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In this work, we study the linewidths of vibrational modes of single dibenzoterrylene (DBT) molecules in paradichlorobenzene (pDCB) and anthracene (AC) crystals at cryogenic temperatures using their vibronic spectra. To identify long-lived modes, these spectra are measured at a high spectral resolution via fluorescence excitation spectroscopy and stimulated emission depletion (STED) spectroscopy with narrowband tunable lasers. We show that the linewidths of some vibrational modes of DBT in pDCB reach values around 2 GHz. This corresponds to a lifetime of 80 ps and is, thus, significantly longer than the typical lifetimes of vibrational modes in the solid state.

We also observe indications of the coherent excitation of a vibronic mode in the electronic ground state of DBT in pDCB. The associated splitting of the absorption profile of a vibronic transition is achieved by tuning an intense control laser on resonance with a transition between two vibronic states with a high Franck-Condon overlap. According to our model calculation, 80 % of the population that is transferred to the vibronic state of the electronic ground state is coherent in this process. If the vibrational lifetimes of certain modes can be extended by decoupling them from crystal phonons, similar schemes may be exploited in future for the coherent transfer of a flying qubit state to a vibrational state of a single molecule.
Johannes Zirkelbach

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Abstract

Dye molecules in organic crystals are excellent single-photon sources and can act as non-linear elements in optical circuits. Since these molecules lack a long-lived spin state, they have previously not been considered for applications that require a quantum memory. In principle, the vibrational modes of single dye molecules in organic crystals could serve that purpose and act as qubits. Due to their coupling to the crystal lattice, the lifetimes of molecular vibrations are often limited to around 10 ps. In the field of cryogenic single molecule spectroscopy, however, the decay constants of vibrational modes have never been studied systematically. This leaves open the possibility that some modes exhibit considerably longer lifetimes.

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A comparison of the vibronic spectra of five DBT molecules in pDCB reveals intriguing systematic variations. The inhomogeneous broadening of the vibrational frequencies is on average narrow (0.9 cm⁻¹), but varies among different vibrational modes. For some modes, the transitions to the electronically
excited state differ considerably from the corresponding transitions to the electronic ground state: the line associated with the mode at 670 cm$^{-1}$ is about nine times broader in the fluorescence excitation spectra than in the STED spectra. The frequency of a mode at 400 cm$^{-1}$ is about 8 cm$^{-1}$ higher in the ground state than in the excited state. We make use of density functional theory calculations of DBT in pDCB matrices to explain the wavenumbers and intensities of the observed vibronic features theoretically.

In another experiment, we observe indications of the coherent excitation of a vibronic mode in the electronic ground state of DBT in pDCB. For this purpose, we tune an intense control laser on resonance with a transition between two vibronic states with a high Franck-Condon overlap. We demonstrate experimentally and theoretically that this configuration leads to a dip in the absorption profile of the upper vibronic state. This effect lies between the regimes of electromagnetically induced transparency and Autler-Townes splitting. According to our model, 80% of the population that is transferred to the vibronic state of the electronic ground state is coherent in this process. Similar approaches could be used to transfer flying qubits to a vibrational state of a molecule and store them there.

In order to use the vibrational states of single molecules in solid-state systems as qubits, their vibrational lifetimes must be extended by several orders of magnitude. Our analysis of the vibrational properties of single DBT molecules in pDCB crystals contributes to an enhanced understanding of the properties of such systems. In future, molecules with long-lived vibrational states might be realized in solid-state systems with engineered phononic properties.
Zusammenfassung


Aus einem Vergleich der vibronischen Spektren von insgesamt fünf DBT Molekülen in pDCB Kristallen ergeben sich weitere interessante Beobachtungen. Die inhomogene Verbreiterung der Schwingungsfrequenzen hängt von der Schwingungsmode ab, ist jedoch mit 0.9 cm\(^{-1}\) im Mittel relativ schmal. Deutlich größere Unterschiede finden wir beim Vergleich der vibronischen Übergänge in den Grundzustand mit den entsprechenden Übergängen in den angeregten Zustand: Die Linie des vibronischen Übergangs in den angeregten Zustand ist bei 670 cm\(^{-1}\) etwa neunmal so breit wie der entsprechende Übergang in den Grundzustand. Eine andere Schwingungsmode bei 400 cm\(^{-1}\) liegt im Grundzustand 8 cm\(^{-1}\) höher als im angeregten Zustand. Mithilfe von Dichtefunktionaltheorie-Simulationen von DBT in pDCB Kristallen können wir den Ursprung der Linien in den gemessenen vibronischen Spektren erklären.


Um Schwingungsmoden einzelner Moleküle in Festkörper-Systemen als Qu-bits zu nutzen, muss deren Lebensdauer deutlich verlängert werden. Unsere Analyse der Schwingungseigenschaften einzelner DBT Moleküle in pDCB Kristallen trägt dazu bei, die Eigenschaften solcher Systeme besser zu verstehen. In Zukunft könnten langlebige Schwingungsmoden realisiert werden, indem die phononischen Eigenschaften der Molekül-Matrix-Interaktion gezielt verändert werden.
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1 Introduction

Molecules consist of atoms that are held together via spring-like forces. The ability to vibrate is therefore a fundamental property of every molecule and its vibrational frequencies are characteristic of its chemical composition. Generally, the interaction of a molecule with light is accompanied by the change in its vibrational state. Thus, molecules are able to convert light to mechanical oscillations on a nanoscopic length scale.

Molecular vibrations play a pivotal role in molecular spectroscopy, serving as a fingerprint for chemical identification [1, 2]. Traditionally, molecular spectroscopy is performed on large ensembles of molecules in gases or the condensed phase. In an effort to reach a level of sensitivity free from restrictions imposed by ensemble averages, cryogenic single molecule spectroscopy was developed around the year 1990 [3, 4]. The polycyclic aromatic hydrocarbon (PAH) molecules used for studies in this field are typically rigid. As a consequence, these molecules are characterized by a strong electronic transition between their vibrationless states, also referred to as 00-zero-phonon-line (00-ZPL) [5]. Single molecule sensitivity is achieved by doping PAH molecules into suitable optically transparent solid host materials at a highly diluted level, enabling access to spectrally isolated 00-ZPL transitions of single molecules. Indeed, the majority of single-molecule studies at cryogenic temperatures has focused on spectroscopy of these 00-ZPL transitions [4, 6]. Details of the vibrational properties of typical systems employed in the field of single molecule spectroscopy have also been investigated, but at a considerably smaller scope.

The concentration of the oscillator strength in the 00-ZPL transition enables efficient interaction of single molecules with light. Based on this property it has been demonstrated that a single molecule can extinguish about 10% of the power of a weak focused laser beam in a free-space configuration [7]. Recently, a landmark experiment realized an extreme level of light-molecule coupling with a single molecule in a microcavity [8]. In that case, 99% of the light incident on the cavity was reflected from the cavity-enhanced 00-ZPL
transition of a single molecule. Other experiments, such as the coupling of molecules to on-chip waveguides [9, 10] or plasmonic structures [11] also benefit from the good light-matter interface provided by the prominent oo-ZPL transition of molecules used in single molecule spectroscopy. These recent experimental efforts have established the building blocks for optical circuits involving single molecules as sources of single photons and as non-linear switching elements [6, 12]. So far, however, molecules in solid-state systems lack long-lived metastable states, which is an essential property of nodes in a quantum network.

In principle, the vibrational states of a polyatomic molecule in its electronic ground state could serve as quantum memory states. Fundamentally, the lifetimes of low-energy vibrational states in isolated molecules are limited by radiative infrared decay, often over a timescale of milliseconds or longer [15–17]. The solid-state environment, however, drastically reduces the vibrational lifetimes of these states by offering many paths for the dissipation of their vibrational energy. While it is considered general knowledge in single molecule spectroscopy that the vibrational states of molecules are short-lived (∼10 ps) in solid-state systems [4, 18, 19], the range of their vibrational lifetimes has yet to be explored experimentally. In other words: it is not known whether there are vibronic states whose lifetimes reach values far above the average. The main reason for the limited knowledge about the lifetimes of vibrational states in cryogenic single molecule spectroscopy is the conventional use of grating spectrometers to measure vibronic spectra of transitions to the electronic ground state. The spectral resolution of these spectrometers is typically limited to ≳10 GHz, making it difficult to identify the widths of states with lifetimes longer than 20 ps.

In addition to the lack of experimental data, the theoretical basis of vibrational relaxation in typical systems of single molecule spectroscopy is poorly understood. In the context of most single molecule experiments it is sufficient to model a molecule as a quantum mechanical two-level system (see Figure 1.1(a)). This model can account for many aspects of the light-molecule interaction, for example saturation effects and non-classical photon statistics [20]. To include additional decay pathways from the electronically excited state to vibrational states of the electronic ground state, the model of a molecule is often extended by a generic additional decay channel that describes red-shifted fluorescence or transitions to the triplet state [21, 22]. A corresponding

---

1 In polyatomic molecules, vibrational states with high energies often decay via intramolecular vibrational redistribution [13, 14].

2
Figure 1.1: Various levels of modeling for the quantum mechanical energy scheme of a molecule to describe its interaction with light. (a) Two-level system. In this model, only the purely electronic zero phonon line (oo-ZPL) transition is taken into account. $|g\rangle$ and $|e\rangle$ denote the vibrational ground states of the electronic ground and excited states. $\Gamma_{eg}$ denotes the rate of spontaneous emission from $|e\rangle$ to $|g\rangle$. (b) Multi-level model for a molecule with vibrational states. The gray box stands for the manifold of vibrational levels, which is not resolved into separate modes in this model. (c) Schematic of the vibrational relaxation cascade model of a molecule in a molecular crystal. $|u\rangle$ and $|v\rangle$ stand for two exemplary vibronic states associated with the electronic ground state. Black arrows indicate possible transitions during the vibrational relaxation cascade.

level scheme is depicted in Figure 1.1(b). The gray box in this scheme represents the complex structure of vibrational states in a polyatomic molecule and their relaxation dynamics. The details of this relaxation process are usually not included in the models of single molecule spectroscopy. As indicated by the level scheme in Figure 1.1(c), the vibrational relaxation dynamics of a molecule in a solid involves a complex cascade of relaxation steps [13, 23]. The rate of each relaxation step is a well-defined property of the molecule, the material of the solid host system, and the strength of their mechanical coupling. For some pure and mixed molecular crystals, these decay dynamics have been explored in great detail [18, 19, 24]. A similar analysis for typical systems of single molecule spectroscopy would improve the understanding of the essential parameters for their vibrational relaxation. These insights may then help in engineering the vibrational relaxation behavior with the goal of generating long-lived vibrational states that could act as single molecule vibron qubits.

In this thesis, we present high-resolution vibronic spectra of single dibenzoterrylene molecules in para-dichlorobenzene and anthracene crystals, two well-established systems in cryogenic single molecule spectroscopy [25, 26]. In that context, we apply a stimulated emission depletion (STED) [27, 28] method to study the linewidths of vibronic states associated with the electronic ground state (see Figure 1.2(a) for a schematic representation). This spectroscopy method offers a markedly enhanced spectral resolution compared to grating spectrometers and reveals a considerable variation in the
linewidths among vibrational modes. For dibenzoterrylene (DBT) in paradichlorobenzene (pDCB), we find that the linewidths of vibronic states vary by more than one order of magnitude, with the lowest linewidths reaching values around 2 GHz, corresponding to a vibrational lifetime of 80 ps.

The STED scheme shown in Figure 1.2(a) leads to an incoherent population transfer, because of the spontaneous vibrational relaxation from \( |w\rangle \) to \( |e\rangle \). By a slight modification of the laser frequencies, it is, however, also possible to achieve coherent population transfer to a vibronic state. The corresponding three-level-like configuration is displayed in Figure 1.2(b). In this thesis, we explore the features and limitations of this effective three-level configuration using vibronic states of DBT in pDCB. Generally, due to the low lifetime of vibronic states in this guest-host system, the total population transferred to a vibronic state in the steady-state remains very small. Nevertheless, we are able to induce a prominent dip in a vibronic line profile by tuning the frequency of an intense control laser on resonance with a transition between two vibronic states with a high Franck-Condon overlap. This is the first demonstration of a three-level effect using two vibronic transitions in a single molecule. If long-lived vibrational states can be realized in the future, such a scheme could be used to coherently store light in the vibration of a single molecule and retrieve it at a later point in time.
This thesis is organized as follows: in chapter 2, we give a brief introduction to cryogenic single molecule spectroscopy. Vibrational states and vibronic transitions in polyatomic molecules are discussed in chapter 3. Since these subjects are typically not treated in detail in the context of single molecule spectroscopy, we dedicate several pages to introducing them. In the same chapter, we also discuss vibrational relaxation in molecular crystals and provide a literature overview of the existing vibronic studies in cryogenic single molecule spectroscopy. In chapter 4, we develop models to describe the interaction of light with a molecule via its vibronic transitions. This covers the theory of incoherent fluorescence excitation, STED spectroscopy, and the coherent processes in a three-level configuration. The experimental setup used for the measurements in this thesis is discussed in chapter 5. The high-resolution vibronic spectra and their analysis are presented in chapter 6. Our measurements were performed in the electronic ground and excited states of six molecules in total. Besides the identification of several particularly narrow vibronic lines, we also discuss some additional intriguing vibronic features in our data, the effect of the host system on the vibronic properties of DBT, and the results of density functional theory calculations. In chapter 7, we show the outcome of the experiments in which a strong control laser was used to induce a dip in a vibronic line profile. Based on the model parameters obtained from that study, we also elaborate on the implications for coherent storage of information in a vibrational state of the molecule. In chapter 8, we discuss several consequences of engineering long-lived vibrational states in the solid state in potential future experiments.
2 Cryogenic single molecule spectroscopy

Cryogenic single molecule spectroscopy is a method used to investigate the properties of single dopant molecules in solid-state environments at liquid helium temperatures where thermal dephasing on the electronic transition is negligible. This provides access to information about electronic and vibrational degrees of freedom on a nanoscopic length scale, without averaging over the properties of a molecular ensemble.

In this chapter, we summarize several principles of cryogenic single molecule spectroscopy. For a more detailed introduction to this subject, we refer the reader to the monograph by Basché et al. [4]. Other useful accounts are given in the recent review article by Toninelli et al. [6] and in previous PhD theses from the Sandoghdar group [29–32].

2.1 Guest-host systems

Cryogenic single molecule spectroscopy is typically performed with PAH molecules such as pentacene (Pc) or terrylene (Tr) that are doped as guest molecules into optically transparent solid-state hosts. The dopant molecules have an electronic transition in the visible or near-infrared spectral range that can be addressed by a narrow-band tunable laser. The hosts are often organic crystals such as naphthalene (Nt) or anthracene (Ac). A single guest molecule usually replaces several molecules of the host crystal after insertion. Non-crystalline materials such as polyethylene (PE) and Shpol’skii matrices such as hexadecane can also be used as solid-state hosts for PAH impurity centers. Figure 2.1 shows an overview of the most commonly studied guest and host molecules in cryogenic single molecule spectroscopy [4, 6].

The experimental approach of doping a solid with the PAH molecules of interest serves several purposes: (1) A suitable host system provides a well-defined environment in which a dopant molecule experiences only minor
Figure 2.1: Overview of common dopant dye molecules and host systems used in single molecule spectroscopy. The dopant molecules have electronic transitions in the visible or near-infrared range of the electromagnetic spectrum. The host systems are transparent in this spectral range, allowing unperturbed optical access to the dopant molecules.
perturbations and is protected from oxidation and other external influences such as fluctuating fields generated by electrical charges. The solid-state environment thus prevents photobleaching and can protect the molecule from processes that induce spectral instabilities. (2) Embedding a molecule in a transparent solid is comparable to fixing it at a certain position in free space. In contrast to cold molecules in supersonic jets or in optical traps, translational and rotational degrees of freedom are not available to a dopant molecule. This greatly simplifies the molecular spectra and excludes spectral broadening via Doppler shifts. Moreover, it is possible to study a single dye molecule at a fixed position over the course of months if the cryogenic conditions are preserved. (3) The density of impurity molecules in a diffraction-limited volume can be controlled by adjusting their doping level in the host system. Reaching the limit of single molecule spectroscopy heavily relies on a reduction of the number of dopant molecules in the focal volume of a laser beam, often to several hundred or thousand molecules. Additionally, inhomogeneities in the nanoscopic environment of each molecule lead to shifts in their resonance frequencies. Because of these molecule-specific spectral shifts, single molecules can be addressed by spectral selection of their non-overlapping electronic transitions if the impurity concentration in the host is low enough (see section 2.4).

2.2 Zero phonon lines and phonon sidebands

Figure 2.2(a) shows the energy level scheme of a dopant molecule in a molecular crystal. The electronic ground state of the PAH molecules studied in cryogenic single molecule spectroscopy is a singlet state \( S_0 \) with paired electrons. From there, the molecule can be optically excited to other electronic singlet states \( S_n \). Triplet states \( T_n \) with unpaired electrons are also eigenstates of the molecule. The energy of the triplet states can split into several sublevels due to magnetic dipole-dipole interactions between their unpaired electrons [4] (not shown in Figure 2.2(a)). Transitions between singlet and triplet states are spin-forbidden and therefore considerably less likely than transitions between singlet states. Important prerequisites for guest-host systems in single molecule spectroscopy are a low intersystem crossing (ISC) rate from \( S_1 \) to the triplet state and a low triplet lifetime [33]. If these conditions are not fulfilled, molecules display a fluorescence blinking behavior and a reduced brightness due to extended dwell times in the dark triplet state.

Each electronic state (\( S_n \) and \( T_n \)) harbors a manifold of vibrational states (see Figure 2.2(a)). Vibrational states are associated with oscillatory movements of the atoms in the molecule [34]. Polyatomic molecules such as the PAH
Figure 2.2: Spectroscopy of molecules in the solid state. (a) Simplified level scheme of a molecule in a solid-state matrix. Of all electronic states, only the first two singlet states ($S_0$ and $S_1$) and the first triplet state $T_1$ are shown. In each electronic state, there is a manifold of vibrational states. Each quantum state of the molecule is accompanied by a phonon sideband (PSB, indicated by the grey bands) due to coupling of the molecule to its solid-state environment. The transitions involving no energy transfer to the matrix (colored arrows) are called zero phonon lines (ZPLs). Intersystem crossing (ISC) is a spontaneous transition between singlet and triplet states. (b) Schematic representation of a low temperature fluorescence excitation spectrum obtained by tuning a laser over the ZPLs indicated by the solid arrows in (a) and their phonon sidebands. The relative amplitudes of the vibronic ZPLs are determined by their Franck-Condon overlaps with the vibrational ground state in $S_0$ (= the initial state) and their relative linewidths. For the vibronic level with the lowest frequency, the first overtone level is shown as well.

molecules used for cryogenic single molecule spectroscopy have many vibrational modes and thus their vibrational manifold forms a complex ladder of quantum states. Due to selection rules for the excitation of vibronic states, not all vibronic states can be directly accessed via vibronic transitions [35–37]. The allowed vibronic transitions are called (Franck-Condon) active transitions. In Figure 2.2(a), the longest horizontal line of each electronic state stands for its respective vibrational ground state, i.e. the state in which no vibrational normal mode of the molecule is excited such that the nuclei of the molecule only undergo zero-point motion. The shorter horizontal lines represent various vibrational normal modes of the molecule. These are vibronic states and are defined by their electronic and vibrational quantum numbers. The overtone and combination modes of the vibronic states are not displayed in the schematic of Figure 2.2(a). Since this thesis is concerned with vibronic transitions, we give a detailed introduction to vibrational states of polyatomic molecules and selection rules for vibronic transitions in chapter 3. We remark that vibronic transitions involve a simultaneous change of the electronic and vibrational state of a molecule. Vibrational transitions, in contrast, are transitions between different vibrational states in the same electronic state (relevant to Raman and infrared spectroscopy).
As indicated in Figure 2.2, each level of the molecule has a phonon sideband (PSB) [38–40]. These sidebands originate from interactions of the molecule with its solid host system. If a PSB is excited, the change in the molecular quantum state involves energy transfer to the solid. If the host system is a molecular crystal, this energy transfer corresponds to the excitation of a crystal phonon. The exact shape and extent of the PSBs vary among guest-host combinations.

Transitions between the internal states of a molecule in a solid are termed zero phonon lines (ZPL). These transitions do not lead to energy transfer to the solid and are marked by the double-headed arrows in Figure 2.2(a). A special transition among the ZPLs is the 00-ZPL, connecting the vibrational ground states of \( S_0 \) and \( S_1 \) (indicated by the blue double-headed arrow in Figure 2.2(a)). In the rigid PAH molecules used for cryogenic single molecule spectroscopy, the 00-ZPL has the highest oscillator strength of all transitions that involve the vibrationless state of either \( S_0 \) or \( S_1 \). The PSB of the 00-ZPL does not play a significant role in many cryogenic single molecule studies since its absorption cross section is weak compared to the 00-ZPL. The strength of the PSB relative to the ZPL transitions is quantified by the Debye-Waller factor \( \alpha_{DW} \), defined as the intensity of the ZPL transition relative to the sum of the intensities in the ZPL and its PSB [39, 41]. Since the transitions to vibronic states are weaker than the 00-ZPL, their PSBs have lower absorption cross sections than the PSB of the 00-ZPL. In many vibronic spectra, the PSBs of vibronic states are therefore difficult to identify. Figure 2.2(b) shows a schematic fluorescence excitation spectrum of the level scheme in Figure 2.2(a). The narrow lines in this spectrum correspond to the ZPL transitions and the broad peaks stand for their respective PSBs.

Figure 2.2(a) does not indicate the decay pathways of the molecular quantum states. A detailed quantitative account of internal relaxation pathways of DBT in pDCB is given in section 4.1 of this thesis. Some general rules for the decay of molecular quantum states are as follows: vibrational states of molecules in solid-state matrices typically have lifetimes around 10 ps, considerably shorter than the electronically excited state (few nanoseconds). The complete dissipation of vibrational energy from a molecule to the matrix usually involves a number of non-radiative relaxation steps. This vibrational relaxation cascade is discussed in more detail in sections 3.3 and 4.1.1. While vibronic states in \( S_1 \) can in principle decay radiatively to vibronic states in \( S_0 \), one typically assumes that all vibronic states in \( S_1 \) first decay non-radiatively to the vibrational ground state of \( S_1 \) (Kasha’s rule [42]). In a subsequent step, \( S_1 \) decays radiatively to \( S_0 \) via spontaneous emission of a single fluorescence
2 Cryogenic single molecule spectroscopy

![Graphs showing lifetime-limit and temperature dependence of the homogeneous linewidth of single DBT molecules in pDCB.](a) Fluorescence excitation scan of the lifetime-limited resonance profile of a single molecule (for $P = 0.03$ nW, $P_{\text{sat}} = 1.4$ nW, and $T < 2$ K). Adapted from [45], with the permission of AIP Publishing. (b) Thermal broadening of the homogeneous linewidth. For DBT in pDCB, the homogeneous linewidth starts to broaden for $T \gtrsim 3$ K. Data of part (b) courtesy of D. Rattenbacher.

Figure 2.3: Lifetime-limit and temperature dependence of the homogeneous linewidth of single DBT molecules in pDCB, recorded in the low excitation regime. (a) Fluorescence excitation scan of the lifetime-limited resonance profile of a single molecule (for $P = 0.03$ nW, $P_{\text{sat}} = 1.4$ nW, and $T < 2$ K). Adapted from [45], with the permission of AIP Publishing. (b) Thermal broadening of the homogeneous linewidth. For DBT in pDCB, the homogeneous linewidth starts to broaden for $T \gtrsim 3$ K. Data of part (b) courtesy of D. Rattenbacher.

photon along the 00-ZPL or allowed vibronic transitions. Transitions to the triplet state additionally lead to the depopulation of $S_1$. In systems selected for single molecule spectroscopy, the timescale of ISC is typically considerably longer than radiative decay of $S_1$, rendering ISC a secondary decay channel for the excited state. The triplet state itself can decay by several processes, for example by coupling to vibrational states of $S_0$ or by the emission of a photon (phosphorescence) [43, 44].

### 2.3 Lifetime-limited linewidths at cryogenic temperatures

The linewidth $\Delta \nu$ of the 00-ZPL transition in a molecule can be expressed as

$$\Delta \nu = \frac{1}{2\pi T_1} + \frac{1}{\pi T_2^*},$$

(2.1)

where $T_1$ denotes the lifetime of the electronically excited state and $T_2^*$ is the pure dephasing time. Typical values of the excited state lifetime $T_1$ are several nanoseconds, corresponding to natural linewidths in the range of 10–50 MHz. At room temperature (RT), dopant molecules are, however, strongly affected by thermally activated processes, e.g. lattice vibrations (= phonons), in the host system [40]. This thermal activity induces dephasing with $T_2^*/T_1 \sim 10^{-5} - 10^{-6}$ on the electronic transition and lead to a broadening of the 00-ZPL to values around 15 THz at RT [46]. By cooling a doped host system to temperatures between 1.4–4 K, thermally induced dephasing can be
completely suppressed in most systems, reaching \( T^* \rightarrow \infty \) [47]. In this case, the linewidth of the 00-ZPL transition is determined by the lifetime of the electronically excited state. Figure 2.3(a) shows an example of a lifetime-limited resonance profile of a single DBT molecule in a pDCB crystal at \( T < 2 \) K, exhibiting a linewidth of 23 MHz. The measurement was performed at a low excitation power to avoid power-broadening effects (see section 2.5). The black line is the fit of a Lorentzian line profile

\[
R(v) = R_{\text{max}} \frac{\Delta v^2/4}{(v - v_0)^2 + \Delta v^2/4} + R_{\text{bg}}
\]  

(2.2)

to the data, where \( R_{\text{max}} \) and \( R_{\text{bg}} \) denote the amplitude of the line profile and the background measured on the detectors, respectively, \( \Delta v \) is the full width at half maximum (FWHM) of the profile and \( v_0 \) is the resonance frequency. The line broadening of the 00-ZPL transition caused by thermal dephasing is shown in Figure 2.3(b) for a single DBT molecule in pDCB. For this guest-host combination, the electronic transition undergoes thermal broadening starting from \( T \gtrsim 3 \) K.

Equation (2.1) also holds for the vibrational states of a molecule [13]. The natural linewidth of these states is typically 100-1000 times broader than the 00-ZPL due to their short vibrational lifetimes around \( T_1 \sim 10 \) ps. At liquid helium temperatures, dephasing of vibrational states can usually be ignored. In contrast to the electronic transition, the lifetime of vibrational states of molecules in the condensed phase depends on the temperature of the surrounding medium. Stimulated emission triggered by thermal phonons leads to an increase of the vibrational relaxation rate with increasing temperature [13, 49]. The scattering of thermal phonons by a molecule can cause additional pure dephasing of the vibrational transition. However, vibrational states often broaden only by one or two orders of magnitude between liquid helium temperature and RT, considerably less than the electronic transition [49–51]. The linewidths of transitions in Raman and infrared spectroscopy, which do not involve a change in the electronic state, can thus be in the order of 100 GHz at RT in the condensed phase [49, 52–54].

In the case of vibronic transitions, the lifetime and pure dephasing of both electronic and vibrational states contribute to the overall linewidth. The absence of thermal dephasing at liquid helium temperatures leads to vibronic spectra that consist of narrow and well separated lines. Figure 2.4(a) shows the emission spectrum of a single DBT molecule in pDCB. This spectrum was recorded by sending the light emitted from the molecule at cryogenic temperatures to a grating spectrometer. As the temperature increases, the
Figure 2.4: Vibronic spectra of single molecules under cryogenic conditions and at room temperature. (a) Fluorescence emission spectrum of a single DBT molecule in a pDCB matrix at $T < 2$ K, recorded using a grating spectrometer. Because electronic dephasing is absent at these temperatures, the vibronic spectrum consists of narrow lines. The molecule was excited via a vibronic transition to $S_1$ (via the 00-ZPL) for the ×1 and ×10 versions (for the ×150 version). Adapted from [45], with the permission of AIP Publishing. (b) Schematic representation of the 00-zero phonon line and its phonon sideband of a single molecule for various temperatures. As the temperature increases, the phonon sideband starts to dominate the spectrum. Reprinted from [38] with permission from Elsevier. (c) Fluorescence emission spectra of Tr:pT at room temperature (a,b; inside plot) and at liquid helium temperature (c; inside plot). Reprinted from [48] with permission from Elsevier.

lines in this spectrum broaden, mainly due to dephasing on the electronic (and not the vibrational) transition. At the same time, the Debye-Waller factor decreases, making the PSB more prominent than the ZPL peaks. Figure 2.4(b) illustrates how the PSB starts to dominate as temperature increases [38, 39]. The RT absorption and emission spectra of molecules in the condensed phases thus mainly consist of the highly overlapping PSBs of their (00- and vibronic) ZPL transitions. Figure 2.4(c) displays the fluorescence emission spectra of Tr molecules in para-terphenyl (pT) at cryogenic temperatures and
2.4 Inhomogeneous broadening

As in other solid-state systems, the hosts used for single molecule spectroscopy contain defects and other perturbations. Therefore, every dopant molecule has a different nanoscopic environment, even in crystalline hosts. The variation of strain and electric field strengths at the positions of the dopant molecules shift their resonance frequencies, usually on a considerably broader scale than the natural linewidth of the 00-ZPL. In this way, every single molecule is not only characterized by its position in the host crystal, but also by the frequency of its 00-ZPL. Figure 2.5 shows a measurement of the spectral distribution of 00-ZPL transitions of single DBT molecules in an Ac host crystal. The ability to spectrally address a single molecule even if hundreds or thousands of molecules are present in the same excitation volume of a laser spot is a key feature of cryogenic single molecule spectroscopy. The variation in the transition frequencies of nominally identical DBT molecules due to their environment is called inhomogeneous broadening.

The center wavelength of the inhomogeneous broadening differs between dye molecules and host crystals. Generally, the wavelength increases with the area of the delocalized electron wave function in the dye molecule. The largest conventionally used molecule in cryogenic single molecule spectroscopy is
DBT (dimensions: \( \sim 14 \, \text{Å} \times 12 \, \text{Å} \); see Figure 2.1 for its chemical structure) with 00-ZPL wavelengths within 740–785 nm, depending on the host system and spectroscopic site [25, 26]. This spectral range is convenient for access by tunable narrow-band Ti:Sapphire lasers. The inhomogeneous broadening of the molecules Tr and dibenzanthanthrene (DBATT) is centered around 570–590 nm [55, 56]. This spectral range is usually accessed by dye lasers.

### 2.5 Light-molecule interaction

The interaction of a single molecule with light is often described by the interaction of a quantum mechanical two-level system with a classical oscillating light field \( \vec{E}(t) \). The two-level approximation is justified for the description of the 00-ZPL since all other resonances of the molecule are spectrally far away. In order to take the triplet state and/or red-shifted decay channels of the molecule into account, additional levels can be added to the decay path of the model without introducing major changes to its qualitative behavior [21, 30, 57].

The behavior of a quantum mechanical two-level system that undergoes spontaneous emission and is driven by a classical light field \( \vec{E}(t) = E_0 \cos(\omega t) \) (see Figure 2.6) can be described by the Lindblad master equation [4, 58, 59] for the density operator \( \hat{\rho} \) of an open quantum system

\[
\partial_t \hat{\rho} = -\frac{i}{\hbar}[\hat{H}, \hat{\rho}] + \sum_k \Gamma_k (\hat{L}_k \hat{\rho} \hat{L}_k^\dagger - \frac{1}{2} (\hat{L}_k^\dagger \hat{L}_k \hat{\rho} + \hat{\rho} \hat{L}_k^\dagger \hat{L}_k)).
\]  

(2.3)

In this equation,

\[
\hat{\rho} = \begin{pmatrix}
\rho_{gg} & \rho_{ge} \\
\rho_{eg} & \rho_{ee}
\end{pmatrix}
\]

(2.4)
denotes the density operator of the two-level system in the basis $I = \{ |g\rangle, |e\rangle \}$ and

$$\hat{H} = \hat{H}_m + \hat{H}_{mf} = \hat{H}_m - \hat{d} \cdot \tilde{E}(t) = \begin{pmatrix} \hbar \omega_g & 0 \\ 0 & \hbar \omega_e \end{pmatrix} - \begin{pmatrix} 0 & \hat{d}_{ge} \\ \hat{d}_{ge} & 0 \end{pmatrix} \cdot \tilde{E}(t)$$ (2.5)

is the Hamilton operator of the molecule ($\hat{H}_m$) and its electrical dipole interaction ($\hat{H}_{mf}$) with the oscillating electric field $\tilde{E}(t)$. $\hbar \omega_g$ and $\hbar \omega_e$ denote the energies of the two states $|g\rangle$ and $|e\rangle$ of the two-level system, respectively. The transition dipole moment $\hat{d}_{ge} = \langle g| \hat{d} |e\rangle$ is assumed to be real-valued. The sum in equation (2.3) is over all (Lindblad) jump operators $\hat{L}_k$ of the system with associated decay rates $\Gamma_k$. For a two-level system without dephasing, the only relevant jump operator is $\hat{L}_{eg} = |g\rangle \langle e|$, describing spontaneous emission along the transition $|e\rangle \rightarrow |g\rangle$. We denote the corresponding decay rate as $\Gamma_{eg}$.

In the rotating wave approximation and a suitable rotating frame (see appendix D.1), the Hamiltonian of the two-level system can be rewritten as

$$\tilde{H} = \hbar \begin{pmatrix} 0 & \Omega/2 \\ \Omega/2 & -\Delta \end{pmatrix},$$ (2.6)

with Rabi frequency $\Omega = -\hat{d}_{ge} \cdot \tilde{E} / \hbar$, detuning of the laser with respect to the transition frequency $\Delta = \omega - \omega_{ge}$, and transition frequency $\omega_{ge} = \omega_e - \omega_g$. Substituting this matrix and the jump operator for spontaneous emission into equation (2.3) results in the optical Bloch equations of a two-level system [20]:

$$\partial_t \rho_{ee} = -\frac{i}{2} \Omega (\tilde{\rho}_{ge} - \tilde{\rho}_{eg}) - \Gamma_{eg} \rho_{ee}$$ (2.7)

$$\partial_t \tilde{\rho}_{ge} = -\frac{i}{2} \Omega (\rho_{ee} - \rho_{gg}) + (i \Delta - \frac{1}{2} \Gamma_{eg}) \tilde{\rho}_{ge} + \frac{1}{2} \Gamma_{eg} \rho_{gg}$$ (2.8)

$$1 = \rho_{gg} + \rho_{ee},$$ (2.9)

where $\tilde{\rho}_{ge} = \tilde{\rho}_{eg}^*$ are the coherences of the density operator in the rotating frame. These equations describe several fundamental properties of the interaction between a quantum mechanical two-level system and a driving laser field, for example (damped) Rabi oscillations and antibunching of the autocorrelation function.
The rate of photons that are spontaneously emitted from the two-level system is $\Gamma_{eg}\rho_{ee}$. Hence, the resonance profile of the two-level system corresponds to the behavior of $\rho_{ee}$ as a function of detuning $\Delta$ in the steady-state. The solution to equations (2.7)-(2.9) for the steady-state population in the excited state $|e\rangle$ can be written as

$$
\rho_{ee}(\Delta) = \frac{1}{2} \frac{S(\Delta)}{1 + S(\Delta)} = \frac{1}{2} \frac{S}{1 + S} \frac{1}{\Delta^2 + \frac{1}{4} \Gamma_{eg}^2 (1 + S)},
$$

(2.10)

with the saturation parameter

$$
S(\Delta) = \frac{\Omega^2 / 2}{\Delta^2 + \Gamma_{eg}^2 / 4}.
$$

(2.11)

By dropping the argument of the saturation parameter, we refer to the on-resonance case, i.e.

$$
S = S(\Delta = 0) = \frac{2\Omega^2}{\Gamma_{eg}^2}.
$$

(2.12)

The steady-state population of $|e\rangle$ has a Lorentzian profile (see equation (2.2)) as a function of laser detuning with amplitude

$$
\rho_{ee,\text{max}} = \frac{1}{2} \frac{S}{1 + S}
$$

(2.13)

and linewidth (full width at half maximum, in units of Hz)

$$
\Delta \nu = \frac{\Gamma_{eg}}{2\pi} \sqrt{1 + S} = \Delta \nu(0) \sqrt{1 + S},
$$

(2.14)

where $\Delta \nu(0)$ denotes the linewidth of the transition in the limit of low excitation power $S \to 0$. Hence, the population in $|e\rangle$ displays a saturation behavior and is limited to a maximum value of $1/2$ in the steady-state. This upper limit of the steady-state population stems from the fact that at high values of $\Omega$, excitation and depletion of the excited state via the resonant laser compensate for each other. The population in $|e\rangle$ reaches $\rho_{ee} = \rho_{ee,\text{max}}/2$ for $S = 1$. In this case the laser-induced Rabi frequency $\Omega$ is comparable to the excited state decay rate $\Gamma_{eg}$.

The photon count rate $R$ measured on a detector is related to the photon emission rate $\Gamma_{eg}\rho_{ee}$ of the (idealized two-level) molecule by a proportionality constant $\eta$ that quantifies the photon collection properties of the optical setup: $R = \eta \Gamma_{eg}\rho_{ee}$. Hence, the line profiles measured in fluorescence excitation experiments are expected to follow the same saturation behavior as the excited
2.5 Light-molecule interaction

Figure 2.7: Saturation behavior of the fluorescence emission from a single DBT molecule in pDCB. (a) Fluorescence excitation scans of the 00-ZPL, recorded at various powers of the excitation laser (0.03 nW to 291 nW). (b) Amplitude (blue dots) and linewidth (orange dots) of the molecular line profiles in (a) as a function of the power of the excitation laser. Black lines: fits of the functions (2.15) and (2.14) to the respective data points ($R_{\infty} = 0.65$ Mcps, $P_{\text{sat}} = 1.4$ nW, $\Delta \nu(0) = 22.5$ MHz).

state population in equation (2.10). The amplitude of the Lorentzian line profiles (2.2) measured on a single photon detector is typically written as

$$R_{\max} = R_{\infty} \frac{S}{1 + S},$$

where $R_{\infty}$ is the maximum possible detected emission from the molecule at resonant excitation. Typical values of $R_{\infty}$ in state of the art single molecule experiments are within 0.1-2 Mcps [6, 11, 25, 30, 31]. A measurement series of fluorescence excitation scans of the 00-ZPL transition at different laser powers is shown in Figure 2.7(a). The behavior of $R_{\max}$ and $\Delta \nu$ of the Lorentzian line profiles of this series is displayed in Figure 2.7(b). The black lines in this figure are fits of the functions (2.15) and (2.14) to the data in this plot, showing very close agreement with the measurements. Since the saturation parameter is proportional to the laser intensity at the position of the molecule, one can write

$$S = \frac{P}{P_{\text{sat}}},$$

in the context of an experiment. The saturation power $P_{\text{sat}}$ depends on the decay rate of the quantum emitter and the excitation efficiency of the optical setup. Typical values of $P_{\text{sat}}$ in single molecule experiments on the oo-ZPL are within 0.1-50 nW [6, 11, 25, 31].

The experiments presented in this thesis all rely on the detection of incoherent fluorescence from single molecules. Since we perform spectroscopy on
vibronic states both in $S_0$ and $S_1$, the two-level model must be extended by the corresponding levels. In chapter 4, we introduce several models describing the interaction of light with vibronic transitions in molecules.

2.6 Developments in single molecule spectroscopy

The early years of single molecule spectroscopy [4] dealt with the improvement of experimental sensitivity, identification of working guest-host systems, and the first demonstrations of several effects characteristic of single quantum emitters, including saturation [21], antibunching [60], spectral jumps [61], and spectral tuning using the Stark effect [62]. Vibronic spectra of single molecules have also been investigated by dispersing their fluorescence with grating spectrometers [63]. These experiments were performed in a free-space configuration, addressing single molecules embedded in bulk host systems using a narrow-band tunable laser.

Later, researchers explored non-linear effects mediated by a single molecule that is simultaneously addressed by two lasers. In this way, the AC-stark shift [64, 65] and the hyper-Raman effect [66] could be demonstrated using single molecules. With an adapted experimental design, it was later shown that a low number of photons can be sufficient to induce such non-linear effects in the light transmitted through the sample [67]. There is also a report about an experiment in which properties of single molecule vibronic states in $S_1$ were derived from ensemble measurements using two-laser saturation spectroscopy [68].

The improvement of light-molecule coupling by solid immersion lenses [7] or near-field approaches [22] enabled experiments in which the intensity of the coherent scattering of a molecule is similar to the intensity of the excitation laser. In these experiments, the propagation of a laser beam can be severely attenuated by the presence of a single molecule in its beam path. Using a micro-cavity, an enhancement of this effect was demonstrated, leading to a reflection of 99% of the incoming laser light by a single molecule [8]. With the help of a second laser, it is possible to use such a system as a switch or to generate light at new frequencies and even to reach the strong coupling limit of cavity quantum electrodynamics [69]. By pumping a molecule with a second laser via a vibronic state, it was also demonstrated that a laser beam can be attenuated or amplified by tuning the intensity of the second laser in a free-space configuration [12].
In the past ten years, researchers started to embed molecules in environments with engineered photonic properties, such as antennas [70, 71], on-chip waveguides [9, 10, 72], and plasmonic nano-structures [11, 73]. While some of these approaches mainly serve the purpose of improving collection efficiency, others can be described in the weak coupling regime of cavity quantum electrodynamics. The combination of single molecules and nano-structured substrates enables a high level of control over the interaction of molecules with light. Some recent approaches to doping nanocrystals with single molecules could help this progress by enabling highly deterministic placement of single emitters on substrates with nano-fabricated structures [74, 75]. A more detailed review of the state of the art in single molecule quantum technology has been published recently [6].

Despite the impressive development of single molecule spectroscopy over the last 30 years, the molecular vibronic linewidths have neither been measured precisely in a systematic way nor fully understood. Recent theoretical publications suggest, however, that interest in the vibronic and phononic properties of single molecule systems is currently increasing [40, 76–78]. In this thesis, we explore ways to experimentally access single molecule vibronic states and their relaxation rates by high-resolution measurements of vibronic spectra for DBT in pDCB (see chapter 6). Since vibronic selection rules and the mechanisms of vibrational relaxation do not belong to the common knowledge of single molecule spectroscopists, we introduce the necessary theoretical foundations in chapters 3 and 4. In this context, we also discuss an experimental arrangement for the coherent excitation of a vibrational state in $S_0$. The corresponding experimental data are presented in chapter 7. The methods and findings presented in this thesis may mark the beginning of a line of research in which vibronic states of molecules are exploited as quantum memory.
3 Vibronic transitions

Molecules exist because it can be energetically favorable for individual atoms to share electrons [79]. The equilibrium positions of atoms in a molecule are determined by a minimum in the energy of the composite system. If nuclei are displaced by a small amount from their equilibrium positions, they experience a restoring force. As a consequence, a molecule can vibrate in different patterns at frequencies that depend on the strength of the restoring forces and the mass of the atoms involved in the oscillation. The spectrum of vibrational frequencies is therefore characteristic for the exact chemical composition and the spatial conformation of a molecule. If an electron is promoted to a different electronic state, e.g. by absorption of a photon, the equilibrium positions of the nuclei in the molecule change. After a change in the electronic state, the nuclei have to re-arrange to reach these new equilibrium positions. This process can trigger the start of a molecular vibration.

Vibronic spectroscopy probes the frequencies, linewidths and intensities of electronic transitions to molecular quantum states in which the molecule is vibrating. While the energy of a vibrational state is mainly associated with the properties of the spatial mode of the vibration, its linewidth depends on the dissipation rate of energy from the vibration. Intensities of vibrational lines depend on the method of interrogation (fluorescence, stimulated emission, infrared or Raman spectroscopy) and are related to the symmetry of the vibration. In this chapter, we introduce the mathematical formalism to describe the vibronic quantum states of molecules (see section 3.1) and their Franck-Condon factors in polyatomic molecules (see section 3.2). Additionally, we give a brief introduction to the theory of vibrational relaxation of molecules in molecular crystals (see section 3.3) and an overview of single molecule vibronic spectroscopy at low temperatures (see section 3.4).
3 Vibronic transitions

3.1 Vibrational quantum states

3.1.1 Normal modes

The vibrational normal modes of a molecule are oscillatory displacement patterns of its nuclei around their equilibrium positions [34, 80]. Mathematically, normal modes are derived from the equations of motion of the nuclei in the approximation of a harmonic potential around their equilibrium positions.

One needs $3N$ coordinates to describe the positions of the nuclei in a molecule with $N$ atoms. We use $(\Delta x_i, \Delta y_i, \Delta z_i)$ to denote the displacement of the $i$th nucleus from its equilibrium position along the axes of a Cartesian coordinate system. Using these displacement coordinates, we define the $3N$ mass-weighted nuclear coordinates $q_j$ according to the following pattern [34]:

$$
q_1 = \sqrt{m_1} \Delta x_1, \quad q_2 = \sqrt{m_1} \Delta y_1, \quad q_3 = \sqrt{m_1} \Delta z_1,
q_4 = \sqrt{m_2} \Delta x_2, \quad q_5 = \sqrt{m_2} \Delta y_2, \quad q_6 = \sqrt{m_2} \Delta z_2,
\vdots
q_{3N-2} = \sqrt{m_{N-1}} \Delta x_{N-1}, \quad q_{3N-1} = \sqrt{m_{N-1}} \Delta y_{N-1}, \quad q_{3N} = \sqrt{m_{N-1}} \Delta z_{N-1}.
$$

In these coordinates, the classical equations of motion can be written as

$$
\frac{d}{dt} \frac{\partial T}{\partial ̇ q_j} + \frac{\partial V}{\partial q_j} = 0, \text{ with } j = 1, 2, \ldots, 3N, \tag{3.2}
$$

with kinetic energy

$$
T = \sum_{i=1}^{3N} \frac{1}{2} \dot{q}_i^2 \tag{3.3}
$$

and the total potential energy $V$. Expanding the potential energy function in terms of the mass-weighted coordinates yields:

$$
V = V_0 + \sum_{i=1}^{3N} \left( \frac{\partial V}{\partial q_i} \right)_0 q_i + \frac{1}{2} \sum_{i,j=1}^{3N} \left( \frac{\partial^2 V}{\partial q_i \partial q_j} \right)_0 q_i q_j + \text{higher terms}. \tag{3.4}
$$

In the harmonic approximation, only the third term of the above equation is retained and the equations of motion can be written as

$$
\ddot{q} + K \cdot ̂\vec{q} = 0, \tag{3.5}
$$

1 The constant term has no effect on the equations of motion and the linear term vanishes at the equilibrium positions of the nuclei by definition.
with $\vec{q} = (q_1, q_2, \ldots, q_{3N})$ and $K_{ij} = (\partial^2 q_i / \partial q_j^2)\mid_0$, the Hessian matrix of the potential energy function in mass-weighted coordinates. The solution of this set of $3N$ coupled differential equations is given by

$$\ddot{q}_i(t) = \ddot{A}_i \cos(\sqrt{\lambda_i}t + \phi_i),$$

(3.6)

where $\ddot{A}_i$ and $\lambda_i$ are related to each other via the eigenvector equation $(K - \lambda_i I)\ddot{A}_i = 0$, where $I$ denotes the identity matrix. The magnitude of $\ddot{A}_i$ and the value of the phase $\phi_i$ are determined by the initial conditions. Non-trivial solutions require $\det(K - \lambda_i I) = 0$. Six of the $3N$ solutions of the above equations have $\lambda_i = 0$, i.e., do not result in an oscillatory behavior. These solutions are related to rotations or translations of the molecule and are not normal modes of vibration (see the textbooks by Wilson et al. [34] and Bunker and Jensen [37] as well as the paper by Ochterski [80] for a more detailed description of how these solutions can be projected out). The remaining solutions are the $N_{\text{vib}} = 3N - 6$ normal modes of the molecule and labeled by the indices $i = 1, 2, \ldots, N_{\text{vib}}$ (linear molecules: $N_{\text{vib}} = 3N - 5$). If a molecule is vibrating in its $i$th normal mode, all of its atoms are moving around their equilibrium position with the same frequency $\sqrt{\lambda_i} / (2\pi)$, the same phase, and (relative) amplitudes defined by the entries of $\ddot{A}_i$. Any general motion of the nuclei in which the center of mass of the molecule is not moving and the molecule is not rotating can be expressed as a linear superposition of these normal modes. The vibrational frequencies of normal modes are in the range between 1–100 THz. Typically, these frequencies are reported as (vibrational) wavenumbers defined via

$$\tilde{\nu} = \nu / c$$

(3.7)

in units of cm$^{-1}$. In equation (3.7), $\nu$ is the frequency of the vibration and $c$ is the speed of light. One wavenumber (1 cm$^{-1}$) corresponds to 30 GHz and a frequency of 1 THz corresponds to about 33 cm$^{-1}$. In this thesis we will use the convention that the mode index $i$ increases with the frequency of the normal mode, i.e. mode 1 has the lowest vibrational frequency and mode $N_{\text{vib}}$ the highest one.

The amplitude vectors $\ddot{A}_i$ are orthogonal with respect to each other and after normalization they form the columns of the $(3N \times N_{\text{vib}})$-matrix [80],

$$I_{\text{mwc}} \equiv (\ddot{A}_1 / |\ddot{A}_1|, \ddot{A}_2 / |\ddot{A}_2|, \ldots),$$

(3.8)

which transforms between the mass-weighted coordinates $\vec{q}$ and the normal coordinates $\vec{Q}$:

$$\vec{q} = I_{\text{mwc}} \cdot \vec{Q} \iff \vec{Q} = I_{\text{mwc}}^T \cdot \vec{q}.$$  

(3.9)
The unit of a normal coordinate is $[\vec{Q}] = [\vec{q}] = \sqrt{kg \cdot m}$. Using the diagonal matrix $\mathbf{M}$ defined by $M_{ii} \equiv m_i$, where $m_i$ is the mass of the atom described by the mass-weighted displacement coordinate $q_i$, one obtains the Cartesian displacements associated with each normal mode as the column vectors of the matrix $\mathbf{l}_{\text{cart}}$:

$$\mathbf{l}_{\text{cart}} \equiv \mathbf{M}^{-1/2} \cdot \mathbf{l}_{\text{mwc}}.$$  \hspace{1cm} (3.10)

The column vectors of $\mathbf{l}_{\text{cart}}$ are in general not orthogonal with respect to each other.\(^2\) More details about different types of coordinate systems used in the context of the molecular normal modes (e.g. internal coordinates) can be found in standard textbooks [34, 37] and papers [36, 80] about this topic.

In appendices C.1 and C.2, we demonstrate how to calculate the normal modes of diatomic and linear triatomic molecules. The resulting normal modes are shown in Figure 3.1(a,b). The approach to finding the normal modes of molecules as large as pDCB or DBT is the same as for small molecules but requires the handling of larger matrices. Details of the algorithm for vibrational analysis used by the software *Gaussian 16* [81], which was used for DBT and pDCB in this thesis, are given in the paper by Ochterski [80]. Figure 3.1(c,d) shows for the examples of pDCB and DBT that molecular normal modes become more complex as the number of atoms in the molecule increases.

A prerequisite for the normal mode analysis described in this section is knowledge of the equilibrium structure of a molecule as well as of the Hessian matrix of the interatomic potential. Density functional theory (DFT) provides methods to find the equilibrium structure of complex molecules by means of numerical optimization. From the optimized molecular structure, one can then also determine the Hessian matrix $\mathbf{K}$ of the potential. All DFT simulations for vibrational modes of DBT presented in this thesis were performed by our collaborators Irena Deperasińska and Boleslaw Kozankiewicz using *Gaussian 16* [81]. An in-depth discussion of DFT methods is outside the scope of this thesis and can be found in the literature, e.g. in [82]. We will mention details about the settings of the DFT simulations where they are relevant.

The equilibrium structures of several stereoisomers of isolated DBT have been published in [83]. The most stable isomer of DBT has been found to be non-planar, is part of the $C_{2v}$ point group (see section 3.1.3 for more details about

\(^2\) Vibrational analysis performed by the density functional theory software *Gaussian 16*, which is used for normal mode calculations in this thesis, returns a normalized version of these column vectors as an output: $\mathbf{l}_{\text{cart, out}, i} = \mathbf{l}_{\text{cart}, i} / |\mathbf{l}_{\text{cart}, i}|$ [80]. The reduced mass $\mu_i$ of normal mode $i$ is defined as $\mu_i \equiv |\mathbf{l}_{\text{cart}, i}|^{-2}$ in *Gaussian 16*.\}
symmetry groups), and is shown in Figure 3.1(d). It has the outer rings of the tetracene unit tilted out of the terrylene plane by an angle of about 26° due to steric hindrance (see Figure 6.18 and [84]). The presence of the strong line at around 290 cm\(^{-1}\) and the two additional lines at 177 cm\(^{-1}\) and 234 cm\(^{-1}\) in experimental fluorescence spectra suggest that DBT maintains a similar conformation with only minor deformations from it when it is embedded into Ac [26, 84, 85], 2,3-dimethylanthracene (DMA) [85], Nt [86], or pDCB [25]. In section 3.2.4, we discuss the general concept of how deformations of a
Figure 3.2: Wavenumbers and symmetries of all vibrational normal modes of isolated DBT in $C_{2h}$-symmetry, resulting from DFT calculations. (a) Wavenumbers and Mulliken symbols of all 168 vibrational modes of isolated DBT resulting from DFT simulations. Wavenumber regions of typical mode patterns are indicated by the colored bars at the side of the plot. (b–e) Examples of four normal modes of DBT in the low, intermediate and high frequency regions, one for every Mulliken symbol in the character table of the $C_{2h}$ group. $A_g$: symmetric under all symmetry operations of the $C_{2h}$-group; $A_u$: antisymmetric under inversion and reflection; $B_g$: antisymmetric under rotation and reflection; $B_u$: antisymmetric under rotation and inversion (see also Figure 3.3). The wavenumbers shown in this figure are not corrected by a linear scaling function (see section 6.3.1).
molecule affect its vibronic spectrum. In section 6.3, we present simulation results of the vibronic spectra of DBT in pDCB crystals and compare them with the spectra of isolated DBT. The displacements of the mode at 290 cm$^{-1}$ (mode 17) are plotted in Figure 3.1(d) (see also [86] for plots of this and the two other prominent low wavenumber modes of DBT).

Figure 3.2(a) shows the frequencies and symmetry properties of the normal modes of DBT as obtained from DFT simulations. Since increasing vibrational frequency indicates stronger binding forces and/or smaller oscillating mass, the wavenumber of a vibration roughly indicates which parts of the molecule are engaged in the oscillation. Low frequency modes typically involve oscillations of larger parts of the molecule (skeletal modes). An example of a skeletal mode of DBT is the ‘butterfly mode’ in which the ‘wings’ of the molecule move as a whole, see Figure 3.2(b). At increasing frequencies, there are modes of the benzene rings, out of/in-plane bending of the C-H bonds (Figure 3.2(c,d)), as well as C–C stretching. The highest frequency modes of DBT are C–H stretch modes which are expected at considerably higher frequencies than all its other modes (Figure 3.2(e)). In this thesis we number the normal modes of DBT according to increasing vibrational frequency resulting from DFT calculations. The symmetry properties of the normal modes of DBT are specified by Mulliken symbols and explained in more detail in section 3.1.3.

### 3.1.2 Vibrational wave functions

The normal mode patterns of a molecule can be found using classical mechanics, but the actual vibrations of a molecule behave quantum mechanically: energy can only be transferred to the vibration in integer multiples of $h\nu$ and even in the lowest energy state the nuclei of the molecule are not at rest but undergo zero-point motion. In this section, we show how the vibrational wave functions of a molecule are derived from the rovibronic Schrödinger equation in the context of the Born-Oppenheimer (BO) approximation. The normal coordinates introduced in the previous section can then be used to separate the vibrational Schrödinger equation of the coupled nuclear motions into a sum of many one-dimensional harmonic oscillator terms. In our arguments and notation of this section we closely follow the presentation in the book by Bunker and Jensen [37].

The quantum mechanical vibrational and rotational behavior of a molecule with $l$ particles ($N$ nuclei, $l-N$ electrons) can be described in a frame moving
with the nuclear center of mass using the rovibronic Schrödinger equation [37, equation (9-48)]:

\[
\left[ \hat{T}_e + \hat{T}_N + V(\vec{R}_N, \vec{r}_e) - E_{\text{rve}} \right] \Phi_{\text{rve}}(\vec{R}_N, \vec{r}_e) = 0,
\] (3.11)

with

\[
\hat{T}_e = -\frac{\hbar^2}{2m_e} \sum_{i=N+1}^{l} \vec{\nabla}_i^2 - \frac{\hbar^2}{2M_N} \sum_{i,j=N+1}^{l} \vec{\nabla}_i \cdot \vec{\nabla}_j = \hat{T}_0^e + \hat{T}_e',
\] (3.12)

\[
\hat{T}_N = -\frac{\hbar^2}{2} \sum_{i=2}^{N} \frac{1}{m_i} \vec{\nabla}_i^2 + \frac{\hbar^2}{2M_N} \sum_{i,j=2}^{N} \vec{\nabla}_i \cdot \vec{\nabla}_j,
\] (3.13)

\[
V(\vec{R}_N, \vec{r}_e) = \sum_{r<s=1}^{l} \frac{C_r C_s e^2}{4\pi \epsilon_0 R_{rs}},
\] (3.14)

where the nuclei and electrons are counted from 1 to \(N\) and from \(N+1\) to \(l\), respectively. \(m_e\) is the mass of an electron, \(m_i\) is the mass of the \(i\)th nucleus, \(M_N\) is the total mass of the nuclei, \(C_i e\) is the charge of particle \(i\), \(R_{rs}\) is the distance between particles \(r\) and \(s\), and the coordinates of the particles (nuclei: \(\vec{R}_N\), electrons: \(\vec{r}_e\)) are defined with respect to the nuclear center of mass. The cross-terms in the kinetic energy operators are related to the transformation to the nuclear center of mass. The wave function \(\Phi_{\text{rve}}\) describes the joint electronic, vibrational, and rotational state of the molecule with energy \(E_{\text{rve}}\).

The rovibronic Schrödinger equation (3.11) can be solved analytically by first applying the BO approximation and then transforming to a suitable coordinate frame that is rotating with the molecule. The BO approximation involves a separation of the rovibronic wave function into a product of an electronic wave function \(\Phi_e(\vec{R}_N, \vec{r}_e)\) and a wave function \(\Phi_N(\vec{R}_N)\) of the nuclear motion. In appendix D.2, we show several steps of the BO approximation that lead to the rotation-vibration Schrödinger equation for the wave function of the nuclear motion \(\Phi_N\):

\[
[\hat{T}_N + V_N(\vec{R}_N)] \Phi_N(\vec{R}_N) = E_{\text{rve}}^0 \Phi_N(\vec{R}_N),
\] (3.15)

with \(V_N = V_{nn} + V_e\), where \(V_{nn}\) stands for the inter-nuclear repulsion and \(V_e\) for the binding potential mediated by the electronic orbital. \(E_{\text{rve}}^0\) is the rovibronic energy of the molecule in the BO approximation.

In a coordinate frame that is moving with the molecular center of mass, the nuclear motion corresponds to rotations and vibrations of the molecule. A
3.1 Vibrational quantum states

Further separation of the rotation-vibration Schrödinger equation (3.15) into two individual equations that describe the rotational and vibrational motion, respectively, can be achieved by a transformation to a coordinate frame that rotates with the molecule. Since we are not dealing with rotational states of molecules in the context of this thesis and the choice of a suitable rotating frame that minimizes coupling between rotational and vibrational motion is non-trivial, we do not reiterate the corresponding derivation here. The books by Wilson et al. [34, chapter 11] and by Bunker and Jensen [37] discuss the related steps in detail. Using the Euler angles $\theta$, $\phi$, and $\chi$ to describe the orientation of the frame that rotates with the molecule, the nuclear wave function can be written as the product $\Phi_N(\vec{R}_N) = \Phi_{\text{rot}}(\theta, \phi, \chi) \Psi_{\vec{v}}(\vec{Q})$ of a rotational wave function $\Phi_{\text{rot}}$ and a vibrational wave function $\Psi_{\vec{v}}$. In the normal coordinate basis, the Schrödinger equation for the vibrational motion is particularly simple [34, 37]:

$$\sum_{k=1}^{N_{\text{vib}}} \left( -\frac{\hbar^2}{2} \frac{\partial^2}{\partial Q_k^2} + \frac{1}{2} \lambda_k Q_k^2 \right) \Psi_{\vec{v}}(\vec{Q}) = E_{\vec{v}} \Psi_{\vec{v}}(\vec{Q}), \quad (3.16)$$

where $\lambda_k$ are the (non-zero) eigenvalues of the Hessian matrix $K$ defined in equation (3.5). Thus, in the normal mode basis, the vibrational Schrödinger equation corresponds to a sum of $N_{\text{vib}}$ independent Schrödinger equations of one-dimensional harmonic oscillators.

The wave function that solves equation (3.16) is [36]:

$$\Psi_{\vec{v}}(\vec{Q}) = \Psi_{v_1}(Q_1) \Psi_{v_2}(Q_2) \cdots \Psi_{v_{N_{\text{vib}}}}(Q_{N_{\text{vib}}}) = \left( \frac{\det(\tilde{\Gamma})}{\pi^{N_{\text{vib}}}} \right)^{1/4} \left(2^{N_{\text{vib}}}(\prod_{i=1}^{N_{\text{vib}}} v_i!)\right)^{-1/2} \exp\left[-\frac{1}{2} \tilde{Q}^T \tilde{\Gamma} \tilde{Q} \right] \prod_{i=1}^{N_{\text{vib}}} H_{v_i}(\tilde{\Gamma}_i). \quad (3.17)$$

This is the product of $N_{\text{vib}}$ single harmonic oscillator wave functions in the normal coordinates $Q_1, Q_2, \ldots, Q_{N_{\text{vib}}}$ with associated vibrational quantum numbers $\vec{v} = (v_1, v_2, \ldots, v_{N_{\text{vib}}})$. The (reduced) frequencies $\tilde{\Gamma}_{ii} = 2\pi\sqrt{\lambda_i}/\hbar = \omega_i/\hbar$ of each oscillator are the entries of the diagonal matrix $\tilde{\Gamma}$ and introduce the quantum mechanical scale for the vibrational wave functions along the normal mode axes. The function $H_i$ denotes the $i$th (physicist's) Hermite polynomial.

---

3 We use $\tilde{\Gamma}$ to denote the matrix of reduced frequencies because the standard notation $\Gamma$ for this matrix is reserved for decay rates in this thesis.
3 Vibronic transitions

(see appendix C.1.2 for more details about harmonic oscillator wave functions). The energy of the vibrational state \( \Psi_\mathbf{\vec{v}}(\mathbf{Q}) \) is

\[
E_\mathbf{\vec{v}} = \sum_{i=1}^{N_{\text{vib}}} \hbar \omega_i (v_i + \frac{1}{2}).
\]  

(3.18)

The vibrational zero-point motion of a molecule follows from equation (3.17) for \( \mathbf{\vec{v}} = \mathbf{0} \):

\[
\Psi_{\mathbf{\vec{v}}=\mathbf{0}}(\mathbf{Q}) = \left( \frac{\det(\mathbf{\tilde{\Gamma}})}{\pi^{N_{\text{vib}}}} \right)^{1/4} \left( 2^{N_{\text{vib}}} \right)^{-1/2} \exp\left[ -\frac{1}{2} \mathbf{\tilde{Q}}^t \mathbf{\tilde{\Gamma}} \mathbf{\tilde{Q}} \right].
\]  

(3.19)

In this state, the variance of the normal coordinate \( Q_i \) is

\[
\Delta Q_{zpm,i}^2 = \langle Q_i^2 \rangle = 1/(2\mathbf{\tilde{\Gamma}}_{ii}) = \hbar/(2\omega_i).
\]  

(3.20)

We will use the zero-point range \( \Delta Q_{zpm,i} \) as the natural scale for the vibrational wave functions and their relative shifts in electronic transitions.

If only a single vibrational quantum number equals one while all others equal zero \( (v_k = 1, v_{\neq k} = 0) \), the fundamental of vibrational mode \( k \) is excited. If instead \( v_k = 1 + n \), the \( n \)th overtone of this mode is excited. Modes for which multiple vibrational quantum numbers are non-zero are combination modes.

As (bra-)ket notation for the vibrational wave function \( \Psi_{\mathbf{\vec{v}}}(\mathbf{Q}) \) of equation (3.17) we use

\[
|\mathbf{\vec{v}}\rangle = |v_1\rangle |v_2\rangle \cdots |v_{N_{\text{vib}}}\rangle.
\]  

(3.21)

For the fundamental of the \( k \)th normal mode we employ the simplified notation

\[
|1_k\rangle = |v_1 = 0\rangle |v_2 = 0\rangle \cdots |v_k = 1\rangle \cdots |v_{N_{\text{vib}}} = 0\rangle,
\]  

(3.22)

similar to the notation used in [87], and we write

\[
|2_k\rangle = |v_1 = 0\rangle |v_2 = 0\rangle \cdots |v_k = 2\rangle \cdots |v_{N_{\text{vib}}} = 0\rangle
\]  

(3.23)

for the first overtone of mode \( k \).

Using \( |S_0\rangle \) and \( |S_1\rangle \) to denote the electronic ground and excited state, respectively, the complete vibronic quantum state \( \Phi_e \Psi_{\mathbf{\vec{v}}} \) of a non-rotating molecule in the BO approximation can be written as:

\[
|S_k, \mathbf{\vec{v}}\rangle = |S_k\rangle |\mathbf{\vec{v}}\rangle,
\]  

(3.24)
with \( k \in \{0, 1\} \). Due to the orthogonality between normal modes in the same electronic state:

\[
\langle S_k, \tilde{v}' | S_k, \tilde{v} \rangle = \langle S_k | S_k \rangle \langle \tilde{v}' | \tilde{v} \rangle = \prod_{i=1}^{N_{\text{vib}}} \delta_{\nu_i, \nu_i'}.
\] (3.25)

Note that while \(|\tilde{v}\rangle\) is a (purely) vibrational state, \(|S_k, \tilde{v}\rangle\) is a vibronic state including vibrational and electronic components. Vibrational states differ depending on the electronic state with which they are associated such that equation (3.25) does not hold if \(|\tilde{v}'\rangle\) and \(|\tilde{v}\rangle\) denote vibrational states associated with different electronic states. A transition \(|S_k, \tilde{v}\rangle \rightarrow |S_{\neq k}, \tilde{v}'\rangle\) is called a vibronic transition (e.g. fluorescence), while \(|S_k, \tilde{v}\rangle \rightarrow |S_k, \tilde{v}'\rangle\) is a vibrational transition (e.g. infrared absorption). In this thesis, we are mainly concerned with vibronic transitions. The overlap between vibronic wave functions associated with different electronic states is discussed in section 3.2.

### 3.1.3 Totally symmetric modes

Transitions to totally symmetric normal modes are generally expected to show the highest intensities in fluorescence spectrum of a molecule in the vibrational ground state if the molecule has the same symmetry in the electronic ground and excited states [35]. This rule is based on the overlap integrals between the vibrational states involved in the vibronic transitions. While the details of these integrals will be discussed in more detail below (section 3.2), we give a brief overview of some important symmetry classifications for molecules in this section using the example of isolated DBT. The discussion can be applied in a similar way to other polyatomic molecules with non-degenerate normal modes.

A totally symmetric normal mode is symmetric under all symmetry operations of the point group of the molecule under consideration. The point group of a molecule is determined based on the set of symmetry operations that map the equilibrium positions of a molecule to themselves. We will not list all possible symmetry operations here (see e.g. [34, 37] for a full list), but merely mention those applicable to the most stable isomer of isolated DBT:

- \( E \): identity
- \( C_2 \): two-fold rotation around the principal symmetry axis of DBT (= the axis parallel to the long side of the terrylene moiety)
- \( i \): inversion
3 Vibronic transitions

The four symmetry operations $E$, $C_2$, $i$, and $\sigma_h$ form the $C_{2h}$ point group and because isolated DBT is symmetric under these operations it belongs to this group. The principal symmetry axis, the inversion center and the mirror plane of a DBT molecule in $C_{2h}$-symmetry are indicated in Figure 3.3(a).

The normal modes of a molecule are either symmetric or antisymmetric under the symmetry operations in the point group of the molecule. This can be expressed via the transformation behavior of the normal coordinates under a symmetry operation:

\[
\text{symmetric: } Q_i \rightarrow +Q_i \quad (3.26) \\
\text{antisymmetric: } Q_i \rightarrow -Q_i. \quad (3.27)
\]

If a mode transforms antisymmetrically under a symmetry operation, its displacement vectors are mapped to the $\pi$-phase shifted version of themselves (see Figure 3.2(b) for a normal mode of DBT, which is antisymmetric under rotation and inversion and symmetric under reflection). For a molecule in a given point group there is a limited number of combinations of how the molecular normal modes can transform under all symmetry operations of the group. These combinations are listed in the lines of the character table of the point group. Each of the lines is one irreducible representation of the point

---

The symbol $C_{2h}$ is part of the Schönflies notation for point groups. All molecules with one two-fold rotation axis and one reflection plane perpendicular to this axis belong to this group (e.g. butane and oxalic acid). See [37] for a definition of all Schönflies symbols.
3.2 Franck-Condon factors

Franck-Condon (FC) factors quantify the overlap between vibrational wave functions associated with two distinct electronic states of a molecule. This overlap is relevant to the selection rules and the relative intensities of vibronic transitions in a molecule. In this section, we give an overview of the theoretical basics of FC overlaps for diatomic (see section 3.2.2) and polyatomic molecules (see section 3.2.3). Many important aspects of the FC physics of DBT are explained by the example of the diatomic molecule, because many modes of DBT are similar between ground and excited states and display negligible mode mixing.

---

5 The $D_{2h}$ group contains all molecules with a two-fold rotation axis, two two-fold rotation axes perpendicular to this axis, and a reflection plane perpendicular to the (main) two-fold rotation axis (e.g. ethene and diborane). The Mulliken symbols of the $D_{2h}$ group are $A_g$, $A_u$, $B_{1g}$, $B_{1u}$, $B_{2g}$, $B_{2u}$, $B_{3g}$, $B_{3u}$ [37].
3.2.1 Franck-Condon principle

The change in the electronic state triggers the rearrangement of the nuclei from the equilibrium positions of the initial state to the equilibrium positions of the final state. Whether a molecular normal mode is excited in this process depends on the difference of the equilibrium positions and on the instantaneous positions of the nuclei at the moment of the electronic state change. The FC principle is the basis on which the relevant quantum mechanical transition probabilities are calculated.

The basic assumption of the FC principle is that the change in the electronic state is so fast compared to the motion of the nuclei that it can be regarded as instantaneous (this is equivalent to the BO approximation). This idea was first raised by Franck in 1926 [91] and was put into a mathematical framework by Condon [92–94]. In a classical picture, the nuclei of the molecule begin to oscillate around their new equilibrium positions starting from their (equilibrium) positions at the moment of the electronic state change [35]. In the quantum mechanical description, the nuclei are delocalized within a range defined by their wave functions and consequently there is a number of vibrational states in which the molecule can end up. The corresponding probabilities are given by the FC factors which are the squared overlap integrals between two vibrational wave functions with shifted origins.

In the dipole approximation, the probability for a radiative transition between an initially excited vibronic state $|S_m, \vec{v}'\rangle$ and a final vibronic state $|S_n, \vec{v}\rangle$ is proportional to the modulus square of the dipole matrix element $\langle S_m, \vec{v}'| \hat{\vec{d}}_{\text{tot}} | S_n, \vec{v} \rangle$. The FC principle applies to transitions between different electronic states ($m \neq n$). In the context of this thesis, we are only concerned with electronic ground and first excited states ($m, n \in \{0, 1\}$). The dipole moment of the molecule can be expressed as

$$\hat{\vec{d}}_{\text{tot}} = e \sum_{i=1}^{N} C_i \vec{R}_i - e \sum_{i=N+1}^{l} \vec{r}_i = \hat{\vec{d}}_N + \hat{\vec{d}}_E,$$

(3.28)
3.2 Franck-Condon factors

with \( \vec{r}_i \), the positions of the electrons and \( \vec{R}_i \), the positions of the nuclei. The matrix element for the dipole transition can be simplified in the BO approximation as follows:

\[
\langle S_m, \vec{v}' | \hat{d}_{\text{tot}} | S_n, \vec{v} \rangle = \langle S_m, \vec{v}' | \hat{d}_N | S_n, \vec{v} \rangle + \langle S_m, \vec{v}' | \hat{d}_E | S_n, \vec{v} \rangle =
\]

\[
= \langle S_m | S_n \rangle \langle \vec{v}' | \hat{d}_N | \vec{v} \rangle + \langle \vec{v}' | \langle S_m | \hat{d}_E | S_n \rangle | \vec{v} \rangle =
\]

\[
(3.29)
\]

where we use the orthogonality of the different electronic states \( \langle S_m | S_n \rangle = \delta_{mn} \), assume that \( m \neq n \), and write \( \hat{d}_0(\vec{Q}) = \langle S_m | \hat{d}_E | S_n \rangle \) for the electronic transition dipole moment. \( \hat{d}_0(\vec{Q}) \) depends on the nuclear positions via the electronic states \([87, 95]\). Developing \( \hat{d}_0(\vec{Q}) \) around small values of the normal coordinates

\[
\hat{d}_0(\vec{Q}) = \hat{d}_0(\vec{Q} = \vec{0}) + \left[ \nabla_{\vec{Q}} \hat{d}_0(\vec{Q}) \right]_0^T \vec{Q} + ...
\]

(3.32)

yields

\[
\langle S_m, \vec{v}' | \hat{d}_{\text{tot}} | S_n, \vec{v} \rangle \approx \hat{d}_0(\vec{Q} = \vec{0}) \langle \vec{v}' | \vec{v} \rangle + \langle \vec{v}' | \left[ \nabla_{\vec{Q}} \hat{d}_0(\vec{Q}) \right]_0^T \vec{Q} | \vec{v} \rangle
\]

(3.33)

by including terms up to the linear order \([87]\). In the case of a weak electronic transition, the linear (Herzberg-Teller \([35]\)) term of the series (3.33) can become important. For strong electronic transitions, this term typically only leads to minor corrections. The integral related to the constant term in equation (3.33),

\[
I(\vec{v}', \vec{v}) = \langle \vec{v}' | \vec{v} \rangle = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} ... \int_{-\infty}^{\infty} \Psi_{\vec{v}'}(\vec{Q}') \Psi_{\vec{v}}(\vec{Q}) dQ_1 ... dQ_{N_{\text{vib}}}
\]

(3.34)

is the FC integral and

\[
FC(\vec{v}', \vec{v}) = |I(\vec{v}', \vec{v})|^2
\]

(3.35)

is the FC factor of the transition between the states \( |S_m, \vec{v}' \rangle \) and \( |S_n, \vec{v} \rangle \). The effect of the molecular vibrations on the electronic dipole moment is thus not taken into account in the FC approximation. By using \( I(\vec{v}', \vec{v}) \) for the overlap integral, we follow the standard notation from the literature. Note that the intensity of a vibronic line is not proportional to \( I(\vec{v}', \vec{v}) \), but to \( FC(\vec{v}', \vec{v}) \). The FC factors fulfill the condition

\[
\sum_{v_1=0}^{\infty} \sum_{v_2=0}^{\infty} ... \sum_{v_{N_{\text{vib}}}=0}^{\infty} FC(\vec{v}', \vec{v}) = 1
\]

(3.36)
3 Vibronic transitions

Figure 3.4: Franck-Condon principle for a diatomic molecule. (a) Vibrational wave functions and probability densities (filled curves with light and dark color, respectively) of two electronic states with the equilibrium positions of the nuclei shifted by $\Delta Q = \Delta Q_{zpm}$. Black lines: potential energy $V = \omega^2 Q^2 / 2$. This picture is applicable to a diatomic molecule or to normal modes of a polyatomic molecule that do not mix between the electronic states. (b) Franck-Condon factors $FC(\nu, \nu')$ for $\Delta Q = \alpha \cdot 2\Delta Q_{zpm}$ (see text and equations (3.40) and (3.41)). Solid lines: same vibration frequency in ground and excited state. Colored dashed lines: $\omega / \omega' = 1.2$. Black dashed line: $FC(0, 2)/FC(0, 1)$. (c) Relative change in the Franck-Condon factor $FC(0, 1)$ for frequency differences of 1% and 2% between ground and excited state.

and can thus be regarded as the probability of decay from an initial state $|\tilde{\nu}'\rangle$ to $|\tilde{\nu}\rangle$. To calculate the FC integral (3.34), one must take into account that the equilibrium positions, normal coordinates, and the curvature of the harmonic potential can change between ground and excited states. Since we are working at low temperatures with vanishing thermal population in the vibrational states, we are mainly interested in the situation in which the initial state is in the vibrational ground state $\tilde{\nu}' = \tilde{0}$, i.e. either $|S_0, \tilde{0}\rangle$ or $|S_1, \tilde{0}\rangle$.

The contribution of the linear term in equation (3.33) is called Herzberg-Teller correction [35, 87]. According to DFT simulations, this term causes intensity corrections in the few percent range compared to the strongest vibronic features for DBT. Herzberg-Teller corrections are thus not expected to be relevant to a theoretical description of the prominent vibronic features discussed in this thesis.

3.2.2 Diatomic molecules

Diatomic molecules only have one vibrational mode, the symmetric stretch mode (see Figure 3.1(a) and appendix C.1). The FC analysis of a diatomic molecule returns the squared overlap integrals $FC(\nu', \nu) = |I(\nu', \nu)|^2$ for transitions from the $\nu'$th overtone of the stretch mode in the initial electronic
3.2 Franck-Condon factors

state to the \( v \)th overtone of the stretch mode in the final electronic state. Note that this situation is significantly less complex than for a polyatomic molecule, where the transition rates between different vibrational modes must be analyzed as well (see section 3.2.3).

Overlap integrals of the vibrational wave functions of diatomic molecules were explicitly calculated for the first time by Hutchisson in 1930 [96]. Later, the calculations were extended to account for frequency differences in ground and excited states [97–99] as well as for anharmonicity of the potential [100, 101]. The theoretical approaches either directly evaluate the integrals of the harmonic oscillator wave functions [97, 98, 102] or make use of an operator approach [99, 101].

Figure 3.4(a) illustrates the vibrational wave functions of \(|S_0\rangle\) and \(|S_1\rangle\) for the case that the distance between the nuclei is larger in \(|S_1\rangle\) than in \(|S_0\rangle\). For such an extended diatomic molecule, the normal coordinates \( Q' \) and \( Q \) in \(|S_1\rangle\) and \(|S_0\rangle\), respectively, are related via

\[
Q' = Q - \Delta Q = Q - \alpha \cdot 2\Delta Q_{zp}\tag{3.37}
\]

with \( \alpha = \Delta Q / (2\Delta Q_{zp}) \in \mathbb{R} \) and \( \Delta Q = \sqrt{\mu \Delta l} \). The reduced mass of the molecule is given by \( \mu = m_1 m_2 / (m_1 + m_2) \), where \( m_1 \) and \( m_2 \) are the masses of the nuclei. \( \Delta l \) denotes the length change in the molecule between \( S_0 \) and \( S_1 \) (see appendix C.1). \( \Delta Q_{zp} \) is the range of the zero-point motion as defined in equation (3.20) and appendix C.1.2. The parameter \( \alpha \) thus quantifies the equilibrium position shift between two electronic states with larger values of \( \alpha \) corresponding to a larger shift. Assuming identical oscillation frequencies \( \omega' = \omega \) in both electronic states and no anharmonic effects leads to the solution (for \( v \geq v' \)):

\[
I(v', v) = \int_{-\infty}^{\infty} \Psi_{v'}(Q') \Psi_{v}(Q) dQ = \alpha^{v-v'} \left( \frac{v!}{v'}! \right)^{\frac{1}{2}} e^{-\frac{1}{2} \alpha^2} L_{v-v'}^m(\alpha^2), \tag{3.38}
\]

where the \( L_n^{m-n} \) are the associated Laguerre polynomials [97–99].

For transitions starting from the vibrational ground state \(|S_i, v' = 0\rangle\), equation (3.38) simplifies to

\[
I(v', 0) = \frac{\alpha^v}{\sqrt{v!}} e^{-\frac{1}{2} \alpha^2} \tag{3.39}
\]

\[ L_0^n(x) = 1, L_1^n(x) = 1 + n - x, \ldots \]
and the corresponding FC factors are given by a Poisson distribution with parameter $\alpha^2$:

$$FC(v' = 0, v) = \frac{(\alpha^2)^v}{v!} e^{-\alpha^2}. \quad (3.40)$$

Figure 3.4(b) shows plots of equation (3.40) for different values of $\Delta Q$ and $v$. For $\Delta Q \ll 2\Delta Q_{zpm}$ a diatomic molecule is most likely to make a transition to the vibrational ground state $|v = 0\rangle$. With increasing $\Delta Q$, the probability of making transitions to states $|v > 0\rangle$ increases. At $\Delta Q = 2\Delta Q_{zpm}$, the molecule is equally likely to decay to $v = 0$ or $v = 1$. For even higher values of $\Delta Q$, the probability of decaying to highly excited vibrational states increases. Note that as a consequence, it is not possible to strongly activate a single vibrational line (e.g. only the fundamental excitation with $v = 1$) in a molecular emission spectrum while keeping all other overtones weak.

The FC integral can also be solved analytically if the vibrational frequencies in ground and excited states differ. For transitions starting from the vibrational ground state one obtains:

$$I(0, v) = \left(\frac{v!}{2^{v-1}}\right)^{\frac{1}{2}} \left(\frac{\omega \omega'}{\omega_+^2}\right)^{\frac{1}{4}} \left(\frac{\omega - \omega'}{\omega_+}\right)^{\frac{v}{2}} e^{-\frac{1}{2} \frac{\omega \omega' \Delta Q^2}{\hbar}}$$

$$\cdot \sum_{j \in A} \frac{(2\omega \omega')^{\frac{j}{2}}}{(\omega_+ \omega_-)^{\frac{j}{2}}} \frac{1}{(v-j)!j!} \left(\frac{\omega_+ \frac{1}{2} \Delta Q}{\hbar}\right)^j \quad (3.41)$$

with $A = \{v \mod 2, v \mod 2 + 2, ..., v\}$, $\omega_+ = \omega + \omega'$, and $\omega_- = \omega - \omega'$ (following Iachello and Ibrahim [100]). This result differs from the result in equation (3.39) because a change in the vibrational frequency affects the width of the vibrational wave functions and thus their overlap integrals. Also note that while equation (3.39) can be regarded as an overlap between a Fock state and a coherent state, equation (3.41) corresponds to the overlap between a Fock state and a squeezed state. In the limit $\omega' \to \omega$ equation (3.41) reduces to equation (3.39). We refer the reader to the various approaches published in [97–100] for the solutions of the integrals $I(v', v)$ given arbitrary values of the quantum numbers $v'$ and $v$ and vibrational frequencies $\omega'$ and $\omega$. In Figure 3.4(c) we show how much the FC factor of the transition from $|v' = 0\rangle$ to $|v = 1\rangle$ is affected if the vibrational frequency differs by 1% and 2% between the two electronic states. The relative probability change $\Delta FC(0, 1)/FC(0, 1)$ is less than 1% for values of $\Delta Q$ that are relevant to DBT (see also section 3.2.3).
3.2 Franck-Condon factors

3.2.3 Polyatomic molecules

The spontaneous decay of a molecule with more than two nuclei can promote it to various vibrational modes. This is related to the fact that the vector $\Delta \vec{R} = \vec{R}_{S_1} - \vec{R}_{S_0}$ connecting the equilibrium positions of the atoms in electronic ground and excited states can contain contributions from many normal modes. If the projection of a normal mode on $\Delta \vec{R}$ is high, the probability of exciting it during spontaneous emission is high. This is one way to phrase the FC principle for polyatomic molecules and the idea inspired by a classical picture that a molecule will start to oscillate in those modes whose turning points correspond to the equilibrium positions in the state from which it decays [35].

In order to solve the FC integral (3.34) for a polyatomic molecule, the normal coordinates in one state need to be expressed in terms of the normal coordinates in the other state. Assuming a linear relationship, one can write

$$\vec{Q}' = J\vec{Q} + \vec{K},$$

(3.42)

a formula first introduced by Duschinsky in 1937 [36, 103, 104]. The Duschinsky matrix $J = (I_{ \text{mwc}})^T I_{ \text{mwc}}$ defines how the normal coordinates of the final state $\vec{Q}$ mix to result in the normal coordinates $\vec{Q}'$ of the initial state. The shift vector $\vec{K} = (I_{ \text{mwc}})^T M^{1/2} \Delta \vec{R}$ is the projection of the equilibrium position change between $S_0$ and $S_1$ to the normal coordinate basis of the initial state.

Throughout this thesis we assume that the molecules do not change their symmetry group between $S_0$ and $S_1$. Duschinsky realized that in this case only modes of the same irreducible representation are mixed by the transformation between electronic states (3.42) (in the $C_{2h}$ group: $A_g$ modes in $S_0$ can be expressed as linear combinations of $A_g$-modes in $S_1$; the same holds for the other Mulliken symbols $A_u$, $B_g$, and $B_u$ of this this point group [103]). Additionally, as already pointed out by Herzberg and Teller in 1933 [35], an entry $K_i$ can only be non-zero if it belongs to a totally symmetric normal coordinate $Q'_i$. Besides that there are other ways than displacement of the nuclei to activate non-totally symmetric modes. These effects include a change in vibrational frequency between the electronic states [36], Herzberg-Teller effects [35, 105–108], isotopic substitution [63, 109], Duschinsky mode mixing [103, 104], or anharmonic effects [110]. The contributions of these effects are, however, mostly (but not always) minor corrections to the structure of the FC spectrum defined by the shifts in the equilibrium positions. As a consequence, if the transition starts in the vibrational ground state, totally symmetric modes are expected to have the highest FC factors [35]. We illustrate one example of this important principle using the linear triatomic molecule in appendix 41.
C.2.2, showing that the FC integral necessarily equals zero for all odd quantum numbers of the antisymmetric stretch mode. For (non-zero) even quantum numbers of this mode, the FC integral only vanishes if the mode has the same frequency in $S_0$ and $S_1$. A rigorous formulation of the symmetry principles that play a role in the relative vibrational intensities and selection rules can be found in the book by Bunker and Jensen [37].

In 1964, Sharp and Rosenstock introduced a method for the calculation of FC factors of polyatomic molecules based on generating functions [36]. Besides general formulas for a number of transitions between states with different vibrational quantum numbers, Sharp and Rosenstock show with their formalism that the transition from $|S_1, \vec{0}\rangle$ to the antisymmetric stretch mode of a linear triatomic molecule only has a non-vanishing FC factor if the vibrational frequencies in the two states are different. Similar approaches and/or notation to that in [36] have been adopted in many subsequent papers on this topic [87, 111–113]. Doktorov et al. introduced an alternative approach in 1975 using coherent states to solve the FC integrals [114–116]. A more detailed overview of the literature on polyatomic FC integrals can be found in section II.A of the paper by Jankowiak et al. [116].

The algorithm used in Gaussian 16 combines the formalism of Sharp and Rosenstock [36] with the iterative approach by Ruhoff et al. [111] to calculate FC factors of polyatomic molecules. As input, it requires the matrices $I_{mwc}$ and $I_{mwc}$, the vibrational frequencies of all modes in both states (the elements of the diagonal matrices $\tilde{\Gamma}'$ and $\tilde{\Gamma}$) and $\Delta \vec{R}$. Using these quantities, the overlap integral between the vibrational ground states of both electronic states can be computed using the formula [36, 87]:

$$I(\vec{0}, \vec{0}) = 2^{N/2} \frac{\det(\tilde{\Gamma}')^{1/4}}{\det(J^t \tilde{\Gamma}' J + \tilde{\Gamma})^{1/2}} \cdot \exp\left(-\frac{1}{2} \vec{K}^t \tilde{\Gamma}' \vec{K} + \frac{1}{2} \vec{K}^t J^t \tilde{\Gamma}' J + \tilde{\Gamma} - 1 J^t \tilde{\Gamma}' J \right).$$

Equation (3.43) and the formulas in appendix D.3 were used to calculate the theoretical vibronic spectra presented in this thesis (e.g. those shown in Figure 3.6 and Figure 6.23).
3.2 Franck-Condon factors

Figure 3.5: Change in the equilibrium positions and the normal mode structure of isolated DBT between $S_0$ and $S_1$ (DFT results). (a,b) Equilibrium structure of DBT in $S_0$ (black and red atoms) and a version in which the atoms are displaced by $20\Delta \vec{R}$ from their positions in $S_0$ (blue and green atoms), shown from two different angles. (c) Entries of the vector $\vec{K}$ from equation (3.42) for the calculation shown in (a,b), but for the actual value of $\Delta \vec{R}$. (d) Diagonal entries of the matrix 2C of isolated DBT indicating typical frequency differences between $S_0$ and $S_1$. (e) Duschinsky matrix $J$ of isolated DBT. In (c,d,e) we assumed that $S_1$ and $S_0$ are the initial and the final electronic states, respectively.

In Figure 3.5(a,b) we show DFT simulations of the equilibrium structure of isolated DBT in $S_0$ together with a version of DBT in which the atoms are displaced 20 times as much as during the actual change between $S_0$ and $S_1$ to make the direction of change visible. The average displacements of carbon and hydrogen atoms between the two electronic states $S_0$ and $S_1$ of DBT are 1.7 pm and 1.2 pm, respectively. Figure 3.5(c) shows the entries of the displacement vector $\vec{K}$ for the case that $S_1$ is the initial and $S_0$ the final electronic state. As predicted, the modes that contribute non-vanishing values to $\vec{K}$ are all totally symmetric. The frequency differences between ground and excited
state normal modes can be quantified using the $C$-matrix from Sharp and Rosenstock [36]:

$$C = 2\tilde{\Gamma}^{1/2}(J^T \tilde{\Gamma} J + \tilde{\Gamma})^{-1}\tilde{\Gamma}^{1/2} - I.$$  \hspace{1cm} (3.44)

In the one-dimensional case, this corresponds to $C = (\omega - \omega')/(\omega + \omega')$ and in the multi-dimensional case it contains additional information about mixed modes. The plot of the diagonal entries of $C$ resulting from the DFT calculations for isolated DBT in Figure 3.5(d) shows that the frequencies of the normal modes do not change significantly between $S_0$ and $S_1$. Note that we show $2C_{ii}$ in the plot because these values correspond to the actual frequency differences. The Duschinsky matrix $J$ resulting from the DFT calculations of isolated DBT in $C_{2h}$ symmetry is shown in 3.5(e). The fact that $J$ only has few off-diagonal entries indicates that modes of DBT do not mix strongly between ground and excited states. The average of the maximum values of $|J_{ij}|$ in each line is 0.95. In this thesis, we assign mode indices to the normal modes according to increasing vibrational frequency (as resulting from Gaussian 16 calculations). Because the order of the vibrational frequencies of the modes changes slightly between $S_0$ and $S_1$ due to changes in the interatomic potential, there are some cases in which two modes change order without mixing. An example of modes that actually do mix strongly are the $B_g$-modes 51, 53, and 61. They combine like $Q'_{51} \approx 0.64Q_{51} + 0.74Q_{53} + 0.19Q_{61}$ to yield the normal modes.

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$^7$ We calculated $J$ based on the normal modes in $S_0$ and $S_1$ as returned by the calculations using Gaussian 16. Since some of the normal modes in $S_1$ are defined with an opposite sign compared to their $S_0$ counterparts, we manually flipped the (arbitrarily defined) signs of those modes $i$ in $S_1$ with $\sum_j J_{ij} < 0$ to remove entries in $J$ that are close to $-1$. 

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Figure 3.7: Displaced harmonic oscillator approximation and full solution of the FC factors for all modes of isolated DBT in $C_{2h}$-symmetry (based on DFT simulations). The data are shown as a function of the mode index $i$ in the electronic ground state $S_0$, which is assumed to be the final electronic state. (a) Black dots: indices $s(i)$ of the modes in the excited state of DBT that match the modes of the ground state of DBT most closely. Orange line: corresponding absolute value of the entry in the Duschinsky matrix. (b) $\alpha$-values resulting from equation (3.46) for all modes of isolated DBT. The mode indices of prominent modes are explicitly indicated by numbers. (c) Comparison of the FC factors obtained from the full model [87] and the displaced oscillator approximation.

coordinate $Q'_{51}$ of the excited state. For modes with mode numbers between 110 and 130, the mode mixing is more pronounced than for the others.

Figure 3.6 displays calculated FC factors of fundamental and higher vibrational excitations of isolated DBT obtained from the algorithm described by Barone et al. [87]. While the 00-ZPL clearly dominates the spectrum, the highest intensities in the vibrational part of the spectrum belong to fundamental excitations. Some overtones and combination modes that involve prominent fundamental excitations have intensities comparable to the intensities of weaker fundamentals. Most of the combination modes are, however, very weak compared to the main vibronic lines.

For DBT one obtains a reasonable approximation for the FC integrals by ignoring the Duschinsky mode mixing. We define a function $s$ that matches the indices of the most similar modes in $S_0$ and $S_1$ and is shown for isolated DBT in Figure 3.7(a). The value of $s(i)$ is the index of the entry in $J_i$ (=ith
column of $J$) with the maximum absolute value. With this definition, one can introduce an approximation for the polyatomic FC integral (3.34) by expressing it as a product of two-dimensional FC integrals [117–119]:

$$I(\vec{v}', \vec{v}) = \langle \vec{v}' | \vec{v} \rangle \approx \prod_{i=1}^{N_{\text{vib}}} \langle v'_s(i) | v_i \rangle.$$  (3.45)

In this approximation, one can assign a parameter

$$\alpha_i = \frac{\Delta Q_i}{2\Delta Q_{i,zpm}} = \sqrt{\frac{\omega_i}{2\hbar}} K_{s(i)}$$  (3.46)

to each mode (as introduced in equation (3.37) for the diatomic molecule; see also equations (3.20) and (3.42)) and write

$$I(\vec{0}, \vec{v}) \approx \prod_{i=1}^{N_{\text{vib}}} \alpha_i^{v_i} e^{-\frac{1}{2} \alpha_i^2}$$  (3.47)

as in equation (3.39). For the 00-ZPL, this yields the FC overlap integral [120]:

$$I(\vec{0}, \vec{0}) \approx \prod_{i=1}^{N_{\text{vib}}} e^{-\frac{1}{2} \alpha_i^2} = e^{-\frac{1}{2} \sum_{i=1}^{N_{\text{vib}}} \alpha_i^2}.$$  (3.48)

This approximation is the displaced harmonic oscillator model of non-mixing normal modes [118].

Equation (3.48) shows that an increasing number of vibrational states and increasing displacement of the nuclei between $S_0$ and $S_1$ lead to a drop in the intensity of the 00-ZPL. Polycyclic aromatic hydrocarbon molecules such as Tr [121], DBT [25, 122], dibenzanthanthrene (DBATT) [123], and many others [4] are attractive for single molecule spectroscopy because of their strong 00-ZPL lines. A strong 00-ZPL provides a high extinction cross section of the molecule and high count rates of indistinguishable photons if used as a single photon source. Often, these molecules are modeled as two-level systems in which the red-shifted emission to vibrational levels and intersystem crossing events act as loss channels. The fact that their 00-ZPL is so dominant implies that the equilibrium positions of their nuclei are very similar for $S_0$ and $S_1$.

For isolated DBT we obtain $FC(\vec{0}, \vec{0}) = 0.32$ in the displaced oscillator model (3.48) (see Figure 3.7(b) for the values of the $\alpha_i$ used for this calculation). The more complex model from Barone et al. [87] yields a similar value of
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\[ FC(\vec{0}, \vec{0}) = 0.31 \] using equation (3.43). Experiments often report the ratio of \( I_{\text{ZPL}} \), the intensity of the 00-ZPL, to \( I_{\text{tot}} \), the total fluorescence emission from the molecule to all states of the electronic ground state.\(^8\) In solid state systems, \( I_{\text{ZPL}}/I_{\text{tot}} \) is smaller than \( FC(\vec{0}, \vec{0}) \) due to energy transfer to the matrix (see section 2.2). The two quantities are connected by the Debye-Waller factor: \( I_{\text{ZPL}}/I_{\text{tot}} = \alpha_{\text{DW}} \cdot FC(\vec{0}, \vec{0}) \).\(^9\) Experimentally, \( I_{\text{ZPL}}/I_{\text{tot}} = 0.33 \) has been reported for DBT:Ac \(^{124}\) and \( I_{\text{ZPL}}/I_{\text{tot}} = 0.44 \) for DBT:pDCB \(^{25}\). There are several possible reasons for why these values are higher than expected based on the DFT calculations mentioned in the previous paragraph. In both experimental studies \(^{25, 124}\), the spectral range of the emission spectrum used to determine the total fluorescence emission did not cover the full range of vibrational modes. Since intensity in some higher-lying vibrational states is missed that way, the experimental values of \( I_{\text{tot}} \) are too small and the resulting values of \( I_{\text{ZPL}}/I_{\text{tot}} \) are biased towards higher values. As stated by Verhart et al. \(^{25}\), their result can additionally be biased by chromatic effects and background. Moreover, according to the calculations shown in section 6.3, crystal-induced deformations lead to an increase of \( FC(\vec{0}, \vec{0}) \) to values around 0.36, yielding a closer agreement between theory and experiment.

Applying equation (3.46) to the DFT simulations for isolated DBT results in \( |\alpha_{17}| \approx 0.44 \) for mode 17 (the most intense vibronic mode, numbered according to the mode order in \( S_0 \)). Based on equation (3.47) of the non-mixing displaced harmonic oscillator approximation, one obtains the relation \( \alpha_i = \langle \vec{0}|\vec{z}_i\rangle/\langle \vec{0}|1_i\rangle \). From the full calculation using the method by Barone et al. \(^{87}\), we obtain the FC factors \( |\langle \vec{0}|1_{17}\rangle|^2 = 5.9\% \) and \( |\langle \vec{0}|2_{17}\rangle|^2 = 0.57\% \), and hence \( |\langle \vec{0}|2_{17}\rangle|/|\langle \vec{0}|1_{17}\rangle| = 0.31 \). The deviation of this value from the value obtained in the non-mixing approximation indicates that the validity of this approximation is limited. Nevertheless, both values show that the vibronic transitions to fundamentals carry considerably more intensity than their overtones or combination modes in DBT.

3.2.4 Deformed molecules

A deformation of the molecule by external forces, e.g. by a host crystal into which the molecule is embedded, leads to a change in the line intensities in its

\(^8\) To prevent confusion regarding the notation, we remark that \( I(\vec{v}, \vec{v}') \) refers to an FC overlap integral and is proportional to the square root of the intensity. \( I_{\text{ZPL}} \) refers to the intensity of the 00-ZPL in a fluorescence emission spectrum.

\(^9\) In general: \( \alpha_{\text{DW}} \leq 1 \). Türschmann et al. estimate \( \alpha_{\text{DW}} \approx 0.66 \) for DBT:Ac \(^9\). Clear et al. obtained similar values \(^{40}\).
Vibronic transitions

fluorescence spectrum. The line intensities change because $\Delta \vec{R}$ will generally change as the molecule is deformed [125]. Additionally, the deformation of a molecule may break some of its symmetries and move it to a group of lower symmetry (i.e. a point group containing fewer symmetry operations). In a group of lower symmetry, more normal modes are totally symmetric, can gain FC overlap, and appear in the fluorescence spectrum. If new lines appear in the emission spectrum of a molecule, this can be used to identify deformations. Matrix-induced conformational changes can also affect the frequencies of the vibrational peaks, but for PAHs the line intensities have been reported to be more sensitive to deformations than the corresponding wavenumbers [109, 126].

Vibronic spectra have been reported to depend on the spectroscopic site of molecules in their host matrix. In a study of Tr:PE by Tchénio et al., molecules could be classified into two categories based on the intensities and positions of lines in their emission spectrum [109, 127]. This may be related to stronger external forces acting on the molecule in crystalline regions of PE compared to amorphous regions. Additionally, the vibrational frequencies increased for the molecules with the lowest oo-ZPL frequencies in the crystalline regions, possibly because they reside in smaller crystal cages. Reversible light-induced spectral jumps of the oo-ZPLs of Tr molecules in pT are accompanied by a change in the relative intensities of two vibrational lines in the emission spectrum [128]. Also for the combinations Tr:pT [126] and Pc:pT [129], the relative line intensities in vibrational spectra have been reported to depend on the spectroscopic site of the oo-ZPL. For DBT:Ac, fewer fluorescence lines have been observed in the red site than in the main site [26, 84]. The vibronic lines of molecules in red sites of DBT:Nt appear more intense than in the main site, indicating large average values of $|\Delta \vec{R}|$ in the red sites [86]. While such observations of site-specific vibronic spectra suggest a relation to the molecular conformation, we are not aware of simulations that are able to explain the variation of vibronic line intensities based on site-specific deformations of the molecules.

In addition to systematic differences between spectroscopic sites, the vibronic spectra differ on the level of individual molecules [126, 129, 130]. In 2,3-dimethylnaphthalene (DMN) [86] and DMA [85], crystals with dipolar disorder, the vibronic lines of out-of-plane modes were observed to differ strongly between molecules. Using quantum chemical simulations, it was found that DBT is pressed into a flatter structure in DMN. Deperasińska et al. conjecture that this leads to stronger interaction of out-of-plane modes with the crystal and causes the larger spread of the vibrational frequencies between molecules.
in DMN. Such observations of inter-molecular differences also indicate that local defects in the matrix can cause intensity changes which are comparable to or even larger than those between different spectroscopic sites. Note that in addition to deformations, differences between individual molecules can be caused by the presence of $^{13}$C isotopes at various positions in some molecules. Tchénio et al. found that replacing a single $^{12}$C atom by a $^{13}$C atom can lead to a wavenumber shift by 2 cm$^{-1}$ and intensity loss of about 30% of a vibronic line of Tr [63].

If the spectra of molecules in a new matrix contain new lines that were not present in previous matrices or are not expected based on normal mode simulations, this indicates matrix-induced deformation. For Tr:pT more lines were observed in the emission spectra than for Tr:PE [126]. Kummer et al. explain the appearance of the mode at around 255 cm$^{-1}$ in Tr:pT by a non-planar conformation of Tr in its electronic ground state. They further propose that the intensity ratio of this mode and a close-by totally symmetric mode can be used to quantify how much Tr is distorted from the planar conformation. The appearance of strong, previously unobserved lines in fluorescence excitation spectra has been reported for Tr:Nt [125, 131] as well as Tr in 2,3-dichloronaphthalene (DCN) and Tr in 2,3-dibromonaphthalene (DBN) [90]. By simulating the effect of crystal-induced geometry changes on the FC factors, these additional lines could also be explained by non-planar deformations of Tr in $S_1$.

The explanation of deformation-induced lines in a spectrum requires appropriate simulation methods. Calculations of the normal mode structure and the wavenumbers of totally symmetric modes serve as a first indication of the wavenumbers at which lines are expected to appear in a spectrum. The empirical methods developed by Ohno [132–134] have been used as a reference for many spectra of PAHs reported in the literature, e.g. in [55, 109]. As an alternative approach, the semi-empirical AM1 method [135] has been used to calculate normal modes [127]. If strong lines appear at positions in a spectrum where no totally symmetric mode is expected this indicates that the molecule has a different equilibrium structure with fewer symmetry elements than assumed for the normal mode calculations.

A pure normal mode analysis of the ground state structure, however, does not provide estimates of the FC factors. In order to obtain FC factors, equilibrium and mode structure of the electronically excited state must be known as well [36]. While simplified empirical approaches such as that of Ohno [118] or the QCFF/PI+CISD method [136] have been applied to estimate FC overlaps [63, 109], an ab initio quantum chemical treatment appears more appropriate.
Figure 3.8: ONIOM calculation for terrylene (Tr) in naphthalene (Nt) and deformation-induced activation of a line in the vibronic spectrum. (a) Optimized conformation of Tr surrounded by 36 Nt molecules. The crystal distorts the planar conformation of the isolated Tr molecule and reduces its symmetry from $D_{2h}$ to $C_i$. The elements of the $C_i$ point group are: identity $E$ and inversion $i$. (b) The crystal-induced deformation leads to activation of a vibronic line close to the strong line at around 250 cm$^{-1}$ as observed experimentally (bottom panel: isolated Tr, middle panel: Tr:Nt). To obtain closer quantitative agreement with the experimental spectra [131], the crystal-induced deformation was enhanced manually (top panel). Parts (a) and (b) reprinted from [125] with permission from Elsevier.

for this purpose. Excited state calculations are challenging and computationally expensive and a topic of active research [137, 138]. Time-dependent DFT (TD DFT) quantum chemical calculations now yield close agreement with experimental findings. Combined with the B3LYP exchange-correlation functional and the 6-31G* or 6-311+G** basis set, TD DFT methods have successfully described spectra of PAHs [139, 140]. Deperasińska et al. and the Kozankiewicz group used these and similar basis sets for TD DFT simulations of Tr and DBT to calculate their vibronic spectra [85, 86, 141]. Vibronic lines caused by deformation can be generated in the simulated spectra by running the vibrational analysis on molecules that were manually deformed away from their optimized equilibrium structure [90, 125]. If such deformation results in a spectrum that reproduces the experimental data, one can assume that it mimics the effect of the crystal.

Including the host matrix in the calculations allows direct simulation of the matrix-induced effects on the conformation of the guest molecule. Molecular dynamics approaches have successfully been used to simulate mixed molecular crystals and to match the substitution sites to spectroscopic sites [84, 142, 143]. Since these simulations resolve the structure of the guest molecule, they
show how the crystal deforms the guest molecule. Using molecular dynamics, Nicolet et al. calculated for DBT:Ac how much the angles between various parts of the molecule differ between the two sites of the Ac crystal as well as compared to the isolated state [84]. Because these simulations are based on a classical picture, however, it is not possible to obtain excited state information from them. TD DFT simulations of a large ensemble of molecules are currently still infeasible due to large computational demands. As a compromise, hybrid methods such as ONIOM\(^1\) have been introduced in which different parts of the problem can be simulated at different levels of accuracy [144, 145]. In the case of a mixed molecular crystal, the guest molecule can be simulated at a high level of accuracy (B3LYP/6-31G(d,p)) while the surrounding crystal molecules are simulated on a molecular dynamics level using for example the UFF force field [146]. This has been applied to Tr:DMN, Tr:Nt, DBT:DMN, DBT:Ac and DBT:DBN by the Kozankiewicz group to optimize the crystal structure and the guest molecule simultaneously, for the electronic ground and excited states [85, 86, 90, 125, 147]. In this way, the crystal-induced deformations and their effect on the FC factors could be simulated in close agreement with experimental observations. The optimized crystal structure and the associated vibronic spectra for Tr:Nt are shown in Figure 3.8. While the example of Tr:Nt demonstrates the state of the art of ab initio simulations applied to the vibronic spectrum of a guest molecule in a mixed molecular crystal, the line intensities in the calculated vibronic spectrum did not show close quantitative agreement with the experimental data. Simulations of highly accurate vibronic spectra thus remain a challenge.

Since computational costs increase with system size, simulations with DBT molecules are generally more demanding than with smaller molecules such as Tr or Pc. Because of its larger size DBT, might also react more to crystal-induced deformation than Tr. From the literature, we are aware of the following molecular dynamics and quantum chemistry optimizations of DBT: isolated DBT was studied using semi-empirical and DFT methods in [83], DBT:Ac by a molecular dynamics approach [84] and by ONIOM [85], DBT:DMN by ONIOM [86], and DBT:DBN by ONIOM [147].

3.3 Vibrational relaxation and cooling in molecular crystals

A vibronic transition promotes a molecule to a vibrational state. How long the molecule stays in that state depends on the possibilities for the molecule to release the vibrational energy to its environment. In molecular crystals, the

\(^1\) ONIOM is an abbreviation for: our own N-layered integrated molecular orbital + molecular mechanics [144].
Vibrational relaxation process involves anharmonic coupling of an initially excited vibrational state to lattice phonons and vibrational states of lower frequency [13, 23]. A typical timescale for vibrational relaxation in molecular crystals is 10 ps, but the observed population relaxation times range from around 1 ps to more than 2 ns for the 606 cm$^{-1}$ mode in isotopically pure benzene [18, 51, 148]. In this section we give an overview of the most important concepts related to vibrational relaxation of molecules in molecular crystals. These processes are responsible for the vibronic linewidths encountered in the following chapters. We also present some information about vibrational cooling, the cascade of vibrational relaxation steps necessary to dissipate the complete vibrational energy of an initially excited vibration to phonons. In our review, we focus on the basic understanding of the processes at low temperatures, similar to the presentation in the book chapter by Dlott [13]. A detailed mathematical treatment of vibrational relaxation theory can be found in [23]. Note that in this section we refer repeatedly to the well-studied molecular crystal Nt. Considerably less literature about vibrational relaxation processes is available for pDCB, which is the matrix used in our experiments.

An isolated molecule in vacuum can release its vibrational energy to the environment only via radiative (infrared) decay. The corresponding decay times depend on the transition dipole moment and have been measured to be on the 10 ms timescale for diatomic molecules in supersonic beams and optical traps [17, 149–151]. Vibrational states of polyatomic molecules with sufficiently high frequency additionally undergo intramolecular vibrational redistribution (IVR) [14, 152]. In this process, the energy of an initially excited mode is distributed inside the same molecule to overtones and combination modes of vibrational modes with lower frequency via Fermi resonance [153]. The corresponding population relaxation times are typically well below 1 ns and often in the few ps range. If the vibrational state belongs to an electronically excited state, its lifetime is additionally limited by the electronic relaxation time [154].

The presence of other molecules in a gas or in the condensed phase offers additional external degrees of freedom for the relaxation of a vibration. In gases, vibrational relaxation occurs via energy transfer from vibration to translation during collisions with other gas molecules. How much this accelerates vibrational relaxation compared to the case of an isolated molecule depends on the exact conditions of the gas. Using the technique of supersonic jet expansion, it is possible to study cold, collision-free molecular ensembles in the gas phase [155].
Coupling to external degrees of freedom in liquids or solids allows faster energy transfer and leads to typical vibrational relaxation times in the 1–100 ps range for polyatomic molecules in the condensed phase [13, 156]. As mentioned above, there are examples of longer-lived vibrational states in the condensed phase as well, for example in benzene. Extreme cases are some liquids of diatomic molecules, for example N\(_2\), in which the vibrational relaxation time is 56 s, probably limited by radiative decay [15, 16, 157]. For the rest of the chapter, we limit our description to vibrational relaxation in molecular crystals. Since vibrational relaxation follows the same principles in pure and mixed molecular crystals, we will start with the description of vibrational relaxation in pure molecular crystals, i.e. crystals containing only one type of molecule.

The vibrational modes in a molecular crystal can be divided into internal modes and external (lattice phonon) modes. Internal modes correspond to vibrational states of the molecules as discussed in section 3.1.1 and external modes describe oscillatory motion of the molecules relative to each other [13, 23]. Additionally, mixed modes that combine internal and external character can exist. Vibrational relaxation in a molecular crystal involves energy transfer from an excited molecular (internal) vibration to (external) vibrations of the crystal lattice. Since most internal states of the molecules have considerably more energy than the available lattice phonons, the direct relaxation of a molecular vibration via the excitation of a single lattice phonon is not the prevailing relaxation mechanism in these systems. Instead, vibrational relaxation typically involves an anharmonic process in which a single internal vibration decays to a lower-lying internal vibration and a lattice phonon. For this process, the phononic density of states of the crystal plays an important role.

The phononic band structures of molecular crystals such as (deuterated) Nt, (deuterated) Ac, and pDCB have been measured using neutron scattering [158–162]. Figure 3.9(a) shows measurements of the phonon bands in deuterated Nt taken from [158]. The three branches that pass the point (\(\vec{k} = \vec{0}, \omega = 0\)) describe the dispersion of acoustic phonons and the other nine branches up to 140 cm\(^{-1}\) belong to optical phonons and librational modes. Acoustic, optical and librational phonon modes are illustrated in Figure 3.9(b). Librational modes are hindered rotations of the molecules. At \(\vec{k}\) close to \(\vec{0}\), molecules of the same unit cell move in the same direction for acoustic phonons and in opposite directions for optical phonons. The band with the highest energy in Figure 3.9(a) has almost no dispersion and describes an internal vibration of the Nt molecule. The butterfly mode of Nt at 180 cm\(^{-1}\) can be regarded as a
3 Vibronic transitions

Figure 3.9: Phononic properties of naphthalene (Nt) and other molecular crystals. (a) Phonon band structure in deuterated Nt measured by coherent inelastic neutron scattering. The cut-off frequency $\Omega_{\text{max}} \sim 180 \text{ cm}^{-1}$ is indicated. © IOP Publishing. Reproduced from [158] with permission. All rights reserved. (b) Illustrations of the acoustic, optical and librational phonon modes in Nt. Reprinted by permission of Springer Nature Customer Service Centre GmbH: Springer Verlag Berlin Heidelberg, Laser Spectroscopy of Solids II edited by M. Yen (1989) [13]. (c) Two-phonon densities of states of various molecular crystals as calculated by Dlott and coworkers. The arrow indicates $2\Omega_{\text{max}}$, the boundary between regime 1 and regime 2 of vibrational relaxation. Reproduced from [18], with the permission of AIP publishing.

mixed mode and is considered part of the phonon modes by Dlott [13]. The upper limit of the phonon modes $\Omega_{\text{max}}$ in Nt is thus around $180 \text{ cm}^{-1}$.

The vibrational modes of a molecular crystal are the solutions of the equations of motion of its atoms in the approximation of a harmonic potential. The higher-order (= anharmonic) terms in the Taylor expansion of the full potential energy lead to a coupling between the harmonic eigenmodes and allow for energy transfer between them [162, 163]. In many cases the cubic terms of the potential series suffice to account for vibrational relaxation processes in molecular crystals. At $T = 0 \text{ K}$ and in the approximation of cubic anharmonic coupling, the vibrational decay rate $\Gamma_{\tilde{v}}$ of a vibrational state $|\tilde{v}\rangle$ with energy $E_{\tilde{v}}$ and $\vec{k} = \vec{0}$ can be written as [162]

$$\Gamma_{\tilde{v}} = \frac{36\pi}{\hbar^2} \sum_{m,n} |B_{lmn}|^2 \delta \left( E_{\tilde{v}}/\hbar - \omega_m(\vec{k}) - \omega_n(-\vec{k}) \right) \quad (3.49)$$
with the cubic anharmonic coupling term

\[ B_{l,m,n} = \frac{1}{3!} \left( \frac{\hbar^3}{2^3 \omega_l \omega_m \omega_n} \right)^{1/2} \left( \frac{\partial^3 V}{\partial Q_l \partial Q_m \partial Q_n} \right)_0. \]  (3.50)

Here, \( l, m \) and \( n \) are indices of the normal coordinates of the crystal (internal modes and phonon modes). The index \( l \) denotes the initial mode and \( \omega_l = E_\vec{v}/\hbar \). \( \omega_m \) and \( \omega_n \) are the frequencies of two accepting modes and \( \pm \vec{k} \) denote the associated wave vectors. The \( \delta \)-function in equation (3.49) guarantees conservation of energy in the relaxation process. The condition of opposite wave vectors \( \vec{k} \) and \( -\vec{k} \) is related to the conservation of momentum. The cubic anharmonic coupling term quantifies how strongly the three modes interact with each other.

According to equation (3.49), a vibrational mode has a high decay rate if many modes with suitable energy and momentum are available and the anharmonic coupling elements (3.50) between initial and final modes have high values. As a simplification for equation (3.49), Dlott and coworkers [18, 50] used the averaged anharmonic approximation which assumes that the decay rate can be written as

\[ \Gamma_\vec{v} \propto \langle V^{(3)} \rangle_l^2 \sum_{m,n} \delta(E_\vec{v} - \hbar \omega_m(\vec{k}) - \hbar \omega_n(-\vec{k})) = \langle V^{(3)} \rangle_l^2 \cdot D(E_\vec{v}), \]  (3.51)

where the average anharmonic coupling element \( \langle V^{(3)} \rangle_l \) quantifies the average coupling between the initial mode \( l \) and all open modes \( m \) and \( n \). The remaining sum over the open modes is the two-phonon density of states \( D(E_\vec{v}) \). Figure 3.9(c) shows examples of the two-phonon densities of states of various molecular crystals calculated by the Dlott group based on measurements of the one-phonon density of states using neutron scattering and vibrational spectroscopy [13, 18]. According to Hill et al. the variation of vibrational relaxation rates between modes can be explained by the variation in the two-phonon density of states, up to about \( \pm 50\% \) [18]. Cubic coupling coefficients have been reported to vary considerably among the allowed transitions between different modes, for example in benzene [164]. Still, averaging over many accepting modes can lead to similar values of the averaged coupling coefficients among the vibrational modes, in particular for larger molecules with many vibrational degrees of freedom. For a detailed discussion of the features visible in the two-phonon density of states plots shown in Figure 3.9(c), we refer the reader to the study by Hill et al. [18].
Energy conservation during the vibrational relaxation process leads to the following classification for vibrational relaxation of internal modes in molecular crystals (via the δ-function in equation (3.49)): if the vibrational frequency of the initial mode $\omega_\vec{v}$ is lower than $2\Omega_{\text{max}}$ (with $\Omega_{\text{max}}$: maximum phonon frequency), it can decay directly to two lattice phonons. Otherwise vibrational decay either requires two internal modes $|\vec{v}_1\rangle$ and $|\vec{v}_2\rangle$ that fulfill $\omega_\vec{v} = \omega_\vec{v}_1 + \omega_\vec{v}_2$ or one internal mode and a lattice phonon of matching frequency. The former condition can usually not be fulfilled by vibrational modes with intermediate frequencies (up to a molecule-dependent vibrational frequency, often $\gtrsim 1000 \text{ cm}^{-1}$) because of the sparsity of lower energy vibrational states. Vibrations in this range hence tend to decay to a lower vibrational state and a phonon. Vibrations with high frequencies, for example the C-H stretches around 3000 cm$^{-1}$, are usually resonant with many overtones and combination modes of lower-lying states and often transfer vibrational energy to them within a few ps via IVR. In Hill et al. [18], these three types of decay are classified into:

- **regime I:** $\omega_\vec{v} < 2\Omega_{\text{max}}$ decay via two phonons
- **regime II:** $\omega_\vec{v} > 2\Omega_{\text{max}}$ decay via one internal mode + one phonon
- **regime III:** $\omega_\vec{v} \gg 2\Omega_{\text{max}}$ intramolecular vibrational redistribution.

The boundary between regime II and regime III is not perfectly defined and depends on the molecular system. Besides the processes mentioned above, internal vibrations of molecules can also relax by coupling to the internal vibrations of neighboring molecules. A full description of the vibrational relaxation dynamics requires these states to be included in the two-phonon density of states [18].

Figure 3.10(a) illustrates possible relaxation steps for regime I and regime II vibrations. The states in the figure are numbered according to increasing frequency, i.e. $\omega_{\vec{v}_i} < \omega_{\vec{v}_j}$ for $i < j$. The length of the two arrows next to the level scheme indicate the maximum step size for cubic anharmonic relaxation in the respective regime of vibrational decay. As visualized in Figure 3.10(a), the number of levels that can be reached in a single vibrational relaxation step varies between the states in regime II. This effect can lead to a variation in the relaxation rates among the vibrational states. Modes in regime I can always directly decay to the vibrational ground state by generating two lattice phonons. The relaxation steps of regime I are visualized by bold arrows since they are typically considerably faster than relaxation in regime II [18].
3.3 Vibrational relaxation and cooling in molecular crystals

Figure 3.10: Vibrational relaxation dynamics in a molecular crystal. (a) Illustration of available vibrational relaxation steps of a molecule in a molecular crystal in the approximation of cubic anharmonic coupling. The levels in this energy scheme stand for vibrational modes of a molecule and the downward arrows indicate possible relaxation steps. The dark and light gray areas indicate the range of the one-phonon density of states and regime I of vibrational relaxation, respectively. Vibrations with frequencies $< 2\Omega_{\text{max}}$ can directly decay to the ground state via two lattice phonons (bold arrows). The maximum step size of vibrational relaxation in regime II is determined by the phonon cut-off frequency $\Omega_{\text{max}}$ and indicated by the length of the upper arrow next to the level scheme. The number of levels that can be reached from each vibrational state in regime II depends on the energy distribution of the levels. (b) Simulation of the vibrational relaxation cascade in Ntmspace, starting from the internal vibration at 1443 cm$^{-1}$. The bars indicate the population of the vibrational states at a given time. Reprinted from [24], with the permission of AIP Publishing.

As suggested by Figure 3.10(a), complete dissipation of vibrational energy of a regime II vibration involves not only one but a number of vibrational relaxation steps. This cascade of vibrational relaxation steps is also called vibrational cooling [18]. Hill and Dlott simulate the vibrational cooling process in Nt using a master equation model based on experimental data [24]. The populations of vibrational states along the relaxation cascade are shown in Figure 3.10(b) as a function of time. These simulations show that the time required for a vibration to relax to the complete ground state can be considerably longer than the vibrational relaxation time of a single step. We remark that the related transient increase and decrease of population in vibrational states along the relaxation cascade can also be measured in experiments (see [165] for related measurements of Nt and Ac in the liquid state). Hill and Dlott estimate the average vibrational cooling rate in Nt to be $(9$ cm$^{-1})$/ps. According to their model, the complete dissipation of the energy of the vibrational mode at 1627 cm$^{-1}$ takes about 150 ps [24]. The timescale of vibrational cooling is
3 Vibronic transitions

thus about one order of magnitude longer than the timescale of vibrational relaxation.

The considerations of the vibrational decay processes in molecular crystals presented so far refer to pure crystals. In our experiments we are, however, dealing with mixed crystals with a low concentration of guest molecules (DBT) in a host crystal (pDCB). The relaxation processes in a mixed crystal follow the same rationale as introduced above for a pure crystal [19]. The most important difference is that the guest molecule decays via coupling to the phonons of the host matrix, which are generally different from phonons of a matrix of the guest molecules. This affects not only the two-phonon density of states but also the strength of the anharmonic coupling. Additionally, the relative importance of coupling to vibrational states between neighboring molecules (two site processes) versus coupling to intramolecular vibrational states can differ among host crystals [19].

As pointed out in section 3.2.3, the symmetry of normal modes is relevant to the intensity distribution in vibronic spectra. Normal mode symmetry can additionally be relevant to vibrational relaxation and thus the linewidth distribution in vibronic spectra. As pointed out by Hill et al. in [18], the non-totally symmetric molecules of Nt tend to relax faster than totally symmetric modes, probably caused by stronger dipole-dipole interactions that mediate interactions with vibrational states of neighboring molecules. Effects like this can lead to a correlation between the symmetry of a vibration and its lifetime. Since the vibronic spectroscopy methods used in this thesis are sensitive to totally symmetric vibrations, we do not expect to observe related effects in our data.

The relaxation times of vibrational modes in several pure and mixed molecular crystals have been measured using time and frequency-resolved Raman and infrared methods [13]. Lists of many vibrational relaxation times for pure benzene, Nt, Ac, and durene have been collected in [18], ranging from 2 ps for a 1451 cm$^{-1}$ infrared active mode in Ac to 2.65 ns for the 606 cm$^{-1}$ mode in benzene. A list of lifetimes of 40 vibrational states in Nt (3–140 ps) has been collected in [24]. In this data set one can clearly see that regime I modes and non-totally symmetric modes of Nt tend to relax faster than regime II modes and totally symmetric modes. Vibrational relaxation data for the mixed molecular crystals Nt in durene and Ac in Nt (<10–140 ps) are shown in [19]. The systems Pc in Nt and Pc in pT were studied in [166], reporting relaxation times between 1–60 ps.
3.4 Vibronic spectroscopy of single molecules at low temperatures

After providing an introduction to the vibronic transition and relaxation properties of molecules, we use this section to summarize the studies about vibronic properties of single molecules at cryogenic conditions. As mentioned in chapters 1 and 2, single molecule spectroscopy has mainly focused on the narrow and intense 00-ZPL transitions. There is, however, also a number of studies about the vibronic properties of single molecules. Such studies are often performed to characterize novel guest-host systems. Some authors additionally provide interpretations of the intensity and wavenumber distribution in the spectra (see also section 3.2.4). Figure 3.11 shows an overview of cryogenic single molecule experiments that included measurements of the vibronic spectrum.

The first fluorescence emission spectra of single molecules under cryogenic conditions were published by Tchénio et al. in 1993 for the systems Pc:pT [63] and Tr:PE [55, 127]. In these studies, the authors excited single dopant dye molecules via their 00-ZPL transitions and guided the fluorescence emission to grating spectrometers to analyze its spectral composition. In the subsequent years, the vibronic spectra of many other guest-host combinations have been studied as well (see Figure 3.11).

Due to the different normal mode structure in the electronic states $S_0$ and $S_1$, the vibronic spectra of electronic transitions $S_1 \rightarrow S_0$ are generally different from the spectra of transitions $S_0 \rightarrow S_1$. Fluorescence emission spectra measure light emitted from spontaneous vibronic transitions associated with the change $S_1 \rightarrow S_0$. A measurement of the spectra associated with the direction $S_0 \rightarrow S_1$ can be performed in the fluorescence excitation mode with a tunable
laser. In addition to the requirement of laser scanning, a clean single molecule excitation spectrum can only be measured if no molecules other than that under study are present in the excitation volume of the laser. Due to these additional complications, it took about ten years from the discovery of single molecule spectroscopy until the first vibronic fluorescence excitation spectra of single molecules were published by Nonn and Plakhotnik in 2001/2 [68, 167]. They used Tr:Nt with reduced doping levels and a two-laser saturation spectroscopy method for their measurements. These very first experiments were, however, still done on samples with multiple molecules in the excitation volume. In 2007, Banasiewicz et al. succeeded in creating Tr:Nt samples of low enough doping that single molecules could be selected by their position on the sample. With this approach, they were able to record clean fluorescence excitation spectra of the 00-ZPL, its PSB, and vibronic transitions along $S_0 \rightarrow S_1$.

The analysis of the vibronic spectra in the context of cryogenic single molecule spectroscopy is usually restricted to the line positions and intensities of the spectral features (see also section 3.2.4). Linewidths of vibronic lines in the electronic ground states are usually not reported. This is probably due to the limited resolution of conventional grating spectrometers ($\geq 10$ GHz), the only instrument used to study vibronic transitions along $S_1 \rightarrow S_0$ so far. For transitions to the electronically excited state ($S_0 \rightarrow S_1$), Nonn and Plakhotnik reported a linewidth of around 30 GHz for two vibronic lines close to 250 cm$^{-1}$ in Tr:Nt [68, 167], but they also report a (non-attributable) feature with a linewidth of about 3 GHz. Schofield et al. measured the line profile of a single vibronic transition of DBT in Ac using fluorescence excitation spectroscopy and obtained a linewidth of 23 GHz [46]. Using the same technique, Lettow et al. reported a vibronic profile with a linewidth of 28 GHz for a single DBATT molecule in n-tetradecane (nT) [172].

In general, spectra recorded by a frequency tuned laser can achieve considerably higher resolution than spectra recorded with a grating spectrometer. In this thesis, we introduce a stimulated emission depletion method to record vibronic spectra of the electronic ground state with a laser scanning method at a high spectral resolution limited by the linewidth of the laser ($<1$ MHz). The related theory will be presented in section 4.3 and the experimental results in chapter 6.
4 Light-vibration interaction

Several important properties of vibronic transitions in molecules are discussed in chapter 3. In the current chapter, we introduce models that describe the interaction of a molecule with light via vibronic transitions, including absorption, stimulated emission, and spontaneous emission. This does not cover vibrational transitions such as spontaneous Raman scattering or infrared absorption, during which the electronic state of the molecules remains unchanged.

The excitation of a molecule via vibronic transitions enables the investigation of the vibrational manifold associated with the electronic excited state by scanning a single tunable laser over the vibronic resonances (see section 4.2). In order to measure properties of the vibrational states of the electronic ground state with a high spectral resolution, we introduce a stimulated emission depletion (STED) scheme in which a second laser is resonant with the transition between excited-state and ground-state vibrational levels. In section 4.3, we describe the associated incoherent population dynamics of the electron in the level structure of the molecule. As shown in section 4.4, it is also possible to observe coherent effects of the interaction of vibrational states and light, leading to line splitting and the coherent excitation of a molecular vibration in the electronic ground state of a molecule.

We infer properties of the molecular vibrational states from the change of the excited state population monitored via emitted fluorescence photons. Proper modeling of this process requires a closer study of the internal decay processes of DBT (see section 4.1) and an analysis of how the excited state population is affected by the presence of two laser fields. Throughout this section we assume a cryogenic environment at temperatures low enough that pure dephasing is negligible and vibrational states are not thermally populated.
4 Light-vibration interaction

4.1 Internal decay processes of DBT in a pDCB crystal

Molecules are complex quantum objects with a large number of quantum states. If one of these states is excited, there is usually a large number of pathways to redistribute this energy inside the molecule and to dissipate it to the environment. Possible relaxation pathways include radiative and non-radiative decay, vibrational relaxation, as well as intersystem crossing, which can be visualized in Jabłoński diagrams (see Figure 4.1(a)). The photophysical behavior of a molecule depends heavily on the relative rates of the possible relaxation processes. If the triplet state is long-lived, for example, the molecule will show an on/off behavior in its emission of photons and consequently a reduced average fluorescence rate.

In this section, we characterize the various relaxation pathways and their rates for DBT in pDCB. We estimate properties of the vibrational relaxation cascade in section 4.1.1, the decay rate of the electronically excited state in section 4.1.3 and the intersystem crossing rate in section 4.1.4. Based on measurements and numbers reported in the literature, we estimate that for DBT in pDCB the fraction of steady-state population in the vibrational manifold as well as in the triplet state is considerably lower than in the electronically excited state. Together with a simplified level scheme for DBT presented in section 4.1.2, this serves as a basis for describing the interaction of light with vibronic states of the molecule in the following sections.

4.1.1 Vibrational relaxation cascade

According to Hill and Dlott [24, 175], one can describe the decay of population from a vibronic state $|S_0, \vec{v}_j\rangle$ to the vibronic ground state $|S_0, \vec{0}\rangle$ via a cascade of incoherent vibrational relaxation steps (see section 3.3). In the current section, we estimate an upper bound for the steady-state population residing in all vibrational states of the electronic ground state using a rate equation model of the vibrational cascade similar to the approach by Hill and Dlott [24].

To model the vibrational relaxation cascade, we use the following notation:

\begin{align*}
|g\rangle = |\vec{v}_0\rangle &= |S_0, \vec{0}\rangle \\
|\vec{v}_j\rangle &= |S_0, \vec{v}_j\rangle \\
|e\rangle &= |S_1, \vec{0}\rangle,
\end{align*}
with the vibronic states $|S_k, \vec{v}\rangle$ as defined in section 3.1.2. The states $|\vec{v}_j\rangle$ include overtones and combination modes and are ordered according to their energy such that $E_{\vec{v}_j} \leq E_{\vec{v}_{j+1}}$, as indicated in Figure 3.10(a). $V_{\text{tot}}$ denotes the number of all relevant vibrational states of $|S_0\rangle$.¹ We write $\Gamma_{\vec{v}_k \vec{v}_j}$ for the vibrational relaxation rate from level $|\vec{v}_k\rangle$ to level $|\vec{v}_j\rangle$ and

$$\Gamma_{\vec{v}_j} = \sum_{i=0}^{j-1} \Gamma_{\vec{v}_j \vec{v}_i}, \quad (4.1)$$

for the total decay rate from $|\vec{v}_j\rangle$ to all energetically lower-lying states $|\vec{v}_i\rangle$ with $i < j$. Using this notation, the rate equation for the population $N_{\vec{v}_j}$ on level $|v_j\rangle$ is given by

$$\partial_t N_{\vec{v}_j} = \Gamma_{ev_{j}} N_e + \sum_{k=j+1}^{V_{\text{tot}}} \Gamma_{\vec{v}_k \vec{v}_j} N_{\vec{v}_k} - \Gamma_{\vec{v}_j} N_{\vec{v}_j} \quad (1 \leq j \leq V_{\text{tot}}). \quad (4.2)$$

In what follows, we consider the steady state case ($\partial_t N_{\vec{v}_j} = 0$) and the symbols $N_{\vec{v}_j}$ denote steady-state populations.

As we show in section 4.3, STED spectroscopy can determine the total relaxation rates $\Gamma_{\vec{v}_j}$ of the totally symmetric vibrational modes of DBT via their linewidth if pure dephasing is negligible. This does not, however, include information about the branching ratio, i.e. about how the total decay rate results from decay to all reachable vibrational modes with lower energy. To estimate the parameters $\Gamma_{\vec{v}_k \vec{v}_j}$, we additionally need to know the one/two-phonon density of states of pDCB [161, 176], the anharmonic coupling parameters and the wavenumbers and decay rates of the non-totally symmetric states (see section 3.3 and table I in [24] for corresponding numbers in $N_t$). Due to our limited knowledge about the phononic properties of pDCB and the decay rates of the vibrational modes of DBT that are not reachable via vibronic transitions, we are not able to model the vibrational relaxation cascade in full detail in this thesis.

Without resolving the exact population distribution inside the vibrational manifold, one can treat it as one effective (cascade) state $|c\rangle$ with population

$$N_c = \sum_{j=1}^{V_{\text{tot}}} N_{\vec{v}_j} \quad (4.3)$$

¹ Relevant states are those that are reachable via radiative decay from $|S_1, \vec{0}\rangle$ or via vibrational relaxation from other vibrational states.
and decay rate $\Gamma_{cg}$. The decay rate $\Gamma_{cg}$ can be found based on the steady-state condition. In the steady-state, the rate at which population is transferred to a level is the same as the rate at which population is transferred from that level to other states. In the model considered here, this means that in the steady-state the population transferred from $|e\rangle$ to $|c\rangle$ is the same as transferred from $|c\rangle$ to $|g\rangle$. With

$$\Gamma_{ec} = \sum_{j=1}^{V_{tot}} \Gamma_{e \bar{v}_j}$$

(4.4)

this condition can be written as

$$\Gamma_{ec} N_e = \sum_{j=1}^{V_{tot}} \Gamma_{\bar{v}_j g} N_{\bar{v}_j} \equiv \Gamma_{cg} N_c$$

(4.5)

and hence

$$\Gamma_{cg} = \frac{\sum_{j=1}^{V_{tot}} \Gamma_{\bar{v}_j g} N_{\bar{v}_j}}{\sum_{j=1}^{V_{tot}} N_{\bar{v}_j}}.$$  

(4.6)

By expressing all steady-state populations $N_{\bar{v}_j}$ in terms of the vibrational decay rates and $N_e$, $\Gamma_{cg}$ can be expressed as a function of the decay rates $\Gamma_{\bar{v}_k \bar{v}_j}$ and $\Gamma_{e \bar{v}_j}$. The steady-state population in $|c\rangle$ is determined by the ratio of the spontaneous relaxation rate to $|c\rangle$ over the spontaneous relaxation rate from $|c\rangle$:

$$N_c = \frac{\Gamma_{ec}}{\Gamma_{cg}} N_e.$$  

(4.7)

The derivation of this equation from the rate equations (4.2) is shown in appendix D.4.

According to the calculations by Hill and Dlott [24], the vibrational cooling process for the highest frequency vibrations in $N_t$ takes place in about 150 ps. The vibrational relaxation cascade involved in this process thus takes about one order of magnitude longer than an individual vibrational relaxation step. Using this number, we obtain an upper bound of

$$\frac{N_c}{N_e} = \frac{\Gamma_{ec}}{\Gamma_{cg}} \leq \frac{\Gamma_e}{\Gamma_{cg}} \leq \frac{1/7 \text{ ns}}{1/150 \text{ ps}} \approx 2\%$$

(4.8)

for the population residing in the vibrational manifold of DBT in pDCB. This is a conservative estimate because we assume that all fluorescence emission ends up in the vibrational state with the longest vibrational cooling time. Moreover, DBT has a larger number of vibrational modes than $N_t$, such that
4.1 Internal decay processes of DBT in a pDCB crystal

Figure 4.1: Internal decay processes of a DBT molecule. (a) Jabłoński diagram of DBT indicating decay processes related to fluorescence (Fluo), vibrational relaxation (VR) and intersystem crossing (ISC). Gray areas indicate phonon sidebands. The weak phonon sidebands of vibrational states are omitted in this illustration. (b) Simplified level scheme and the spontaneous decay rates $\Gamma_{ij}$ used for modeling. $W_p$ denotes the (pump/excitation) laser-induced transition rate between $|g\rangle$ and $|w\rangle$.

IVR becomes relevant for vibrations with lower wavenumber compared to Nt and increases the overall decay speed.

Since level $|c\rangle$ is almost empty for DBT in pDCB, we omit it in the models used to fit the data. As shown in section 4.2, the results are almost unaffected by this approximation. We also assume that vibrational states that are populated by photoexcitation or stimulated emission relax directly to their associated electronic states ($|S_0\rangle$ or $|S_1\rangle$) at the rate given by their linewidth without triggering a vibrational relaxation cascade. This approximation is good for low wavenumber states which are routinely pumped in STED spectroscopy [24], but becomes worse for high wavenumber states, for which the process of vibrational cooling takes longer. But with the same argument as above, the population in $|c\rangle$ will still be considerably smaller than in the vibrational ground state. We note, however, that if only a single vibrational state $|\tilde{v}_j\rangle$ is long-lived, ignoring the vibrational relaxation cascade can lead to erroneous results. Also, if the laser-induced transition rates in the STED scheme are similar to the vibrational relaxation rates, vibrational states can start to be populated and the details of the vibrational relaxation cascade can become relevant. In the experiments presented in this thesis, however, we do not explore the corresponding parameter range.
4.1.2 Simplified level scheme for DBT

For model calculations of the laser-induced population dynamics in DBT we use simplified level schemes such as that shown in Figure 4.1(b). The states of the scheme shown in Figure 4.1(b) are defined as follows:

\[
|g\rangle = |S_0, \tilde{0}\rangle \quad \text{vibrational ground state of the electronic ground state}
\]

\[
|c\rangle \quad \text{vibrational cascade \textquoteleft state\textquoteright\ of the electronic ground state}
\]

\[
|t\rangle = |T_1, \tilde{0}\rangle \quad \text{vibrational ground state of the triplet state}
\]

\[
|e\rangle = |S_1, \tilde{0}\rangle, \quad \text{vibrational ground state of the electronic excited state}
\]

\[
|w\rangle = |S_1, \tilde{v}_w\rangle \quad \text{(pumped) vibrational state of the electronic excited state}
\]

With a laser induced pump rate \( W_p \) on the transition \(|g\rangle \leftrightarrow |w\rangle\), the system of rate equations corresponding to the model in Figure 4.1(b) is given by:

\[
\begin{pmatrix}
N_g \\
N_c \\
N_t \\
N_e \\
N_w
\end{pmatrix}
= \begin{pmatrix}
0 & \Gamma_{cg} & \Gamma_{tg} & \Gamma_{eg} & 0 \\
0 & -\Gamma_{cg} & 0 & \Gamma_{ec} & 0 \\
0 & 0 & -\Gamma_{tg} & \Gamma_{et} & 0 \\
0 & 0 & 0 & -\Gamma_e & \Gamma_{we} \\
0 & 0 & 0 & 0 & -\Gamma_{we}
\end{pmatrix}
\begin{pmatrix}
N_g \\
N_c \\
N_t \\
N_e \\
N_w
\end{pmatrix}
+ \begin{pmatrix}
W_p(N_w - N_g) \\
0 \\
0 \\
0 \\
W_p(N_g - N_w)
\end{pmatrix}, \quad (4.9)
\]

with \( \Gamma_e = \Gamma_{eg} + \Gamma_{ec} + \Gamma_{et} \) and \( N_g + N_c + N_t + N_e + N_w = 1 \). In this model, we assume that the state \(|w\rangle\) decays directly to \(|e\rangle\) at a rate \( \Gamma_{we} \) without undergoing a vibrational cascade. Moreover, we ignore radiative transitions from vibrationally excited states in \( S_1 \) to states in \( S_0 \).

Solving equation (4.9) under steady-state conditions (\( \partial N_i = 0 \)) yields the saturation behavior of the population \( N_e \) in the electronically excited state:

\[
N_e = \frac{1}{K} \frac{\Gamma_{we} S_p}{\Gamma_e} \frac{S_p}{1 + S_p}, \quad (4.10)
\]

with saturation parameter

\[
S_p = \frac{KW_p}{\Gamma_{we}} \quad (4.11)
\]

and

\[
K = 2 + \frac{\Gamma_{we}}{\Gamma_e} \left( 1 + \frac{\Gamma_{ec}}{\Gamma_{cg}} + \frac{\Gamma_{et}}{\Gamma_{tg}} \right) \geq 2. \quad (4.12)
\]
If $K$ increases, the maximum reachable steady-state population in $|e\rangle$ drops and as a consequence the saturation power drops as well. In the limits of vanishing population in $|c\rangle$ ($\Gamma_{ec}/\Gamma_{cg} \to 0$) and $|t\rangle$ ($\Gamma_{et}/\Gamma_{tg} \to 0$), and assuming fast vibrational relaxation $\Gamma_{we}/\Gamma_e \gg 2$, one obtains $K \to \Gamma_{we}/\Gamma_e$ and $N_e(S_p \to \infty) = 1$. Since the internal decay parameters of DBT are close to this limit (see sections 4.1.1 and 4.1.4), we expect that strong pumping of a vibronic state in $S_1$ allows the transfer of almost all electronic population to the electronically excited state $|e\rangle$ of DBT.

In the rate equation model (4.9), the steady-state populations in $|c\rangle$ and $|t\rangle$ are related to the excited state population $N_e$:

$$N_c = \frac{\Gamma_{ec}}{\Gamma_{cg}} N_e \quad (4.13)$$

$$N_t = \frac{\Gamma_{et}}{\Gamma_{tg}} N_e. \quad (4.14)$$

These equations demonstrate an important characteristic of the population dynamics inside the molecule: the ratio of population rate to depopulation rate of a level determines how much population accumulates in the level in the steady-state. For the exemplary level scheme used in this section, the population in the triplet state $|t\rangle$ exceeds the population in the excited state $|e\rangle$ if $\Gamma_{et} > \Gamma_{tg}$. In that case, the triplet state acts as a bottleneck in which considerable population is trapped.\(^2\) We show in section 4.1.4 that the triplet state of DBT carries negligible steady-state population, similar to the population in $|c\rangle$ estimated in section 4.1.1.

The population in the pumped vibronic state $|w\rangle$ is

$$N_w = \frac{\Gamma_e}{\Gamma_{we}} N_e. \quad (4.15)$$

$N_w$ is expected to be considerably smaller than $N_e$ because typically $\Gamma_{we} \gg \Gamma_e$. The vibrational ground state of the electronic excited state $|e\rangle$ thus acts as a metastable state in the level system shown in 4.1(b). In many cases it is therefore a valid approximation that all population resides in $|g\rangle$ and $|e\rangle$ while all other states are empty.\(^2\)

\(^2\) A related example from the literature is Tr:Ac with $\Gamma_{et}/\Gamma_{tg} \approx 5.6 \cdot 10^3$ [177].
If the molecule is not pumped via the level $|w\rangle$ but via $|e\rangle$, the system of rate equations for the model in Figure 4.1(b) is given by [30, 57]:

$$
\begin{pmatrix}
N_g \\
N_c \\
N_t \\
N_e \\
N_w
\end{pmatrix} =
\begin{pmatrix}
0 & \Gamma_{cg} & \Gamma_{tg} & \Gamma_{eg} & 0 \\
0 & -\Gamma_{cg} & 0 & \Gamma_{ec} & 0 \\
0 & 0 & -\Gamma_{tg} & \Gamma_{et} & 0 \\
0 & 0 & 0 & -\Gamma_e & \Gamma_{we} \\
0 & 0 & 0 & 0 & -\Gamma_{we}
\end{pmatrix}
\begin{pmatrix}
N_g \\
N_c \\
N_t \\
N_e \\
N_w
\end{pmatrix}
+ \begin{pmatrix}
\tilde{W}_p (N_e - N_g) \\
0 \\
0 \\
\tilde{W}_p (N_g - N_e) \\
0
\end{pmatrix}.
$$

(4.16)

In this case, the saturation behavior of the excited state population can be written as

$$
N_e = \frac{1}{2\tilde{K}} \frac{\tilde{S}_p}{1 + \tilde{S}_p},
$$

(4.17)

with saturation parameter

$$
\tilde{S}_p = \frac{2\tilde{K}\tilde{W}_p}{\Gamma_e}
$$

(4.18)

and

$$
\tilde{K} = 1 + \frac{1}{2} \left( \frac{\Gamma_{ec}}{\Gamma_{cg}} + \frac{\Gamma_{et}}{\Gamma_{tg}} \right).
$$

(4.19)

In this case, we obtain $\tilde{K} \rightarrow 1$ for vanishing population in $|c\rangle$ and $|t\rangle$, reproducing the result derived for a two-level system in section (2.5). Consequently, we find $N_e (\tilde{S}_p \rightarrow \infty) = 1/2$ for the maximum population in $|e\rangle$, which is determined by the equilibrium between absorption and stimulated emission along the 00-ZPL.

### 4.1.3 Excited state decay rate

The state $|e\rangle$ decays via radiative emission of a fluorescence photon within $\sim 10$ ns, about three orders of magnitude slower than the typical timescale of vibrational relaxation. Intersystem crossing also contributes to depopulation of $|e\rangle$, but for DBT this takes place at a rate that is negligible compared to radiative decay. In this section, we present measurements of the (total) decay rate of the electronic excited state of a single DBT molecule in pDCB, an important parameter for the models presented below.

The excited state decay rate $\Gamma_e$ can be determined via the fluorescence lifetime of a molecule. We used pulsed excitation and time-correlated detection of fluorescence photons to measure the fluorescence lifetime of a selected DBT
4.1 Internal decay processes of DBT in a pDCB crystal

Figure 4.2: Measurement of the excited state lifetime of a single DBT molecule (mol. 1). (a) Sketch of a simplified version of the optical setup for pulsed excitation and time-correlated photon detection. APD – avalanche photo diode, BS – beam splitter, FPD – fast photodiode, LP – longpass filter, PM – polarization-maintaining fiber, PP – pulse picker, TCSPC – time correlated single photon counting module, Ti:Sa – pulsed Ti:Sapphire laser. (b) Histogram of time-resolved fluorescence detection of a DBT molecule after pulsed excitation (blue), instrument response function of the APD (black dashed line), and a fit of an exponential function to the data (orange dashed line). (c) Fluorescence excitation scan of the 00-ZPL of the same molecule as in (b) in the low excitation regime with a Lorentzian fit (orange dashed line). Part (c) adapted from [45], with the permission of AIP Publishing.

molecule in pDCB (mol. 1, see table 6.1). For the experiment we selected every 20th pulse from a pulsed Ti:Sapphire laser (Mira 900, Coherent; rep. rate: 76.2 MHz; bandwidth: 200 GHz) with a pulse picker (PulseSelect, APE Berlin; settings: division ratio: 20, pulse width: 4 ns, Po: 16.5 W) and used it to excite the molecule via a low-frequency vibrational state at 291 cm$^{-1}$ (see Figure 6.3(a)). The pulse picker was triggered by the output of a fast photodiode (FPD 510-FV, Menlo Systems) and provided synchronized output pulses that served as the sync signal for the TCSPC module (PicoHarp 300, PicoQuant). As illustrated in the simplified sketch of the optical setup shown in Figure 4.2(a), the laser pulses were guided to the molecule in the cryostat and the fluorescence emission from the molecule was collected using an avalanche photodiode (SPCM-AQR-14, Perkin Elmer). The TCSPC module was used in start-stop mode to collect a histogram of the time delays of the fluorescence.
photons with respect to the laser-triggered sync signal. The resulting fluorescence decay curve, the instrument response function of APD and TCSPC module, and a fit of an instrument-corrected exponential decay function are shown in Figure 4.2(b). Note that the molecule studied in this experiment was the only DBT molecule in the excitation volume. This is an ideal condition to study fluorescence decay of a single molecule because the spectrally broad excitation pulses cannot excite any other molecules, which would lead to unwanted background signals. Similar measurements with single Tr molecules [90, 168] and DBATT molecules [178] under cryogenic conditions have been reported in the literature.

The fit of the exponential decay function yields a fluorescence lifetime of $T_1 = \frac{1}{\Gamma_e} = 7.00\, \text{ns}$. The corresponding lifetime-limited linewidth is $1/(2\pi T_1) \approx 22.7$ MHz and agrees closely with the FWHM of the fluorescence excitation profile of the 00-ZPL recorded using low excitation power (see Figure 4.2(c)). This indicates that pure dephasing on the electronic transition is negligible for the studied molecule, as expected at $T \approx 25$ mK. We assume that the linewidths of the other molecules studied in chapter 6 (22–26 MHz) are also lifetime-limited. Under this assumption, the excited state lifetimes of these molecules are in the range of 6–7.5 ns (see table 6.1).

**4.1.4 Intersystem crossing**

The spins of the outer pair of electrons are typically paired (singlet state), but can also be promoted to an unpaired (= triplet) state. After a transition to the triplet state, the molecule does not emit a photon for a period that is determined by the triplet state lifetime. This on/off-behavior effectively chops the photon stream emitted by a molecule under cw-excitation into bunches and can be detected via a bunching peak in the autocorrelation function of the photon arrival times at the detector. The amplitude and the decay time of the bunching peak can be used to determine the intersystem crossing rates into and out of the triplet state [123, 179, 180]. The amplitude of the bunching peak increases with excitation laser power because the dark periods create more clearly defined bunches if the average photon emission rate is high. The decay time of the bunching peak is a measure of the typical duration of the bunched photon streams [179].

The triplet yield $\phi_t = \frac{\Gamma_{et}}{(\Gamma_{eg} + \Gamma_{ec} + \Gamma_{et})}$ of dye molecules used in cryogenic single molecule spectroscopy has been reported to vary by many orders of magnitude, depending on the combination of molecule and host crystal [33]. For Tr in Ac, high triplet yields of around $3 \times 10^{-3}$ with triplet lifetimes around
4.1 Internal decay processes of DBT in a pDCB crystal

$1/\Gamma_{tg} \approx 500 \mu s$ have been observed [177]. In this case, the first excited singlet state of the guest molecule has more energy than the lowest triplet state of the host molecule, enabling a transition to the triplet manifold of the guest molecule via the host matrix. The triplet occupation of DBT has been reported to be very low in Ac ($\phi_t = 10^{-7}$ and $1/\Gamma_{tg} = 40 \sim 200 \mu s$ at 1.4 K [26]; $1/\Gamma_{tg} = 1.5 \mu s$ at RT [181]) and Nt (according to Jelezko et al. [122]: either $\phi_t < 4 \cdot 10^{-6}$ or $1/\Gamma_{tg} < 10 \mu s$). Because DBT is a relatively large dye molecule, the energy of its triplet state is expected to be very low, leading to the low ISC rates into the triplet state and the short triplet lifetime [83]. For DBT in pDCB no results for triplet yield and lifetime have been published thus far. Verhart et al. [25] report bunching contrasts between 2–6% and correlation times between 1-100 µs for three DBT molecules in pDCB, indicating variation in the ISC behavior between molecules.

To estimate the average population of the triplet state of DBT in pDCB, we performed autocorrelation measurements with a single DBT molecule under cw-excitation of the prominent vibronic state at 291 cm$^{-1}$ at different excitation powers (mol. 1, see table 6.1 and Figure 6.3). The fluorescence photons emitted by the molecule were measured in an HBT-setup (see Figure 5.1). On the timescale of the spontaneous emission rate, we observe an antibunching dip characteristic for single photon emission (see Figure 4.3(a)). The antibunching data are consistent with the model

\[ g_d^{(2)}(\tau) = \int_{-\infty}^{\infty} g^{(2)}(\tau - \tau') \cdot \text{IRF}(\tau') d\tau', \quad (4.20) \]

where

\[ g^{(2)}(\tau) = 1 - e^{-\left(1 + S_p\right)|\tau|/T_1} \quad (4.21) \]

is the expected functional form of the autocorrelation function as a function of delay $\tau$ [124] and IRF is the two-detector instrument response function. The predictions of equation (4.20) are plotted as black lines in Figure 4.3(a) and were obtained without the need for fitting. The excited state lifetime $T_1 = 7$ ns of the studied molecule has been determined using pulsed excitation (see section 4.1.3). The saturation parameter $S_p$ of each measurement has been determined independently from a fluorescence excitation measurement (see section 6.1.2) and we assume that the background signal is negligible ($B = 0$). At the lowest power setting used we obtain $g^{(2)}(0) = 0.15$, a value limited by the timing jitter of photo-detection in the APDs and not by background fluorescence photons. The measured amplitude of the antibunching dip drops with increasing excitation power because the dip narrows with increasing saturation parameter but the two-detector time-resolution of our APDs is
Figure 4.3: Autocorrelation function of the arrival times of photons emitted by a single DBT molecule for different excitation powers (mol. 1). (a) Antibunching on the timescale of 10 ns due to single photon emission. Black lines are theory curves (see text), numbers indicate the saturation parameters. Data are displayed with an offset of 0.2 between each power setting. The dashed black line is the two-detector IRF (not normalized), shifted by 25 ns from the origin. (b) Bunching on the timescale of 10 µs due to intersystem crossing. Data are displayed with an offset of $2 \cdot 10^{-3}$. (c, d) Bunching contrast $C$ and decay constant $\lambda$ obtained from fits to the data shown in (a). The black line in (c) is the fit of a saturation curve $C_\infty S_p/(1 + S_p)$. The dashed black line in (d) is the average over all points except the one at $S=0.2$.

limited to about 1 ns. The corresponding two-detector instrument response function is shown as a black dashed line in Figure 4.3(a).

As shown in Figure 4.3(b), we observe a weak bunching peak in the autocorrelation function on the timescale of 10 µs. The peak can be fitted by a mono-exponential function

$$g^{(2)}(\tau) = 1 + C e^{-\lambda |\tau|},$$

with amplitude $C$ and decay parameter $\lambda$. From a fit of the function $C(S_p) = C_\infty S_p/(1 + S_p)$ to the saturation curve of the bunching amplitude $C$ shown in Figure 4.3(c) we obtain $C_\infty = 3.6 \cdot 10^{-3}$. Based on the model given in [179] and some adaptations for the case of vibronic pumping instead of pumping
4.2 Fluorescence excitation spectroscopy

Vibrational states in the electronically excited state of DBT can be excited by light in the near-infrared. In fluorescence excitation spectroscopy, the red-shifted fluorescence is collected while the laser frequency is scanned over vibrational transitions. In the following sections, we present models describing this process (see section 4.2.1) and compare the power needed to saturate a vibrational transition and the 00-ZPL (see section 4.2.2). We remark that by ‘pump’ and ‘excite’ we refer to the same process. In the equations,
we use the index p for quantities related to the pumping/excitation of the molecule.

### 4.2.1 Fluorescence excitation of a vibronic transition

We use the level scheme shown in Figure 4.1(b) to model the excitation of a molecule via a vibrational state. Note that this scheme does not take radiative transitions from vibrationally excited states in $S_1$ into account. The rate equations describing the population distribution in the level scheme of Figure 4.1(b) are given in equation (4.9). Based on a comparison with the results of a
Lindblad master equation treatment (see appendix D.6) one can relate the rate $W_p$ to the Rabi frequency $\Omega_p$, induced by the pump laser:

$$W_p(\Delta_p) = \frac{\Omega_p^2 \Gamma_{we}}{4(\Delta_p^2 + \Gamma_{we}^2/4)},$$ (4.25)

where $\Omega_p = -\vec{d}_{gw} \cdot \vec{E}_p / \hbar$ and $\vec{E}_p$ is the amplitude of the electric field of the pump laser $\vec{E}(t) = \vec{E}_p \cos(\omega_p t)$ at the position of the molecule. $\Delta_p = \omega_p - \omega_{gw}$ denotes the detuning of the pump laser with respect to the frequency of the vibronic transition $|g\rangle \leftrightarrow |w\rangle$.

Inserting the detuning-dependent pump rate from equation (4.25) into the results from section 4.1.2 yields the resonance behavior of the population in the levels $|e\rangle$ and $|w\rangle$:

$$N_e(\Delta_p) = \frac{1}{K} \frac{\Gamma_{we}}{\Gamma_e} \frac{S_p(\Delta_p)}{1 + S_p(\Delta_p)},$$ (4.26)

$$N_w(\Delta_p) = \frac{\Gamma_e}{\Gamma_{we}} N_e(\Delta_p)$$ (4.27)

with the detuning-dependent saturation parameter

$$S_p(\Delta_p) = \frac{K \cdot W_p(\Delta_p)}{\Gamma_{we}}$$ (4.28)

and $K$ as defined in equation (4.12). The population in the states $|e\rangle$ and $|w\rangle$ (and all others except for $|g\rangle$) has a Lorentzian line profile as a function of laser detuning and a linewidth of $\Delta \nu_0 = \Gamma_{we} / (2\pi)$ in the limit of low excitation power.\(^3\) With increasing light intensity, the amplitude of the line profile exhibits the saturation behavior described by equation (4.26) and the linewidth displays power-broadening described by the function:

$$\Delta \nu = \Delta \nu_0 \sqrt{1 + S_p}.$$ (4.29)

Figure 4.4(a) shows $N_e$ and $N_w$ for the model parameters $M_{00}$ and $\Omega_p = \sqrt{\Gamma_e \Gamma_{we}}$ (corresponds to $S_p \approx 1$). The population of $|c\rangle$ resulting from the model parameters $M_{tc}$ is limited to $N_c < 1\%$.

\(^3\) If radiative transitions from $|w\rangle$ to (vibrational) states in $S_0$ are taken into account, the linewidth in the low excitation limit increases to $(\Gamma_{we} + \Gamma_{ww}) / (2\pi)$, where $\Gamma_{ww}$ is the radiative decay rate of $|w\rangle$. We assume that vibrational relaxation is considerably faster than electronic relaxation ($\Gamma_{we} \gg \Gamma_{ww}$) and neglect this contribution.
4 Light-vibration interaction

Figure 4.4: Excitation of a molecule via a vibronic transition and via the oo-ZPL transition. (a) Population of the states $|e\rangle$ and $|w\rangle$ under vibronic excitation for parameters $M_{00}$ (see Table 4.1) and $\Omega_p = \sqrt{\Gamma_w \Gamma_e}$. The black dashed line shows $N_e$ for the parameters $M_{t\epsilon}$. $N_e$ and $N_w$ do not change appreciably in this situation. (b) Saturation behavior of $N_e(\Delta_p = 0)$ for the cases in which the molecule is excited via a vibronic line and via the oo-ZPL (colored lines: $M_{00}$ and assuming $\eta_p = \tilde{\eta}_p$). The black dashed line shows $N_e$ in the case of vibronic pumping if vibrational states and triplet state are included in the model ($M_{t\epsilon}$). (c) Power-broadening behavior of the linewidth of the pumped states ($M_{t\epsilon}$).

In section 6.1.2, we show how the model discussed in this section can be extended by additional vibronic levels and a background term that accounts for absorption via PSBs. These extensions are necessary to fit the experimental data presented in section 6.1.

4.2.2 Vibronic vs. oo-ZPL excitation

We observe that it takes about four orders of magnitude more power in experiments to saturate the molecule if it is excited via a vibronic state compared to excitation via the oo-ZPL. This difference is due to the different decay rates of the pumped states, the different FC factors of both transitions and the fact that about twice as much population can be transferred to the excited state if the molecule is pumped via a vibronic state. In this section we give an estimate for the expected ratio of the excitation powers $P_p / \tilde{P}_p$ based on the model from section 4.2.1. A similar relation has been used by Nonn and Plakhotnik to estimate expected photon counts in their vibronic pumping experiments [167].
With $\Omega_0 = -\langle S_0 | \hat{d} | S_1 \rangle \cdot \vec{E}/\hbar \propto \sqrt{P_p}$ and

$$\Omega_p = -\langle g | \hat{d} | w \rangle \cdot \vec{E}/\hbar = I(\vec{0}, \vec{v}_w) \cdot \Omega_0 = I(\vec{0}, \vec{v}_w) \cdot \sqrt{\eta_p P_p} \quad (4.30)$$

$$\tilde{\Omega}_p = -\langle g | \hat{d} | e \rangle \cdot \vec{E}/\hbar = I(\vec{0}, \vec{0}) \cdot \Omega_0 = I(\vec{0}, \vec{0}) \cdot \sqrt{\tilde{\eta}_p \tilde{P}_p}, \quad (4.31)$$

we can write the saturation parameters of a molecule pumped via $|w\rangle$ and via $|e\rangle$ as:

$$S_p = \frac{K W_p}{\Gamma_{we}} = \frac{K \Omega_p^2}{\Gamma_{we}^2} = \frac{K \cdot I(\vec{0}, \vec{v}_w)^2}{\Gamma_{we}} \eta_p P_p \quad (4.32)$$

$$\tilde{S}_p = 2 \frac{\tilde{K} \tilde{W}_p}{\Gamma_e} = 2 \frac{\tilde{K} \tilde{\Omega}_p^2}{\Gamma_e^2} = 2 \frac{\tilde{K} \cdot I(\vec{0}, \vec{0})^2}{\Gamma_e^2} \tilde{\eta}_p \tilde{P}_p. \quad (4.33)$$

The proportionality factors $\eta_p$ and $\tilde{\eta}_p$ quantify differences in excitation efficiency related to variations in the alignment of the excitation laser between vibronic and oo-ZPL pumping. The ratio of excitation powers required to reach equal saturation parameters $S_p = \tilde{S}_p$ is given by:

$$\frac{P_p}{\tilde{P}_p} = 2 \frac{\tilde{K}}{K} \left( \frac{\Gamma_{we}}{\Gamma_e} \right)^2 \left( \frac{I(\vec{0}, \vec{0})}{I(\vec{0}, \vec{v}_w)} \right)^2 \eta_p \rightarrow 2 \frac{\Gamma_{we}}{\Gamma_e} \left( \frac{I(\vec{0}, \vec{0})}{I(\vec{0}, \vec{v}_w)} \right)^2. \quad (4.34)$$

The limit indicated by the arrow in equation (4.34) describes the case $\Gamma_{ec}/\Gamma_{cg} \rightarrow 0$, $\Gamma_{et}/\Gamma_{tg} \rightarrow 0$, $\Gamma_{we}/\Gamma_e \gg 2$ and $\eta_p = \tilde{\eta}_p$. Inserting typical values for DBT in pDCB yields

$$\frac{P_p}{\tilde{P}_p} \approx 2 \cdot \frac{10 \text{ GHz} \cdot (2\pi) 0.33}{0.06} \approx 5 \cdot 10^3, \quad (4.35)$$

based on DFT results for the FC overlaps for the oo-ZPL and the transition between $|g\rangle$ and the strongest vibrational line of isolated DBT (see Figure 3.6). This value for the ratio of required pump powers roughly agrees with our experimental observations (see section 6.1.2).

Figure 4.4(b) shows the saturation behavior of $\rho_{ee}$ under vibronic pumping and oo-ZPL pumping as a function of $\tilde{S}_p$. The saturation parameter under vibronic pumping is related to $\tilde{S}_p$ via $S_p = (\tilde{P}_p/P_p)\tilde{S}_p$ with $\tilde{P}_p/P_p$ from equation (4.34). The figure shows that vibronic pumping allows the transfer of almost all population to $|e\rangle$ at the cost of considerably increased laser power. The difference between the models $M_{00}$ and $M_{tc}$ mainly appears as a small difference in the maximum population in $N_e$ under vibronic pumping. The
4 Light-vibration interaction

Figure 4.5: Experimental scheme and examples of stimulated emission pumping (SEP) measurements with molecules in the gas phase. (a) Level scheme of the SEP method. The two states $|\nu\rangle$ and $|w\rangle$ are (ro-)vibronic states in two different electronic states of a molecule. (b) A vibronic transition in $I_2$, measured using the SEP technique. $\Delta I/I$ is the normalized depletion of the fluorescence signal induced by the dump laser. The linewidth of the depletion signal ($\sim 600$ MHz) is limited by the bandwidth of the lasers. Reprinted from [183], with the permission of AIP Publishing. (c) Several fluorescence dips indicating vibronic transitions in benzonitrile-$H_2O$. Reprinted with permission from [184]. © The Optical Society.

power-broadening behavior of the linewidth of the pumped states under vibronic and 00-ZPL pumping is shown in Figure 4.4(c).

4.3 Stimulated emission depletion spectroscopy

In chapter 6, we present experimental results for a stimulated emission depletion spectroscopy scheme applied to single DBT molecules in pDCB. In STED spectroscopy one (pump) laser populates the excited state $|e\rangle$ via excitation of a vibronic level while another (depletion) laser depletes $|e\rangle$ via stimulated emission to vibrational levels of the electronic ground state. The depletion is monitored via the reduction of the fluorescence signal from $|e\rangle$. Some of the literature about methods similar to STED spectroscopy is covered in section 4.3.1. In section 4.3.2, we introduce a model of STED spectroscopy to provide a basic understanding of the process.

4.3.1 Literature on stimulated emission pumping and STED

A method very similar to STED spectroscopy has been reported by Kittrell et al. in 1981 using $I_2$ molecules in the gas phase [183]. The level scheme of their stimulated emission pumping (SEP) method is shown in Figure 4.5(a). Using SEP, Kittrell et al. were able to detect vibrational states of $I_2$ by the depletion of the fluorescence signal induced by the frequency-scanned depletion laser (see Figure 4.5(b) for an example). Since SEP requires two resonance conditions to be fulfilled at the same time, it reduces the complexity of rotational-vibrational
spectra of molecules in the gas phase considerably. SEP can thus serve as a spectroscopic tool, but it is also useful to transfer population to selected vibrational states of a molecule. By combining the excitation of a selected vibrational state using (pulsed) SEP with a delayed probe pulse, researchers have studied the subsequent temporal relaxation behavior of the prepared vibrational state. This method has been applied to more complex molecules such as para-difluorobenzene and benzonitrile [184, 185], yielding vibronic spectra like the one reprinted in Figure 4.5(c), exhibiting multiple characteristic lines. For some other polyatomic molecules including DFCO and formaldehyde, IVR processes have been investigated using line profiles recorded using STED spectroscopy [186, 187]. More references about SEP experiments can be found in the review article by Hamilton et al. [187].

Depending on the exact configuration of the experiment, the resolution in many SEP studies has been limited by the bandwidth of the (pulsed) lasers or by rotational contours of the investigated states [184, 187]. SEP techniques have traditionally been applied to gas phase systems or molecules in supersonic jets, in which vibrational states typically have longer lifetimes than in the condensed phase. In these experiments, the pulses from the pump and dump lasers usually address the same upper state within a time window that is shorter than the vibrational relaxation of that state. At the same time, the pump and dump laser pulses should have a negligible temporal overlap to avoid coherent effects that can lead to complex temporal behavior of the population. If this condition is fulfilled, simple rate equation approaches are sufficient to model the fluorescence depletion in SEP experiments [183].

An approach very similar to the SEP method has found a very prominent application in the context of stimulated emission depletion (STED) microscopy. STED microscopy achieves super-resolution using spatially modulated depletion to reduce the effective size of fluorescent spots on the sample [27, 188]. The basic principle and kinetic models to describe the population distribution in SEP and STED are very similar. Because STED deals with molecules in the condensed phase, fast relaxation to the vibrational ground state can be assumed such that the pump and depletion laser can be chosen to be resonant between two separate sets of levels. This is different than in the gas phase and renders coherent effects unimportant. While STED was first introduced in pulsed mode, it has also been shown to work with cw-lasers [189]. STED being primarily a microscopy technique, the spectral behavior of the depletion has only played a minor role in this field. There are, however, also investigations into the efficiency of stimulated emission at different wavelengths of the depletion laser [190, 191]. In dedicated experimental settings, such schemes can be
used to study fast internal processes in molecules [192]. Recently, Malein et al. demonstrated the use of STED spectroscopy for the investigation of PSBs of color centers in hexagonal boron nitride [28].

In this thesis, we apply STED spectroscopy to single DBT molecules in molecular crystals at cryogenic temperatures. These experiments differ from SEP spectroscopy in the gas phase because rotational and translational degrees of freedom are not available to the molecule and coupling to the matrix phonons leads to fast vibrational relaxation of the pumped state to the vibrational ground state of $S_1$. Unlike in STED microscopy, which is predominantly performed at RT, the molecules in our experiments have narrow vibronic transitions because electronic dephasing is absent at cryogenic temperatures. The cryogenic environment and embedding into the crystal additionally prevent photobleaching, enabling measurements of the same single molecule over periods of months. This makes high-resolution vibronic spectroscopy on the single molecule level and the subsequent exploration of intermolecular variation caused by local defects in the crystal possible. Since pump and depletion laser are resonant with two separate sets of levels in our experimental approach, coherent effects are not expected to play a role, even though we use cw-lasers without temporal separation. The resolution of STED spectroscopy for the measurement of vibronic linewidths is limited by the linewidth of the scanned laser. Due to the contribution of the electronic decay rate to the total linewidth of a vibronic transition, the resolution for the measurement of vibrational linewidths is limited by the linewidth of the 00ZPL in our experiments ($\sim 30$ MHz; see the next section for more details).

4.3.2 STED spectroscopy of a vibronic transition

The level scheme in Figure 4.6(a) describes STED spectroscopy of a transition $|e\rangle \leftrightarrow |v\rangle = |S_0, \vec{v}_v\rangle$ that involves a vibrational state in the electronic ground state. The model displayed in Figure 4.6(a) neither includes a triplet state nor a vibrational cascade because these states carry negligible population in DBT in pDCB (see sections 4.1 and 4.2). We also assume that $|v\rangle$ decays directly to $|g\rangle$ at a rate $\Gamma_{vg}$ corresponding to its lifetime-limited linewidth and we ignore the spontaneous emission from $|e\rangle$ to $|v\rangle$ (corresponds to $\Gamma_{ev} = 0$).

4 There is a report about STED microscopy at 76 K [193]. Spectroscopic details of the vibronic linewidths are not provided there, however.
4.3 Stimulated emission depletion spectroscopy

![Figure 4.6: Model for stimulated emission depletion spectroscopy (STED) of a single vibronic state. (a) Level scheme used for STED model calculations. The pump and depletion processes are induced by two cw-lasers that are resonant with the respective transitions. (b) Stimulated emission dip in the excited state population induced by scanning the depletion laser detuning at various depletion laser powers and $S_p = 1$. (c) $N_e(\Delta_d = 0)$ as a function of pump and depletion saturation parameters. (d) Same data as in (b), but represented as depletion factor $D$. (e) Saturation of the on-resonance depletion factor $D(\Delta_d = 0)$ as a function of $S_d$ for different values of $S_p$. (f) Power broadening of the Lorentzian profile of $D$ as a function of $S_d$.](image)

The rate equations describing the population distribution in the level scheme shown in Figure 4.6(a) are

$$\begin{pmatrix}
N_g \\
N_v \\
N_e \\
N_w
\end{pmatrix} =
\begin{pmatrix}
0 & \Gamma_{vg} & \Gamma_e & 0 \\
0 & -\Gamma_{vg} & 0 & 0 \\
0 & 0 & -\Gamma_e & \Gamma_{we} \\
0 & 0 & 0 & -\Gamma_{we}
\end{pmatrix}
\begin{pmatrix}
N_g \\
N_v \\
N_e \\
N_w
\end{pmatrix}
+ \begin{pmatrix}
W_p(N_w - N_g) \\
W_d(N_e - N_v) \\
W_d(N_v - N_e) \\
W_p(N_g - N_w)
\end{pmatrix}. \quad (4.36)$$
In the steady-state, the pump rate $W_p$ is given by equation (4.25) and the depletion rate $W_d$ can be expressed as

$$W_d = \frac{\Omega_d^2 (\Gamma_e + \Gamma_{vg})}{4(\Delta_d^2 + (\Gamma_e + \Gamma_{vg})^2/4)}. \quad (4.37)$$

The Rabi frequency $\Omega_d = -\vec{d}_v \cdot \vec{E}_d / \hbar$ is induced by the depletion laser that generates the field $\vec{E}(t) = \vec{E}_d \cos(\omega_d t)$ at the position of the molecule and is detuned by $\Delta_d = \omega_d - \omega_{ve}$ with respect to the frequency $\omega_{ve}$ of the transition $|v\rangle \leftrightarrow |e\rangle$. A derivation of the relation between $W_d$ and $\Omega_d$ from the Lindblad master equation can be found in appendix D.7.

The analytical solution for the excited state population in the model (4.36) can be expressed as:

$$N_e = (1-a)N_{e,\text{max}} \frac{S_p}{1+S_p} \left(1 - \frac{S_d}{1+S_d}\right) + aN_{e,\text{max}} \frac{S_p}{1+S_p}, \quad (4.38)$$

with pump saturation parameter $S_p$ as in equation (4.28) in the limit $\Gamma_{et}, \Gamma_{ec} \to 0$, the maximum population in $|e\rangle$,

$$N_{e,\text{max}} = \frac{\Gamma_{we}}{\Gamma_e} \frac{1}{K}, \quad (4.39)$$

with $K = 2 + \Gamma_{we}/\Gamma_e$, the depletion saturation parameter

$$S_d = \frac{(\Gamma_e + \Gamma_{vg})\Gamma_{we} + 2(\Gamma_e + \Gamma_{vg} + \Gamma_{we})W_p}{\Gamma_{vg}(\Gamma_{we}W_p + \Gamma_e(\Gamma_{we} + 2W_p))}W_d, \quad (4.40)$$

and a factor $a$ defined by:

$$a = \frac{\Gamma_e\Gamma_{we} + 2\Gamma_e W_p + \Gamma_{we} W_p}{(\Gamma_e + \Gamma_{vg})\Gamma_{we} + 2(\Gamma_e + \Gamma_{vg} + \Gamma_{we})W_p}. \quad (4.41)$$

Plots of $N_e(\Delta_d)$ for $S_p = 1$ and various values of $S_d$ are shown in Figure 4.6(b). The depletion laser causes a Lorentzian depletion dip in the excited state population that becomes deeper and broader with increasing depletion laser power. By defining the depletion factor as the normalized, depletion laser-induced decrease in excited state population

$$D = \frac{N_e(S_d = 0) - N_e(S_d)}{N_e(S_d = 0)}, \quad (4.42)$$
and inserting equation (4.38), one obtains

\[ D = (1 - a) \frac{S_d}{1 + S_d}. \] (4.43)

This shows that the depletion factor induced by the depletion laser displays a typical saturation behavior with \( D \propto S_d/(1 + S_d) \) and associated linewidth broadening \( \Delta \nu = \Delta \nu_0 (1 + S_d)^{1/2} \), where \( \Delta \nu_0 = \Gamma_{vg} + \Gamma_e \). Since \( \Delta \nu_0 \to \Gamma_e \) for \( \Gamma_{vg} \to 0 \), the resolution of the STED scheme for vibrational linewidths is limited by the decay rate of the oo-ZPL transition. This is not a limiting factor for the measurement of the vibrational relaxation rates of DBT in pDCB, because for this system the vibrational states have \( \Gamma_{vg} \gg \Gamma_e \). Plots of the depletion factor \( D \) and its saturation behavior resulting from the model discussed in this section are shown in 4.6(d–f). Note that the factor \( a > 0 \) limits the maximum possible depletion factor to \( D < 1 \). This is related to residual population in the pumped vibronic states and becomes relevant if the transfer rates induced by pump and stimulated emission are comparable to the vibrational relaxation rates. Figure 4.6(e) shows that the maximum depletion factor is reduced at higher pump powers. Our STED experiments were performed at \( S_p \approx 1 \), corresponding to \( W_p \approx \Gamma_e \ll \Gamma_{we} \), such we did not enter this regime.\(^5\)

To provide a more intuitive understanding of the relation (4.40) between depletion saturation parameter \( S_d \) and depletion rate \( W_d \), we simplify it using the assumptions \( \Gamma_{we} \approx \Gamma_{vg} \) and \( \Gamma_e \ll \Gamma_{vg} \). In this case, we obtain the equation

\[ W_d \approx W_p + \Gamma_e + 2 \Gamma_e W_p / \Gamma_{vg} S_d. \] (4.44)

For \( S_p = 1 \), i.e. \( W_p \approx \Gamma_e \), we obtain \( W_d = 2 \Gamma_e S_d \) or \( \Omega_d^2 = 2 \Gamma_e \Gamma_{vg} S_d \). Generally, if the molecule is pumped at a higher rate, one also needs to use a higher depletion power to reach saturation of the stimulated transition. While the rate \( W_d \) required to reach saturation is in the order of \( \Gamma_e \) for low \( W_p \ll \Gamma_e \), it increases considerably for high values \( W_p \gg \Gamma_e \).

If one or several vibrational states exhibit slow relaxation rates, for example in the order of \( \Gamma_e \) or slower, the level scheme shown in Figure 4.6(a) is not appropriate. For vibronic states in \( |S_1\rangle \), hot luminescence transitions \( |S_1, \vec{w}\rangle \to |S_0, \vec{v}\rangle \) become an important depopulation mechanism if their vibrational relaxation is slow enough [154]. Additionally, the time required for vibrational relaxation, a proper modeling of the vibrational relaxation cascade may be necessary as well.

---

\(^5\) If the transition rates induced by pump and depletion lasers are as fast as vibrational relaxation, a proper modeling of the vibrational relaxation cascade may be necessary as well.
cooling extends with the vibrational lifetimes, leading to a larger fraction of population residing in the vibrational cascade. This, in turn, leads to a decrease in the fluorescence emission rate of the molecule.

In appendix D.8, we show how the model discussed in this section can be extended by additional vibronic levels and a background term that accounts for absorption via PSBs. These extensions are necessary to fit the experimental data presented in section 6.2.

4.4 Splitting of a vibronic line

In the STED spectroscopy scheme presented in the previous section, the two lasers are resonant with two disjoint sets of molecular quantum states, which are connected to each other via incoherent vibrational relaxation. For this reason, the coherences in the equations of motion of the density matrix can be replaced by incoherent transfer rates $W_p$ and $W_d$ to obtain the steady-state behavior. If, however, both lasers are simultaneously resonant with the same (upper) vibronic state of the molecule, the coherent evolution of the density matrix elements becomes relevant to the description of the resulting non-Lorentzian resonance profiles. A strong second (control) laser that is resonant between the upper state and the equivalent vibronic state in $S_0$ can induce a dip in the resonance profile of the upper vibronic state.

We have experimentally observed the splitting of a vibrational level by tuning a strong laser beam to the corresponding transition between two vibronic states. The data from this experiment are presented and discussed in chapter 7. In section 4.4.1, we provide an overview of some basic understanding and the literature related to coherent effects in non-linear excitation schemes of quantum emitters. A model describing the essential processes that are relevant to our experiments is introduced in section 4.4.2. In section 7.2, the model is extended by some additional effects that are visible in our data but not related to the dip in the resonance. Throughout section 4.4 and chapter 7 we use QuTiP [59] to calculate the results of the Lindblad master equation model.

4.4.1 Coherent effects in three-level systems

The off-diagonal elements of the density matrix, i.e. the coherences, describe the phases of the quantum states of an atom or molecule relative to the field of the driving laser. One consequence of the coherences is the Rabi oscillations of the population between two quantum states driven by a resonant light field.
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Figure 4.7: Electromagnetically induced transparency (EIT) in (effective) three-level systems. (a) Typical EIT level scheme with probed transition $|1\rangle \leftrightarrow |3\rangle$ and a second transition state $|2\rangle \leftrightarrow |3\rangle$ addressed by the control laser. (b) Behavior of imaginary and real part of the linear susceptibility of the transition $|1\rangle \leftrightarrow |3\rangle$ in a three-level system with control laser off (dashed lines) and on (solid lines). The presence of the control laser field suppresses absorption in a narrow spectral window within the resonance. (c) Example of EIT in Li$_2$, measured via fluorescence. Reprinted Figures (a,b) with permission from [194]. Copyright (2005) by the American Physical Society. Reprinted Figure (c) with permission from [195]. Copyright (2010) by the American Physical Society.

This type of internal dynamics within a quantum system cannot be described using an incoherent rate equation treatment.

The interplay between the coherences becomes more complex in systems with three quantum states that are addressed by two lasers. An important line of work with such systems was triggered by several publications around the year 1990, discussing the phenomenon of electromagnetically induced transparency (EIT) [196, 197]. In these works it was shown that a strong (control) laser that is resonant between the probed state $|3\rangle$ and a metastable state $|2\rangle$ can suppress the optical absorption of another (probe) laser on the transition $|1\rangle \leftrightarrow |3\rangle$. The typical EIT-level scheme is shown in Figure 4.7(a). In such an arrangement, the medium becomes transparent for the probe laser in a narrow spectral window defined by the frequency of the control laser. The real and imaginary parts of the linear susceptibility of this three-level model are displayed in Figure 4.7(b). The transparency effect can be understood via the destructive interference of the excitation pathway $|1\rangle \rightarrow |3\rangle$ with a second excitation pathway $|1\rangle \rightarrow |3\rangle \rightarrow |2\rangle \rightarrow |3\rangle$ driven by the control laser and the coherences between the quantum states [194]. A detailed overview of EIT and related phenomena such as Autler-Townes splitting (ATS), slow light, and coherent population trapping can be found in the extensive review article by Fleischhauer et al. [194] and textbooks about quantum optics including that by Scully and Zubairy [198]. One example of an experimental realization of
EIT in Li$_2$ is shown in Figure 4.7(c). In this case, the induced transparency is monitored via a dip in the fluorescence emission.

The transparency dip of EIT can be described by a model of two coupled oscillators [199, 200]. In this analogy, the two oscillators correspond to the coherences $\hat{\rho}_{13}$ and $\hat{\rho}_{12}$ between the states of the three-level system. The coupling strength between the oscillators is determined by the Rabi frequency $\Omega_c$ of the control laser. A narrow transparency dip only exists if the linewidth of one oscillator is considerably smaller than the linewidth of the other oscillator. For EIT in a three-level system, the state $|2\rangle$ must thus be long-lived with a low dephasing rate. If the linewidth of level $|2\rangle$ is comparable to the linewidth of the probed state $|3\rangle$, the control laser cannot induce a narrow transparency dip. In this case, increasing the coupling strength by increasing the power of the control laser leads to a splitting of the resonance profile of the transition $|1\rangle \leftrightarrow |3\rangle$ into two separate Lorentzian lines. This corresponds to a (linear) AC-stark effect or ATS, caused by the intense field of the control laser on the transition $|2\rangle \leftrightarrow |3\rangle$, probed via the transition $|1\rangle \leftrightarrow |3\rangle$. Hence, depending on the exact properties of the atomic or molecular states and the power of the control laser, one can observe EIT, ATS, or a transition between the two regimes [200–202].

Usually, both EIT and ATS experiments have been performed on ensembles of atoms, in the gas phase. There are, however, also reports about EIT and ATS experiments on the single emitter level in a variety of different systems. Transparency effects have been observed for single Rb atoms in a cavity [203], trapped $^{138}$Ba$^+$ ions in free space [204], and superconducting qubits [205]. Moreover, ATS with single quantum dots [206] and single silicon vacancy centers [207] has been demonstrated. While there are also single molecule ATS experiments [64, 67], they have been performed while both lasers were (near-)resonant with the 00-ZPL transition of the molecule.

In our experiment, the states of the model system shown in Figure 4.7(a) correspond to

\begin{align}
|1\rangle &= |g\rangle = |S_0, \vec{0}\rangle \\
|2\rangle &= |v\rangle = |S_0, \vec{v}_v\rangle \\
|3\rangle &= |w\rangle = |S_1, \vec{v}_w\rangle.
\end{align}

The states $|g\rangle$, $|v\rangle$, and $|w\rangle$ are displayed in Figure 4.8(a). Here, $|\vec{v}_v\rangle$ and $|\vec{v}_w\rangle$ are fundamental excitations of an equivalent normal mode in $S_0$ and $S_1$, respectively. Since $|v\rangle$ is a vibronic state with a fast relaxation rate, our system does not fulfill the conditions for EIT, in which state $|2\rangle$ exhibits a long
coherence time. The configuration in our experiment further differs from
typical EIT configurations because state $|w\rangle$ decays quickly to a metastable
state $|e\rangle = |S_1, \vec{0}\rangle$ that relaxes to the ground state at a rate that is slow compared
to the decay of $|v\rangle$ and $|w\rangle$. Moreover, we do not monitor the transmission
of the probe laser but the fluorescence from the molecule. Nevertheless, our
system behaves according to the mechanisms of three-level systems addressed
by two laser fields. In the following section we develop a model that describes
the most relevant processes for the experiment discussed chapter 7. For this,
we adopt some of the methods presented in the theses of Weatherall [208]
and Fisher [209].

4.4.2 Four-level model for vibronic line splitting

We use a Lindblad master equation model based on the level scheme shown
in Figure 4.8(a) to describe the splitting of a vibronic line profile. Besides the
three states $|g\rangle$, $|v\rangle$, and $|w\rangle$ from a typical EIT-configuration, this scheme
includes the excited state $|e\rangle$ that acts as a metastable state on the decay path
from $|w\rangle$ to $|g\rangle$. $\Omega_p$ denotes the Rabi frequency of the probe laser, $\Omega_c$ the
Rabi frequency of the control laser. Since the vibrational frequencies $\omega_{gv}$
and $\omega_{ew}$ of the normal modes associated with $|v\rangle$ and $|w\rangle$ are usually similar,
the frequency of the transition $|v\rangle \leftrightarrow |w\rangle$ is similar to the frequency of the
00-ZPL. Therefore, the control laser generally interacts with the transition
$|g\rangle \leftrightarrow |e\rangle$ as well. We label the Rabi frequency induced by the control laser
on this transition by $\beta_g \Omega_c$. To avoid the molecule being pumped effectively
via the control laser, the vibrational frequencies $\omega_{gv}$ and $\omega_{ew}$ should ideally
differ considerably.

We model the coherent light-molecule interaction of the system shown in
Figure 4.8(a) in the framework of the Lindblad master equation discussed
in section 2.5 [208, 209]. The Hamiltonian of this model (in the basis $I =
\{|g\rangle, |v\rangle, |e\rangle, |w\rangle\}$) is given by

$$\hat{H} = \hat{H}_m + \hat{H}_{mf},$$

(4.48)

with the Hamiltonian of the molecule

$$\hat{H}_m = \begin{pmatrix}
\hbar \omega_g & 0 & 0 & 0 \\
0 & \hbar \omega_v & 0 & 0 \\
0 & 0 & \hbar \omega_e & 0 \\
0 & 0 & 0 & \hbar \omega_w
\end{pmatrix}$$

(4.49)
Figure 4.8: Excited state population in a four-level model for the splitting of a vibronic line. (a) Level scheme. See the main text for the description of the symbols. (b-f) Excited state population as a function of probe and control laser detuning for the parameters listed in column $M_{vw}$ of Table 4.1 and (except where otherwise stated): $\Omega_p = 2(\Gamma_e \Gamma_{we})^{1/2}$, $\Omega_c = \Gamma_{ve}$, $\beta_g = 1$, $\Delta_p = 0$, and $\Delta_c = 0$. (b) For increasing values of $\Omega_c$, the dip in the resonance profile of $|w\rangle$ increases until it starts to split into two lines. (c) Changing the frequency of the control laser moves the spectral position of the dip in the resonance profile of $|w\rangle$. (d) A decrease in of the vibrational relaxation rate of $|v\rangle$ leads to narrower transparency dips. (e) Scanning the control laser while the molecule is pumped via $|w\rangle$ leads to a dip for $\omega_c = \omega_{vw}$ due to the splitting of the transition $|g\rangle \leftrightarrow |w\rangle$. Interaction with the 00-ZPL transition for $\omega_c = \omega_{ge}$ either leads to absorption or stimulated emission, depending on whether the molecule is pumped below or above saturation. (f) Detuning the probe laser slightly from the resonance with $|w\rangle$ leads to a dispersive profile around $\omega_c = \omega_{vw}$.

and the Hamiltonian $\hat{H}_{mf}$ describing the interaction between the molecule and the incident classical light field $\vec{E}(t)$ in the dipole approximation:

$$\hat{H}_{mf} = -\hat{\vec{d}} \cdot \vec{E}(t).$$  \hspace{1cm} (4.50)

The light field $\vec{E}(t)$ is the sum of probe and control laser fields:

$$\vec{E}(t) = \vec{E}_p \cos(\omega_p t) + \vec{E}_c \cos(\omega_c t).$$  \hspace{1cm} (4.51)
4.4 Splitting of a vibronic line

We assume that the frequency of the probe laser $\omega_p$ is close to the frequency of the transition $|g\rangle \leftrightarrow |w\rangle$ (i.e. $|\omega_p - \omega_{gw}|/\Gamma_{we} \sim 1$) and that the frequency of the control laser $\omega_c$ is close to the frequency of the transition $|v\rangle \leftrightarrow |w\rangle$ and the frequency of the oo-ZPL (i.e. $|\omega_c - \omega_{vw}|/\Gamma_{vg} \sim 1$ and $|\omega_c - \omega_{ge}|/\Gamma_{vg} \sim 1$). At the same, we assume that $\omega_p$ and $\omega_c$ have a large frequency difference ($|\omega_p - \omega_c|/\Gamma_{we} \gg 1$).

In the basis of the molecular states, the dipole operator can be expressed as

$$\hat{d} = \sum_{i,j \in I} |i\rangle \langle i| \hat{d} |j\rangle \langle j| = \begin{pmatrix} 0 & 0 & \hat{d}_{ge} & \hat{d}_{gw} \\ 0 & 0 & \hat{d}_{ve} & \hat{d}_{vw} \\ \hat{d}_{ge} & \hat{d}_{ve} & 0 & 0 \\ \hat{d}_{gw} & \hat{d}_{vw} & 0 & 0 \end{pmatrix}$$ (4.52)

with $\hat{d}_{ij} = \langle i| \hat{d} |j\rangle$ and the phases of the molecular states chosen such that the transition dipole elements are real numbers. In equation (4.52), we utilize that $\langle S_k | \hat{d} | S_k \rangle = 0$ and that the studied vibronic modes are not infrared active.

To apply the rotating-wave approximation, we transform $\hat{H}_{mf}$ to the interaction picture using the operator $\hat{U} = e^{i\hat{H}_m t/\hbar}$. The effect of this transformation on the dipole operator is:

$$\hat{d}_I = \hat{U} \hat{d} \hat{U}^\dagger = \begin{pmatrix} 0 & 0 & \hat{d}_{ge} e^{-i\omega_{get}} & \hat{d}_{gw} e^{-i\omega_{gwt}} \\ 0 & 0 & \hat{d}_{ve} e^{-i\omega_{vet}} & \hat{d}_{vw} e^{-i\omega_{vwt}} \\ \hat{d}_{ge} e^{i\omega_{get}} & \hat{d}_{ve} e^{i\omega_{vet}} & 0 & 0 \\ \hat{d}_{gw} e^{i\omega_{gwt}} & \hat{d}_{vw} e^{i\omega_{vwt}} & 0 & 0 \end{pmatrix}$$ (4.53)

with $\omega_{ij} = \omega_j - \omega_i$. The Hamiltonian in the interaction picture is then given by

$$\hat{H}_I = \hat{U} \hat{H}_{mf} \hat{U}^\dagger = -\hat{d}_I \cdot \vec{E}.$$ (4.54)

In the rotating wave approximation, we only keep the slowly varying terms in this Hamiltonian, i.e. those terms which contain the difference between a laser frequency and a (nearly) resonant transition frequency. These terms
are the ones oscillating at \( \omega_p - \omega_{gw} \), \( \omega_c - \omega_{vw} \), and \( \omega_c - \omega_{ge} \). Applying this approximation yields:

\[
\hat{H}_{\text{RWA}} = -\frac{1}{2} \begin{pmatrix}
0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 \\
(d_{ge} \cdot \vec{E}_c)e^{i(\omega_{ge} - \omega_c) t} & 0 & 0 & 0 \\
(d_{gw} \cdot \vec{E}_p)e^{i(\omega_{gw} - \omega_p) t} & (d_{vw} \cdot \vec{E}_c)e^{i(\omega_{vw} - \omega_c) t} & 0 & 0
\end{pmatrix} + \text{h.c.,}
\]

where h.c. denotes the Hermitian conjugate of the previous term in the equation. Back in the Schrödinger picture (\( \hat{H}_{\text{RWA}} = \hat{U}^\dagger \hat{H}_{\text{RWA}} \hat{U} \)), the transition frequencies vanish and we obtain

\[
\hat{H}_{\text{RWA}} = \hbar \left( \begin{pmatrix}
0 & 0 & \beta_g \Omega_c e^{i\omega_c t} & \Omega_p e^{i\omega_p t} \\
0 & 0 & 0 & \Omega_c e^{i\omega_c t} \\
\beta_g \Omega_c e^{-i\omega_c t} & 0 & 0 & 0 \\
\Omega_p e^{-i\omega_p t} & \Omega_c e^{-i\omega_c t} & 0 & 0
\end{pmatrix}\right)
\]

with the (real) Rabi frequencies \( \Omega_p = -\vec{d}_{gw} \cdot \vec{E}_p / \hbar \), \( \Omega_c = -\vec{d}_{vw} \cdot \vec{E}_c / \hbar \), and \( \beta_g \Omega_c = -\vec{d}_{ge} \cdot \vec{E}_c / \hbar \) as indicated in Figure 4.8(a).

In a next step, we remove the time-dependencies in the Hamiltonian by transforming the system to a rotating frame. A method for finding the operator \( \hat{R} \) that generates the rotation matrix \( e^{-i\hat{R}} \) is given in the thesis of Fisher [209, chapter 3.2]. As described there, one can use the ansatz

\[
\hat{R} = c_{gw} \sigma^z_{gw} + c_{vw} \sigma^z_{vw} + c_{ge} \sigma^z_{ge}
\]

to solve the equations

\[
[\hat{R}, \hat{\sigma}^x_{gw}] = i \omega_p t \cdot \hat{\sigma}^y_{gw} \\
[\hat{R}, \hat{\sigma}^x_{vw}] = i \omega_c t \cdot \hat{\sigma}^y_{vw} \\
[\hat{R}, \hat{\sigma}^x_{ge}] = i \omega_c t \cdot \hat{\sigma}^y_{ge},
\]

where the operators are defined as

\[
\hat{\sigma}^x_{mn} = |m\rangle\langle n| + |n\rangle\langle m| \\
\hat{\sigma}^y_{mn} = -i(|m\rangle\langle n| - |n\rangle\langle m|) \\
\hat{\sigma}^z_{mn} = |m\rangle\langle m| - |n\rangle\langle n|.
\]
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Evaluating the commutators leads to the system of equations

\[
\begin{pmatrix}
2 & 1 & 1 \\
1 & 0 & 2 \\
1 & 2 & 0 \\
\end{pmatrix}
\begin{pmatrix}
c_{gw} \\
c_{vw} \\
c_{ge} \\
\end{pmatrix}
= \begin{pmatrix}
\omega_p t \\
\omega_c t \\
\omega_c t \\
\end{pmatrix}
\] (4.64)

for the cofficients of \( \hat{R} \). Solving this system of equations for the coefficients \( c_{ij} \) and using equation (4.63) we can write the rotation matrix in the basis of molecular states as:

\[
\hat{R} = \frac{1}{2}
\begin{pmatrix}
\omega_p t & 0 & 0 & 0 \\
0 & (2\omega_c - \omega_p) t & 0 & 0 \\
0 & 0 & (\omega_p - 2\omega_c) t & 0 \\
0 & 0 & 0 & -\omega_p t \\
\end{pmatrix}
\] (4.65)

The Hamiltonian in the rotating frame is given by

\[
\hat{H} = e^{-i\hat{R}}(\hat{H}_m + \hat{H}_{RWA})e^{i\hat{R}} + \hbar \partial_t \hat{R}.
\] (4.66)

Inserting the above result for \( \hat{R} \), we obtain

\[
\hat{H} = \frac{\hbar}{2}
\begin{pmatrix}
2\omega_g + \omega_p & 0 & \beta_g \Omega_c & \Omega_p \\
0 & 2(\omega_v + \omega_c) - \omega_p & 0 & \Omega_c \\
\beta_g \Omega_c & 0 & 2\omega_e - 2\omega_c + \omega_p & 0 \\
\Omega_p & \Omega_c & 0 & 2\omega_w - \omega_p \\
\end{pmatrix}
\] (4.67)
and by shifting the energy axis such that the ground state energy is zero (i.e. subtract $\hbar/2(2\omega_g + \omega_p)$ from the diagonal), we arrive at:

$$
\hat{H} = \frac{\hbar}{2} \begin{pmatrix}
0 & 0 & \beta_g \Omega_c & \Omega_p \\
0 & 2(\omega_{gv} + \omega_c - \omega_p) & 0 & \Omega_c \\
\beta_g \Omega_c & 0 & 2(\omega_{ge} - \omega_c) & 0 \\
\Omega_p & \Omega_c & 0 & 2(\omega_{gw} - \omega_p)
\end{pmatrix}
$$

(4.68)

$$
= \hbar \begin{pmatrix}
0 & 0 & \beta_g \Omega_c/2 & \Omega_p/2 \\
0 & \Delta_c - \Delta_p & 0 & \Omega_c/2 \\
\beta_g \Omega_c/2 & 0 & -\Delta'_c & 0 \\
\Omega_p/2 & \Omega_c/2 & 0 & -\Delta_p
\end{pmatrix}
$$

(4.69)

with the detunings $\Delta_p = \omega_p - \omega_{gw}$, $\Delta_c = \omega_c - \omega_{vw}$, and $\Delta'_c = \omega_c - \omega_{ge}$.

Spontaneous electronic and vibrational decay processes are described by the jump operators:

$$
\hat{L}_{we} = |e\rangle\langle w| 
$$

(4.70)

$$
\hat{L}_{eg} = |g\rangle\langle e| 
$$

(4.71)

$$
\hat{L}_{ev} = |v\rangle\langle e| 
$$

(4.72)

$$
\hat{L}_{vg} = |g\rangle\langle v| 
$$

(4.73)

with the corresponding decay rates $\Gamma_{ij}$ indicated in Figure 4.8(a).

Figure 4.8 shows the results of QuTiP calculations of the model Hamiltonian (4.69) combined with the Lindblad decay operators from equations (4.70)–(4.73). Unless otherwise stated, the parameters used for these calculations are listed in column $M_{vw}$ of Table 4.1 and were chosen to resemble the case studied experimentally in chapter 7. This means in particular that the difference between the vibrational frequencies of $|v\rangle$ and $|w\rangle$ is large (here: $\omega_{ge} - \omega_{vw} = 10 \cdot \Gamma_{we}$), such that the control laser is not simultaneously resonant with the oo-ZPL transition and $|v\rangle \leftrightarrow |w\rangle$. In this case, the resonance profiles of the vibronic level and the oo-ZPL transition do not overlap considerably and can be treated as separate phenomena. Additionally, we use $\Gamma_{vg} = 0.5\Gamma_{we}$, similar to the case in our experiment.

The dip emerging in the vibronic resonance profile of $|w\rangle$ with increasing control laser power is shown in Figure 4.8(b) via the excited state population of the molecule. As the control laser is detuned from the exact resonance
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with the transition $|v\rangle \leftrightarrow |w\rangle$, the position of the dip in the resonance profile changes (see Figure 4.8(c)). With increasing (vibrational) lifetime of the state $|v\rangle$, the dip in the resonance profile becomes narrower and deeper, as shown in Figure 4.8(d).

If the control laser is scanned while the probe laser is at a fixed frequency, one observes a dip for $\Delta_c = 0$, because the splitting of the vibronic line reduces the absorption cross section of the molecule at the frequency of the probe laser (see Figure 4.8(e)). For $\omega_c = \omega_{ge}$, i.e. the case that the control laser is resonant with the oo-ZPL transition, one observes either a dip or a peak in the excited state population, depending on whether the molecule is pumped above $S_p = 1$ via the probe laser or not. Below saturation, the excited state can additionally be pumped via the oo-ZPL. Above saturation, the excited state is depleted by stimulated emission along the oo-ZPL. Depending on the detuning of the probe laser, the dips in the scan of the control laser have a symmetric or asymmetric profile (see Figure 4.8(f)).
5 Experimental setup

In this chapter we describe the experimental setup used for the measurements presented in chapters 6 and 7. The setup consists of a confocal microscope and a closed-cycle dilution cryostat to study single molecules in molecular crystals at cryogenic temperatures. Two lasers were coupled to the beam path of the microscope to perform the non-linear spectroscopy experiments.

In section 5.1, we provide a detailed description of the optical setup and its components. The sample preparation methods of the DBT:pDCB and DBT:Ac samples used for the measurements in chapters 6 and 7 are described in section 5.2. In section 5.3, we discuss our design of an insert that enables free space optical access to single molecules in the dilution cryostat. Additionally, we show transmission measurements of planar and wedged cryostat windows, we list the temperatures reached inside the cryostat under various conditions, and we quantify the effect of vibrations on the measured fluorescence signal of a single molecule.

5.1 Optical setup

We used a confocal microscope to optically access the samples in the cryostat. Similar optical setups are described in other theses of the Sandoghdar group [30, 31, 210]. Two tunable narrow-band lasers were coupled to the beam path of the microscope to perform the vibronic spectroscopy experiments presented in chapters 6 and 7. A sketch of the optical setup is shown in Figure 5.1. The two separate beam paths shown on the left side of the figure are used for polarization and intensity control of the two laser beams.

The beam shown on the upper left side in Figure 5.1 is mainly used as the pump or control laser. It is generated by a tunable Ti:Sapphire laser (Matisse, Sirah) that is stabilized by a reference cavity. The laser wavelength is read out by a wavemeter (WS6-200, HighFinesse) at an absolute accuracy of 200 MHz.

and a resolution of 4 MHz. The laser light is coupled to a polarization maintaining fiber (PM780-HP, Thorlabs; collimation: AC254-030-B, Thorlabs) to guide it from a dedicated laser lab to the lab of the dilution cryostat. The polarizer (Glan-Taylor polarizer, Thorlabs) and half-wave plate (AHWP05M-630, Thorlabs) in front of the fiber are used to match the laser polarization to the fiber. The half-wave plate (AHWP05M-600, Thorlabs) and polarizer (LPVIS050-MP2, Thorlabs) behind the fiber define the initial polarization of the light on the optical table around the cryostat. The laser power in front of the fiber was often around 200 mW. The laser filter (FESH0750, Thorlabs) is used to remove red-shifted photons created by the strong laser light inside the optical fiber. Those background photons can reach the detectors without much attenuation if their frequency falls in the same spectral range as the detection bandpass window. The type of the laser filter was chosen in such a way that its spectral blocking range overlaps with the detection bandpass window. By slight tilting of the laser filter, the position of the filter edge was fine-tuned for optimal background suppression. In our experiments, the laser filter was crucial to obtaining spectra with low background. To stabilize the laser intensity on the optical table around the cryostat, we sampled the laser intensity using a photodiode (PDA36A-EC, Thorlabs; beam sampler: BSF10-B, Thorlabs) and used a home-made PID-controller to adjust the intensity in the first diffraction order of an AOM (MT200-A0.5-VIS, AA Opto-Electronic) in front of the fiber. The half- and quarter-wave plate (AQWP05M-630, Thorlabs;
5.1 Optical setup

AQWP05M-600, Thorlabs) behind the beam sampler were used to match the polarization of the laser to the direction of the transition dipole moment of the investigated molecule. The intensity of the beam could be adjusted in steps by a filter wheel equipped with neutral density filters (NE5xxB-B, Thorlabs) between the beam splitter of the intensity stabilization and the wave plates (not shown in Figure 5.1).

The setup for the second (mainly depletion or probe) laser\(^1\), shown in the lower left part of Figure 5.1, is very similar to the one of the first laser. Because this laser was often scanned over broad spectral ranges (\(~10\) THz), its intensity was stabilized behind the wave plates (AHWP10M-980, Thorlabs; AQWP10M-980, Thorlabs) to compensate for etaloning caused by these optical elements. Optional neutral density filters (NExxB-B, Thorlabs; not shown) were sometimes introduced into the beam path but many measurements were performed without such filters. The elements in the beam path of the second laser are (from left to right): a narrow-band tunable Ti:Sapphire laser (SolsTiS, MSquared) with reference cavity, a high precision wavemeter (WS7, HighFinesse; absolute accuracy: 60 MHz, resolution: 2 MHz), an AOM (MT200-Ao.5-800, AA Opto-Electronic), a linear polarizer (LPNIRE100-B, Thorlabs), a half-wave plate (WPH05M-780, Thorlabs), a home-made PID controller, a polarization-maintaining fiber (PM630-HP, Thorlabs; incoupling: RMS10X, Thorlabs; collimation: AC254-030-B, Thorlabs), a half-wave plate (400–850 nm, Thorlabs), a linear polarizer (LPVIS100-MP2, Thorlabs), a laser filter (depending on experiment: 750 LP ET, Chroma; FESH0750, Thorlabs; FF01-775/SP-25, Semrock), a half-wave plate (AHWP05M-980, Thorlabs), a quarter-wave plate (AQWP05M-980, Thorlabs), a wedged beam sampler (BSF10-B, Thorlabs), and a photodiode (PDA36A-EC, Thorlabs). The use of an appropriate laser filter for background suppression is important for this beam path because of the high laser powers coupled into the optical fiber. This even holds if the detection window is blue-detuned with respect to the laser frequency (as in many STED spectroscopy measurements of chapter 6), probably because of anti-Stokes light created in the fiber.

Both beams are combined to a common beam path in a 50/50 cube beam splitter (CCM1-BS014/M, Thorlabs). A second, wedged beam splitter guides a fraction of the laser light to the excitation path. For samples 1 and 2 (see Table 5.1) we used a reflection/transmission ratio of 3/97 (BSF10-B, Thorlabs). To increase the laser power in front of the cryostat for the measurements in chapter 7, we replaced the beam splitter by one with a 30/70 splitting

\(^1\) This laser was also used for the fluorescence excitation experiments of section 6.1 and section 6.4.
ratio for sample 3 (BSS11, Thorlabs). The combination of a scanning mirror (FSM-300, Newport) and a 4f-system (2x AC508-300-B, Thorlabs) enables lateral scanning of the laser spot over the sample in the cryostat [31]. The focus of the laser light is created by an aspheric lens (C330TMD-B, Thorlabs) with a numerical aperture of 0.7 and a working distance of 1.8 mm. For the experiments with DBT in pDCB, we used high-index solid immersion lenses (SIL) to improve the coupling of light to single molecules [30]. The SILs used for the experiments are ZrO$_2$ ($n = 2.14$ at $\lambda = 740$ nm) half-ball lenses with a radius of 3 mm (A.W.I. Industries) and antireflection coating. For the experiments with DBT in Ac, no SILs were used.

In the detection path, fluorescence light from the molecule is separated from the intense laser light using a narrow spectral bandpass created by several (tunable) long- and shortpass filters (TLP01-790-25x36, Semrock; 750 LP ET, Chroma; TSP01-790-25x36, Semrock; FF01-758/SP-25, Semrock; FESH0750, Thorlabs) and a narrow bandpass filter (770-1-OD4, Alluxa) or combinations thereof. The exact arrangement of these filters depends on the spectral range accessed by the lasers in a given experiment. Most of the time, we filtered out a single spectral line (either the 00-ZPL or the strongest vibronic line) from the molecular fluorescence (see also Figure 6.1). Restricting detection to a single spectral line instead of a broader spectral region increases the spectral range accessible to the scanned (typically: depletion) laser without leaking through the filter.

The detection path has a camera (Zyla 4.2P, Andor) for the optical alignment of the setup and the initial identification of molecules on a sample using wide-field illumination. For wide-field illumination, we inserted a lens (AC254-300-B) between the two beam splitters shown in the center of Figure 5.1. A spectrometer (SP-2-500i, Princeton Instruments; grating: 1800 g/mm with blaze angle at 500 nm; camera: PIXIS: 400 BR, Princeton Instruments) accessed via a multi-mode fiber (FG050LGA, Thorlabs) was used for the detection of spectrally dispersed fluorescence. Most of the experiments in chapters 6 and 7 were performed using confocal excitation and fluorescence detection via APDs (SPCM-AQR-14, Perkin Elmer). The TTL pulses from the APDs were counted and routed to a PC using a DAQ-Card (USB-6363-BNC, National Instruments). A dedicated experiment control script (LabVIEW, National Instruments) was used to record the APD signal in sync with the wavemeter output and other signals from the experiment. For autocorrelation measurements, we arranged two APDs in an HBT-setup and used a PicoHarp 300 (PicoQuant) for time-correlated single photon counting.
5.2 Sample preparation

In the context of this thesis, we studied DBT in the organic host crystals pDCB and Ac. Most of the experiments were performed with DBT in pDCB. The steps of the corresponding sample preparation procedure are described in section 5.2.1. The vapor-phase growth technique used to create doped Ac crystals is explained in section 5.2.2.

5.2.1 DBT in para-dichlorobenzene

In this section, we describe the preparation of pDCB crystals that are sparsely doped with DBT molecules for our experiments of chapters 6 and 7. We used fused silica substrates with two etched nanochannels to create a confined space for the doped pDCB crystal. A sketch of the sample design is shown in Figure 5.2. The dimensions of the nanochannels on the samples used in this thesis are listed in Table 5.1. Initially, the bare substrate was heated to 120 °C for some minutes. Then, a SIL was mounted on the substrate using a spring steel clamp that was screwed to the sample holder (see Figure 5.2 and Figure 5.6(a,b)). The sample holder has a 2.5 mm diameter hole at the opposite side of the SIL in order to transmit most of the light that is focused on the sample. Details about the use of SILs in the context of single molecule spectroscopy can be found in the PhD thesis of G. Wrigge [30].
DBT:pDCB was prepared at a low molar concentration of about 20–30 ppb, and ground into a very fine power using a spatula. To bring the doped pDCB crystal into the nanochannel, the powder was first arranged on the channel substrate around the SIL. Then the sample holder was heated on a heating plate (setpoint: 80 °C) until the crystal power melted and moved into the channels due to capillary forces. We stored the sample holder for about 2 min in a water bath at 4 °C to quickly cool the massive sample holder and the pDCB crystal. In the next step, the crystal under the SIL was remelted 1 to 3 times with the help of a soldering iron whose tip was brought into contact with the substrate and the side of the SIL (temperature ~ 350 °C). According to our experience, remelting the crystal improves the spectral stability of DBT molecules in pDCB. A microscope image of the remelted crystal in the nanochannels of sample 1 is shown in Figure 5.6(c). It takes several hours until the samples reach temperatures below 0 °C in the cryostat. Before that, they are exposed to pressures < 10^{-5} mbar in the vacuum can of the cryostat. To prevent sublimation of the pDCB crystal during this time, we applied a layer of Apiezon N vacuum grease (M&I materials) around the interface between SIL and substrate using a fine syringe needle (see Figure 5.2 and Figure 5.6(b)). Then we cleaned the bottom surface of the sample holder using ethanol, blow-dried the sample with nitrogen, and mounted it on the nanopositioners in the cryostat as shown in Figure 5.4.

5.2.2 DBT in anthracene

Ac crystals doped with DBT were created by a vapor-phase growth technique [211], using the same steps and apparatus as described in the PhD thesis by D. Wang [212].

Initially, zone-refined anthracene (> 99.5%, TCI) was mixed with DBT (Dr. W. Schmidt, Laboratory for PAH Research, Greifenberg, Germany) at a mass ratio

<table>
<thead>
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<th>sample</th>
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<th>molecule ids</th>
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<th>channel width</th>
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<td>460 nm</td>
<td>250 µm</td>
</tr>
<tr>
<td>4</td>
<td>DBT:Ac</td>
<td>6</td>
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<td></td>
<td></td>
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</table>

Table 5.1: Molecules and samples studied in this thesis.
of 24 ppm and melted to create a doped crystal. Some of the doped crystal was then placed in a vial and enclosed under nitrogen atmosphere. Using a heat gun set to 320 °C, the crystals in the vial were heated until they started to melt and sublimate. Then, the heat gun was removed and fresh nitrogen at room temperature was used to flush the vial. In this process, DBT-doped Ac crystals form on a cover glass that was placed inside the vial. To transfer these crystals to a fused silica substrate that is compatible for operation in the cryostat, we gently removed them from the cover glass using a spatula.

The fused silica substrate with the Ac crystals was mounted to a sample holder similar to the one shown in Figure 5.6(a) for cooldown in the dilution cryostat. Note that in contrast to the pDCB samples, we did not use a SIL for the measurements with Ac. Therefore, the Ac crystals were not enclosed in a vacuum-tight environment. Ac has a lower sublimation rate than pDCB at room temperature. Nevertheless, if we placed relatively few and thin Ac crystals in the cryostat, they sublimated completely before the base temperature was reached. To avoid this, we used a high number of Ac crystals on the sample substrate, in some regions even densely stacked on top of each other. In this manner, we were able to preserve sufficient Ac crystals for single molecule experiments at low temperatures.

5.3 Dilution cryostat

A dilution cryostat reaches temperatures well below the boiling points of $^4$He ($T_b = 4.21$ K) and $^3$He ($T_b = 3.19$ K) by exploiting a phase separation in liquid $^3$He/$^4$He mixtures into a $^3$He-rich and $^3$He-poor phase at $T < 0.88$ K. The transition of $^3$He atoms from the concentrated to the diluted phase leads to a cooling effect with sufficient cooling power to reach temperatures as low as 2 mK. Details about the physical and technical details of $^3$He/$^4$He dilution cryostats as well as about the fascinating behavior of the quantum liquids $^3$He and $^4$He can be found in the monograph by Pobell [213]. The lower temperatures reached in a dilution cryostat compared to a $^4$He bath cryostat may help to reduce spectral diffusion of molecules triggered by thermally activated processes. Since the experiments presented in this thesis have been performed with molecule-crystal systems in which molecules are spectrally stable and thermal dephasing is negligible for $T \leq 3$ K (see Figure 2.3(b)), the lower temperatures reached by the dilution cryostat were not necessary for obtaining the results presented in this thesis. In future experiments with novel phononic environments, however, the mK-temperatures may help to improve spectral stability of single molecules. We note that the closed cycle operation of the dilution cryostat facilitates its daily operation considerably,
Experimental setup

5.3 Cryostat model and sample holder insert

For our experiments we used a commercial closed-cycle dilution cryostat (BF-LD250, Bluefors). It contains two closed systems in which helium circulates to provide the cooling effect. A pulse tube cooler containing only $^4$He cools the cryostat to about 4 K. The $^3$He/$^4$He mixture circulates in a separate system that is precooled by the pulse tube cooler and in which a turbo pump generates the pressure necessary to condense the mixture and to drive the cooling transitions of the $^3$He atoms between the two phases. The mixture is additionally guided through a cold trap at liquid nitrogen temperatures to clean it of contamination.

Our cryostat model includes a heavy aluminum top frame for passive vibration isolation from the vibrations induced by the pulse tube and the turbo pump. Additionally, a helium battery connected to the 4 K plate is available, permitting several hours of cryostat operation while the pulse tube cooler is turned off. Inside the cryostat, there is a sequence of connected plates with temperatures decreasing from the top to the bottom (see Figure 5.3): the...
5.3 Dilution cryostat

50 K plate, 4 K plate, still plate, cold plate, and mixing chamber (MXC) plate. The interior of the cryostat is protected by three radiation shields that are connected to the still plate, the 4 K plate, and the 50 K plate, respectively. All these shields are enclosed by the outermost can which is vacuum-tight. The radiation shields and the vacuum can each contain five openings (four on the sides, one at the bottom) for free space optical access through optional windows. A check after the initial setup of the cryostat in a configuration where all windows were blind flanged yielded a base temperature of \(< 7 \text{ mK}\) on the MXC plate. The cooling power at 20 mK (100 mK) was measured to be 17 \(\mu\)W (480 \(\mu\)W). In our experiments, we used only one set of four windows on one side of the cryostat while the others remained covered by blind flanges.

We designed an insert for the cryostat to mount samples in the optical path defined by the window positions, about 17 cm below the MXC plate. Important considerations for the design of the insert were (i) good thermal contact of the sample to the MXC plate, (ii) the ability to adjust the lateral sample position as well as the focus of the laser beam during the operation of the cryostat, and (iii) stability with respect to vibrations. Figure 5.4 shows our design of the insert. The sample is accommodated in the sample holder and can be moved in the plane normal to the incident beam using two nanopositioners. We used the nanopositioner model ANPx101/RES/LT (Attocube) for movements parallel to the base plate (x-direction) and ANPz102/RES/LT (Attocube) for movements perpendicular to it (y-direction). For position control and readout of the nanopositioners we used the dedicated piezo motion controller ANC350 (Attocube). The laser beam is focused by an aspheric lens (C330TMD-B, Thorlabs/Lightpath) with an NA of 0.7 and a working distance of 1.8 mm. The nanopositioner mounted on the asphere holder (ANPx101/RES/LT) is used to adjust the focal plane of the laser beam. We realized in the course of this thesis that the asphere model C330TMD-B displays a poor (off-axis) imaging performance compared to other models with similar NA and working distance (for example: model 355330 from Lightpath).

In a dilution cryostat, the sample is cooled by thermal contact with the MXC plate. Establishing a good thermal link between the sample and the MXC plate is therefore crucial to provide sufficient cooling power at the position of the sample. Obstacles to the heat flow can be materials with low thermal conductivity, such as the titanium from which the nanopositioners are made, long or thin rods through which the heat needs to be transported, and weak (bolted) connections between two objects [213]. Because of its high thermal conductivity at low temperatures, we used oxygen-free copper (Cu-OFE) coated with gold (5 \(\mu\)m thickness) for all the materials that are shown in gold in Figure 103.
Figure 5.4: Cryostat insert for thermal contact and optical access to the sample. (a) Description of the most important parts of the cryostat insert. The direction of the laser beam (z) is indicated. (b) Central part of the insert shown from a different angle than in (a). (c,d) Complete insert shown from different angles than in (a). Screws, wires, and flexible connections of the thermal couplers are not shown. See Figure 5.5 for photographs of the insert.
5.3 Dilution cryostat

Figure 5.5: Photographs of the open dilution cryostat and the insert. (a) View into the cryostat after removing the vacuum can and the radiation shields. The uppermost plate visible in the image is the 4 K-plate. The cryostat insert at the bottom (marked by the white dashed frame) is attached to the mixing chamber plate. (b) Detailed view on the insert from the side. The cables attached to the rod on the left side are connected to the controller of the nanopositioners. (c) Photograph of the aspheric lens in front of the sample holder. (d) View on the sample holder from the direction opposite to the direction of laser propagation. Photograph in (d) courtesy of Friederike Herget (Max Planck Institute for the Science of Light).

5.4. The gold coating prevents oxidation and improves the thermal contacts. By means of the massive rods (diameters: 19 mm and 29 mm) and strongly bolted and/or clamped joints, we established good thermal links between the parts of the insert. The sample is brought into thermal contact with the MXC plate via the massive copper rod in the center of the insert. A flexible thermal coupler (ATC100/60, Attocube; thermal conductivity 15 mW/K) connecting the sample holder to the rod allows to move the sample using the nanopositioners while the thermal contact is maintained. The actual copper bands of the thermal couplers are not shown in Figure 5.4, but they can be seen in the photographs in Figure 5.5. Figure 5.4 only shows the two ending plates of the ATC100, one of which is underneath the sample holder while the other one is mounted on the bottom of the central rod. The same type of thermal coupler was used to connect the asphere holder to the central rod. We used brass for screws ending in copper threads to match the thermal expansion of screw and thread. Since both copper and brass are soft materials, the torque that can be
5 Experimental setup

![Sample holder and sample preparation for cryogenic operation. (a) Photograph of a sample holder with a sample and SIL mounted on it. (b) Photograph of a sample mounted with SIL on the sample and prepared for cooldown. The vacuum grease around the SIL protects the pDCB crystal under the SIL from sublimation. (c) Microscope image of a pDCB crystal in 250 µm wide nanochannels recorded through the SIL in a cross-polarization configuration. Different domains of the crystal appear at different brightness.](image)

applied to the screws in this case is limited. Whenever possible, we therefore avoided screwed connections into copper. To mount the exchangeable base plate to its support, stainless steel screws and nuts were strongly tightened while the aluminum frames shown in Figure 5.4 protected the copper from indentations. Stainless steel screws and nuts were also used to tighten the clamps of the adapter plate and base plate support to the four long rods. The wire thermalizers mounted on the base plate were used to cool the cables of the nanopositioners (see photographs in Figure 5.5). The temperature sensor mounted on the side of the central rod (RuO$_2$ sensor in gold-plated copper housing, Bluefors; calibrated until 7 mK) shows similar temperatures to the MXC plate sensor (ΔT ≤ 1 mK), indicating a good thermal link.

The small circuit board shown in Figures 5.4 and 5.5 is used to connect the nanopositioners to wires from the piezo controller (ANC350) for motion control and position read-out. The wires attached to the left rod visible in Figures 5.5(a,b) connect the circuit board to low-ohmic wires (< 4 Ohm for the position control and < 14 Ohm for the resistive read-out) from the MXC plate to the top of the cryostat. The two temperature sensors (in the sample holder and at the central rod) are connected to corresponding plugs at the cold plate for four-point measurements using a dedicated scanner (Lakeshore, Model 372). Besides the wires for the nanopositioners and the temperature sensors, no further electrical connections were used for the insert.

One of the sample holders used in this thesis is shown in Figure 5.6(a). It is designed for 0.5 mm thick samples that are mounted on the holder via a spring steel clamp together with a SIL on top of the sample. The sample
holder is partially hollow such that a RuO$_2$ temperature sensor (RX-102B-CB, Lake Shore) can be mounted for a temperature measurement close to the sample. The sensor is calibrated until 17 mK. It is placed inside of the sample holder to protect it from thermal radiation that may influence its readings. By mounting the sensor on the base plate without further protection, however, we measured resistances associated with temperatures below the calibrated range. This suggests that the thermal radiation does not have a major effect on the measurements. Temperature readings at the sample holder, the central rod of the insert, and the MXC plate under different conditions are shown in Table 5.2. During operation of the cryostat, the temperature at the sensor in the sample holder reached minimum values around 24 mK. The increase compared to the temperature at the central rod is probably caused by the limited thermal conductivity of the ATC100/60 and the higher number of screwed connections between sample holder and MXC plate.

In the experiments of chapters 6 and 7, we routinely sent laser powers of around 100 µW or more into the cryostat. Under intense laser illumination, we observed a pronounced temperature increase at the sample holder (see Table 5.2 for some examples). In a typical STED spectroscopy experiment, we measured more than 100 mK at the sample holder. We do not know, however, how these temperatures are related to the (local) temperature around the molecules investigated in our experiments. The thermal contact between the fused silica sample substrate and the sample holder, i.e. an insulator and a metal, is expected to be weak at low temperatures [213]. Therefore the temperature in the crystal is expected to be higher than the temperature measured at the sample holder, in particular under illumination by a laser. For the experiments presented in this thesis, the most relevant thermal effect is dephasing induced by thermally active crystal phonons. As shown in section 4.1.3, we obtained lifetime-limited linewidths of single molecules in the cryostat. This shows that under illumination of a laser, the local temperature around a DBT molecule remains lower than about 3 K (see also section 2.3). One way to determine the local temperature around an investigated molecule could be via the thermal phonon population. This population can be probed using fluorescence excitation measurements as shown in Figure 7.6(b), in which thermal phonons and photons with frequencies below the 00-ZPL transition combine to excite the molecule via the 00-ZPL. A fit of a model that takes the density of states and their thermal population into account may then allow estimation of the local temperature [40].
Figure 5.7: Time scales of the cooldown and warm-up of the dilution cryostat equipped with the insert and windows. (a,c) Temperature measured at the 50 K plate and the 4 K plate during the cooldown and warm-up of the cryostat, respectively. Both processes take about 30 h due to the massive insert mounted to the MXC plate for our experiments. The dashed line in (c) shows the warm-up of the 4 K plate if the exchange gas is introduced not at the beginning of the warm-up, but at the time indicated by the arrow. (b) Temperature at the MXC plate, the central rod of the insert, and the sample holder after the condensation of the He mixture is started. The arrow indicates the time at which the voltage applied for resistive readout of the nanopositioners is turned off.

### 5.3.2 Operation of the cryostat

The cooldown of the cryostat takes place in two steps. The initial cooling to 4 K is accomplished using the pulse tube cooler. Typical cooldown curves of this step are shown in Figure 5.7(a). The stages below the 50 K plate reach $T \lesssim 4$ K after 30 h of continuous pulse tube operation. As indicated in Figure 5.3, the MXC plate is lifted by approximately 3.5 mm in this process due to thermal contraction. We note that the cooldown time shown in Figure 5.7(a) is longer than for an empty cryostat, because of the approximately 9.5 kg of copper attached to the MXC plate in our setup. Additional cooling from 4 K to mK-temperatures happens after the circulation and condensation of the $^3$He/$^4$He-mixture is started. The cooldown curves of the MXC plate and the sample insert are shown in Figure 5.7(b). It takes about 2 h to cool the insert from 4 K to base temperature. In the example shown in Figure 5.7(b), the voltage applied to the nanopositioners for resistive readout was turned off at the time indicated by the arrow. This eliminates the associated ohmic heating and allows the insert to reach the final base temperature. The temperature at the sample holder routinely reached base temperatures around 24 mK.
5.3 Dilution cryostat

<table>
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<th>$T_{\text{rod}}$ (mK)</th>
<th>$T_{\text{sh}}$ (mK)</th>
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<td>260</td>
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Table 5.2: Temperatures measured in the cryostat under different conditions. $T_{\text{MXC}}$ : temperature at the MXC plate, $T_{\text{rod}}$ : temperature at the central copper rod of the insert, $T_{\text{sh}}$ : temperature at the sample holder.

A warm-up of the cryostat from base temperature to room temperature also takes about 30 h (see Figure 5.7(c)). The standard warm-up procedure introduces a small amount of atmospheric contact gas into the cryostat at the beginning of the warm-up process. This accelerates the temperature increase considerably as illustrated in Figure 5.7(c). Since a sample exchange requires the cryostat to be opened, the cooldown and warm-up times limit the throughput to about 1 sample/3 days for this system.

While the cryostat is being operated, the pulse tube induces vibrations with a frequency of about 1.4 Hz. Together with other sources, such as the turbo pump of the mixture circuit, these vibrations excite mechanical modes of the cryostat. At low frequencies, horizontal swinging vibrations of the cryostat in its supporting frame dominate the spectrum. Although we expect our heavy insert to damp the amplitude of these vibrations, we still see signatures of the pulse tube vibrations in our data. Figure 5.8(a) shows a fluorescence time trace from a molecule under excitation of a vibronic line at fixed laser frequency, recorded with an integration time of 1 ms. The power spectrum of such a time trace clearly indicates the pulse tube frequency at 1.43 Hz as well as its overtones and additional modes (see Figure 5.8(b)). One strategy to remove the modulation of the emission by the pulse tube frequency from the data is to average them over one cycle, i.e. over $T \approx 701$ ms. The effect of such averaging is shown in Figure 5.8(a): while averaging over 70 ms leads to noticeable oscillations, an average over $T = 701$ ms yields a signal with considerably smaller fluctuations. Additionally, the Fano factor of the signal (variance/average)
Figure 5.8: Modulation of the fluorescence signal caused by vibrations of the cryostat. (a) Fluorescence time trace under stationary excitation of a vibronic transition in a single DBT molecule recorded with 1 ms integration time. The orange and red curve are moving averages over 70 and 701 data points of the data, respectively. (b) Power spectrum of the time trace (1 ms) from (a). The insert shows the low frequency region around the fundamental pulse tube peak. (c) Fano factors and signal-to-noise ratio (SNR) for various bin sizes of a rolling average applied to 100 s of the signal shown in (a). The black dashed line indicates the period of the pulse tube oscillation.

around $T = 701$ ms attains values close to one, indicating that the signal is almost shot noise-limited (see Figure 5.8(c)). In the experiments presented in chapters 6 and 7, we mostly used an integration time of $\Delta t \sim 70$ ms and then a rolling average over ten recorded data points. Note that the exact behavior and statistics of time traces such as the one shown in Figure 5.8(a) depend on the details of the laser focus.

### 5.3.3 Optical access

We used parallel and wedged fused silica windows with AR-coating (wavelength ranges 400–900 nm and 400–1100 nm; $R_{\text{av}} < 0.5\%$; UQG Optics) to enable free-space optical access to the sample inside the cryostat. For all experiments shown in this thesis, only one side of the cryostat was equipped with a set of four windows that were arranged as illustrated in Figure 5.9(a,d). The other window openings remained closed by flanges. Replacing a set of flanges by a set of windows led to an increase in the base temperature by about 1.5 mK, probably due to additional radiative heating by thermal radiation from the environment (see Table 5.2). It turns out that the initially used planar windows lead to etaloning of the transmitted laser intensity with a contrast of about 10%. Figure 5.9(b) shows a measurement of the transmission through one and a stack of four planar windows. The measurement was performed
Figure 5.9: Transmission through parallel and wedged cryostat windows. (a,d) Dimensions (in mm) and arrangement of the planar and wedged cryostat windows. The windows are mounted at an angle of 3° w.r.t. the normal direction. Drawing is not to scale. (b,e) Transmission spectra of a single window and a stack of four planar (b) and wedged (e) windows. (c,f) Fluorescence excitation measurements of a part of the phonon sideband using planar (c) and wedged (f) windows. The etaloning in the measurement with planar windows shown in (c) has similar contrast and periodicity to the transmission measurement in (b).

with a tunable laser and a photodiode. The periodicity of the etaloning of a single planar window is consistent with its window thickness of 2 mm. Arranging four planar windows in a sequence leads to more irregular oscillations of the transmission behavior with an amplitude of about 10%. This effect remains unnoticed if single 00-ZPLs are investigated because their spectral width is negligible compared to the periodicity of the etaloning. For spectrally broad structures such as the PSB of the 00-ZPL, however, it does have a visible effect as shown in Figure 5.9(c). We attribute the modulation of the detected intensity in this fluorescence excitation measurement of the phonon sideband mainly to etaloning caused by the parallel cryostat windows (data from mol. 5, see Table 6.1). After replacing the parallel windows with wedged windows, which do not support the Fabry-Perot modes of a plane-parallel cavity, we did not observe this type of intensity modulation anymore as shown in Figure 5.9(f) for an equivalent measurement to that in (c). A transmission measurement through a single and four stacked wedged windows confirmed that no etaloning is present with these windows, see Figure 5.9(e). The wedged window were only used for sample 3 (see Table 6.1). To reduce the total deflection of the beam caused by the wedged geometry of the windows, we arranged them in the staggered configuration shown in Figure 5.9(d).
6 High-resolution vibronic spectroscopy of single molecules

In this chapter we present high-resolution vibronic spectra of single DBT molecules in pDCB and Ac. We employ fluorescence excitation and STED spectroscopy to measure the properties of vibronic levels in the electronic excited and ground states, respectively. Our study marks the first application of STED spectroscopy to single molecules in the solid state and yields a considerable improvement in the spectral resolution of transitions to the electronic ground state compared to conventional measurements with grating spectrometers. By this approach, we were able to identify several narrow vibronic transitions with linewidths around 2 GHz. We provide detailed analyses of our spectroscopic findings as well as their intermolecular distribution and compare them with the intensity distribution in vibronic spectra resulting from DFT calculations.

This chapter is organized as follows: in section 6.1, we present broadband vibronic fluorescence excitation spectra of single DBT molecules in pDCB crystals. In this context, we discuss the properties of several prominent vibronic features in the electronically excited state, their saturation behavior, and their intermolecular variation. In section 6.2, we describe the results of single molecule STED spectroscopy on DBT in pDCB, including relevant experimental parameters and the intermolecular statistics of prominent vibronic features. Additionally, we compare the vibronic wavenumbers and linewidths of electronic ground and excited states and identify several noteworthy differences. To examine the intensity distribution in the measured vibronic
Figure 6.1: Experimental schemes used for fluorescence excitation and STED experiments.
(a) Simplified level scheme showing vibronic states associated with the electronic states $S_0$ and $S_1$. The gray areas indicate the region of the PSB of the 00-ZPL transition. (b–e) Transitions addressed by pump and depletion laser in the different spectroscopy schemes and the corresponding emission band filtered out for fluorescence detection. For measurements of the vibronic manifold (b,d) we filtered out a narrow spectral region around the 00-ZPL to measure the excited state population. For measurements of the PSB of the 00-ZPL (c,e), we instead detected the emission to the prominent vibronic level at around 290 cm$^{-1}$ to avoid leakage of the laser light close to the 00-ZPL through the detection bandpass.

spectra further, we compare our experimental findings with the results of DFT calculations in section 6.3. It transpires that the pDCB crystal must be included in these simulations to achieve close agreement between theory and experiment. By comparing vibronic spectra of DBT in pDCB with spectra recorded in Ac in section 6.4, we further explore the effect of the host system on the vibronic properties of the dopant molecules. In section 6.5 we discuss several consequences of our experimental findings and suggest next steps for experiments that may lead to an extension of the vibrational lifetimes of single dye molecules in solid state environments.

The data presented in this chapter were recorded using various arrangements of the pump and depletion laser as well as the detection bandpass. These arrangements are summarized in Figure 6.1. For scans of the vibronic manifold, we filtered out the light emitted in a narrow spectral range ($\sim$ 2 nm) around the 00-ZPL transition. If the frequency of a laser needed to be tuned close to the frequency of the 00-ZPL transition for us to explore its PSB, the detection bandpass window was adapted such that light emitted to the prominent vibronic level around 290 cm$^{-1}$ reached the detector and the rest was blocked. The typical detuning rate of the scanned laser during the broadband vibronic measurements was 2 GHz/s. For detailed scans of spectrally narrow features, the scan speed could be reduced. The fluorescence count rate was measured using an integration time of 70 ms and then smoothed by a running average.
filter covering ten data points to average out the vibrations induced by the pulse tube cooler (see section 5.3.2).

We denote the count rate detected by the APD in our setup by $R$, while $R_\infty$ stands for the (extrapolated) maximum detected rate if the molecule is at full saturation. The spontaneous decay rate from state $|i\rangle$ to state $|j\rangle$ is denoted by $\Gamma_{ij}$. Because this is common practice in single molecule spectroscopy, we report the vibronic linewidth $\Gamma_{ij}/(2\pi)$ in the units of GHz instead of the decay rate $\Gamma_{ij}$. We use angular brackets $\langle \cdot \rangle$ to denote intermolecular averages.

## 6.1 Fluorescence excitation spectroscopy of vibronic transitions

Fluorescence excitation experiments enable the investigation of the vibronic manifold associated with the electronically excited state of a single molecule using a tunable laser. A requirement for obtaining clean vibronic fluorescence excitation spectra of single molecules is the use of sufficiently low doping levels such that only a single molecule is present in the beam path of the laser. As shown in section 6.1.1, we successfully realized this condition in our experiments with DBT in pDCB. In section 6.1.2 we show that we obtain almost background-free single molecule emission signals from DBT while exciting a vibronic transition, even at excitation powers exceeding 2 mW. As shown in sections 6.1.3 and 6.1.4, we recorded fluorescence excitation spectra of four molecules in pDCB within 0–800 cm$^{-1}$ by scanning a laser over a spectral range of about 25 THz. Fitting the rate equation model (see section 6.1.2) to these data sets allows us to compare the intermolecular variation of wavenumbers, relaxation rates and intensities of several vibronic states in section 6.1.4. In section 4.2, we introduce models that can be fitted to the data obtained from fluorescence excitation measurements. In section 6.1.5, we additionally present some observations related to combination modes and the overtone associated with the prominent vibronic level at 291 cm$^{-1}$. The corresponding fluorescence excitation measurements of DBT in Ac are discussed separately in section 6.4.

### 6.1.1 Limit of a single DBT molecule per excitation volume

For studies of vibronic excitation spectra of single molecules, we applied low doping levels of DBT in pDCB. Together with the confinement in the thin nanochannels described in section 5.2.1, nominal molar doping levels between 20–30 ppb often led to crystals in which less than a single DBT molecule
Figure 6.2: Fluorescence excitation scans of the 00-ZPL resonances of single DBT molecules in pDCB. (a) Confocal fluorescence excitation scan over a range of more than 2 THz around the normal spectral site of DBT in pDCB (mol. 1). A scan in the low excitation regime resolving the linewidth of the narrow line of this molecule is shown in Figure 4.2(c). Adapted from [45], with the permission of AIP Publishing. (b) Normalized fluorescence excitation spectra of the 00-ZPLs of all molecules studied in this chapter. The spectra are plotted with an offset. The indices of the molecules are ordered according to increasing 00-ZPL frequency.

was found per diffraction-limited excitation volume of the laser. This was confirmed by confocal fluorescence excitation scans over the typical spectral range of the inhomogeneous broadening of the normal site of DBT in pDCB [25]. Figure 6.2(a) shows a case in which only a single 00-ZPL was found within a range of more than 2 THz. Since we also scanned the spectral region of the red site of DBT in pDCB [25] in our STED experiments, we are confident that in this case there is only a single DBT molecule in the excitation volume of the laser. The photophysical properties of the five DBT molecules in pDCB crystals studied in this chapter are listed in Table 6.1. This table defines the numbers by which we refer to the different molecules in this chapter (mol. 1 to mol. 5) and the colors used to identify each molecule in plots in which properties of the molecules are compared. The properties of the DBT molecule in Ac (mol. 6) are discussed in section 6.4. As shown in Figure 6.2(b), a single 00-ZPL clearly dominated the excitation spectrum in the spectral range of the normal site of DBT in pDCB. The 00-ZPL resonances of all five molecules are distributed around the center of the inhomogeneous broadening at $\sim 402.76$ THz as reported by Verhart et al. for DBT in bulk pDCB [25]. We note that for some crystal samples taken from a prepared DBT:pDCB stock with 20–30 ppb molar doping level, we could not find any molecules. However, other samples taken from the same crystal stock contained dense regions with many sharp 00-ZPLs in the range of the inhomogeneous broadening. We attribute these differences to variations in the density of DBT in the pDCB crystal power used for sample
6.1 Fluorescence excitation spectroscopy of vibronic transitions

preparation. At the positions of molecules 1, 2, and 4, we found no indication of any other molecules in the same excitation volume. Thus, we could record fluorescence excitation spectra of the vibronic manifold at positions without spectral lines associated with other impurities.

<table>
<thead>
<tr>
<th>Mol.</th>
<th>Sample</th>
<th>$\omega_{ge}/2\pi$ (GHz)</th>
<th>$\Gamma_e/2\pi$ (MHz)</th>
<th>$T_1$ (ns)</th>
<th>$\bar{\nu}_w$ (cm$^{-1}$)</th>
<th>$\Gamma_{we}/2\pi$ (GHz)</th>
<th>Color</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3</td>
<td>402574.7 (~2)</td>
<td>22.8</td>
<td>7.00</td>
<td>290.7</td>
<td>10.9</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>2</td>
<td>402575.4</td>
<td>26.3</td>
<td>6.05*</td>
<td>290.4</td>
<td>11.8</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>1</td>
<td>402666.8</td>
<td>31.6</td>
<td>5.04*</td>
<td>290.5</td>
<td>11.9</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>2</td>
<td>402826.2 (0.1)</td>
<td>28.2</td>
<td>5.64*</td>
<td>290.6</td>
<td>12.5</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>2</td>
<td>402894.6 (0.1)</td>
<td>26.0</td>
<td>6.12*</td>
<td>290.6</td>
<td>10.4</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>4 (Ac)</td>
<td>381806.5</td>
<td>40.0</td>
<td>3.98*</td>
<td>294.4</td>
<td>21</td>
<td></td>
</tr>
</tbody>
</table>

Table 6.1: Photophysical properties of the molecules studied in the fluorescence excitation and STED experiments. The molecules of the experiments with pDCB are ordered according to the frequencies of their 00-ZPLs. $\omega_{ge}/(2\pi)$: 00-ZPL frequency; the number in brackets indicates range of spectral jumps (if observed). $\Gamma_e/(2\pi)$: 00-ZPL linewidth in the low excitation limit. $T_1$: lifetime of $|S_1, \hat{0}\rangle$ (*: calculated via $1/\Gamma_e$). $\bar{\nu}_w$: vibrational wavenumber of the most prominent vibronic state in $S_1$. $\Gamma_{we}/(2\pi)$: linewidth of the most prominent vibronic state in $S_1$.

6.1.2 Saturation behavior of vibronic transitions

Figure 6.3 shows a single molecule fluorescence excitation measurement recorded at various excitation powers in the spectral range around the prominent vibronic line at 291 cm$^{-1}$ (mol. 1). These measurements were performed using the arrangement displayed in Figure 6.1(b) with excitation powers up to 2.2 mW. We remark that all laser powers reported in this thesis were measured in front of the cryostat. The resulting line profiles show two defined peaks and a broad feature in the upper half of the scanned spectral range. We attribute the two peaks to two distinct vibronic levels (see Figure 6.23 and Table 6.2 for the assignment of these modes) and the broad feature to PSBs of lower-lying vibronic states and vibronic combination modes of the molecule. Since the broad feature becomes visible for high excitation powers in the order of 100 µW, it might be interpreted as laser-induced background fluorescence. For samples with higher doping levels, we regularly observe a spectrally flat fluorescence background that is not related to the emission from the investigated molecule. If the signal at position ② was associated with this type of background signal, one would observe the same increments
Figure 6.3: Saturation scan of a single DBT molecule in pDCB (mol. 1) via excitation of a vibronic transition. (a) Fluorescence excitation scan of the range around the most prominent vibronic line of DBT in pDCB (around 291 cm\(^{-1}\)) at various excitation powers. The laser powers associated with three of the curves are indicated. (b) Intensities at points 1 and 2 of the spectral profile shown in (a) as a function of excitation power. The solid black line is a fit of the function \(R_\infty P_p/P_{sat}/(1 + P_p/P_{sat})\) to the blue data points \((P_{sat} = 18.6 \mu W)\). The dashed black line shows the same function but with \(P_{sat} \rightarrow 250 \cdot P_{sat}\). (c,d) Emission spectra in the range around the 00-ZPL under excitation at the frequencies indicated by 1 (c) and 2 (d) in the fluorescence excitation scans of (a). Excitation power: 2.2 mW, integration time: 2 s. The transmission behavior of the detection bandpass is indicated by the grey line (arbitrary units).

with increasing laser power at position 1. Between 0.98 mW and 2.2 mW, however, the signal at 1 stays almost constant while it strongly increases at 2. Therefore, we assume that the signal observed while exciting the molecule at the frequency 411.500 THz is fluorescence from the molecule.

As a cross-check, we recorded emission spectra while pumping the molecule at the frequencies 411.291 THz 1 and 411.500 THz 2 using a laser power of 2.2 mW (see Figures 6.3(c,d)). In both spectra we see one sharp line at the frequency of the 00-ZPL of the molecule and its PSB, which is truncated in these measurements by the detection bandpass filter. This observation
6.1 Fluorescence excitation spectroscopy of vibronic transitions

confirms that we are pumping the molecule not only at the defined vibronic peak \( \text{peak 1} \) but also at the spectral position indicated by \( \text{peak 2} \). We assume that the measurements shown in Figure 6.3(a) are background-free, containing no significant contributions besides the emission of the molecule. This assumption is supported by the accurate description of the antibunching measurements shown in Figure 4.3(a) by a theory curve without fit parameters under the assumption of negligible background. We remark that performing an experiment with such low background, even at high laser powers around 2 mW, required thorough adjustment of the laser filter to suppress red-shifted light generated in the fiber.

The blue symbols in Figure 6.3(b) show the maximum values of the line profiles in Figure 6.3(a). A fit of equation (2.15) to the data yields a saturation power of \( P_{\text{sat}} = 18.6 \mu W \) and a maximum fluorescence detection rate of \( R_\infty = 716 \text{ kcps} \) for excitation at 411.291 THz. The laser power of 2.2 mW thus corresponds to a saturation parameter of \( S_p = 118 \) via vibronic excitation. We remark that the saturation power of the excitation via a vibronic level is about a factor of two higher than expected from equation (4.35) and from the saturation power for excitation via the 00-ZPL of mol. 1 \( \tilde{P}_{\text{sat}} = 1.4 \text{ nW} \). This difference might be caused by suboptimal alignment of the laser in the excitation measurement of the vibronic level (affecting the factor \( \eta_p \) in equation (4.34)) and by the chromatic behavior of the aspheric lens, which is discussed in more detail in section 6.1.3.

The orange points in Figure 6.3(b) show the intensity in Figure 6.3(a) upon excitation at 411.500 THz. Their dependence on the laser power can be described by a saturation curve with \( P_{\text{sat},2} = 250 \cdot P_{\text{sat}} \) and \( R_{\infty,2} = R_\infty \), shown by the dashed line in the plot. We note that the typical pump powers used to record STED spectra are \( \lesssim 100 \mu W \) and hence considerably lower than the maximum power applied during the saturation scan shown in the current section.

The measurements in Figure 6.3(a) show that the resonance frequency of DBT is exceptionally stable in pDCB crystals under intense laser illumination. Laser powers around 100 µW have been reported to cause consistent spectral shifts of the 00-ZPL in the order of 10 GHz for DBT in Ac and DBT in DBN \([214]\). These shifts do not require the laser to be resonant with the molecule and can be explained by photoionization events. In the measurements of Figure 6.3(a), we applied powers in the order of 1 mW over several minutes and we did not observe spectral shifts comparable to the width of the vibronic line. During the broadband STED experiments, we applied powers around 100 µW to the sample and observed stable emission from the molecule over hours. A continuous spectral shift of the molecular resonance frequency towards
higher or lower frequencies in the order of GHz would lead to a consistent drop in the fluorescence signal over time. We did not notice such an effect during our measurements.

All molecules presented in this chapter were investigated over timescales of more than one month. A comparison of the 00-ZPL transition frequencies at different times during these measurement periods showed a variation of $\lesssim 0.1$ GHz for most molecules. Only for mol. 1 did we notice a change in its transition frequency over time ($\sim 2$ GHz), possibly caused by the high excitation power applied during the measurements such as the one shown in Figure 6.3. A frequency change in 2 GHz corresponds to a wavenumber change of 0.07 cm$^{-1}$ and is small on the scale of most vibronic linewidths. For the evaluation of the fluorescence excitation and STED spectra in this thesis we assume a constant 00-ZPL frequency.

The spectral profile shown in Figure 6.3(a) illustrates a general challenge in fitting models to vibronic spectra, especially for large molecules such as DBT. A priori it is unclear how many vibrational modes contribute to an observed line profile and should thus be included in a model for fitting. First principle simulations of DBT do not provide wavenumber and intensity predictions that are accurate enough to serve as a basis for fitting (see section 6.3 for more details on the accuracy of DFT calculations). Therefore, we decided to fit the data of DBT using models for which the number of vibronic resonances was determined heuristically based on a visual inspection of the data.

In order to fit the data from a fluorescence excitation scan of overlapping vibronic states, the model for a single vibronic transition discussed in section 4.2.1 must be extended. In Figure 6.4(a), we show the level scheme of a model that includes two defined vibronic states $|w\rangle = |S_1, \tilde{v}_w\rangle$ and $|x\rangle = |S_1, \tilde{v}_x\rangle$ together with a spectrally flat ‘level’ $|E\rangle$, representing absorption via weak additional channels such as the PSBs of vibrational states and weak combination modes. The state $|x\rangle$ stands for a second (Lorentzian) vibronic level that has a spectral overlap with the vibronic level $|w\rangle$ and relaxes at a rate $\Gamma_{xe}$. The state $|E\rangle$ describes all additional absorption pathways of the molecule and we assume that it relaxes at the same rate as $|w\rangle$, i.e. $\Gamma_{Ee} = \Gamma_{we}$. Note that the laser-induced transitions shown in Figure 6.4(a) are all driven by the same laser that induces an (on-resonance) Rabi frequency $\Omega_p$ on the transition $|g\rangle \leftrightarrow |w\rangle$. The parameters $\beta_x$ and $\beta_E$ scale the Rabi frequency $\Omega_p$ according to the (relative) FC overlaps of the levels $|x\rangle$ and $|E\rangle$ with the level $|g\rangle$. We

---

1 We have no means of measuring the (effective) decay rate of the auxiliary state $|E\rangle$.
6.1 Fluorescence excitation spectroscopy of vibronic transitions

Figure 6.4: Simultaneous saturation behavior of two overlapping vibronic levels and a spectrally flat absorption feature. (a) Level scheme used to describe the simultaneous excitation of a molecule via two vibronic states |w⟩ and |x⟩ as well as a spectrally flat feature |E⟩. (b) Normalized population of |e⟩ for a level scheme with the parameters $M_{wx}$ and various values of the pump Rabi frequency $\Omega_p$. $N_{e,\infty} = 0.995$. (c) Saturation behavior of the (normalized) population in |e⟩ at the three detunings indicated in (b). Black lines are fits of the function $\Omega_p^2/c/(1 + \Omega_p^2/c)$ to the data.

define the laser detuning with respect to the state |w⟩, i.e. $\Delta_p = \omega_p - \omega_{gw}$. As such, the pump rates $W_{p,i}$ of the states |i⟩ are given by:

$$W_{p,w}(\Delta_p) = \frac{\Omega_p^2 \Gamma_{we}}{4(\Delta_p^2 + \Gamma_{we}^2/4)} \quad (6.1)$$

$$W_{p,x}(\Delta_p) = \frac{\beta_x^2 \Omega_p^2 \Gamma_{xe}}{4((\Delta_p - \delta_{xw})^2 + \Gamma_{xe}^2/4)} \quad (6.2)$$

$$W_{p,E}(\Delta_p) = \frac{\beta_E^2 \Omega_p^2}{\Gamma_{ee}} \quad (6.3)$$

with $\delta_{gx, gw} = \omega_{gx} - \omega_{gw}$, the difference of the resonance frequencies of the states |w⟩ and |x⟩. Equation (6.3) includes the assumption that the pump rate of the state |E⟩ is independent of the laser frequency, leading to a spectrally flat profile. We use rate equations analogous to the set of equations (4.9) but adapted to the level scheme shown in Figure 6.4(a) to describe the steady-state distribution of population in this model.
The rate equations of the model shown in Figure 6.4(a) are given by:

\[
\begin{pmatrix}
N_g \\
N_e \\
N_w \\
N_x \\
N_E
\end{pmatrix}
= 
\begin{pmatrix}
0 & \Gamma_{eg} & 0 & 0 & 0 \\
0 & -\Gamma_{eg} & \Gamma_{we} & \Gamma_{xe} & \Gamma_{Ee} \\
0 & 0 & -\Gamma_{we} & 0 & 0 \\
0 & 0 & 0 & -\Gamma_{xe} & 0 \\
0 & 0 & 0 & 0 & -\Gamma_{Ee}
\end{pmatrix}
\begin{pmatrix}
N_g \\
N_e \\
N_w \\
N_x \\
N_E
\end{pmatrix}
+ 
\begin{pmatrix}
W_{p,w}(N_w - N_g) + W_{p,x}(N_x - N_g) + W_{p,E}(N_E - N_g) \\
0 \\
W_{p,w}(N_g - N_e) \\
W_{p,x}(N_g - N_x) \\
W_{p,E}(N_g - N_E)
\end{pmatrix}
\tag{6.4}
\]

and

\[
N_g + N_e + N_w + N_x + N_E = 1,
\tag{6.5}
\]

with the pump rates \(W_{p,i}\) as defined in equations (6.1)–(6.3). One can add more simultaneously pumped vibronic levels \(|i\rangle\) to the set of equations (6.4) by adding terms in the same pattern as for the states \(|w\rangle\) and \(|x\rangle\). The analytical solutions of these equations can be obtained with the help of computer algebra software. These solution are not shown here because they are large expressions.

The (normalized) spectral profiles \(N_e/N_{e,\infty}\) at various values of the pump Rabi frequency \(\Omega_p\) are shown in Figure 6.4(b). Here, \(N_{e,\infty}\) is defined as the value of \(N_e\) in the limit of infinite laser power, i.e. \(N_{e,\infty} = N_e(\Omega_p \to \infty)\). The parameters \(M_{wx}\) used for the plots in this figure are listed in Table 4.1 and chosen to create a spectral profile similar to the experimental data shown in Figure 6.3(a). By normalization of the model using \(N_{e,\infty}\), the difference between a model that includes states \(|c\rangle\) and \(|t\rangle\) and a model without these states is negligible. Figure 6.4(c) shows the saturation behavior of the spectral profile at the three detunings indicated in Figure 6.4(b).

Spectral profiles such as that shown in Figure 6.4(a) cannot be described by a sum of two independent Lorentzian line shapes from equation (4.26) and a background term. This can be appreciated from the fact that the sum of two profiles \(N_e(\Delta_p)\) given by equation (4.26) can be larger than 1. Instead, all three pumping processes are coupled via the saturation of the molecule leading to a more complex line shape. A (summed) Lorentzian model only works as
6.1 Fluorescence excitation spectroscopy of vibronic transitions

Figure 6.5: Fit of the rate equation model (6.4) to the data of Figure 6.3. (a) Blue lines: data from Figure 6.3(a). Orange dashed lines: fit of the rate equation model (6.4) to the data. The level names assigned to the data are indicated in the plot. (b) Squared Rabi frequencies resulting from the fit shown in (a). The dashed black lines are linear fits to the circular data points, for which $R/R_\infty < 0.8$ over the full spectral range of the measurement. The square data points in (b,c) indicate cases for which $R/R_\infty > 0.8$ at the position of the peak associated with level $|w\rangle$. (c) Vibrational relaxation rates of the levels $|w\rangle$ and $|x\rangle$ resulting from the fit shown in (a). The dashed lines indicate averages over the circular data points (defined as in (b)). See the main text for comments regarding the deviations at higher laser powers.

long as the vibronic features do not overlap much. In this thesis, we fit the experimental fluorescence excitation spectra using rate equation models such as the one shown in 6.4(a). Depending on the number of discernible vibronic features in a fluorescence excitation scan, we adjust the number of levels in the model before fitting. We then fit the analytical solutions of the rate equations for $N_e(\Delta p)/N_{e,\infty}$ to the (normalized) data $R(\Delta p)/R_\infty$. Figure 6.5 and section 6.1.4 show examples of data from fluorescence excitation experiments together with fits of the models like the one described by Figure 6.4(a).

Pumping a molecule simultaneously via multiple excitation pathways can in principle lead to interference effects between the coherences induced in the molecule. The configuration shown in Figure 6.4(a) is reminiscent of a V-configuration known from electromagnetically induced transparency in three-level systems [215, 216]. We checked whether coherent effects should be expected in our fluorescence excitation measurements by using QuTiP simulations [59], but we did not find indications of significant changes of the line profile compared to the rate equation treatment.

We used the rate equations (6.4) to fit the vibronic profile shown in Figure 6.3(a). This model assumes two localized vibronic states at $\omega_{gx}/(2\pi) = 411.220$ THz and $\omega_{gw}/(2\pi) = 411.291$ THz together with a spectrally flat absorption feature $|E\rangle$. The parameters $\Omega_p$, $\beta_x$, $\beta_E$, $\Gamma_{we}$, $\Gamma_{xe}$, $\omega_{gw}$, and $\omega_{gx}$ were used...
as free parameters at each power setting and $\Gamma_{eg}$ was fixed at the value determined using the time-resolved measurements discussed in section 4.1.4. In order to fit the model, we normalized the data using $R_\infty$ obtained from the fit to the saturation curve shown in Figure 6.3(c). Then, we fitted the function $N_e(\Delta_p)/N_{e,\infty}$ resulting from the rate equations (6.4) to the normalized data.

The spectral profiles resulting from the fit are shown as orange dashed lines in Figure 6.5(a). The associated values of $\Omega^2_p$ and $(\beta_x \Omega_p)^2$ are shown for all laser powers in Figure 6.5(b). As expected, these values increase monotonically with laser power. The fit results for $\Omega^2_p$ of the transition $|g\rangle \leftrightarrow |w\rangle$ deviate from the linear behavior indicated by the black dashed lines at high laser powers. We attribute these deviations to the fact that the errors in the estimation of $R_\infty$ have a strong effect on the estimation of $\Omega^2_p$ if the molecule is close to full saturation, i.e. if $R \approx R_\infty$. Therefore, fit parameters from measurements close to saturation can be unreliable. To limit the error propagation from $R_\infty$ to our estimation of the decay rate, we only take measurements with $R/R_\infty < 0.8$ into account. In this case, a 1% relative error in $R_\infty$ translates to less than 5% relative error in $\Omega^2_p$. The fit results associated with measurements for which $R/R_\infty < 0.8$ are plotted using circular symbols in Figures 6.5(b,c).

Figure 6.5(c) shows the fit results for the decay rates $\Gamma_{we}$ and $\Gamma_{xe}$. Since the fitted rate equation model (6.4) intrinsically describes power-broadening, these fit results are expected to be independent of the laser power. However, small errors in $R_\infty$ also affect the fit results for the decay rates. For that reason, the fit results for $\Gamma_{we}$ and $\Gamma_{xe}$ at high laser powers deviate from the constant behavior at low laser powers. The dashed lines in Figure 6.5(c) indicate the average values of the (reliable) fit results for the decay rates with $R/R_\infty < 0.8$: $\Gamma_{we}/(2\pi) = 10.9$ GHz and $\Gamma_{xe}/(2\pi) = 8.6$ GHz. These values agree with the extrapolated linewidth of these transitions in the low excitation regime as determined by Lorentzian fits to the data. The corresponding vibrational lifetimes in the case of negligible pure dephasing are $\tau_w = 15$ ps and $\tau_x = 19$ ps.

We remark that thermally induced pure dephasing in the order of 1 GHz might be present in the data of Figure 6.5 at high laser powers $P_p \gtrsim 500 \mu W$. Because of the strong saturation effects and the complexity of the vibronic line profile, it is difficult to extract accurate information about thermal broadening effects on this scale from our data. The constant fit results for the vibronic linewidth of $|x\rangle$ in the range $P_p \lesssim 500 \mu W$ suggest that thermal broadening is negligible for that range of laser powers. Since the broadband spectra used for analysis of the vibronic linewidths were recorded at $P_p \lesssim 200 \mu W$, we do not expect them to be affected by thermal broadening.
6.1 Fluorescence excitation spectroscopy of vibronic transitions

Figure 6.6: Fluorescence excitation spectrum of the PSB and vibronic levels of mol. 1. The phonon sideband (gray area and left intensity axis, \(R_\infty = 150 \text{ kcps}\)) and the vibronic levels (right intensity axis, \(R_\infty = 773 \text{ kcps}\)) were recorded at \(P_p = 201 \mu\text{W}\) and different settings of the detection bandpass filter as indicated by the level schemes. See the main text for a comment about the intensity drop between the gray part and the white part of the spectrum. A magnified version of the high-frequency range of the spectrum is shown as a black line. The black dashed line at the bottom shows the limits of the scan regions between which the focus of the laser was optimized. Adapted from [45], with the permission of AIP Publishing.

6.1.3 Fluorescence excitation scan of the vibrational manifold of the excited state

Figure 6.6 shows a fluorescence excitation scan of the vibronic manifold of mol. 1 up to approximately 800 cm\(^{-1}\), recorded by scanning the laser frequency with \(P_p = 201 \mu\text{W}\) over a spectral range of approximately 25 THz (or 50 nm). The spectral range of the PSB is shown with a gray background. As indicated by the inserted level scheme, the gray range was recorded using the experimental configuration displayed in Figure 6.1(c). The rest of the spectrum was measured using the arrangement in Figure 6.1(b). The detected count rates differ because of the different branching ratios of the two selected transitions. The maximum count rates \(R_\infty\) under excitation of the vibronic level at 291 cm\(^{-1}\) were 150 kcps and 773 kcps in the two configurations, respectively. We remark that the ratio of these values (150/773 \(\sim\) 0.2) agrees closely with what is expected based on the results of DFT calculations, predicting FC factors of around 6\% and 35\% for the most prominent vibronic transition \(|S_1, \vec{0}\rangle \rightarrow |S_0, \vec{v}\rangle\) and the oo-ZPL transition, respectively (see Figures 3.6 and 6.23).

To correct for the background fluorescence caused in some measurements by red-shifted light from the optical fiber, we moved the sample by several \(\mu\text{m}\) to a
point without any molecule in the beam path using the nanopositioners. Then we scanned the laser frequency over the spectral range of the fluorescence excitation measurement to record the background signal $R_{bg}$ on the APD. The APD signal from the fluorescence excitation scan of the molecule was corrected by $R \rightarrow R - R_{bg}$. One problem with this procedure can be that the background recorded at a different position of the sample differs from the background at the position of the molecule. For most of the spectra presented in this thesis, $R_{bg}$ appeared to account for background contributions of the laser. One exception is the part of the spectrum in Figure 6.6 shown on a gray background. In this case we attribute the intensity drop between the gray part of the spectrum and the white part of the spectrum to uncorrected laser-induced background in the measurement of the PSB region.

In Figure 6.6, the PSB of the 00-ZPL is clearly visible in a range up to around 150 cm$^{-1}$. It has a maximum at around 35 cm$^{-1}$ and several broad peaks, some of which may be attributable to internal modes of DBT that amalgamated with the matrix [168, 217]. The first sharp vibronic feature of an internal mode of DBT appears at 145 cm$^{-1}$. An in-depth analysis of the PSB of DBT in pDCB is outside the scope of this thesis, but we note that our spectra contain several details that can serve as experimental benchmarks for theoretical calculations. One such detail is the broad peak at around 128 cm$^{-1}$ that appears next to a broad dip between 100 cm$^{-1}$ and 120 cm$^{-1}$.

The part of Figure 6.6 with white background shows vibronic features of DBT within a laser scan range of around 20 THz. The extent of this spectrum is limited by the wavelength range accessible to the Ti:Sapphire laser used for this measurement ($\lambda \geq 700$ nm). We are not aware of other high-resolution fluorescence excitation spectra of single molecules recorded over a comparable range of frequencies. The good signal-to-noise ratio (SNR) of our measurement allows us to identify many vibronic transitions at a high level of detail. In sections 6.1.4 and 6.1.5, we provide quantitative analyses of the most prominent vibronic features.

According to numerical simulations provided by Thorlabs, the focal shift of the aspheric lens used in our experiments is about 1 µm per 5 THz at the optical frequencies of our measurements. Since the axial extent of the PSF of the aspheric lens is in the order of 1.5 µm in pDCB, the laser intensity at the position of the molecule is expected to change considerably as the laser frequency is scanned over an interval of 5 THz. This effect is also responsible

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2 Similar spectra were reported by the group of B. Kozankiewicz [85, 86, 131, 169] with Tr and DBT in various matrices. Due to the laser scanning technique applied in these experiments, their resolution was limited to $\geq 30$ GHz.
for the decrease in intensity with increasing wavenumber in fluorescence emission spectra recorded in our setup (see Figure 2.4(a)).

To compensate for the focal shift in our fluorescence excitation and STED measurements, we divided the scanned spectral range into several subsections of about 10 THz each and optimized the excitation (or depletion) efficiency in each range. This was achieved by making the laser beam slightly divergent or convergent by adjusting the axial position of the collimating lens behind the optical fiber in our setup (see Figure 5.1). We determined the optimal axial position of the collimating lens by optimizing the fluorescence signal on the APD while the laser was resonant with a prominent spectral feature close to the center of each scan range. The aspheric lens in the cryostat was not moved in this process to maintain the collection efficiency.

We note that there can be additional effects related to the chromatic behavior of the excitation efficiency: (1) Letting the beam diverge to compensate for the focal shift can lead to clipping of the beam at the edge of the asphere and thus limit how much the focus can be optimized. (2) Letting the beam converge can lead to an under-filling of the asphere and hence a drop in the numerical aperture. (3) The highest focus quality is expected at the design wavelength of our asphere model, which is at 830 nm. We did not perform detailed measurements and simulations to quantify the contributions of each of these effects. In future experiments, the use of a suitable achromatic cryostat objective instead of an aspheric lens will obviate the need for realignment.

The values of the squared Rabi frequencies $\Omega_p^2$ of $\Omega_d^2$ of vibronic transitions reported below can be affected by chromatic and alignment-related effects. Since we found quite consistent behavior of the relative squared Rabi frequencies among the five investigated molecules (see Figures 6.8 and 6.14), we assume that the excitation and depletion efficiencies were similar for each vibronic feature. The relative squared Rabi frequencies are proportional to the relative FC factors of the investigated vibronic transitions only under the assumption of a constant laser intensity at the position of the molecule.

### 6.1.4 Intermolecular variation

Figure 6.7 shows fluorescence excitation spectra of mol. 1, mol. 2, and mol. 5. The positions of all prominent features in the spectra are similar across these molecules. Some small peaks are present only in one spectrum and the relative intensities of some vibronic features vary between the molecules. As discussed in sections 3.2.3 and 3.2.4, we attribute differences between the
Figure 6.7: Fluorescence excitation spectra of some vibronic levels of mol. 1, mol. 2, and mol. 5. Pump powers: 201 µW, 35 µW, and 31 µW, respectively. Magnified versions of parts of each spectrum are shown as black lines. The numbers at the top of the plot indicate the (approximate) wavenumbers (unit: cm\(^{-1}\)) of the vibronic features included in the more detailed analyses shown in Figures 6.8 and 6.9. The black dashed lines show the borders of the scan regions between which the focus of the laser was optimized.

spectra of single DBT molecules in a pDCB matrix mainly to differences in the molecular conformation due to local matrix defects and isotopic substitution of individual \(^{12}\)C atoms by \(^{13}\)C. In section 6.3, we present related results from quantum chemical calculations. The partly blurred background in the spectra of mol. 2 and mol. 5 in Figure 6.7 is caused by etaloning in the planar windows and residual red-shifted background fluorescence.

We selected those prominent vibronic features that are marked in the spectra of Figure 6.7 for a more detailed analysis. Their vibrational wavenumbers \(\tilde{\nu}_w\), relaxation rates \(\Gamma_{we}\), and Rabi frequencies \(\Omega_p\) were determined by fitting the rate equation model described in section 6.1.2 to the measurements. For the fit, we used sections of \(\pm 5\) cm\(^{-1}\) around the selected features and estimated \(R_\infty\) for each molecule using a saturation measurement of the vibronic level at 291 cm\(^{-1}\). Based on the features in the data, we decided on the number of levels to be included in the model. Plots of some of the vibronic features together
6.1 Fluorescence excitation spectroscopy of vibronic transitions

Figure 6.8: Intermolecular variation of the vibronic levels in $S_1$. (a) Selected features in the normalized fluorescence excitation spectra of mol. 1 ($P_p = 201 \mu W$), mol. 2 ($P_p = 35 \mu W$), mol. 4 ($P_p = 100 \mu W$), and mol. 5 ($P_p = 31 \mu W$). The black dashed lines are fits of the rate equation model described in section 6.1.2 to the data of mol. 1. The vertical dashed lines point to the vibrational wavenumbers $\bar{\nu}_w$ of the different vibronic features and molecules. The numbers at the top of the plot are the average linewidths $(\Gamma_{we}/(2\pi))$ and the range of the vibrational wavenumbers of the levels $|\nu\rangle$ included in the rate equation model. Adapted from [45], with the permission of AIP Publishing. (b) Distribution of the vibronic wavenumbers around the average wavenumber of each level. (c) Distribution of the vibronic linewidths. (d) Distribution of the relative Rabi frequencies $\Omega_p^2/\Omega_{p,\text{max}}^2$. In (d) we only show the values obtained for the molecules mol. 1, mol. 2, and mol. 5.

with the fits of the rate equation model are shown in Figure 6.8(a). This figure shows that the vibrational wavenumbers of the vibronic levels in $S_1$ differ among the investigated molecules. The corresponding wavenumber ranges are indicated at the top of Figure 6.8(a). Since we used different excitation

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3 These plots also contain data from mol. 4. The complete spectrum of mol. 4 is not shown in Figure 6.7 because it contains vibronic features from a second molecule in the excitation volume. For mol. 3, no fluorescence excitation spectrum was measured.
powers for the measurements of the different molecules, the amplitudes and linewidths of the vibronic features cannot be readily compared. The results of the rate equation model fits do, however, yield values of the decay rates $\Gamma_{we}$ of the vibronic states $|S_1, w\rangle$. The average linewidths $(\Gamma_{we}/2\pi)$ over the four molecules included in this analysis are also printed at the top of Figure 6.8(a).

More details of the intermolecular distribution of the model parameters are shown in Figure 6.8(b–d). Part (b) of the figure shows the variation in the vibrational wavenumbers of the selected vibronic features among the four investigated molecules. While the vibrational frequency does not vary much for some modes (e.g. $291 \text{ cm}^{-1}$ and $457 \text{ cm}^{-1}$), it shows a broader distribution for others (e.g. $177 \text{ cm}^{-1}$ and $670 \text{ cm}^{-1}$). This suggests that some vibrational modes are more robust against external perturbations than others. The average wavenumber range over all molecules and modes shown in Figure 6.8(b) is $0.9 \text{ cm}^{-1}$.

The distribution of the linewidths $\Gamma_{we}/(2\pi)$ over the four investigated molecules is displayed in Figure 6.8(c). Similar to the frequencies of the vibrational modes, the vibrational relaxation rates differ between modes and molecules. The drop in the vibrational relaxation rate between the mode at $234 \text{ cm}^{-1}$ and the mode at $288 \text{ cm}^{-1}$ may be related to the transition between regime I and regime II of vibrational relaxation (see section 3.3). The average linewidth range over all features shown in Figure 6.8(c) is $5.1 \text{ GHz}$.

Figure 6.8(c) shows the squared pump Rabi frequencies $\Omega_p^2$, normalized individually for each molecule by the maximum pump Rabi frequency of the transition to the mode at $291 \text{ cm}^{-1}$. Due to possible changes in the excitation efficiency between vibronic modes associated with the chromatic aberrations and the re-alignment steps during the full measurement (see section 6.1.3), it remains unclear how much of the variation between the molecules is actually related to a variation between the FC factors. We note, however, that the results of the relaxation rates $\Gamma_{we}$ shown in Figure 6.8(c) are not biased by this effect. The data for mol. 4 are not shown in Figure 6.8(d), because there are clear indications of non-optimal laser realignment between the two scan regions.

### 6.1.5 Combination modes

The fluorescence excitation spectra in Figure 6.7 contain some features that can be attributed to combination modes of the prominent mode at $291 \text{ cm}^{-1}$ with other strong modes in the vibronic spectrum. In Figure 6.7, these modes
are marked by “291+x”, where x is the (approximate) wavenumber of the second vibration involved in the combination mode. Since the FC factor of the transition to a combination mode scales with the product of the FC factors of the corresponding transitions (in the non-mixing approximation given by equation (3.45)), transitions to modes that combine two modes with high FC factors are expected to have the highest intensities of all available combination modes. We denote the wavenumbers and relaxation rates of combinations of the modes \(|w\rangle\) and \(|x\rangle\) by \(\tilde{\nu}_{w+x}\) and \(\Gamma_{w+x,e}\), respectively.

Figure 6.9(a) shows fluorescence excitation measurements of several combination modes of DBT in pDCB. We assign the two modes around 580 cm\(^{-1}\) to the combination mode of the modes at 288 cm\(^{-1}\) and 291 cm\(^{-1}\) and the first overtone of the mode at 291 cm\(^{-1}\). We extracted the wavenumbers and vibrational relaxation rates of the combination modes by fitting the rate equation model described in section 6.1.2 to the data. Figure 6.9(b) shows the difference between the combination mode wavenumbers and the sum of the wavenumbers of the corresponding fundamental vibrations. The wavenumbers of most combination modes tend to be smaller by about 0.1 cm\(^{-1}\) than the sum of the
fundamental mode wavenumbers. The vibrational relaxation rates of the combination modes resulting from the rate equation model fit are shown in Figure 6.9(c). They are plotted in units of the summed vibrational relaxation rates of the corresponding fundamental modes. The observation that the values in Figure 6.9(c) are scattered around 1 suggests independent decay behavior of both fundamental modes. A detailed analysis of the wavenumber and linewidth properties of the combination and overtone modes is outside the scope of this thesis.

Based on the relative squared Rabi frequencies of the fundamental and the first overtone of the mode at 291 cm$^{-1}$, we can estimate the $\alpha$-parameter of the non-mixing displaced harmonic oscillator model presented in section 3.2.3. Assuming identical excitation efficiencies in the wavenumber ranges around the spectral range of the fundamental and the overtone, we estimate $\alpha$ from the fit results via:

$$\langle \alpha \rangle = \left( \sqrt{\frac{\Omega_{p,w}^2}{\Omega_{p,w}^2 + \Omega_w^2}} \right) = 0.24$$

for the mode at 291 cm$^{-1}$ using the data from the molecules mol. 1, mol. 2, and mol. 5. The overtone modes of all other prominent vibrational modes in our spectra are weak, however, rendering an equivalent analysis difficult.

### 6.2 Stimulated emission pumping spectroscopy

In single molecule spectroscopy, vibronic states in $S_0$ are typically characterized by fluorescence emission spectra that are recorded using grating spectrometers. The spectral resolution of conventional grating spectrometers is typically limited to $\gtrsim 10$ GHz or 0.3 cm$^{-1}$. Therefore, the relaxation rates of vibrational modes in $S_0$ have not been measured precisely for single dopant molecules in molecular crystals and it is unclear whether some lines are narrow.

In the following sections, we present results from STED experiments with single DBT molecules in pDCB crystals. To our knowledge, this is the first time STED spectroscopy has been applied to single molecules. A similar approach was used recently to measure PSBs of defects in hexagonal boron nitride [28]. Based on our measurements, we can calculate the vibrational relaxation rates of many modes in the electronic ground state of DBT. We observe that the vibrational relaxation in $S_0$ rates are, on average, considerably smaller than in $S_1$ (up to a factor of nine). The lowest linewidths measured by our method are around 2 GHz, corresponding to vibrational lifetimes of around 80 ps.
6.2 Stimulated emission pumping spectroscopy

In section 6.2.1, we present the spectrum of a single DBT molecule, recorded over a broad spectral range and including the PSB of its 00-ZPL. In section 6.2.2 the dependence of the excited state depletion on the power of the depletion laser is analyzed in terms of the parameters of the rate equation model from section 4.3.2 and appendix D.8. The variation in the STED spectra between different molecules is studied in section 6.2.3, together with the properties of some combination and overtone modes. In section 6.2.4, we compare the mode wavenumbers, relaxation rates, and relative intensities of selected modes in $S_0$ and $S_1$. Some levels with particularly low linewidths are discussed in section 6.2.5.

6.2.1 Stimulated emission pumping spectrum of a single DBT molecule

Figure 6.10 shows a STED spectrum of mol. 1, covering the spectral range 0–1600 cm$^{-1}$. The measurement of the PSB (gray area) was performed in the experimental configuration shown in Figure 6.1(e). The rest of the spectrum was recorded using the arrangement shown in Figure 6.1(d). Because the tunable Ti:Sapphire laser used for these measurements could be scanned in a spectral range between about 300–430 THz and the 00-ZPL transition of mol. 1 was at 402.57 THz, we were able to cover a broader range of vibrational
6 High-resolution vibronic spectroscopy of single molecules

levels in the STED measurements compared to the fluorescence excitation measurements in section 6.1. In principle we could have also reached the high wavenumber region of the C-H stretch modes at $> 3000 \text{ cm}^{-1}$ with our tunable laser, but during the experiments performed for this thesis, we did not attempt to access this range.

As indicated in the caption of Figure 6.10, we used higher pump and depletion laser powers for the PSB measurement to improve the SNR. The saturation parameters $S_p$ were obtained from saturation measurements of the pumped vibronic level in the respective experimental arrangements. The higher pump saturation power observed for the scan of the PSB can be attributed to sub-optimal alignment of the pump laser focus in this case. To compensate for the chromatic aberrations of the aspheric lens we divided the vibronic part of the spectrum into four regions for which the laser focus was optimized individually. More details of chromatic effects in our measurements are given in section 6.1.3.

To remove background induced by the pump and depletion laser, we determined their contributions individually and subtracted them from the total APD count rate $R$ obtained from a STED measurement. The background induced by the pump laser was measured by scanning the pumped vibronic level and fitting a Lorentzian model including an offset term to the data. Since the pump saturation parameters in our STED measurements were $S_p \sim 1$, the off-resonant pumping of the molecule described in section 6.1.2 is expected to be very weak. Therefore, we directly used the offset term resulting from the fit to estimate the pump laser induced background count rate $R_{bg,p}$. To estimate the background count rate $R_{bg,d}$ induced by the depletion laser, we blocked the pump laser and scanned the depletion laser over the complete spectral range covered in the STED measurement. The total APD count rate of an STED experiment was then corrected using $R \rightarrow R - R_{bg,p} - R_{bg,d}$.

During the course of our experiments, we observed that accurate alignment of the laser filters can reduce the background levels of both lasers to negligible values. Therefore, we assume that background in a STED measurement mainly stems from light created in the fibers that was not filtered out. We also noticed that the application of a longpass filter behind the fiber of the depletion laser leads to a decrease of the background in the configuration shown in Figure 6.1(d). Since the detection bandpass is blue-detuned with respect to the depletion laser frequency in this case, we presume that anti-Stokes Raman scattering in the fiber can also contribute to background terms. Generally, with increasing sample number from 1 to 3 as defined in Table 6.1, the background suppression efficiency improved due to better alignment of the laser filters.
and the implementation of the wedged windows until we obtained almost background-free scans for mol. 1 on sample 3.

The STED spectra in Figures 6.10 and 6.11 show a large number of vibronic features with a high spectral resolution. A detailed analysis of each feature in this rich data set, including a first principles explanation of its vibronic line profile, is beyond the scope of this thesis but could be an interesting topic for a separate theoretical analysis. In the following sections, we characterize some properties of the STED spectroscopy method in more detail and report quantitative results related to the wavenumbers, vibrational relaxation rates and relative depletion Rabi frequencies of selected prominent modes in the STED spectra of five DBT molecules in pDCB.

6.2.2 Saturation behavior of stimulated vibronic transitions

The stimulated emission induced by the depletion laser exhibits a saturation behavior (see section 4.3 for a theoretical derivation). As a consequence, the relative amplitudes of the vibronic features in a STED spectrum depend on the power of the depletion laser and differ from the relative amplitudes of the lines in a fluorescence emission spectrum.

Figure 6.11 shows the saturation effect of STED spectroscopy by comparing the data from Figure 6.10 ($P_d = 102 \, \mu W$) with a STED spectrum recorded at a higher depletion laser power ($P_d = 550 \, \mu W$). Because of saturation, the depletion of the weak features shows a larger relative increase compared to the depletion of the most prominent features between these two depletion power settings. The data in Figure 6.11 were recorded with the same settings of the pump laser and are plotted without offset between the scans. The decrease in the fluorescence baseline between the vibronic features at the depletion laser power of 550 $\mu W$ is caused by stimulated emission from $|S_1, 0\rangle$ to PSBs of vibrational states and weak vibrational (combination) modes of DBT. This is equivalent to the broadband absorption in high power fluorescence excitation scans around the 291 cm$^{-1}$ mode of $S_1$, indicating that the molecule can absorb light even if the depletion laser is not resonant with a discrete vibrational feature (see also section 6.1.2). The broad depletion dip between 270 cm$^{-1}$ and 350 cm$^{-1}$ appears to result from the sum of the PSBs of the strong vibronic features with lower wavenumbers. As mentioned below, we cannot exclude that thermal dephasing also contributes to the drop in the fluorescence baseline for $P_d = 550 \, \mu W$. 

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Figure 6.11: STED spectra of mol. 1, recorded at the depletion laser powers 102 µW and 550 µW. The horizontal black dashed line shows the fluorescence level in a configuration in which the depletion laser is blocked. The vertical black dashed lines show the limits of the scan regions between which the focus of the depletion laser was optimized.
The FC factors and linewidths vary among the vibronic transitions in a DBT molecule in pDCB. As a consequence, the saturation parameters $S_d$ of the depletion process and the associated power-broadening of a vibronic line vary among the transitions in a STED spectrum that was recorded at a fixed power of the depletion laser. Measurements with negligible power-broadening of the vibronic lines can be obtained by adjusting the power of the depletion laser individually for each transition to reach the low excitation limit $S_d \ll 1$. Alternatively, one can record one STED spectrum at a single laser power and correct for the power-broadening effects in the data analysis. Since recording a background-corrected STED spectrum over a spectral range of 1600 cm$^{-1}$ takes about 2 days, we used the latter approach in this thesis. To correct for power-broadening, we fit a rate equation model to the STED data that intrinsically takes the saturation behavior of the depletion and the related power-broadening into account. This model is analogous to the model for the data from fluorescence excitation measurements introduced in section 6.1.2 but adapted to the case of (potentially overlapping) vibronic transitions in STED spectroscopy. Details about the underlying equations can be found in appendix D.8. To fit the model to the data, we first calculate the excited state depletion factor from the data via $D = \left( R(P_d = 0) - R(P_d \neq 0) \right) / R(P_d = 0)$, where $R(P_d = 0)$ is the (background-corrected) rate of photons from the pumped molecule that is measured at the APD if the depletion laser is off [183]. The value of $R(P_d = 0)$ is determined from a saturation measurement of the pumped vibronic state (see section 6.1.2 for an example). For the model, we used the independently determined vibrational relaxation rate $\Gamma_{we}$, electronic decay rate $\Gamma_{eg}$, and pump saturation parameter $S_p$ as fixed parameters. Then we fitted the depletion factor $D = \left( N_e(\Omega_d = 0) - N_e(\Omega_d \neq 0) \right) / N_e(\Omega_d = 0)$ resulting from the model in appendix D.8 to the data.

In Figure 6.12(a), we show data from a saturation measurement of the prominent level around 290 cm$^{-1}$ in $S_0$, including fits of the rate equation model. As in $S_1$, there is a small satellite level at around 288 cm$^{-1}$ (state $|u\rangle$) and spectrally broad depletion (‘state’ $|G\rangle$) that becomes visible for higher depletion laser powers. Fit results for the squared depletion Rabi frequencies $\Omega_d^2$ and relaxation rates $\Gamma_{vg}$ and $\Gamma_{ug}$ of $|u\rangle$ and $|v\rangle$, respectively, are shown in Figures 6.12(b,c). We obtained similar values for the relaxation rates for depletion values of the peaks in the range $0.05 < D < 0.9$ (level $|v\rangle$). For very low depletion values $D \ll 0.05$, the noise of the fluorescence baseline can affect the fit results. For high depletion values $D > 0.9$, small errors in the estimation of $R(P_d = 0)$ have a significant impact on the fit results. The measurements used for the intermolecular comparison presented in section 6.2.3 were performed with depletion values in a range $0.05 < D < 0.9$ and thus yield reliable fit results.
The highest depletion reached in the data set of Figure 6.12(b) amounts to $D \sim 0.98$. In this case, the depletion laser removed almost all population from the excited state $|e\rangle$. Note that due to the short vibrational lifetime of the state $|v\rangle$, this population mainly resides in $|g\rangle$ and only a fraction of less than 0.2% is expected to be in the vibronic state $|v\rangle$. Thus, selective preparation of vibrational states, for which stimulated emission pumping has been used in gas phase studies (see section 4.3.1), is of limited use in a solid-state system such as DBT in pDCB due to the fast vibrational relaxation times.

According to the fit results, the relaxation rate of the state at around 290 cm$^{-1}$ is very similar in both electronic ground and excited states of mol. 1 ($S_0$: $\Gamma_{vg}/(2\pi) = 10.5$ GHz, $S_1$: $\Gamma_{we}/(2\pi) = 10.9$ GHz). The same holds for the state at 288 cm$^{-1}$ ($S_0$: $\Gamma_{ug}/(2\pi) = 8.2$ GHz, $S_1$: $\Gamma_{xe}/(2\pi) = 8.6$ GHz).

The model of STED spectroscopy presented in section 4.3.2 predicts that the ratio of the saturation powers for pumping the molecule via $|g\rangle \rightarrow |w\rangle$ to stimulated emission along the transition $|e\rangle \rightarrow |v\rangle$ is $P_{sat,p}/P_{sat,d} \approx 1/2$ for $S_p = 1$ if the decay rates of the addressed vibrational states are identical. From our experiments with mol. 1 we determined the values $P_{sat,p} = 19 \mu W$ and $P_{sat,d} = 11 \mu W$. The difference in the experimental saturation power ratio

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Figure 6.12: Dependence of the STED spectra on the power of the depletion laser. (a) Depletion around the vibronic level at 290 cm$^{-1}$ recorded at different depletion laser powers. Higher depletion laser power leads to increasing depletion. Orange dashed lines are fits of the model described in appendix D.8. The assignments of the levels $|v\rangle$, $|u\rangle$, and $|G\rangle$ used in the model are indicated in the plot. (b) Squared Rabi frequencies resulting from the fit. The black dashed lines show fits of a function $\Omega_d^2 = m \cdot P_d$ to the circular data points. The circular data points in (b,c) indicate depletion factors $D$ within $0.05 < D < 0.9$ over the full spectral range of the measurement. The square data points in (b,c) indicate fit results with $D < 0.05$ or $D > 0.9$ and are unreliable due to a low SNR or because the maximum depletion values are close to saturation (see the main text for more details). (c) Vibrational relaxation rates of the levels $|v\rangle$ and $|u\rangle$ resulting from the fit. The dashed lines and numbers indicate averages over the circular data points.
compared to the value expected based on the rate equation model may be caused by different qualities of the foci of pump and depletion lasers.

Similar to the case of the vibronic saturation measurements in $S_1$ (see Figure 6.5) it is not trivial to separate thermally induced pure dephasing from saturation effects in the data in Figures 6.11 and 6.12. Dephasing on the electronic transition leads to a decrease in the absorption cross sections of the vibronic transitions and could explain the drop in the total fluorescence signal in Figure 6.11 by rendering the pumping of the molecule less efficient. Based on linewidth measurements of the vibronic levels in the spectrum of Figure 6.11 recorded with $P_d = 550 \, \mu W$ and the drop of the baseline fluorescence signal in this figure, we estimate that the dephasing contribution to the total linewidth is limited to $2\Gamma^*/(2\pi) \leq 1 \, \text{GHz}$ at this laser power.

### 6.2.3 Intermolecular variation

Figure 6.13 shows high-resolution STED spectra of the five DBT molecules in Table 6.1. The spectra were recorded at pump saturation parameters $S_p \sim 1$ and powers of the depletion laser within 100–225 $\mu W$. Since the STED spectra of the five molecules were recorded using slightly different arrangements of the experimental setup (wedged or planar windows; with or without laser filters), some of them display systematic oscillations of the baseline signal. We only picked intense vibronic features, which could be clearly separated from the behavior of the background, for the analysis in this thesis. Like the fluorescence excitation spectra of various molecules discussed in section 6.1.4, the vibronic spectra of different DBT molecules in pDCB displayed in Figure 6.13 are very similar. The prominent vibronic features are shared by all molecules.

A detailed inspection of the variation between molecules reveals additional information on a more fine-grained scale. This analysis is enabled by the high wavenumber accuracy (around 2 MHz, limited by the resolution of the wavemeter and assuming a correct 00-ZPL transition frequency) and resolution (around 2 MHz, limited by the resolution of the wavemeter since the linewidth of the laser is $< 1 \, \text{MHz}$) of our STED measurements. We remark that it is difficult to reach a comparable wavenumber accuracy and resolution with a grating spectrometer over a comparable spectral range. Fine gratings ($\geq 1600 \, \text{g/mm}$) that offer a spectral resolution of $\sim 0.7 \, \text{cm}^{-1} \approx 20 \, \text{GHz}$ typically cover a range of approximately 300 $\text{cm}^{-1}$ and need to be rotated during measurements of a broad spectral range. To compensate for (non-linear) distortions along the wavelength axis incurred by the optics of the spectrometer...
Figure 6.13: STED spectra of all molecules listed in Table 6.1. Depletion factors are normalized and indicated for every scan. The numbers at the top of the plot indicate the approximate wavenumbers of the vibronic features, and depletion powers are indicated for every scan. The black dashed lines show the borders of the scan regions between which the focus of the laser has been optimized.

Vibrational wavenumber (cm$^{-1}$) vs. Depletion factor (norm.)
and rotations of the grating, one must calibrate the wavelength axis thoroughly using many reference measurements. Provided that STED measurements are performed with a stable tunable laser with an accurate wavemeter, they reach a high wavenumber accuracy without additional calibration efforts (see section 5.1 for more details of the components used). Similarly, the intensity distribution measured with grating spectrometers can be affected by the wavelength-dependent response of camera pixels and other chromatic effects in the optical setup. An accurate estimation of the intensities with a spectrometer thus requires a dedicated calibration of the intensity axis. STED spectroscopy is not affected by these effects since the detected light has a constant wavelength.

Figure 6.14(a) shows several selected vibronic features from Figure 6.13. These data demonstrate the high spectral resolution of the STED method. Some notable observations are the appearance of the additional satellite peak next to the level at 290 cm$^{-1}$ for molecules mol. 2 and mol. 3 and the two peaks at around 665 cm$^{-1}$ appearing only for molecules mol. 2 and mol. 4.

From fits of the rate equation model from appendix D.8, we determined the wavenumbers $\tilde{\nu}$, vibrational relaxation rates $\Gamma_{vg}$, and (squared) depletion Rabi frequencies $\Omega_d^2$ for all vibronic features marked in Figure 6.13. The fits of the rate equation model to some STED transitions of mol. 1 are shown as black dashed lines in Figure 6.14(a). On top of this plot, we indicate the average relaxation rates and the intermolecular range of vibrational wavenumbers for each mode. Similar to the observation in $S_1$, the width of the intermolecular distribution of the wavenumbers differs considerably between the vibrational modes in $S_0$ (see also Figure 6.14(b)). The average wavenumber range over all molecules and investigated modes is 0.9 cm$^{-1}$.

As shown in Figure 6.14(c), the vibrational relaxation rates are also scattered between molecules. As in $S_1$, there is a marked decrease in the average relaxation rate between the mode at 233 cm$^{-1}$ and the mode at 288 cm$^{-1}$. The average linewidth range in $S_0$ over all molecules is 4.7 GHz. A more detailed comparison of the parameters of the vibronic states in $S_0$ and $S_1$ is shown in section 6.2.4.

Figure 6.14(d) shows the intermolecular distribution of the (relative) squared depletion Rabi frequency $\Omega_d^2$. The most prominent mode is the one around 290 cm$^{-1}$ together with the two modes at 177 cm$^{-1}$ and 234 cm$^{-1}$. The values $\Omega_d^2/\Omega_{d,max}^2$ of the modes at 177 cm$^{-1}$ and 234 cm$^{-1}$ vary considerably between the molecules and are weakest for mol. 3 and strongest for mol. 2. We do not attribute this effect to aberrations of our setup since we do not observe the
6 High-resolution vibronic spectroscopy of single molecules

Figure 6.14: Intermolecular variation of the vibronic levels in $S_0$. (a) Selected features from the STED spectra of all five molecules in Table 6.1. The black dashed lines are fits of the rate equation model described in appendix D.8 to the data of mol. 1. The vertical dashed lines indicate the vibrational wavenumbers $\bar{\nu}_v$ of the different vibronic features and molecules. The numbers at the top of the plot are the average linewidths $\langle \Gamma_{\nu_d}/(2\pi) \rangle$ and the range of the vibrational wavenumbers of the levels $|\nu\rangle$ included in the rate equation model. Adapted from [45], with the permission of AIP Publishing. (b) Distribution of the vibronic wavenumbers around the average wavenumber of each level. (c) Distribution of the vibronic linewidths. (d) Distribution of the relative Rabi frequencies $\Omega_d^2$.

The same consistent ordering of $\Omega_d^2/\Omega_{d,\text{max}}^2$ between molecules for other modes. Potentially, the variation of $\Omega_d^2/\Omega_{d,\text{max}}^2$ of the modes at 177 cm$^{-1}$ and 234 cm$^{-1}$ is caused by different degrees of deformation of DBT along the directions of the corresponding mode vectors.

Figure 6.15 shows more detailed data and fit results for combination modes in $S_0$ that involve the mode at 290 cm$^{-1}$. The analysis shown in the different parts of this figure is equivalent to the analysis for modes in $S_1$, discussed in section 6.1.5. Generally, the wavenumber of the combination modes tends to be slightly lower ($\sim 0.1$ cm$^{-1}$) than the sum of the fundamental mode wavenumbers (see
6.2 Stimulated emission pumping spectroscopy

Figure 6.15: Combination modes and first overtone of the vibrational mode at 290 cm\(^{-1}\) in \(S_0\) shown for all molecules in Table 6.1. (a) Depletion profiles of some combination modes and the overtone mode of the level at 290 cm\(^{-1}\). The black dashed lines in (a) are fits of the rate equation model described in appendix D.8. The vertical dashed lines mark the wavenumbers \(\tilde{\nu}_{v+u}\) of the fitted resonances of each molecule. The numbers at the top of the plot indicate the average linewidths \(\langle \Gamma_{v+u, e}/(2\pi) \rangle\) and the range of the vibrational wavenumbers of the combination modes \(|v + u⟩\) included in the rate equation model. Line colors indicate molecules as defined in Table 6.1. (b) Difference between the combination mode frequency and the sum of the associated fundamental mode frequencies. (c) Ratio of the combination mode linewidth and the sum of the linewidths of the associated fundamental mode frequencies.

Figure 6.15(b)). As in \(S_1\), the mode 290 + 288 is an exception, displaying a higher wavenumber than the sum of the wavenumbers of its fundamentals. The relaxation rates of the combination modes are roughly equal to the sum of the relaxation rates of the fundamental modes (see Figure 6.15(c)). We note that the fit results of some vibronic features shown in Figure 6.15(c)) may be affected by the noise in the data. Using the same method as described in section 6.1.5, we obtain \(\langle \alpha \rangle = 0.31\) for the mode at 290 cm\(^{-1}\) by comparing \(\Omega_0^2\) of its fundamental excitation and its first overtone. This value agrees closely with the corresponding result from the DFT calculations for isolated DBT (\(|\langle 2_17|\vec{0}\rangle/\langle 1_17|\vec{0}\rangle| = 0.31\)) and the deformed versions of DBT discussed in section 6.3.2.

6.2.4 Comparison of modes in \(S_0\) and \(S_1\)

Figure 6.16 shows the fit results of the rate equation model for vibronic transitions \(|S_1, \vec{0}\rangle \rightarrow |S_0, \vec{v}\rangle\) from STED experiments (blue) and transitions
\[ |S_0, \vec{0} \rangle \rightarrow |S_1, \vec{w} \rangle \] from fluorescence excitation experiments (orange) in a combined plot.

There are several notable observations relating to these plots. As shown in Figure 6.16(a), the average wavenumbers of the vibrational modes tend to be larger in \( S_0 \) than in \( S_1 \). This suggests that the average binding forces between the nuclei are smaller in \( S_1 \), as expected for an electronically excited state. The mode with \( \langle \tilde{\nu} \rangle = 402.9 \text{ cm}^{-1} \) in \( S_0 \) has \( \langle \tilde{\nu} \rangle = 395.0 \text{ cm}^{-1} \) in \( S_1 \), a difference of almost \( 8 \text{ cm}^{-1} \) or \( 230 \text{ GHz} \). In the plots of Figures 6.8 and 6.14, we show the same range of \( 15 \text{ cm}^{-1} \) around these modes to demonstrate that there are no other vibronic features in the spectral vicinity. Together with the results of the splitting experiments shown in chapter 7, this demonstrates that these spectral features belong to an equivalent vibronic mode. A wavenumber shift of a similar magnitude has been reported by Carlson and Wright for a vibrational mode in Pc in benzoic acid [105].

Figure 6.16(b) shows that the deviations of the wavenumbers from the average wavenumber are similar in \( S_0 \) and \( S_1 \) for each molecule and each mode. This indicates that the effects leading to the intermolecular wavenumber variation are similar in both electronic states. The observation that mol. 2 and mol. 4 tend to have wavenumbers below the average suggests that these molecules are embedded in similar nano-environments.

Figure 6.16(c) shows the average relaxation rates (normalized by \( 2\pi \)) of the modes in \( S_0 \) and \( S_1 \). Figure 6.16(d) displays the corresponding relaxation rates of the individual molecules. The drop in the (average) relaxation rates between the mode at \( 234 \text{ cm}^{-1} \) and \( 288 \text{ cm}^{-1} \) is most likely related to a change in the vibrational relaxation mechanism from regime I to regime II as described by the Dlott group [13] and discussed in section 3.3 of this thesis. In this context it is notable that the line profile of the mode at \( 234 \text{ cm}^{-1} \) has an asymmetric shape, both in \( S_0 \) and \( S_1 \). One way to explain asymmetric line profiles of a vibrational state is via a marked change in the phononic density of states at its vibrational frequency [218]. In the specific case of the modes at \( 234 \text{ cm}^{-1} \) in DBT in pDCB, the asymmetry may be related to a drop in the two-phonon density of states of pDCB around that frequency (see section 6.5.1 for a more detailed discussion). Additionally we observe that for most modes, the average relaxation rates are considerably higher in \( S_1 \). The mode at \( 670 \text{ cm}^{-1} \) has a particularly large difference between relaxation rates in both states \( (S_0: \Gamma_{vg}/(2\pi) = 4 \text{ GHz} \) and \( S_1: \Gamma_{we}/(2\pi) = 36 \text{ GHz} \). An interesting question arises as to whether this marked difference in relaxation rates is caused by changes in the coupling to the phonons of the matrix, by changes in the number of reachable internal vibrations of DBT due to wavenumber shifts of the vibrational states between
6.2 Stimulated emission pumping spectroscopy

Figure 6.16: Parameters resulting from a fit of the rate equation models to the data from fluorescence excitation (orange) and STED measurements (blue). (a) Difference of the average wavenumbers in $S_0$ and the average wavenumbers in $S_1$. (b) Deviation of the vibrational wavenumbers from the average (in each state). Dashed black lines indicate the average wavenumbers, the scale bar quantifies the extent of the deviations from the average. The tick marks on the vertical axis are the average wavenumbers of the modes in $S_0$. (c) Average linewidths of the vibronic transitions. (d) Deviation of the individually measured linewidths from the average linewidths. (e) Average relative squared Rabi frequencies. (f) Deviation of the relative squared Rabi frequencies from the average relative squared Rabi frequency. Adapted from [45], with the permission of AIP Publishing.

$S_0$ and $S_1$, or by coupling to different fast relaxation channels (see section 6.5.1 for a more detailed discussion).

Figure 6.16(e) shows the relative squared Rabi frequencies of the stimulated transitions. Note that we did not include the $S_1$-data of mol. 4 in this plot, because they showed signs of suboptimal alignment in one scan region. The relative rates behave very similarly in both electronic states, indicating an effective compensation for the chromatic effects in our optical setup. The drop in the average Rabi frequency for the modes in $S_1$ with the highest wavenumbers could, however, be caused by chromatic effects. The deviations of the Rabi frequencies obtained for modes at 177 cm$^{-1}$ and 234 cm$^{-1}$ in $S_0$ are the most prominent ones of the modes that were studied for both molecules.
(see Figure 6.16(f)). This may indicate that the FC factors of these modes are very sensitive probes for individual deformations of the molecules by the crystal matrix. We do not, however, observe the same behavior in $S_1$. Possibly, the different conformation of DBT in its electronically excited state renders its low-wavenumber modes less susceptible to inhomogeneities in the crystal environment.

### 6.2.5 States with low relaxation rates

For the prominent vibronic states investigated using fluorescence excitation and STED spectroscopy, we found a considerable spread of linewidths, corresponding to lifetimes in the range between roughly 4–40 ps (see section 6.2.4). The narrowest linewidth of a prominent line was found for the vibronic state at 670 cm$^{-1}$ in $S_0$, with $\Gamma_{vg}/(2\pi) \sim 4$ GHz. Some less intense features in the vibronic spectra exhibit even narrower linewidths. The corresponding data are displayed in Figure 6.17.

Around 300 cm$^{-1}$, we found narrow vibronic states both in $S_0$ and $S_1$. The colored lines in Figure 6.17(a) show the normalized depletion from STED measurements of the five molecules studied in this chapter. The gray lines show the (normalized) result of fluorescence excitation measurements in the same spectral range. The black dashed lines in this plot are fits of the sum of two Lorentzian functions (2.2) to the data. The numbers next to the peaks are the linewidths obtained from the fits. In contrast to the evaluations shown above, we fit a Lorentzian model instead of the rate equation model to the data to show the linewidth of the measured features directly without intrinsic correction for power-broadening effects. Since the amplitude of the spectra shown here is rather low, power-broadening effects are small in the measurements shown in Figure 6.17. The narrowest linewidths in the measurements at 300 cm$^{-1}$ are around 2 GHz, both in $S_0$ and $S_1$. The relaxation pathways of these states thus appear to be similar in both electronic states.

Around 725 cm$^{-1}$, we found one distinct vibronic line in the STED spectra (see Figure 6.17(b)), but not in the fluorescence excitation spectra. Lorentzian fits to this line also yield narrow linewidths as low as 2 GHz. While the wavenumber of this line is around 728.5 cm$^{-1}$ for most molecules, we found it at 724.9 cm$^{-1}$ for mol. 2.

In addition to the isolated Lorentzian peaks shown in Figures 6.17(a,b), we found highly overlapping vibronic levels in the spectral region around 330 cm$^{-1}$ (see Figure 6.17(c) for the data of mol. 1; for the other molecules the spectra
6.2 Stimulated emission pumping spectroscopy

Figure 6.17: Examples of vibronic transitions with narrow linewdths. (a,b) Colored lines: STED spectra of narrow lines around 300 cm\(^{-1}\) and 725 cm\(^{-1}\), respectively, shown as normalized depletion factor \(D\). The data are plotted with an offset for each molecule. Black dashed lines: fits of Lorentzian profiles to the data. The numbers next to the peaks are the linewidths resulting from the fits (unit: GHz). The solid gray lines in (a) are data from fluorescence excitation measurements in the same spectral range. The linewidths of the Lorentzian profiles in the excitation spectra are similar to the STED spectra. (c) Normalized depletion measured for mol. 1 using two different scan speeds of the depletion laser (0.5 GHz/s and 2 GHz/s, respectively) around 330 cm\(^{-1}\) at \(P_d = 102 \mu W\). Dashed black lines: fits of a Lorentzian profile to a narrow feature in the spectrum. Orange dashed line: the same spectral range recorded with a grating spectrometer (taken from the fluorescence emission spectrum of mol. 1 shown in Figure 2.4(a)). Parts (a) and (b) adapted from [45], with the permission of AIP Publishing.

were similar but exhibited a worse SNR). To check the effect of the laser scan speed on the resulting linewidths, we measured this profile once at the standard scan speed of 2 GHz/s and once at 500 MHz/s. A comparison of the outcomes of both scans demonstrates the noise level in these recordings and that the standard scan speed of 2 GHz/s does not have a major blurring effect on measurements of states with linewidths in the order of 2 GHz. Because the vibronic features are not clearly separated in this spectral range it is difficult to fit a model to these data. In Figure 6.17(c), we also show a measurement of the same spectral range performed with a grating spectrometer (taken from
Figure 2.4(a)). The SNR of the spectrometer data is limited because of the relatively low intensity of the vibronic feature. A comparison with the STED data reveals the enhancement of the spectral resolution achieved via STED spectroscopy. The fluorescence excitation spectrum of mol. 1 does not contain comparable fine vibronic features around $330 \, \text{cm}^{-1}$. Instead, it contains three broad vibronic peaks around $325 \, \text{cm}^{-1}$.

6.3 Density functional theory calculations

In this section, we present the results of DFT calculations for DBT and use them to assign molecular normal modes to the vibronic features observed in our experiments. A close agreement between the simulation results and experimental data requires the pDCB crystal to be included in the simulations.

In section 6.3.1, we show DFT results for the geometry of isolated DBT in $C_{2h}$-symmetry. We also describe the method used in this thesis to correct the wavenumbers of the DFT results. Additionally, we estimate the effects of Herzberg-Teller corrections and $^{13}$C substitution on the vibronic spectra. In section 6.3.2, we present the results of ONIOM simulations that include a shell of pDCB molecules around the DBT molecule. The changes in the spatial conformation of DBT in the crystal and the effects on its vibronic spectra are also analyzed.

All DFT calculations discussed in the context of this thesis were performed by Irena Deperasińska and Boleslaw Kozankiewicz from the Institute of Physics at the Polish Academy of Sciences in Warsaw. They also provided mode assignments and suggestions for how to embed DBT in pDCB for the calculations (see section 6.3.2).

6.3.1 Isolated DBT

The equilibrium structure and the normal modes of isolated DBT in the electronic states $S_0$ and $S_1$ were calculated using the Gaussian 16 software package [81]. The calculations were performed with the B3LYP functional and the 6-31G(d,p) basis set. Results of similar calculations for three stereoisomers of isolated DBT were published by Deperasińska et al. in 2010 [83]. The FC factors were calculated using the results from the Gaussian 16 calculations and the procedure described by Barone et al. [87] (see also appendix D.3 for the most relevant formulas used in the context of this thesis).
Figure 6.18 shows the most stable stereoisomer of isolated DBT ($C_{2h}$ symmetry) in the electronic state $S_0$ from three different perspectives. The $z$-axis of the coordinate system used here coincides with the long axis of the terrylene moiety of DBT. In Figure 6.18(a), various planes of the molecule are marked together with the corresponding normal vectors $\vec{n}_i$ on the planes defined by the surrounding carbon atoms. As indicated in Figure 6.18(b), the angle between the central part of the DBT molecule ($\vec{n}_1$) and an outer ring of the tetracene moiety ($\vec{n}_2$) is $13.0^\circ$ in this configuration of DBT. The angle between the central part and an outer naphthalene unit ($\vec{n}_3$) is $26.4^\circ$. The total tilt angle between the naphthalene unit and the outer ring of tetracene amounts to $39.5^\circ$. The perspective used in Figure 6.18(c) shows that the normal vectors $\vec{n}_2$ and $\vec{n}_3$ are tilted with respect to the central normal vector $\vec{n}_1$ only around the long axis of the terrylene moiety. In $S_1$, the angles between $\vec{n}_1$ and $\vec{n}_2$ as well as between $\vec{n}_1$ and $\vec{n}_3$ are $15.3^\circ$ and $25.3^\circ$, respectively.

The DFT results for the normal mode wavenumbers of isolated DBT are shown in Figure 3.2. These values tend to deviate systematically from the vibrational wavenumbers found in experiments. This is caused by several simplifications underlying the DFT calculations, such as the assumption of...
High-resolution vibronic spectroscopy of single molecules

Since the approximated harmonic potential is steeper than the actual anharmonic potential, the wavenumbers of vibrational modes are usually overestimated by the DFT calculations. It is customary to correct the wavenumbers resulting from DFT calculations using a scaling function. Palafox recommends using the linear function \( \tilde{\nu}_{\text{exp}} = a + b \cdot \tilde{\nu}_{\text{sim}} \) for wavenumber correction [219]. The parameters \( a \) and \( b \) depend on the functional and basis set used for the DFT simulations, the molecule, and the type of normal modes under consideration. Typical values of scaling factors for PAHs and B3LYP/6-31G(d,p) are around \( b \sim 0.96 \) [140, 220].

To assign the normal modes resulting from DFT simulations to the vibronic peaks observed in the STED spectra from section 6.2, we plotted the experimental results and the FC factors from DFT simulations against the vibrational wavenumber (see Figure 6.19). The blue lines in Figure 6.19 display the values of \( \Omega_{p}^{2}/\Omega_{p,\text{max}}^{2} \) of the selected modes in \( S_0 \), averaged over all five molecules (see section 6.2.3). The dashed orange lines in Figure 6.19 mark all FC factors with values \( FC > 0.1\% \) that result from DFT simulations of isolated DBT. For the plot, the FC factors were normalized by the highest FC factor of mode 17. Then we assigned the DFT results to the experimental features based on the similarity of the wavenumbers and the FC intensity while using a ‘pre-scaling’ factor of 0.96 for the wavenumbers of the DFT results. For this procedure, we restricted ourselves to the few selected fundamental modes from section 6.2.3. Additional features have not been included in this analysis because they were either combination modes or difficult to fit using a model with an unambiguous number of peaks due to their complex multi-modal structure. We indicate the mode numbers of the calculated modes that were assigned to the experimental modes in Figure 6.19. The features at 765 cm\(^{-1}\) and 768 cm\(^{-1}\) were assigned (simultaneously) to mode 59. The feature at 784 cm\(^{-1}\) was assigned to mode 63. Table 6.2 lists all the mode assignments. The experimental and theoretical wavenumbers of the matched modes are shown in the inset of Figure 6.19 together with a linear fit. The fit parameters \( a = 15.2 \text{ cm}^{-1} \) and \( b = 0.955 \) agree closely with the literature on similar systems [106, 219–222]. The mean absolute deviation of the nine modes from the fitted line is 3.1 cm\(^{-1}\).

The experimental and theoretical line intensities in Figure 6.19 differ considerably for some modes (e.g. for mode 9 and mode 24; see also Figure 6.23(a,d)). These differences can be attributed to crystal induced deformation of the molecule (see section 6.3.2). With HT corrections and \(^{13}\)C substitution there are, however, also mechanisms that cause a redistribution of intensity between vibronic lines without deformation of the molecule. DFT calculations predict that the (pure) HT intensities are by about four orders of magnitude smaller.
6.3 Density functional theory calculations

Figure 6.19: Mode assignments and wavenumber scaling for results from DFT simulations of isolated DBT. The main plot shows the average experimental mode wavenumbers \( \langle \omega_p \rangle \) from the STED spectra (blue lines) and the normalized FC factors resulting from DFT calculations (orange dashed lines). The STED spectrum of mol 1 is shown by a gray line. The modes from the DFT simulations assigned to the experimental data are indicated by arrows with solid lines in the plot. The arrows with the dashed lines indicate assignments to features in the data that were not analyzed in more detail. The numbers shown in the plot are the mode numbers of the DFT simulations. The inset shows the relation between the average experimental mode wavenumbers \( \langle \bar{\omega}_\text{exp} \rangle \) and the wavenumbers resulting from DFT calculations \( \bar{\omega}_\text{sim} \). The black line shows a linear fit to the data. The parameters of the fit function are indicated in the plot.
Table 6.2: Assignments of the vibrational modes of DBT analyzed in this thesis.

<table>
<thead>
<tr>
<th>Mode</th>
<th>(\langle \tilde{\nu} \rangle)</th>
<th>(\langle \Gamma \rangle)</th>
<th>(\langle \Omega^2 / \Omega^2_{\max} \rangle)</th>
<th>#</th>
<th>(FC_r)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>69.0 cm(^{-1})</td>
<td>3.0 GHz</td>
<td>0.36</td>
<td>10</td>
<td>0.90</td>
</tr>
<tr>
<td>2</td>
<td>69.3 cm(^{-1})</td>
<td>3.0 GHz</td>
<td>0.36</td>
<td>10</td>
<td>0.90</td>
</tr>
<tr>
<td>3</td>
<td>69.6 cm(^{-1})</td>
<td>3.0 GHz</td>
<td>0.36</td>
<td>10</td>
<td>0.90</td>
</tr>
<tr>
<td>4</td>
<td>69.9 cm(^{-1})</td>
<td>3.0 GHz</td>
<td>0.36</td>
<td>10</td>
<td>0.90</td>
</tr>
<tr>
<td>5</td>
<td>70.2 cm(^{-1})</td>
<td>3.0 GHz</td>
<td>0.36</td>
<td>10</td>
<td>0.90</td>
</tr>
</tbody>
</table>

Note: \(\langle \tilde{\nu} \rangle\): average experimental wavenumber (unit: cm\(^{-1}\)); \(\langle \Gamma \rangle\): average vibrational linewidth (unit: GHz); \(\langle \Omega^2 / \Omega^2_{\max} \rangle\): average relative squared pump/depletion Rabi frequency; \# mode number in the respective simulation (ordered according to increasing wavenumber); FC factor, relative to mode 17.
6.3 Density functional theory calculations

Figure 6.20: Effect of the substitution of a single $^{12}$C atom by a $^{13}$C atom (at position 2 indicated in Figure 6.18) on the FC factors of transitions from $S_1$ to $S_0$ in isolated DBT. Only FC factors of the fundamental modes with $FC > 5 \cdot 10^{-4}$ are displayed. The inserts show the regions in which lines are activated by the substitution in more detail and the numbers in the inserts indicate the mode numbers. Mode numbers with an asterisk belong to the DBT molecule with the $^{13}$C atom. The $x$- and $y$-axes of the insets show wavenumbers in cm$^{-1}$ and FC factor in %, respectively. The wavenumbers have been scaled by the function shown in the inset of Figure 6.19.

than the corresponding FC factors of the assigned modes in Figure 6.19 (see equation (3.33)) [87]. Moreover, weak vibronic transitions are predicted to gain not more than $\sim 1\%$ of the intensity of the most prominent vibronic line at 290 cm$^{-1}$ via HT effects in isolated DBT. For the rather coarse description of the vibronic spectra provided in the context of this thesis, we therefore ignore the contribution of HT effects.

Substitution of a $^{12}$C atom by a $^{13}$C atom breaks the symmetry of the molecule. Depending on the position at which the $^{13}$C is substituted, the molecule can lose all of its symmetries or retain some of them. This can lead to the redistribution of intensity and vibrational frequencies in the vibronic spectrum. For large molecules such as DBT, the substitution of a single $^{12}$C atom by a $^{13}$C atom can be regarded as a perturbation from the ideal geometry of the molecule. Therefore, the spectrum is not expected to change completely but rather to exhibit some wavenumber shifts and a moderate redistribution of intensity between the vibronic transitions. Based on the natural abundance of 1.1% of $^{13}$C, the chance that a DBT molecule contains a $^{13}$C atom is approximately 28%. Thus, the probability that none/one/two of the five DBT molecules that are studied in this chapter contain/s a single $^{13}$C atom amounts to 19%/38%/29%. Together with the many possible sites for the substitution of a $^{13}$C atom in DBT, these considerations imply that isotopic substitution can account for individual differences between the five vibronic
spectra recorded in our experiments but not for consistent behavior among all molecules.

Figure 6.20 shows DFT results for isotopically pure DBT and for a DBT molecule in which the single $^{12}$C atom at position 2 indicated in Figure 6.18(a) has been replaced by a $^{13}$C atom. The wavenumbers of the modes shown in the plot change on average by less than 0.2 cm$^{-1}$ after adding the $^{13}$C atom. As shown by the inserts in Figure 6.20, the FC intensities redistribute slightly around the modes 27 and 117 because of the substitution. The maximum FC factor change is expected for mode 27, from 1.7% to 1.3%. A detailed data analysis and the comparison with the calculated spectra for all possible substitution sites of $^{13}$C atoms in DBT may lead to the unique identification of isotopic substitution effects via lines that are activated for individual molecules only. In the context of this thesis we do not, however, aim at explaining the individual differences between the experimental vibronic spectra of the investigated molecules. Instead, we focus on the explanation of the most prominent features in the spectra that are similar across all molecules.

6.3.2 DBT in pDCB

The intensity distribution in vibronic spectra of molecules in solids reflects their deformation due to the forces exerted on them by the surrounding medium. In section 3.2.4, we discuss several examples from the literature in which the appearance of vibronic lines could be explained by crystal-induced deformations and symmetry breaking. To perform such studies computationally, the embedding of the molecule in the host crystal must be known. This information is typically deduced from the alignment of the transition dipole moment with respect to the crystal axes and the results of molecular dynamics simulations. In our study, we did not record directional information on the alignment of DBT with respect to the axes of the pDCB crystal. We nevertheless present two suggestions for how DBT could be embedded in the pDCB crystal and the vibronic spectra resulting from DFT structure calculations of DBT surrounded by a shell of pDCB molecules.

The structure optimization of DBT in pDCB was performed with the help of the ONIOM method [223], similar to the methods presented in several publications by the Kozankiewicz group [86, 90, 125]. In these calculations, the structure of DBT was calculated to high precision at the B3LYP/6-31G(d,p) level while the rigid pDCB molecules were simulated at the semi-empirical PM3 level. Since it was computationally too demanding to calculate the normal mode structure of the complete system in the electronic excited state,
the ONIOM simulations were used to determine the geometrical structure of the deformed DBT molecule in the crystal. DBT in its deformed structure was then taken out of the crystal, and the normal modes and FC factors were determined in the same way as for isolated molecules. In this approach, the calculation is performed on a structure that is not at the minimum of the internuclear potential $V$ introduced in equation (3.4). The conditions for the harmonic approximation are thus not fulfilled, and the application of the standard normal mode analysis methods to the results of this calculation can be considered a perturbative treatment. An indication that the structure can be regarded as a minor perturbation from the equilibrium configuration is that all normal mode frequencies resulting from the calculations are positive.

A molecular crystal consisting of pDCB can exist in different states, labeled as $\alpha$, $\beta$, and $\gamma$-phase [224, 225]. By slow variation of the temperature, a pDCB crystal can be adiabatically transferred from one phase to the other [226]. After a slow cooldown to liquid helium temperatures, pDCB is expected to be in the $\gamma$-phase [25, 227], but the $\alpha$- and $\beta$-phases can also be transferred to 4 K by corresponding cooling protocols [224, 226]. In our experiments, we did not determine the phase of the pDCB crystal around the investigated molecules. Therefore, we can only speculate about the environment of the studied DBT molecules. To demonstrate the kind of effects that a pDCB crystal can have on the vibronic spectra of DBT, we present two simulations with DBT in pDCB for pDCB in the $\alpha$-phase and the $\gamma$-phase. The way DBT was embedded into these structures was determined based on an educated guess. There are many other options for the embedding of a DBT molecule within these crystals, in particular because the pDCB molecules are considerably smaller than a DBT molecule.

Figure 6.21 shows optimized structures of DBT molecules in $\alpha$-pDCB and $\gamma$-pDCB in a wireframe representation. The information about the crystal structures was taken from the literature ($\alpha$-pDCB: [228], CCDC$^4$ ID: 129368; $\gamma$-pDCB: [229], CCDC ID: 1137445). The perspectives along the various crystal axes reveal the differences between the arrangements of the pDCB molecules in both phases. Hydrogen atoms are omitted from the figure. In the $\alpha$-phase, DBT replaced seven pDCB molecules, and 62 pDCB molecules were arranged around the DBT molecule to simulate the crystal. In the $\gamma$-phase, DBT replaced six pDCB molecules, and 44 pDCB molecules were used to represent the crystal.

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$^4$ CCDC: Cambridge Crystallographic Data Centre.
The deformation of the DBT molecules compared to the isolated case is hard to appreciate by eye from Figure 6.21. Therefore we display a close-up of the optimized structures of the DBT molecules in Figure 6.22, including the angles between the central unit and the outer rings of the molecule as defined in Figure 6.18(a). For the plot in Figure 6.22, the molecules have been aligned with respect to the coordinate system of the isolated DBT molecule by rotating them in such a way that the sum of squared distances between identical atoms is minimized. The presence of the pDCB shell leads to a compression of the DBT molecule to a flatter structure, resulting in smaller angles between the planes of the molecule compared to the isolated conformation. The total angle between a naphthalene unit and an outer ring of the tetracene moiety in the $x$-$y$-plane is $28.3^\circ$ in the $\alpha$-phase and $32.2^\circ$ in the $\gamma$-phase (isolated DBT: $39.5^\circ$). Compression of DBT in a crystal environment has also been reported for DBT:DMN [86]. Moreover, the pDCB crystal induces an internal twist in the DBT molecule. This can be recognized from the different perspectives shown in Figure 6.22. The internal twisting of DBT leads to small angles.
Figure 6.22: Angles between different parts of DBT molecules resulting from ONIOM simulations of plausible embeddings of DBT in \( \alpha \)- and \( \gamma \)-pDCB (left and right column, respectively). (a,b) Conformation of isolated DBT in \( C_{2h} \) symmetry, shown for reference (taken from Figure 6.18). (c,f) View along the terrylene moiety of DBT. The angles indicated in the plot show that the DBT molecule is compressed to a flatter structure in the crystal. (d,g) View along the tetracene moiety of DBT. The crystal leads to twists in the DBT molecule such that in the the normal vectors on the naphthalene unit and the outer rings of the tetracene unit are in the \( y-z \)-plane not parallel to the normal vector on the central unit. (e,h) Distance of the atoms from their equivalent counterparts after the application of the four symmetry operations of the \( C_{2h} \) point group. For rotations (\( C_2 \)) and reflections (\( \sigma_h \)), the molecules are not mapped onto themselves. The indices of the atoms are defined in Figure 6.18(a). Adapted from [45], with the permission of AIP Publishing.
between the normal vectors \( \vec{n}_i \) in the \( y-z \)-plane. For isolated DBT, the normal vectors are parallel in this plane.

Due to the twist of the different sub-units of the DBT molecules the symmetry of the molecule decreases from \( C_{2h} \) to \( C_i \), a point group that only contains the symmetry elements \( E \) (identity) and \( i \) (inversion). The reduction in symmetry can be quantified by applying all symmetry operations of the \( C_{2h} \) group to the deformed structures of DBT shown in Figure 6.22.\(^5\) While identity \( E \) and inversion \( i \) map the DBT molecule to itself, rotation \( C_2 \) and reflection \( \sigma_h \) leave some distance between the actual and the expected positions (see Figure 6.22(e,h)). As discussed in several publications by the Kozankiewicz group [90, 125] and in section 3.2.4, the reduction of the molecular symmetry changes the selection rules for vibronic transitions and can lead to the activation of new lines in the vibronic spectra.

Figure 6.23 shows the experimentally measured intensities for transitions \( S_1 \rightarrow S_0 \) as probed by STED spectroscopy (normalized via \( \langle \Omega^2_p/\Omega^2_{p\text{,max}} \rangle \), see section 6.2), the corresponding vibronic spectra calculated for the deformed DBT molecules from the \( \alpha \)- and \( \gamma \)-phase simulations, and the vibronic spectrum of isolated DBT. To improve readability, we only show fundamental modes in the calculated vibronic spectra. The prominent modes of DBT, which were analyzed in the experiment and are shown as black lines in Figure 6.23(a), also correspond to fundamental excitations. The regions of overtones and combination modes of these prominent modes are shown by orange lines in the experimental spectrum. The peaks in these regions are not expected to be reproduced by the calculated spectra.

The mode indices of relevant simulated modes are shown in Figure 6.23(b-d). Here, the large numbers indicate those modes that were assigned to the prominent experimental modes of Figure 6.23(a). The smaller italic numbers are additional modes that are visible in the data but not analyzed in more detail in the context of this thesis. The red numbers indicate simulated modes that show major deviations from the experimental results. Due to changes in the mode order related to small frequency shifts in the different conformations, the mode indices of equivalent modes differ slightly between the panels (b-d) of Figure 6.23. A list of the mode assignments and experimental measurements is provided in Table 6.2.

\(^5\) To quantify the effect of a symmetry operation on a molecule, we determine the distances of all atoms after the application of the symmetry operation with respect to the expected positions for a molecule of the \( C_{2h} \) group, i.e. the positions of the atoms assuming that the molecule is symmetric under each symmetry operation.
6.3 Density functional theory calculations

The experimental spectrum, the wavenumbers of all simulated spectra are scaled by the linear correction functions: 0.952 \cdot \bar{\nu} + 15.9 \text{ cm}^{-1} (\alpha\text{-pDCB}), 0.951 \cdot \bar{\nu} + 14.9 \text{ cm}^{-1} (\gamma\text{-pDCB}) and 0.955 \cdot \bar{\nu} + 15.9 \text{ cm}^{-1} (\text{-pDCB}) from the experimental spectra. The wavenumbers of all simulated spectra are scaled by the linear correction functions: 0.952 \cdot \bar{\nu} + 15.9 \text{ cm}^{-1} (\alpha\text{-pDCB}), 0.951 \cdot \bar{\nu} + 14.9 \text{ cm}^{-1} (\gamma\text{-pDCB}) and 0.955 \cdot \bar{\nu} + 15.9 \text{ cm}^{-1} (\text{-pDCB}) from the experimental spectra.

The measured wavenumbers indicate additional modes not observed experimentally. The smaller italic numbers indicate additional modes measured in the text. Red numbers indicate features that deviate from observed features. The calculated spectra are shown in Figure 6.23.(b/c/d) for the embedding of DBT in pDCB.

The largest numbers are the mode numbers of the prominent modes, as shown in Figure 6.21(a)/6.21(b)/6.18. The large numbers are the mode numbers of the prominent modes assigned to the experimentally observed features. The smaller italic numbers indicate additional modes mentioned in the text. Red numbers indicate features that deviate from the experimental spectrum. Only the calculated spectra, only the calculated spectra, only the calculated spectra, only the calculated spectra, only the calculated spectra, only the calculated spectra, only the calculated spectra.

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Adapted from [45], with the permission of AIP Publishing.
A comparison of the spectra shown in Figure 6.23 reveals the effect of deformations on the selection rules for vibronic transitions. For the deformed DBT molecules considerably more vibronic transitions are active than for the isolated molecule. All of these modes are $A_g$ modes in the $C_i$ group. One of the activated peaks belongs to mode 16, which is an inactive $B_g$ mode in isolated DBT, and is present both in $\alpha$- and $\gamma$-pDCB. We assign this mode to the vibronic feature at 288 cm$^{-1}$ next to the prominent mode at 290 cm$^{-1}$ (see Figures 6.12(a) and 6.14(a)). The modes 10, 14, 43, and the states around mode 86 are other examples of transitions that are present in the experimental data and appear only in the simulated spectra of deformed DBT. Deformation of DBT also leads to a redistribution of intensity between vibronic transitions. The most relevant changes occur for modes 9 and 24 of isolated DBT. The (relative) intensity in mode 24 of isolated DBT appears higher than in the experimental observations and is redistributed over modes 25 and 26 in the deformed molecules. In this way, the relative intensities between the modes at 290 cm$^{-1}$ and 403 cm$^{-1}$ are represented more accurately by the theoretical spectra. The calculated intensity of the prominent mode 9 is predicted to decrease in our $\alpha$-pDCB calculations, while the $\gamma$-pDCB calculations predict an increase in its transition strength compared to isolated DBT.

Mainly because of the behavior of mode 9 in the theoretical spectra, the results for $\alpha$-pDCB are in closer agreement with our experimental data. By studying other possible ways DBT can be embedded into pDCB crystals, it may also be possible to identify a configuration in $\gamma$-pDCB that yields vibronic spectra that agree more closely with the experimental data. The use of the ONIOM method, including the assumption of a rigid pDCB crystal structure, and the calculation of the vibronic spectra using deformed DBT molecules that were taken out of the crystal may also distort the resulting vibronic spectra. Further improvements of DFT methods and available computational power may enable full quantum mechanical simulations of DBT molecules and surrounding crystals in future. The results presented here show, however, that DFT methods provide very valuable insight into the vibronic spectra of systems as complex as DBT in pDCB. This may prove useful in future predictions of the vibronic properties of new molecule/matrix combinations.

In the spectral regions with narrow vibronic transitions shown in Figure 6.17, our theoretical analysis only predicts an active mode (mode 20) around 330 cm$^{-1}$. No active modes are expected around 300 cm$^{-1}$ and 725 cm$^{-1}$, even in the spectra that take pDCB molecules into account. This may be related to an inaccurate representation of the molecular deformation by DFT calculations or to a different mechanism of line activation for these states. The origin of the
Figure 6.24: Comparison of experimental and simulated vibronic spectra of DBT in pDCB for the electronic transition $S_0 \to S_1$. In the calculated spectra, only fundamental modes are shown for clarity. The description of this figure is analogous to Figure 6.23, with the difference that the data were obtained from fluorescence excitation spectra instead of STED spectra. The blue line in (a) shows the fluorescence excitation spectrum of mol. 1. The orange lines in (a) indicate overtones and combination modes. The scaling functions used to correct the wavenumbers from the DFT simulations are: $0.957 \cdot \tilde{\nu} + 14.9$ cm$^{-1}$ ($\alpha$-pDCB), $0.951 \cdot \tilde{\nu} + 16.1$ cm$^{-1}$ ($\gamma$-pDCB), and $0.96 \cdot \tilde{\nu} + 15.1$ cm$^{-1}$ (isolated DBT). Adapted from [45], with the permission of AIP Publishing.

The analysis of the spectrum becomes increasingly complex towards higher vibrational frequencies because the features in the spectrum overlap and it can be difficult to determine the number of levels required to fit to the data. Additionally, the line profiles of the vibronic modes at higher frequencies can be complex vibronic line shape at 330 cm$^{-1}$ (see Figure 6.17(c)) is an interesting topic for further analysis as well.
be affected by IVR processes. Based on a comparison of our simulations with the experimental data, we speculate that the levels at 1161 cm$^{-1}$ and 1250 cm$^{-1}$ undergo IVR (or Fermi resonance). The peaks at 1161 cm$^{-1}$ may originate from mode 101 that splits into a doublet via IVR (see Figure 6.23(a) for these data at a higher resolution). The complex line profile at 1250 cm$^{-1}$ may originate from mode 111 undergoing IVR to a multitude of lower-lying states (see section 6.5 for more details).

Figure 6.24 displays experimental and theoretical spectra of transitions from $S_0$ to $S_1$, which are probed via fluorescence excitation spectroscopy. The effects of the deformation on the vibronic spectra are similar to the effects described above for transitions $S_1 \rightarrow S_0$. Again, due to the relative FC factor of mode 9, the spectra obtained from the simulations with $\alpha$-pDCB appear to match the experimental data more closely than the results for $\gamma$-pDCB. In contrast to the calculated spectrum shown in Figure 6.23(b), mode 16 is not active in the calculation displayed in Figure 6.24(b). The modes assigned to the prominent experimental features are listed in Table 6.2.

### 6.4 Comparison between para-dichlorobenzene and anthracene

The experimental observations and DFT simulations in the previous sections show the effect of the pDCB crystal on the vibronic spectrum of a DBT molecule. In the current section, we present some vibronic spectra of a single DBT molecule in an anthracene crystal. These spectra differ significantly from the corresponding spectra in pDCB crystals, demonstrating the role of the host system in the vibronic properties of the guest molecules.

Vibronic spectra of DBT in Ac have been measured with grating spectrometers in various studies [9, 26, 124, 174]. There is also a report about fluorescence excitation scans of single DBT molecules in Ac by Makarewicz et al. [85]. The resolution in this experiment was limited, however, because the laser was scanned in $\sim 45$ GHz steps.

For our experiment, we created DBT-doped Ac crystals using the saturated vapor phase growing method described in section 5.2.2. The resulting crystals typically display high doping levels. A typical confocal fluorescence excitation scan of one Ac crystal is shown in Figure 2.5, exhibiting a high number of 00-ZPL transitions close to 785 nm. Despite the high doping level in most crystals, we could also identify spatial regions with approximately one molecule per excitation volume. Figure 6.25(a) shows a scan of the inhomogeneous broadening of DBT in Ac that is clearly dominated by a single 00-ZPL. We
Figure 6.25: Spectral properties of a single DBT molecule (mol. 6) in an anthracene crystal at cryogenic temperatures. (a) Fluorescence excitation scan around the inhomogeneous broadening of DBT in Ac. The 00-ZPL of mol. 6 is considerably more pronounced than all other 00-ZPLs in this spectrum, indicating that only mol. 6 is well positioned within the laser focus. (b) Emission spectrum of mol. 6, recorded while exciting the molecule via a vibronic transition (blue) and via the 00-ZPL (black; around 18x magnified version).

refer to this molecule as mol. 6 (see also table 6.1). The fluorescence emission spectrum of this molecule is shown in Figure 6.25(b). At the position of mol. 6, we recorded vibronic fluorescence excitation spectra and STED spectra to characterize the vibronic properties of the molecule. We remark that these experiments were performed before several parameters of the experimental setup and recording procedures had been optimized: the parallel windows were still in place (see section 5.3.3), no laser line filters were used (see section 5.1), and no thorough scans of the molecular saturation behavior and the background were performed in conjunction with the vibronic scans. However, since we recorded the fluorescence excitation and STED spectra discussed below at several powers in the low excitation regime, we are able to estimate the lifetime-limited linewidths of the vibronic transitions by Lorentzian fits and linear extrapolation of the linewidth.

Figure 6.26(a) shows a fluorescence excitation scan of mol. 6 in a spectral range of around 10 THz at $P_p = 200 \mu W$, covering several vibronic transitions in the low wavenumber region. We attribute the increase in the fluorescence baseline with laser frequency to uncorrected red-shifted light created by the intense laser in the optical fiber (see section 5.1). A comparison with the fluorescence spectrum of mol. 1 (DBT in pDCB) reveals clear differences between the two host systems. Instead of the prominent line at 177 cm$^{-1}$ in pDCB, we find four peaks in Ac. In the bulk spectrum of DBT in Ac reported by Makarewicz et
High-resolution vibronic spectroscopy of single molecules

Figure 6.26: High-resolution vibronic spectra of single DBT molecules in anthracene and para-dichlorobenzene crystals. (a) Fluorescence excitation spectra. The spectrum in the Ac crystal exhibits a gradual increase in the baseline due to (uncorrected) background from the laser. The numbers shown in the plot are the vibrational wavenumbers and the homogeneous linewidths of the vibronic transitions in the low excitation limit obtained from saturation scans. The magnified part of the spectrum shows a satellite peak that overlaps with the most prominent vibronic peak. (b) STED spectra of the same molecules as in (a). The main reason for the improved SNR in the pDCB measurements is the use of a SIL in the corresponding experiments. For the linewidths reported in the STED spectrum, we cannot exclude thermal broadening effects incurred by the laser.

al. [85] one can also see a vibronic feature in this spectral range, but the single peaks are not resolved there. Instead of the broad asymmetric line at 234 cm\(^{-1}\) in pDCB, we find a combination of a narrower line and a broad weak vibronic feature in Ac. Furthermore, a prominent feature at 253 cm\(^{-1}\) is present in Ac, with no counterpart in pDCB. The most intense vibronic mode has a similar frequency in pDCB and Ac, but lies systematically higher by approximately 3 cm\(^{-1}\) in Ac at 294.4 cm\(^{-1}\). Its linewidth is around twice as high in Ac compared to pDCB.
Comparison between para-dichlorobenzene and anthracene

to pDCB and closely agrees with the measurement by Schofield et al. [46]. This observation indicates that the Ac crystal offers this mode more possibilities for vibrational relaxation than pDCB. The fluorescence excitation spectrum of DBT in Ac shown in Figure 6.26(a) exhibits fewer weak vibronic features than the vibronic spectrum in pDCB. This may be caused by the fast laser scan speed of 10 GHz/s used in the case of Ac compared to 2 GHz/s for pDCB, causing a suppression of weak vibronic features.

Figure 6.26(b) also shows a STED spectrum of DBT in Ac. The spectrum was recorded with $P_p = 320 \mu W$ and $P_d = 150 \mu W$. A comparison with the spectrum of mol. 1, which was recorded with $P_p = 18 \mu W$ and $P_d = 102 \mu W$, shows the effect of a SIL on the results of STED spectroscopy: by increasing both excitation and collection efficiency, a higher SNR can be reached while applying less laser power if a SIL is used (effective integration times in these measurements are 701 ms/800 ms for pDCB/Ac). We are not certain whether thermal broadening can be excluded for total laser powers as high as 0.3-0.5mW during the STED measurements in Ac. Therefore, the numbers stated in 6.26(b) might not correspond to the lifetime limit of each line.

The STED spectrum and the fluorescence excitation spectrum of DBT in Ac are similar. The level close to 400 cm$^{-1}$ is 11 cm$^{-1}$ higher in the electronic ground state than in the electronically excited state. In pDCB, the prominent line close to 400 cm$^{-1}$ displays a similarly strong shift, in accordance with the DFT results (see section 6.3.2). We remark that we only studied the vibronic spectra of mol. 6 in our experiment and that we cannot exclude that this molecule exhibits exotic vibronic properties due to a unique nano-environment. The positions of the peaks in the vibronic spectra of DBT in Ac reported by Makarewicz et al. [85] are, however, similar to our measurements. This suggests that the molecule studied by us is representative for the embedding of DBT in Ac. Besides the appearance of some additional lines in Ac, another difference between the fluorescence excitation and STED spectra is the linewidth of the most prominent vibronic feature. While one can recognize a satellite peak that merges with the most prominent feature for transitions $S_0 \rightarrow S_1$, an equivalent effect for $S_1 \rightarrow S_0$ is not clearly detectable. Potentially, however, the higher linewidth in the STED spectra is caused by two overlapping vibronic features.

The difference between the vibronic spectra in pDCB and Ac suggests that DBT assumes different conformations in the two host systems. We did not perform DFT calculations of DBT in Ac, but we expect that it is possible to predict the corresponding vibronic spectra using calculations similar to those presented in section 6.3.2. The dependence of the vibronic line positions and
linewidths on the properties of the host system may play an important role in
the search for vibronic states that are useful for quantum technologies.

6.5 Discussion

In sections 6.1 and 6.2, we present high-resolution vibronic spectra of single
DBT molecules in pDCB crystals. Spectra of transitions $S_0 \rightarrow S_1$ were acquired
using fluorescence excitation scans. To measure transitions $S_1 \rightarrow S_0$, we
applied STED spectroscopy. STED spectroscopy yields considerably higher
resolution than grating spectrometers and enables precise estimations of the
relaxation rates of vibronic states in $S_0$. To the best of our knowledge, our study
marks the first systematic investigation of the related vibronic linewidths at
a resolution exceeding 10 GHz. The narrowest transitions identified in our
measurements have linewidths of 2 GHz, well below the average linewidth
of molecules in organic crystals. The detailed observations obtained via the
STED method present an important extension of the knowledge of vibrational
properties in the electronic ground state of these systems. We remark that the
application of STED to spectroscopy purposes differs from the well-known
method of STED microscopy that is used to achieve super-resolution in the
spatial domain [27].

Even though vibronic states in $S_1$ can be accessed by fluorescence excitation
spectroscopy, in the same way as the thoroughly studied 00-ZPL transitions,
the literature provides very little information about excited state vibronic
linewidths of single molecules [68, 167]. Our study closes this gap with the
measurements and analyses in section 6.1. Moreover, the single molecule
fluorescence excitation spectra presented here cover a broader range than
previous reports in the literature [85, 86, 90, 131, 168, 169].

In collaboration with Irena Deperasińska and Boleslaw Kozankiewicz, we
augmented the study by DFT calculations of DBT in pDCB of section 6.3. The
results indicate that accurate simulations of the vibronic spectra of polyatomic
molecules such as DBT in molecular crystals are possible. By comparing the
vibronic spectra of DBT in pDCB with the spectra in Ac in section 6.4, we
demonstrated the effect of the host crystal on the vibrational properties and
selection rules of vibronic transitions.

6.5.1 Spectroscopic details

In this section, we discuss several noteworthy observations in the vibronic
spectra of DBT in pDCB. A detailed theoretical treatment of some of the
6.5 Discussion

Figure 6.27: Spectroscopic details of STED measurements. (a) Asymmetric line profile around 234 cm⁻¹ (normalized). Dotted line: Lorentzian fit to the low frequency side of the profile (shown only up to the peak). Black dashed line: Lorentzian fit to the high frequency side of the peak (shown over the complete spectral range). (b) Linewidth ratio of the fits to the high frequency against low frequency side of the spectrum as a function of peak wavenumber. (c) Complex line profiles around 1250 cm⁻¹.

non-Lorentzian vibronic line shapes is beyond the scope of this thesis and could be a subject for future studies.

Mode at 234 cm⁻¹: The state at 234 cm⁻¹ (mode 13) has an asymmetric line profile both in $S_0$ and $S_1$. Figure 6.27(a) shows the (normalized) STED data around that spectral range for each molecule. Since the linewidth of the vibronic state at 234 cm⁻¹ is broad, the asymmetry of its line profile is also visible in the emission spectra presented in the first study of single DBT molecules in pDCB by Verhart et al. [25]. In spectra of DBT in Ac, we do not observe an asymmetry for the corresponding mode.

A similar asymmetric line profile of a Raman line at 440 cm⁻¹ in ZnO has been explained by an abrupt change in the two-phonon density of states at this vibrational frequency. We conjecture that the same mechanism is responsible for the line shape of the level at 234 cm⁻¹. According to Jongenelis et al., the highest phonon frequency in $\alpha$-pDCB is at 117 cm⁻¹ (for $\vec{k} = \vec{0}$ and $T = 1.4$ K) [224]. Other results for the one-phonon density of states in $\alpha$-pDCB at 295 K roughly agree with this finding [161, 230]. Assuming negligible dispersion of the phonon mode at 117 cm⁻¹, the cutoff of the two-phonon density of states in $\alpha$-pDCB is thus expected at $2\Omega_{\text{max}} = 2 \times 117 \text{ cm}^{-1} = 234 \text{ cm}^{-1}$, exactly at the position of the state with the asymmetric line profile. The reason for

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6 The asymmetry of the vibronic line is not discussed by Verhart et al. in [25], probably because the effect is rather subtle in their spectra.
the asymmetry may thus be a change in the vibrational relaxation type from regime I to regime II within the spectral profile of the state at 234 cm$^{-1}$. This mechanism could consequently render the level broader at lower frequencies.

To quantify the asymmetry of the line profile, we divided it into two parts at the position of its peak. Then we fitted the width of Lorentzian profiles to the low and high frequency parts of the profile, shown as dotted and dashed lines in Figure 6.27(a), respectively. The fits to the high frequency part are plotted over the complete spectral range to visualize the asymmetry of the line. There appears to be a trend of increasing asymmetry as the peak of the profile approaches 234 cm$^{-1}$. As shown in Figure 6.27(b), the ratio of linewidths obtained for the high and low frequency sides of the spectrum decreases with increasing peak wavenumber. This trend is an additional indication that supports the hypothesis of a frequency-dependent relaxation rate. Since $\gamma$-pDCB has phonon modes at frequencies up to 133 cm$^{-1}$ [224], the asymmetry of the line profile at 234 cm$^{-1}$ may serve as an indication that the pDCB crystal in our experiment is actually in the $\alpha$-phase. In future theoretical and experimental efforts one could aim for a more quantitative understanding of the line asymmetry and potentially use it to determine the phase of the pDCB crystal.

Mode at 670 cm$^{-1}$: As shown in Figure 6.16(d), we found that the linewidths of vibronic states in $S_1$ are on average broader than in $S_0$. Similar observations have been reported in the literature, e.g. by Carlson and Wright who found a 3.5-fold difference of the relaxation rates of a vibrational mode in Pc in benzoic acid [105]. In their case the linewidth change is correlated with a change in the vibrational frequency of that state. This shift moves the vibrational frequency to a spectral range with a higher number of relaxation channels. Of the modes analyzed in this thesis, the most extreme linewidth difference was observed for mode 49 at 670 cm$^{-1}$. According to our measurements, the linewidth of this state is $\langle \Gamma_{we} \rangle / (2\pi) = 36.2$ GHz in $S_1$ and $\langle \Gamma_{vg} \rangle / (2\pi) = 4.0$ GHz in $S_0$. At the same time, the vibrational wavenumbers differ by less than 1 cm$^{-1}$ between $S_0$ and $S_1$ for all investigated molecules. Spectral variations of the two-phonon density of states can therefore not explain the linewidth difference. In the context of the theory of anharmonic vibrational relaxation discussed in section 3.3, the vibrational relaxation rate also depends on the anharmonic coupling strength of an excited vibrational mode to modes available for decay. Possibly, the changed conformation of the molecular skeleton of DBT and the (slightly) changed mode pattern of mode 49 in $S_1$ compared to $S_0$ lead to a markedly enhanced coupling of the mode to the pDCB matrix and thus accelerated vibrational decay. In an attempt to ascertain whether specific parts or motion
patterns of the DBT molecule are responsible for (anharmonic) coupling to the matrix, we looked for correlations between the measured linewidths and properties of the assigned theoretical modes. These properties included the in-plane vs. out-of-plane motion of the atoms with respect to the terrylene and tetracene planes of DBT, the oscillation amplitudes of the hydrogen and carbon atoms as well as of each individual atom. In these investigations, we could not, however, identify a simple property of a normal mode that has predictive power with respect to its vibrational relaxation rate.

An alternative explanation for the increased linewidth of mode 49 in \( S_1 \) is other fast decay channels that are not related to the excitation of matrix phonons. However, since fluorescence decay is expected to take place on the nanosecond timescale and transitions to the triplet on the microsecond timescale, it remains unclear, what other types of decay channels could explain the experimentally observed linewidth difference. We remark that the wavenumber difference between the red site and the normal site of DBT in pDCB was reported to be 670 cm\(^{-1}\) [25]. Potentially, this can help to explain the broad linewidth of mode 49 in fluorescence excitation scans. Whatever mechanism is responsible for this observation, its explanation presents an exciting topic for future theoretical investigations.

**Modes at 1162 cm\(^{-1}\) and 1250 cm\(^{-1}\):** IVR (or Fermi resonance) requires a combination of two (or more) modes to be resonant with a fundamental mode of the same symmetry [153]. Additionally, these modes must be coupled via an anharmonic term in the internuclear potential. We did not perform a systematic analysis to identify Fermi resonances/IVR in the experimentally recorded spectra. A comparison of the vibronic features at 1162 cm\(^{-1}\) (see Figure 6.23(a)) and 1250 cm\(^{-1}\) (see Figure 6.27(c)) with the simulated spectra in Figure 6.23(b,c,d) suggests, however, that the multi-peak structure of the levels results from Fermi resonances of modes 101 and 111 with other combination modes of DBT, respectively. Fermi resonances lead to line doublets and complex line profiles such as those observed around 1162 cm\(^{-1}\) and 1250 cm\(^{-1}\) and are often discussed in the context of infrared spectroscopy [231–234]. Since DBT is a large molecule with many vibrational modes, the density of combination and overtone modes is high and the condition for Fermi resonance can be fulfilled. If the interpretation of Fermi resonance is correct, our data suggest that mode 111 shown in Figure 6.23 exhibits particularly strong anharmonic coupling to other close-by modes, leading to the very complex line profile. The variation between the measured STED profiles of mode 111 among the different molecules may be related to slight variations in the combination mode frequencies and the coupling strengths. In-depth analyses
of the underlying processes and decay pathways are promising subjects for future theoretical studies.

### 6.5.2 Outlook and applications

Single molecule spectroscopy enables access to information on a nanoscopic length scale, encoded in the electronic transitions of a dopant molecule embedded in a solid. This notion has first and foremost been applied to the spectral position of the 00-ZPL transition, which is highly sensitive to electric fields and other perturbations in its environment [4, 6]. Vibronic transitions have been studied in this context as well, either to identify systematic deformation of molecules in a solid [90, 125] or to study intermolecular differences that suggest different nano-environments [109, 127].

Single molecule STED spectroscopy, as developed in this thesis, presents an important extension of the toolbox for single molecule interrogation at a high resolution. Besides revealing linewidth information that may be blurred in measurements with grating spectrometers, the enhanced resolution of STED spectroscopy also makes it possible to sample the intermolecular distribution of vibrational wavenumbers with high precision. In combination with accurate simulations of the molecular spectra, STED measurements of the vibronic spectrum of a molecule enable an accurate reconstruction of its spatial conformation. In a similar way, STED measurements of vibronic lines could exploit the molecule as a sensor for external perturbations, e.g. for strain applied to the host crystal. In contrast to the one-dimensional shift of the 00-ZPL, the vibronic spectrum provides multi-dimensional information via the changes in the multiple vibronic lines. This could enable the reconstruction of parameters such as the strain direction. It may be promising to explore the use of STED spectroscopy of vibronic lines for sensing applications in future experiments.

The DFT calculations of the vibronic spectra of DBT in pDCB presented in section 6.3.2 resemble the experimentally observed data. Experiences with the same approach have shown, however, that the intensities predicted by the DFT calculations can also deviate from the experimental findings [125]. To some extent, these deviations may be caused by the lack of ONIOM simulations of the electronically excited state. Such simulations could not be performed in the context of this thesis because of their high computational demands. For future studies of the vibronic properties of single organic molecules, accurate theoretical vibronic spectra would be useful as a benchmark. Based on accurate calculations, the intensity deviations of each molecule from the theoretical
6.5 Discussion

expectation could be interpreted in terms of its individual deformation or isotopic composition. Moreover, it would not be necessary to estimate the number of vibronic features included in a fit of the vibronic line shapes at an empirical level. Full quantum mechanical DFT calculations of the guest-host systems under study could provide higher theoretical accuracy in future. We note that if the harmonic approximation is used, an accurate prediction of the vibronic spectra additionally requires mode-specific correction for the biased wavenumbers (see also section 6.3.1).

Our main motivation for applying STED spectroscopy to single molecules has been to explore the linewidths of vibronic states in $S_0$. Using STED, we found for DBT:pDCB that vibronic transitions to $S_0$ are on average considerably narrower than transitions to $S_1$ (see section 6.2.3) and that some states can have linewidths as low as 2 GHz (see section 6.2.5). While theories and examples of the explanation of vibrational relaxation rates of molecules in (mixed) molecular crystals are available, we have not attempted to explain the measured linewidths in the context of anharmonic relaxation theory [13, 24]. One ingredient missing for performing such an analysis is the wavenumbers of the non-totally symmetric modes of DBT in pDCB, which are not accessible via STED spectroscopy. Additionally, the existing level of accuracy of the phonon density states of pDCB in the literature [159, 161] might not be sufficient for a complete lifetime analysis of the vibrational states. A detailed understanding of vibrational relaxation for DBT in pDCB may thus require additional experimental efforts to perform neutron scattering measurements of the phononic properties of pDCB and infrared studies of the DBT lines that do not appear in the vibronic spectra. Based on these measurements, full theoretical models of the vibrational relaxation cascade could be established [24].

The differences between the vibronic properties of DBT in pDCB and DBT in Ac discussed in section 6.4 demonstrate the influence of the host system on both the wavenumbers and linewidths of vibronic states of the guest molecule. In an effort to identify long-lived vibrational states that are useful for applications in quantum information processing applications, it is an interesting question whether guest-host systems with naturally long-lived vibrational states exist. For this purpose, the linewidths of vibronic states in the typical guest-host systems of single molecule spectroscopy could be cataloged using STED spectroscopy. Even if no vibrational states with lifetimes longer than 100 ps are found in this endeavor, it could help to identify properties of the host systems that favor slow vibrational relaxation.
In the search for long-lived vibrational states, one could also explore novel guest-host combinations. Long vibrational lifetimes may be encountered in host systems with a low cut-off frequency $\Omega_{\text{max}}$, because this limits the available step size in regime II of cubic anharmonic vibrational relaxation (see section 3.3). Systems with a natural phononic band gap would also be of interest because they could exclude certain step sizes for vibrational relaxation. The organic crystals para-dibromobenzene (pDBB, C$_6$H$_4$Br$_2$) and para-diiodo-benzene (pDIB, C$_6$H$_4$I$_2$) could, for example, be worth exploring in this context. Studies of their lattice modes suggest that these systems have a spectral band of low phonon density [161, 235, 236]. We do not know the crystal structures of pDBB and pDIB at liquid helium temperatures. If the crystal structure and the embedding of DBT in these crystals are similar to pDCB, it would be possible to study the effect of the crystal on the vibronic linewidths while the line intensities remain similar. Due to the heavy bromide and iodide atoms in the pDBB and pDIB matrices, one additionally expects an acceleration of the intersystem crossing rates in these matrices [25, 182].

In order to change the mechanical coupling between guest molecules and their solid-state host, one may also adapt geometrical properties of the composite system. Certain phononic properties of nanocrystals [74, 75] may, for example, differ from the properties of the bulk material and affect the vibrational relaxation behavior of the dopant molecules. We note that it was shown recently in simulations that a single phonon mode of an Ac nanocrystal can become long-lived if the phononic properties of the sample substrate are engineered appropriately [78]. Alternatively, one could place molecules on surfaces of molecular crystals, coverslips [237, 238], NaCl or KCl layers [107, 239–241], 2D materials [242], or effectively one-dimensional systems [243]. In such systems, the vibrational relaxation rates may be reduced by adapting the mechanical degrees of freedom (phonon density of states) and the interaction strength of the molecules with their surroundings. A first challenge in all of these approaches will be to establish the conditions for high spectral stability of the molecular transitions. If photostable emission from single molecules in such environments can be achieved, a detailed exploration of their vibronic properties using fluorescence excitation and STED spectroscopy could reveal interesting findings, potentially including long-lived vibrational states.
7 Vibronic line splitting

The STED method presented in section 4.3 and chapter 6 relies on the incoherent redistribution of population in a molecule using two laser beams that interact with separate sets of vibronic states. In a similar experimental scheme it is possible to induce a dip in the absorption profile of a vibronic level at the single molecule level via the interference of two coherent excitation pathways. Here, we report the experimental realization of this effect via scanning a first (= probe) laser frequency over the resonance of a vibronic state $|\nu\rangle$ in $S_1$ while a second (= control) laser is resonant with a transition between $|\nu\rangle$ and a vibronic state $|\nu\rangle$ in $S_0$.

Models of the line splitting effect in (effective) three-level systems are introduced in section 4.4. The molecular system used in our experiment is presented in section 7.1. In that context we also discuss criteria to be met by the molecular states for an experimental realization of coherent effects with vibronic levels. In section 7.3, we show the experimental data and the parameters of the models from section 4.4 describing these data. Some consequences of our observations regarding coherent transfer of population are discussed in section 7.4.

7.1 Molecular system

The experiments presented in this chapter were performed with a single DBT molecule in a pDCB crystal (mol. 1 from Table 6.1). The vibronic level structure of this molecule has been determined at a high resolution using fluorescence excitation measurements and STED spectroscopy (see chapter 6). Figure 7.1 displays those molecular quantum states that are used for the vibronic line splitting experiments of this chapter, as well as their transition frequencies and linewidths. The control laser is tuned on resonance with the transition between the fundamental excitation of mode 24 in both $S_0$ and $S_1$, i.e. between $|\nu\rangle = |S_0, 1_{24}\rangle$ and $|\nu\rangle = |S_1, 1_{24}\rangle$ (see section 3.1.2 for the notation). Here, we use the mode numbering for isolated DBT (see Table 6.2) since the assignments
Figure 7.1: Level scheme indicating those states of the DBT molecule that are used for the vibronic level splitting experiment (mol. 1). The transition frequencies and linewidths of the states were determined using fluorescence excitation and STED measurements. According to these measurements, the difference between the transition frequencies of the 00-ZPL and the transition $|v⟩ \leftrightarrow |w⟩$ is $\nu_{gw} = 233 \text{ GHz}$. The excited state population was measured via fluorescence emission from $|e⟩$ to a narrow spectral window around the vibronic mode $|S_{0,17}\rangle$ at 290 cm$^{-1}$.

of the simulated peaks for DBT in pDCB are not perfectly clear. We selected mode 24 because its vibrational frequency differs considerably between the two electronic states: $\tilde{\nu}_v = 403.4 \text{ cm}^{-1}$ in $S_0$ and $\tilde{\nu}_w = 395.6 \text{ cm}^{-1}$ in $S_1$. This large spectral separation makes it possible to tune a strong control laser on resonance with the transition $|v⟩ \leftrightarrow |w⟩$ while avoiding to pump the molecule via the oo-ZPL transition.$^1$ Since both $|v⟩$ and $|w⟩$ are vibronic states, they decay quickly via coupling to matrix phonons. Therefore, the three levels used in Figure 7.1 do not constitute a typical lambda-system with two long-lived ground states. Nevertheless, this scheme of molecular states enables the observation of three-level effects in a regime between EIT and Autler-Townes splitting.

Figure 7.2(a) shows calculations of the splitting behavior in the four-level model of section 4.4.2 using the parameters from Figure 7.1 and $\beta_g = 0$ ($\beta_g\Omega_c$ denotes the Rabi frequency on the oo-ZPL transition). According to this model, the Rabi frequency of the control laser must be in the order of the vibrational relaxation rates ($\Omega_p^2 \sim \Gamma_g \Gamma_{we}$) to induce a splitting dip (probe laser parameters in Figure 7.2(a): $\Omega_p^2 = \Gamma_e\Gamma_{we}$ and thus $S_p \approx 1$; see Figure 7.2(b) for results with other values of $\Omega_p^2$). In order to reach such values of $\Omega_c$ in our experiments with control laser powers while not exceeding the mW-level, it

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$^1$ The frequency difference between the states $|v⟩$ and $|w⟩$ is $\nu_{vw} = \nu_{ev} - \nu_{gw} + \nu_{ge}$. For $\nu_{ew} = \nu_{gw}$, the transition frequency of the oo-ZPL coincides with $\nu_{vw}$.
Figure 7.2: Control laser Rabi frequency $\Omega_c$ required to induce a dip in a vibronic line profile. (a) Excited state population in the four-level model of section 4.4.2 with the parameters shown in Figure 7.1, $\Omega_p^2 = \Gamma_{eg} \Gamma_{we}$ and $\beta_g = 0$. (b) Relative depth of the splitting dip ($\Delta p = 0$) versus control laser Rabi frequency for various values of the probe laser Rabi frequency. With increasing values of $\Omega_p$, higher values of $\Omega_c$ are required to induce a dip in the resonance profile. (c) Relative (squared) control laser Rabi frequency for the case that the modes of $|v\rangle$ and $|w\rangle$ are equivalent ($s(v) = w$) compared to the case that they are different ($s(v) \neq w$). The $\alpha_i$-parameters quantify the displacement of the potential energy surfaces along the mode $i$ in the non-mixing displaced harmonic oscillator approximation. For DBT: $\alpha_i \approx 0.4$ (indicated by the black dashed line). We note that the non-mixing displaced harmonic oscillator model only allows for a coarse approximation.

was crucial to set the control laser on resonance with a transition between equivalent normal modes in $S_0$ and $S_1$. For molecules such as DBT, the FC factors of these transitions are typically more than two orders of magnitude higher than the FC factors of vibronic transitions between non-equivalent normal modes [105, 141, 244, 245]. As a consequence, considerably less laser power is required if the control laser is resonant between equivalent modes.

We present a related calculation in the displaced harmonic oscillator approximation of non-mixing normal modes in appendix D.11. The outcome of this calculation is shown in Figure 7.2(c) as the ratio of the Rabi frequencies $\Omega_c$ for the case that $|v\rangle$ and $|w\rangle$ are equivalent modes ($s(v) = w$) versus the case that they are different modes ($s(v) \neq w$). This figure shows that transitions between equivalent modes are considerably easier to drive for molecules such as DBT with $\alpha_i \approx 0.4$. Therefore, we selected the transition between the (equivalent) modes 24 in $S_0$ and $S_1$ for our experiments (see Figure 7.1).

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2 We call a mode of $S_1$ equivalent to a mode in $S_0$ if their vibrational displacement patterns are almost identical and, correspondingly, the related entry of the Duschinsky matrix has a high (absolute) value (see section 3.2.3 for more details).

3 See section 3.2.3 for the definition of the function $s$. 
remark, however, that the non-mixing displaced harmonic oscillator model only allows for a coarse approximation to illustrate the overall behavior. More accurate numerical values can be obtained from DFT calculations.

### 7.2 Seven-level model for fitting

The model introduced in section 4.4.2 includes all relevant processes to describe the splitting effect of a vibronic line in the presence of a metastable electronic state \( |e\rangle \). This model is, however, not suitable to fit the data from our measurements discussed below, because it does not capture some additional effects. Most importantly, the strong control laser leads to excited state depletion via transitions to the PSB of the 00-ZPL (corresponds to STED of \( |e\rangle \) via a transition to the PSB of \( |g\rangle \)), even if it is detuned far away from the 00-ZPL resonance. This effect is relevant because the resonance between \( |v\rangle \) and \( |w\rangle \) is at a lower frequency than the 00-ZPL and needs to be included in the model. Moreover, the probe laser does not only pump the molecule via a single isolated vibronic state \( |w\rangle \) in our experiment. Instead, the resonance of another vibronic state \( |x\rangle \) and additional spectrally broad absorption of the molecule must be taken into account.

Figure 7.3(a) shows the level scheme of the model used to fit the experimental data of this chapter. Besides the states \( |g\rangle \), \( |v\rangle \), \( |e\rangle \), and \( |w\rangle \) defined in section 4.4.2, this model contains some additional states, which are also used in the context of fluorescence excitation and STED spectroscopy in sections 6.1.2 and 176.
appendix D.8, respectively: a state $|G\rangle$ that stands for the PSB of the $00$-ZPL in $S_0$, a state $|x\rangle = |S_1, \vec{v}_x\rangle$ that stands for a second vibronic level close to the main vibronic level $|w\rangle$, and a state $|E\rangle$ that stands for weak broadband absorption of the molecule in $S_1$. Since the decay rates of the broad ‘states’ $|G\rangle$ and $|E\rangle$ were not experimentally accessible to us, we assume that $\Gamma_{Gg} = 1/(1\text{ ps})$ and $\Gamma_{Ee} = \Gamma_{we}$. These assumptions are heuristic and not of major relevance to the behavior of the model, except for rendering the states $|G\rangle$ and $|E\rangle$ short-lived with negligible population in the steady-state. Similar to the procedure in section 6.1.2 and appendix D.8, we additionally make the states $|G\rangle$ and $|E\rangle$ infinitely broad by assuming that the laser is always resonant with them.

The method for determining the Hamiltonian of the model displayed in Figure 7.3(a) is equivalent to the method applied in section 4.4.2. We do not repeat the full derivation here and show some intermediate steps in appendix D.9. These steps include the approximation that several transition dipole moments are small, either because they are part of the same electronic state or because of small FC factors. The Hamiltonian in the rotating wave approximation and in the frame without explicit time-dependencies is given by:

$$
\hat{H} = \hbar \begin{pmatrix}
0 & 0 & 0 & \beta_g \Omega_c/2 & \beta_p \Omega_p/2 & \Omega_p/2 & \beta_x \Omega_p/2 \\
0 & \Omega_{gg} & 0 & \beta_c \Omega_c/2 & 0 & 0 & 0 \\
0 & 0 & \Delta_c - \Delta_p & 0 & 0 & \Omega_c/2 & 0 \\
\beta_g \Omega_c/2 & \beta_c \Omega_c/2 & 0 & -\Delta_c - \delta_{vw,ge} & 0 & 0 & 0 \\
\beta_e \Omega_p/2 & 0 & 0 & 0 & -\Delta_p - \delta_{gw,ge} & 0 & 0 \\
\Omega_p/2 & 0 & \Omega_c/2 & 0 & 0 & -\Delta_p & 0 \\
\beta_x \Omega_p/2 & 0 & 0 & 0 & 0 & 0 & -\Delta_p - \delta_{gw,gx}
\end{pmatrix}
$$

with frequency spacings

$$
\delta_{vw,ge} = \omega_{vw} - \omega_{ge} \quad (7.2)
$$

$$
\delta_{gw,ge} = \omega_{gw} - \omega_{gE} \quad (7.3)
$$

$$
\delta_{gw,gx} = \omega_{gw} - \omega_{gx} \quad (7.4)
$$

and basis $I = \{|g\rangle, |G\rangle, |v\rangle, |e\rangle, |E\rangle, |w\rangle, |x\rangle\}$. We additionally assume that $\omega_{gG} \rightarrow -\Delta_c - \delta_{vw,ge}$ as well as $-\Delta_p - \delta_{gw,ge} \rightarrow 0$. The first assumption is equivalent to the assumption that the control laser is always resonant with the transition $|e\rangle \leftrightarrow |G\rangle$. The second assumption means that the probe laser is always resonant with the transition $|g\rangle \leftrightarrow |E\rangle$ (the phonon wing states ‘move’ with the laser frequencies). Thus, the states $|G\rangle$ and $|E\rangle$ act as spectrally broad states without assigning unrealistically high decay rates to them. More realistic models of the PSB could be implemented as in the work by Clear.
et al. [40]. Since we are only concerned with a spectrally confined region of the PSB, however, we consider the model proposed by us as appropriate to describe our data.

The plot in Figure 7.3(b) shows the result of QuTiP simulations using the Hamiltonian from equation (7.1) and Lindblad decay terms corresponding to the decay processes marked in Figure 7.3(a). The parameters of the model were chosen to resemble some of the data discussed in the next section: \( \Delta_c = 0 \), \( \Gamma_{we}/(2\pi) = 25 \text{ GHz} \), \( \Gamma_{xe} = \Gamma_{Ee} = \Gamma_{we} \), \( \Gamma_{vg} = \Gamma_{we}/2 \), \( \Gamma_{eg} = 1/(7 \text{ ns}) \), \( \Gamma_{gg} = 1/(1 \text{ ps}) \), \( \delta_{gw,gx} = 7 \cdot \Gamma_{we} \), \( \delta_{vw,ge} = -10 \cdot \Gamma_{we} \), \( \Omega_p^2/(\Gamma_{eg}\Gamma_{we}) = 1.5 \), \( \beta_g = 0.25 \), \( \beta_x = 0.5 \), \( \beta_g = 0 \), and \( \beta_G = 0.1 \). The values of \( \Omega_c^2 \) are provided in Figure 7.3(b). In contrast to the results of the four-level system displayed in Figure 4.8, the extended model of the current section can account for a flat background absorption next to the probed state due to PSBs and weak combination modes. While an increasing power level of the control laser leads to a splitting of the line profile of the vibronic transition \(|g⟩ ↔ |w⟩\), it also reduces the overall population in \(|e⟩\) by triggering stimulated emission along the transition \(|e⟩ ↔ |G⟩\). Note that this behavior is distinct from the case shown in Figure 4.8(b), in which the amplitude of the splitting peaks only decreases slightly as \( \Omega_c \) becomes larger. The control laser does not induce a splitting of the level \(|x⟩\), because we assumed that the transition dipole moment \( \vec{d}_{vx} \) is negligible due to the low FC overlap between excitations of non-equivalent vibrational normal modes. See appendix D.11 for a calculation of the related FC overlaps of equivalent and different normal modes.

### 7.3 Vibronic line splitting measurements

The optical setup used for the experiments of this chapter is the same as the one used for STED spectroscopy in chapter 6. A sketch of the setup is shown in Figure 5.1. The splitting of the vibronic excitation line was detected via red-shifted fluorescence from the electronically excited state \(|e⟩\) (see Figure 7.1).

The experiment was performed at a probe laser power of \( P_p = 0.58 \text{ mW} \) and control laser powers up to \( P_c = 2.65 \text{ mW} \). By a suitable arrangement of the laser filters and the detection bandpass filter, we were able to reduce the background light leaking from the probe laser to the detectors to a negligible

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4 Actually \( \beta_g \approx 1 \). By setting \( \beta_g = 0 \) we assume that effects related with an interaction of the control laser with the 00-ZPL transition can be ignored. Due to the large frequency difference between the 00-ZPL transition and the resonance between \(|v⟩\) and \(|w⟩\), this assumption is justified as long as \( \Delta_c \approx 0 \).
7.3 Vibronic line splitting measurements

value (see also the related discussion in section 6.1.2). The intense control laser, however, led to a count rate offset of \( R_c \) on the detectors. We measured this offset in a configuration in which the probe laser was blocked and subtracted the related count rate from the total APD count rate: \( R \rightarrow R - R_c \). In appendix D.10 we show the raw data \( R \) and \( R_c \) as a function of the control laser power. The offset \( R_c \) might in part be caused by red-shifted light created by the intense control laser in the fiber that was not completely suppressed by the laser line filter and leaked to the detectors. Additionally, \( R_c \) may contain fluorescence from the molecule excited via the control laser. In our experimental scheme, the control laser was tuned to about 230 GHz below the 00-ZPL transition. Since this detuning is large compared to the linewidth of \( |e \rangle \) (23 MHz), direct excitation of the 00-ZPL transition can be excluded here (see also Figure 7.6(b)).

Excitation of \( |e \rangle \) via thermally excited phonons and photons from the control laser could, however, contribute to \( R_c \), in particular at the highest powers of the control laser for which both the laser-induced excitation rate and the heating effect on the sample have the highest values. Given the low saturation parameter of our experiments and the low values \( R_c < 0.1 \cdot R_\infty \), it appears reasonable to subtract \( R_c \) from the raw count rate \( R \) and to fit a model to the data in which pumping of the molecule via the control laser is neglected (see also the discussion in appendix D.10). To estimate the excited state population from the measured fluorescence rate, we divided the (background-corrected) APD count rate by the saturation count rate \( R_\infty \), i.e. we assumed that \( \rho_{ee} = (R - R_c)/R_\infty \). The value of \( R_\infty = 145 \text{ kcps} \) was determined independently by a saturation measurement of the prominent vibronic level at 291 cm\(^{-1}\) using the same settings of the detection bandpass as for the measurements presented here (see appendix D.10).

Figure 7.4 shows a fluorescence excitation measurement in a spectral range of 400 GHz around the transition frequency to the probed state \( |w \rangle = |S_{1,24} \rangle \). In the spectral vicinity of \( |w \rangle \) we detected another state \( |x \rangle \) at a detuning of \( \delta_{gw,gx}/(2\pi) = 143 \text{ GHz} \). By fitting the seven-level model from section 7.2 to the data of Figure 7.4, we determined the linewidth of state \( |x \rangle \) to be \( \Gamma_{xe}/2\pi = 32.3 \text{ GHz} \) in the low excitation limit. For the fit of the seven-level model, we used \( \Omega_c = 0 \) because the control laser was blocked during the measurement. For the transition frequencies \( \omega_{ge}, \omega_{gv} \) and \( \omega_{ew} \) as well as for the relaxation rates \( \Gamma_{vg}, \Gamma_{eg} \), and \( \Gamma_{we} \), we used the values that have been determined independently via the vibronic spectroscopy methods of chapter

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5 The on-resonance saturation parameter of a 2 mW laser on the oo-ZPL transition is expected to be around \( 10^6 \). The effective saturation parameter, however, is reduced by a factor of about \( \Gamma_{eg}^2/4/(\omega_{gw} - \omega_{gv} + \omega_{eg})^2 + \Gamma_{eg}^2/4 \) \( \approx 2.5 \cdot 10^{-10} \) compared to this value because of the detuning.
Figure 7.4: The spectral region around the probed vibronic level $|w⟩ = |S_{1}, 1_{2g}⟩$, measured with $P_{p} = 0.58 \text{ mW}$ while the control laser was blocked ($P_{c} = 0$). There is a weaker vibronic state $|x⟩$ in the spectral vicinity of $|w⟩$. The dashed orange line is a fit of the seven-level model from section 7.2 to the data. The dashed black line shows the contribution attributed to absorption via the spectrally broad state labeled $|E⟩$.

After the characterization of the probed state $|w⟩$ and its spectral neighborhood, we progressed to the vibronic splitting experiments applying the scheme displayed in Figure 7.1. The control laser was tuned to the frequency $ν_{c} = 402341.5 \text{ GHz} \approx ν_{gw} - ν_{gv}$, i.e. to $Δ_{c} ≈ 0$. Figure 7.5(a) shows the change in the line profile of $|w⟩$ as the power of the control laser is increased to values up to $P_{c} = 2.65 \text{ mW}$. As expected based on the models discussed in section 4.4, this leads to the appearance of a dip in the line profile. The black dashed lines are fits of the seven-level model from section 7.2 to the data. For these fits, only the Rabi frequency of the control laser $Ω_{c}$ and the strength of the PSB
Figure 7.5: Control laser induced dip in a vibronic line profile versus power of the control laser. (a) The vibronic line profile of level $|w\rangle$ recorded via red-shifted fluorescence for various powers of the control laser power. The line profiles are displayed without offsets between the scans. The baseline between these scans drops with increasing control laser power because of stimulated emission along the transition from $|e\rangle$ to the PSB of the 00-ZPL transition (see also the processes illustrated in the simplified level scheme; p: probe laser, c: control laser). Fits of the seven-level model from section 7.2 are shown as dashed black lines. The fit is not shown in the region $Δp ∈ [-80 GHz, -50 GHz]$ to provide a better impression of the behavior of the data. The dashed orange line is the fit of a Lorentzian model to the measurement with the highest control laser Rabi frequency. (b) Rabi frequency of the control laser $Ω_c$ as determined from a fit of the seven-level model from section 7.2 to the data. The black line shows the fit of the function $Ω_c/(2\pi) = a \sqrt{P_c}$ to the data points. (c) Saturation parameter of the baseline depletion resulting from the fit of the seven-level model to the data. The black line shows the fit of a linear function to the data points.
absorption $\beta_G$ were used as free parameters. Because of the large detuning with respect to the 00-ZPL transition, we assumed that $\beta_g = 0$ (i.e. no stimulated transitions along the 00-ZPL) and we (arbitrarily) defined $\Gamma_{gg} = 1/1 \text{ps}$ for the decay rate of the PSB state $|G\rangle$ (see section 7.2). All other variables of the model were determined by the independent measurements described above.

The close agreement between data and fit in Figure 7.5(a) indicates that the model accounts for all relevant effects in our measurements. This includes, in particular, the effect that the overall fluorescence signal drops with increasing power of the control laser. The seven-level model explains that effect via depletion of $|e\rangle$ by stimulated emission to the PSB of the 00-ZPL transition. Figure 7.5(b) shows the Rabi frequencies of the control laser $\Omega_c$ resulting from the fit. As indicated by the solid black line, these Rabi frequencies are proportional to the square root of the control laser power. At the maximum control laser power of $P_c = 2.65 \text{ mW}$, the Rabi frequency between $|v\rangle$ and $|w\rangle$ reaches a value of about $\Omega_c/(2\pi) = 17 \text{ GHz}$. Figure 7.5(c) shows the saturation parameter $(\beta_G \Omega_c)^2/(\Gamma_{eg} \Gamma_{gg})$ of the control laser-induced depletion process caused by transitions $|e\rangle \rightarrow |G\rangle$, where $|G\rangle$ stands for the PSB of the 00-ZPL (see section 7.2 for more details about this process). The fact that this saturation parameter reaches a value larger than unity means that more than half of the original population in $|e\rangle$ is transferred to PSB states at the highest power of the control laser via stimulated emission.

In the case of ATS, the line profile can be described by the sum of two Lorentzian functions whose resonance frequencies differ by the Rabi frequency of the control laser [246, 247]. To test whether such a model can account for our data, we fitted the sum of two Lorentzians to the measurement with the highest control laser power. The result of this fit is shown as an orange dashed line in Figure 7.5(a). The dip in the measured resonance profile is deeper than what can be explained by the Lorentzian model. This is related to additional, EIT-like quantum coherent effects and confirms that our measurements are performed in the regime between EIT and ATS [200–202].

Figure 7.6(a) shows the results of an experiment, in which the detuning $\Delta_c$ of the control laser was varied while its power was kept constant at $P_c = 1.63 \text{ mW}$, the second highest power in the series of Figure 7.5. A change in the control laser frequency moves the position of the dip in the fluorescence profile. The frequency differences of the control laser $\Delta \nu_c$ with respect to the frequency used in the experiments of Figure 7.5 are denoted in Figure 7.6(a). Using these values and the parameters determined from the fits described in the previous paragraphs leads to the theory curves shown as black dashed lines in
7.3 Vibronic line splitting measurements

Figure 7.6: Effects of detuning the control laser. (a) Profiles of the vibronic transition $|g\rangle \leftrightarrow |w\rangle$ for values of the control laser detuning $\Delta c$ denoted in the plot and a control laser power of $P_c = 1.63 \text{ mW}$. The data are plotted with an offset for better readability. The dashed lines are theory curves of the seven-level model from section 7.2. The detuning of the control laser frequency $\Delta \nu_c$ with respect to its value $\nu_c = 402.341.5 \text{ GHz}$ in the experiments of Figure 7.5 is indicated for each scan. (b) Scan of the control laser frequency while the molecule is pumped via the level $|w\rangle$ with $\Delta_p = 0$ at different powers of the probe laser indicated in the plot ($P_p = 0.58 \text{ mW}$). The 00-ZPL transition appears as a peak or a dip in these scans, depending on whether the probe laser pumps the molecule below or above $S_p = 1$. A Lorentzian fit to the line profile of the 00-ZPL results in a linewidth of about 14 GHz for $P_p = 0$ due to power-broadening induced by the control laser. The line splitting effect for $\nu_c = \nu_{gw} - \nu_{gv} \approx 402.34 \text{ THz}$ appears as a dip in the spectra. The detected fluorescence increases with control laser frequency because of stimulated emission and excitation of the PSB of the 00-ZPL transition. The horizontal black line serves as a guide to the eye. The level schemes indicate the relevant processes associated with the different frequencies of the control laser.

Figure 7.6(a). These theory curves match the data of our experiment closely without any further fit parameters. This serves as an additional confirmation that the model developed in section 7.2 provides an accurate description of the processes that are relevant to the experiment.

Figure 7.6(b) shows the APD count rate measured while the probe laser excited the molecule via the state $|w\rangle$ at different powers (with $\Delta_p = 0$) and the control laser was scanned over a range of 700 GHz at a power of $P_c = 0.58 \text{ mW}$. If the probe laser is blocked ($P_p = 0$), the control laser excites the molecule via the 00-ZPL transition and its PSB. Since the power of the control laser is considerably higher than the saturation power of the 00-ZPL transition, it broadens the spectral profile of the 00-ZPL transition to about 14 GHz. Note that the molecule is also excited in a small spectral region below the 00-ZPL
transition. In this range, thermally excited phonons and the incident photons combine to reach the energy required to excite the molecule. With increasing temperature, the PSB wing extends towards lower energies because thermal phonons at higher energies are available [40]. This process could partially be responsible for the control-laser induced background rate $R_c$ discussed in appendix D.10.

The absorption features of the 00-ZPL and the PSB are also present if the molecule is pumped below saturation ($P_p = 0.1\,\text{mW}$). In this case, a dip appears about 232 GHz below the 00-ZPL transition frequency. This dip is centered around the frequency $\nu_c = \nu_{ge} - \nu_{vw}$ for which the resonance condition for the line splitting effect is fulfilled. We note that the frequency for which we observe the dip differs by about 1 GHz from what we expected based on the vibronic level structure measurements (see Figure 7.1). Most likely, this is related to a small spectral jump of the 00-ZPL during the STED measurements, leading to an error in the estimated vibronic wavenumber of $|\nu|$. This error ($\sim 1\,\text{GHz} = 0.03\,\text{cm}^{-1}$) is small compared to the linewidths of the vibronic states involved in the splitting experiment presented above and can therefore safely be neglected.

If the molecule is pumped above saturation ($P_p = 1.2\,\text{mW}$), the 00-ZPL feature changes from a peak to a dip. Under this condition, population is inverted on the transition $|g\rangle \leftrightarrow |e\rangle$ and stimulated emission on the 00-ZPL transition dominates over absorption [12]. The dip related to the line splitting maintains a similar shape below and above saturation. Figure 7.6(b) also shows that stimulated emission to the PSB of the 00-ZPL is a relevant process. The decrease in the fluorescence signal towards lower frequencies of the control laser marks the low frequency region of the PSB measured via a STED process (see Figure 6.10 for a full spectrum). At the position of the splitting dip, the baseline drop due to stimulated emission is clearly visible.

### 7.4 Discussion

In section 7.3 we demonstrate that the ground state and two vibronic states of a DBT molecule can be used as an effective three-level system. By tuning an intense control laser on resonance between the two vibronic states, a dip can be induced in the line profile of the transition between the ground state and the upper vibronic state. Therefore, the intensity of the control laser can be used as a knob to modify the absorption of the probe laser by the molecule. So far, non-linear effects in cryogenic single molecule spectroscopy have only been demonstrated in the spectral vicinity of the strong 00-ZPL transition [64, 67, 68]. Our experiments mark the first demonstration of non-linear optics in
a three-level configuration with two vibronic transitions of a single molecule in the solid phase.

The dip in the line profile of the upper vibronic state cannot be explained purely by ATS, which splits a single resonance line into two Lorentzian resonances (see the orange dashed line in Figure 7.5(a)). The fact that the dip induced in the resonance profile is deeper than can be explained by ATS indicates an additional quantum interference effect, which is typical for EIT. Due to the fast relaxation rate of the lower vibronic state, our experiment is, however, not in a regime in which narrow EIT dips can be induced in the probed resonance profile. Instead, the observations shown in Figures 7.5 and 7.6 are a mixture of both EIT and ATS [200–202, 248].

Since EIT is an established method for optically controlled access to quantum memory states [249], we expect that this process also plays a role in the experiments reported here. In the pioneering experiments with quantum memories accessed by EIT, a light pulse has been coherently transferred to spin states in atomic vapors with the help of a control laser [250, 251]. In these experiments, the stored light pulse could be retrieved after storage times in the order of 1 ms by quickly ramping up the power of the control laser field. In our case, phase-information of the driving light is coherently transferred to the quantum mechanical phase of the vibrational wave function of \(|u\rangle\). This raises the question whether coherent storage and retrieval schemes, similar to the quantum memory experiments with atomic vapors, are possible using vibronic states of a single molecule. We note that quantum memory schemes exploiting ATS have recently also been proposed and successfully demonstrated on the single photon level [252, 253].

Using the model fitted to our data, we can estimate the fraction of the population in \(|u\rangle\) with a defined phase with respect to the driving fields. The population in state \(|u\rangle\) is described by the operator

\[
\hat{\rho}_{uv} = \hat{\sigma}_{g'v}^\dagger \hat{\sigma}_{gv}
\]  

with \(\hat{\sigma}_{gv} = |g\rangle\langle v|\). By expressing the \(\hat{\sigma}\)–operators in terms of their fluctuations \(\delta \hat{\sigma}\) from their averages \(\langle \hat{\sigma} \rangle = \langle \hat{\sigma} \rangle + \delta \hat{\sigma}\), we obtain:

\[
\langle \hat{\rho}_{uv} \rangle = \left( \langle \hat{\delta}_{g'v}^\dagger \rangle + \delta \hat{\delta}_{g'v}^\dagger \right) \left( \langle \hat{\delta}_{gv} \rangle + \delta \hat{\delta}_{gv} \right) = |\bar{\rho}_{gv}|^2 + \langle \delta \hat{\delta}_{g'v}^\dagger \delta \hat{\delta}_{gv} \rangle
\]  

with the matrix element \(\bar{\rho}_{gv} = \langle \hat{\delta}_{g'v}^\dagger \rangle\) from the density matrix. Hence the population can be separated into two parts: one is related to the absolute square of the coherence of the transition (coherently transferred population) and
the other is related to its fluctuations (incoherently transferred population). While the coherent part has a well-defined phase relation with respect to the driving light fields, the phase of the incoherent part is randomized because of spontaneous emission [30, 254]. Spontaneous decay along $|e\rangle \rightarrow |v\rangle$ (and the dynamics of the vibrational relaxation cascade) additionally contributes to the incoherent population of $|v\rangle$.

Figure 7.7 shows the coherent population $|\tilde{\rho}_{gv}(\Delta_p = 0)|^2$ and the total population $\rho_{vv}(\Delta_p = 0)$ obtained from the density matrix resulting from the model fits to the data of Figure 7.5(a). Because of the fast vibrational relaxation rate of $|v\rangle$, the total electronic population transferred to $|v\rangle$ is smaller than $10^{-3}$ (see Figure 7.7(a)). For values around the highest control laser Rabi frequency in our experiment, $\Omega_c/(2\pi) \sim 17$ GHz, our model predicts that the coherently transferred population outweighs the incoherently transferred population of $|v\rangle$. The branching ratio $\Gamma_{ev}/(\Gamma_{eg} + \Gamma_{ev})$ of spontaneous emission to the level $|v\rangle$ studied in our experiment is expected to be in the order of 1%. As shown in Figure 7.7(a), the incoherent population transferred via this channel is expected to be small. For weaker control fields, the incoherent population transferred by spontaneous decay rises faster with the branching ratio than for strong control fields because more population can be transferred to $|e\rangle$ if the dip induced by the control laser is small.
Figure 7.7(b) shows the ratio of the coherent population to the total population in $|v\rangle$. For our experimentally determined parameters and the highest power of the control laser used, we estimate this ratio to be around 80%. This is in stark contrast with the behavior of the population in STED spectroscopy discussed in chapter 6, where the population transfer is purely incoherent. As shown in Figure 7.7(c), there is an optimal value of $\Omega_c$ for maximum transfer of population to $|v\rangle$. The population in $|v\rangle$ decreases for high values of $\Omega_c$ because of the splitting dip that emerges around $\Delta_p = 0$ and reduces the interaction strength of the probe laser with the molecule.

Coherent population transfer to $|v\rangle$ is a useful tool for work in quantum memories. The fast vibrational relaxation rates of the vibronic states of DBT in pDCB limit the storage times to the range of $\sim 10$ ps. Future experiments would benefit from vibrational states that protect the coherence of the memory state for a longer time than the current value. If the decay rates of vibrational states could be reduced to values below the electronic decay rate, i.e. $\Gamma_{vg} < \Gamma_{eg}$, EIT-schemes with $|e\rangle$ as an upper state will be possible. Reduced vibrational relaxation rates would also reduce the laser power required to effectively drive the control laser transition. This, in turn, will reduce the cross-talk with PSB states and other vibronic states in the spectral vicinity. The exploration and engineering of solid state systems with increased vibrational lifetimes thus poses an important challenge for future experiments [78].

---

6 Due to the lower decoherence rate of $|e\rangle$ compared to the decoherence rate of vibronic states of DBT:pDCB, coherent population transfer to a vibronic state of $S_0$ is generally more efficient in the typical guest-host systems of single molecule spectroscopy if $|e\rangle$ is used as upper state.
8 Concluding remarks

The experimental methodology presented in this thesis enables spectroscopic access to vibronic states of single molecules in cryogenic solid-state matrices at a high spectral resolution. Our results show that the line profiles and linewidths of a given vibronic mode are similar among different molecules. This confirms that the vibrational relaxation behavior is a well-defined property of a guest-host system, determined by the mutual (anharmonic) coupling between its various mechanical degrees of freedom.

Many applications in quantum information science require quantum states with markedly longer lifetimes than the typical values around 10 ps observed in molecular crystals. Our study shows that there is considerable variation between the vibrational lifetimes of different vibronic modes in a single dopant molecule. Some modes are sufficiently decoupled from their environment to reach vibrational lifetimes up to 80 ps. Other studies in isotopically pure benzene have detected a vibrational mode relaxing within 2.65 ns [148] (corresponding to a linewidth of 60 MHz), a value comparable to the radiative lifetime of the electronically excited state. These observations raise the interesting questions as to whether it is possible for vibrational lifetimes of dopant molecules in solid-state systems to be prolonged by phononic engineering that decouples them from vibrational dissipation channels.

Even if a molecule is perfectly decoupled from its mechanical environment (e.g., in vacuum), the lifetimes of its vibronic states are not indefinite. Vibronic states in \( S_1 \) can decay via spontaneous emission, limiting their maximum lifetimes to values around 10 ns [154, 255]. States with high vibrational energy can decay by coupling to internal modes of the molecule (IVR) at ps-ns timescales [14, 152]. The lifetimes of low frequency states in \( S_0 \), however, have the potential to reach the the longest vibrational lifetimes in a polyatomic molecule, ultimately limited by radiative infrared decay.
Successfully decoupling a molecule from its mechanical environment has several consequences for its photophysical behavior. The presence of long-lived vibrational states increases the cycling time, i.e. the average time for a complete decay to the energetic ground state. This reduces the brightness of the molecule and the power required to saturate its transitions. Moreover, transitions to long-lived vibronic states can be driven with less laser power due to their reduced linewidth. If vibrational states reach lifetimes at the μs-level or longer, one might start to observe a fluorescence blinking behavior, similar to the case in which a long-lived triplet state is present in the molecule. We also expect that if molecules can be isolated from their environment to some extent, they will likely exhibit not only one but multiple vibrational states with long lifetimes.

Long-lived vibrational states of single dye molecules in the solid state would enable a number of interesting experiments. For example, the three-level scheme studied in chapter 7 would work with considerably lower laser powers and preserve the phase information for longer periods of time. Under these conditions, pulsed storage and retrieval experiments using a single vibration of a single molecule could be realized. One could also study the entanglement properties of a molecule with long-lived vibronic states. The frequency of a photon emitted by a polyatomic molecule is entangled with the final vibrational state of the spontaneous vibronic transition. Long vibrational lifetimes would allow the experimental study of such vibration-photon entanglement. Note that the absence of rotational states in solid-state molecules facilitates such studies by reducing the number of spectral lines. Vibration-photon entanglement could further be used in more complex experiments to entangle vibrational states of two molecules. We remark that theoretical studies of entanglement involving molecular vibrations are currently scarce in the literature. A deeper understanding of the related processes would help in the design of corresponding experiments.

One important difference between vibrational states and spin states is the frequencies of their transitions. While low frequency vibrational states have frequencies in the order of 10 THz, transitions between spin states are typically at the few GHz-level. Hence, different light sources are required for state preparation using Rabi-pulses in these systems. Since light sources in the 10 THz-range are not readily available, Rabi pulses for vibrational states could be applied using a combination of two light fields in the visible range, similar to the approach described in [256]. This would also address the issue that vibrational states form a ladder of states with (almost) equidistant step size,
making it difficult to address a single transition directly (in contrast to a two-level system).

In section 6.5.2, we discuss several possible approaches that might decouple molecules sufficiently from their environment to achieve long vibrational lifetimes. If experiments to realize such states succeed, they will open up an exciting new research direction in the future. In combination with further improvements to integrated nanophotonic platforms, single organic molecules and their vibrational modes might become relevant systems for quantum information processing within the next decades.
Bibliography


Bibliography


Bibliography


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A Abbreviations

A.1 Molecules

<table>
<thead>
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<th>Abbreviation</th>
<th>Full Name</th>
<th>Abbreviation</th>
<th>Full Name</th>
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</thead>
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<tr>
<td>Ac</td>
<td>Anthracene</td>
<td>Pc</td>
<td>Pentacene</td>
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<tr>
<td>DBATT</td>
<td>Dibenzanthanthrene</td>
<td>pDBB</td>
<td>para-Dibromobenzene</td>
</tr>
<tr>
<td>DBT</td>
<td>Dibenzoterrylene</td>
<td>pDCB</td>
<td>para-Dichlorobenzene</td>
</tr>
<tr>
<td>DBN</td>
<td>2,3-Dibromonaphthalene</td>
<td>pDIB</td>
<td>para-Diiodobenzene</td>
</tr>
<tr>
<td>DCN</td>
<td>2,3-Dichloronaphthalene</td>
<td>PE</td>
<td>Polyethylene</td>
</tr>
<tr>
<td>DMA</td>
<td>2,3-Dimethylnaphthalene</td>
<td>PMMA</td>
<td>Polymethylmethacrylate</td>
</tr>
<tr>
<td>DMN</td>
<td>2,3-Dimethylnaphthalene</td>
<td>PrC</td>
<td>Perylenecarboximides</td>
</tr>
<tr>
<td>nH</td>
<td>n-Hexadecane</td>
<td>pT</td>
<td>para-Terphenyl</td>
</tr>
<tr>
<td>nT</td>
<td>n-Tetradecane</td>
<td>TDI</td>
<td>Terrylene-diiimide</td>
</tr>
<tr>
<td>Nt</td>
<td>Naphthalene</td>
<td>Tr</td>
<td>Terrylene</td>
</tr>
</tbody>
</table>

Table A.1: List of abbreviations used for molecules in this thesis.

A.2 List of abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
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</tr>
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<tbody>
<tr>
<td>ATS</td>
<td>Autler-Townes splitting</td>
</tr>
<tr>
<td>BO</td>
<td>Born-Oppenheimer</td>
</tr>
<tr>
<td>CCDC</td>
<td>Cambridge Crystallographic Data Centre</td>
</tr>
<tr>
<td>DFT</td>
<td>Density functional theory</td>
</tr>
<tr>
<td>EIT</td>
<td>Electromagnetically induced transparency</td>
</tr>
<tr>
<td>FC</td>
<td>Franck-Condon</td>
</tr>
<tr>
<td>FWHM</td>
<td>Full width at half maximum</td>
</tr>
<tr>
<td>IVR</td>
<td>Intramolecular vibrational redistribution</td>
</tr>
<tr>
<td>PAH</td>
<td>Polycyclic aromatic hydrocarbon</td>
</tr>
<tr>
<td>PSB</td>
<td>Phonon sideband</td>
</tr>
<tr>
<td>RT</td>
<td>Room temperature</td>
</tr>
<tr>
<td>SEP</td>
<td>Stimulated emission pumping</td>
</tr>
<tr>
<td>SNR</td>
<td>Signal-to-noise ratio</td>
</tr>
<tr>
<td>STED</td>
<td>Stimulated emission depletion</td>
</tr>
<tr>
<td>TD DFT</td>
<td>Time-dependent density functional theory</td>
</tr>
</tbody>
</table>

Table A.2: List of abbreviations used in this thesis (except for names of molecules).
B Glossary

**Combination mode** – A molecular vibrational state with at least two non-zero vibrational quantum numbers. In a combination mode, the nuclei of a molecule oscillate according to a superposition of the displacement patterns associated with multiple normal modes.

**Duschinsky mixing** – If a (vibrational) normal mode in one electronic state can be expressed as a linear combination of two or more normal modes in another electronic state, then these normal modes undergo Duschinsky mixing [103].

**Fermi resonance** – If a normal mode of a molecule (coincidentally) has the same energy and symmetry as a mode with multiple vibrational quanta of the same molecule, then these modes are in Fermi resonance [153]. This can lead to intensity redistribution between the modes and a splitting or shift of their resonance frequencies.

**Herzberg-Teller effect** – Vibronic transitions to a normal mode of a molecule can be activated if the electronic transition dipole moment depends on the normal coordinate of this normal mode. This mechanism is called the Herzberg-Teller effect and can lead to the activation of vibronic transitions in cases in which the (static) transition dipole moment of an electronic transition vanishes [35].

**Intramolecular vibrational redistribution (IVR)** – Relaxation of a vibrational normal mode of a molecule via transfer of its energy to multiple (lower energy) normal modes of the same molecule. This process requires the initial and final states to have the same (total) energy (i.e. to be in Fermi resonance) and to be anharmonically coupled. IVR is most relevant to states with high vibrational energy (≥1500 cm⁻¹).

**Irreducible representation of a point group** – (Simplified description) The elements of a point group are symmetry operations (e.g. the elements of the $C_{2h}$ point group are: identity, two-fold rotation, inversion, and reflection w.r.t. a plane normal to the rotation axis). Combining two symmetry operations in sequence corresponds to a single symmetry operation of the same group (e.g. in the $C_{2h}$ point group: two-fold rotation followed by inversion = reflection). It is possible to describe the elements of a point group using simple integer
numbers that combine under multiplication in the same way as the elements of the point group (e.g.: (identity, two-fold rotation, inversion, reflection) = (1,-1,-1,1)). The set of the simplest representations of a point group are its irreducible representations (see [37] for a rigorous definition). Every point group has the totally symmetric representation in which each symmetry element is represented by 1.

**Mulliken symbol** – Each irreducible representation of a symmetry point group is labeled by a Mulliken symbol (e.g. A\_g or B\_u in the C\_2\_h point group). Since each normal mode of a molecule transforms according to an irreducible representation of the molecule, one can assign a Mulliken symbol to each mode.

**Normal mode of a molecule** – A (vibrational) normal mode of a molecule is an oscillatory displacement pattern of its nuclei around their equilibrium positions at a fixed frequency and phase. In the system of mass-weighted coordinates, the displacement vectors of the molecular normal modes (describing the relative displacement amplitudes of the nuclei) are orthogonal with respect to each other.

**Phonon** – A fundamental excitation of a lattice mode in a crystal.

**Phonon sideband (PSB)** – A broad feature in the spectrum of a molecule in a solid-state matrix that appears next to a zero phonon line and is associated with energy transfer to the matrix.

**Point group (of a molecule)** – The (symmetry) point group of a molecule (e.g. the C\_2\_h point group) contains all symmetry operations under which the molecule can be mapped to itself.

**Totally symmetric normal mode** – A totally symmetric normal mode of a molecule is symmetric (i.e. mapped to itself) under all symmetry operations of the molecular point group.

**Vibrational cooling** – A term used to describe the dissipation of the complete vibrational energy in a molecule to its environment, usually involving a vibrational relaxation cascade (see [18]).

**Vibrational relaxation** – The decay of a vibrational quantum state of a molecule via transfer of its vibrational energy to states in the molecule with lower energy and/or to the environment.

**Vibrational relaxation cascade** – Sequence of vibrational relaxation steps involved in the dissipation of the vibrational energy in a molecule to its environment.
**Vibronic spectrum** – A molecular spectrum resulting from vibronic transitions (e.g. a fluorescence emission spectrum).

**Vibronic state** – A state of a molecule defined by its electronic and vibrational quantum numbers.

**Vibrational transition** – A transition between vibrational states of a molecule during which one or several vibrational quantum numbers change while the electronic state of the molecule remains the same.

**Vibronic transition** – A transition between two electronic states of a molecule that involves a change in its vibrational state.

**Zero phonon line (ZPL)** – A line in a molecular spectrum associated with a transition in the molecule that does not involve energy transfer to the solid-state environment.

**oo-zero phonon line (oo-ZPL)** – The line in a molecular spectrum associated with the transition between the vibrational ground states of the electronic ground and excited states.
C Normal mode analysis

In the following sections, we explicitly calculate the normal modes of a diatomic and a linear triatomic molecule.

C.1 Diatomic molecule

Many important concepts relating to normal modes, vibrational wave functions and FC physics can be understood by analyzing the properties of a diatomic molecule, which only has a single vibrational mode. FC active vibrational modes of polyatomic molecules that do not mix between ground and excited states behave like independent harmonic oscillators, equivalent to the stretch mode of a diatomic molecule. This section presents some steps of the vibrational analysis of a diatomic molecule.

C.1.1 Normal modes

For the treatment of the diatomic molecule we restrict ourselves to one dimension (x-axis). The positions and masses of the two nuclei are denoted by \(x_i\) and \(m_i\) (\(i = 1, 2\)). The equilibrium positions of the nuclei are \(x_{i,0}\) and the deflections from equilibrium \(\xi_i = x_i - x_{i,0}\) (see Figure C.1(a)). Their mass-weighted displacement coordinates are defined as \(q_i = \sqrt{m_i} \xi_i\). Under the assumption of the harmonic potential

\[
V(\xi_1, \xi_2) = \frac{k}{2}(\xi_2 - \xi_1)^2 = \frac{k}{2} \left( \frac{q_2}{\sqrt{m_2}} - \frac{q_1}{\sqrt{m_1}} \right)^2, \tag{C.1}
\]

we obtain the Hessian matrix

\[
V^{(2)} = \frac{k}{\sqrt{m_1 m_2}} \begin{pmatrix}
(m_2/m_1)^{1/2} & -1 \\
-1 & (m_1/m_2)^{1/2}
\end{pmatrix} \tag{C.2}
\]

in the mass-weighted frame.
C Normal mode analysis

Figure C.1: Normal coordinate and vibrational wave function of the diatomic molecule. (a,b) Schematic of the diatomic molecule in two different equilibrium positions $x_{i0}$ and $x'_{i0}$. $\xi_i$ denotes the displacement of atom $i$. (c) Relative orientation of the normal coordinate of the stretch mode in the frame of the Cartesian displacements for $m_1 = m_2$ ($Q_1$) and $m_1 = 4m_2$ ($\tilde{Q}_1$). Dashed line: translation of the molecule. (d) Effect of changing the equilibrium length of a molecule on the wave functions of the vibrational ground state, plotted as a function of the normal coordinate in the state with shorter length (blue: original length; green: $\Delta l = \Delta Q_{zpm}/\sqrt{\mu}$).

Diagonalization of $V^{(2)}$ yields the eigenvalues and eigenvectors

$$\lambda_1 = \frac{k}{\mu}, \quad \vec{A}_1 \propto (-\sqrt{m_2/m_1}, 1)^t \quad (C.3)$$

$$\lambda_2 = 0, \quad \vec{A}_2 \propto (\sqrt{m_1/m_2}, 1)^t, \quad (C.4)$$

with the reduced mass of the system $\mu = m_1 m_2/(m_1 + m_2)$. In the case $m_1 = m_2 = m$, the reduced mass is $\mu = m/2$, while for $m_1 \gg m_2, \mu \to m_2$. Solution 1 is the only vibrational normal mode of this molecule, a symmetric stretch mode. The displacements are in opposite directions and the relative amplitude of the Cartesian displacements is inversely proportional to the ratio of the masses: $|\xi_1/\xi_2| = m_2/m_1$. The frequency of the stretch mode is given by $\omega = \lambda_1^{1/2} = (k/\mu)^{1/2}$. Solution 2 corresponds to translation of the molecule along the $x$-axis, as indicated by its zero frequency and equal (non mass-weighted) Cartesian displacements of both nuclei in the same direction. This solution is thus not a normal mode of vibration. By discarding solution 2 and normalizing $\vec{A}_1$ we obtain the vector

$$I_{mwc} = (I_{mwc,1}) = \left(\frac{-(\mu/m_1)^{1/2}}{(\mu/m_2)^{1/2}} \right) \left(\begin{array}{c} -\sin(\gamma) \\ \cos(\gamma) \end{array}\right) \text{ for } m_1 = m_2 = \frac{1}{\sqrt{2}} \left(\begin{array}{c} -1 \\ 1 \end{array}\right), \quad (C.5)$$
with $\gamma = \arccos((\mu/m_2)^{1/2})$. This vector enables the transformation between the normal coordinate $Q_1$ of the stretch mode and mass-weighted Cartesian displacements $\vec{q} = (q_1, q_2)^t$ via $\vec{q} = I_{\text{mwc}} \cdot Q_1$. Multiplication by $M^{-1/2}$ yields a vector whose entries are proportional to the actual Cartesian displacements

$$I_{\text{cart}} = (I_{\text{cart},1}) = M^{-1/2} I_{\text{mwc}} = \begin{pmatrix} -\mu^{1/2}/m_1 \\ \mu^{1/2}/m_2 \end{pmatrix}. \quad (C.6)$$

The displacements of the nuclei in the stretch mode are $\xi' = I_{\text{cart}} \cdot Q_1$. While $I_{\text{mwc}}$ is unitless, the entries of $I_{\text{cart}}$ have the unit kg$^{-1/2}$, and $[Q_1] = \text{kg}^{1/2}\text{m}$. The normal coordinate $Q_1$ of the stretch mode can be expressed in terms of the Cartesian displacements using the (generalized) left-sided inverse $I_{\text{cart}}^{-1} = I_{\text{mwc}} M^{1/2}$:

$$Q_1 = \sqrt{\mu}(\xi_2' - \xi_1') \quad \text{symmetric stretch}. \quad (C.7)$$

The normal coordinate only changes if the distance between the nuclei is altered.

If the equilibrium positions of the nuclei change according to $x_{i,0} \rightarrow x_{i,0}'$ this leads to a length change $\Delta l = (x_{2,0}' - x_{1,0}') - (x_{2,0} - x_{1,0})$ of the molecule (see Figure C.1(a,b)). The normal coordinate $Q_1'$ defined with respect to the new equilibrium positions can thus be expressed via the original normal coordinate as

$$Q_1' = \sqrt{\mu}(\xi_2' - \xi_1') = Q_1 - \sqrt{\mu}\Delta l, \quad (C.8)$$

where $\xi_i' = x_i - x_{i,0}'$ are the displacements of the nuclei measured with respect to the new equilibrium positions.

**C.1.2 Vibrational wave functions**

The Hamiltonian for the vibrational motion of the diatomic molecule is a single term of the sum given in equation (3.16):

$$\hat{H} = \hat{T} + \hat{V} = \frac{1}{2} \hat{Q}^2 + \frac{1}{2} \omega^2 \hat{\Omega}^2, \quad (C.9)$$

which corresponds to the Schrödinger equation of a harmonic oscillator with unit mass. In equation (C.9), we drop the index of the coordinate $Q_1$ of the
C Normal mode analysis

The solutions of the one-dimensional stationary Schrödinger equation of a harmonic oscillator potential \( \hat{H} \Psi_v = E_v \Psi_v \) are given by

\[
\Psi_v(Q) = \left( \frac{\gamma}{\pi} \right)^{1/4} \frac{1}{2^v \sqrt{v!}} \frac{1}{2} H_v(\gamma^{1/2} Q) e^{-\gamma Q^2/2}, \tag{C.10}
\]

with quantum number \( v \in \mathbb{N}_0^+ \), \( \gamma = \omega/\hbar \) and the \( v \)th physicist’s Hermite polynomial \( H_v(z) \) [95].¹ The energy eigenvalues of these states are given by

\[
E_v = \hbar \omega (v + \frac{1}{2}). \tag{C.11}
\]

and the corresponding vibrational wave functions for \( v = 0, 1, 2 \) are:

\[
\Psi_0(Q) = \left( \frac{\gamma}{\pi} \right)^{1/4} e^{-\gamma Q^2/2} \tag{C.12}
\]

\[
\Psi_1(Q) = \left( \frac{\gamma}{4 \pi} \right)^{1/4} (2 \gamma^{1/2} Q) e^{-\gamma Q^2/2} \tag{C.13}
\]

\[
\Psi_2(Q) = \left( \frac{\gamma}{64 \pi} \right)^{1/4} (4 \gamma Q^2 - 2) e^{-\gamma Q^2/2} \tag{C.14}
\]

See Figure 3.4(a) for plots of these wave functions and the related probability distributions. The variance of \( Q \) in the state with quantum number \( v \) is given by \( \langle \hat{Q}^2 \rangle_v = (v + 1/2)/\gamma \) [257]. For \( v = 0 \) we obtain the value \( \langle \hat{Q}^2 \rangle_0 = 1/(2\gamma) \) and the corresponding standard deviation \( Q_{zpm} = (\hbar/(2\omega))^{1/2} \) quantifying the range of the zero-point motion of the atoms.

C.1.3 Franck-Condon factors

The FC integrals for a diatomic molecule that changes its length by \( \Delta l \) between electronic ground and excited states are

\[
I(\tilde{v}', \tilde{v}) = \langle \tilde{v}' | \tilde{v} \rangle = \int_{-\infty}^{\infty} \Psi_{v'}(Q') \Psi_v(Q) dQ
\]

\[
= \int_{-\infty}^{\infty} \Psi_{v'}(Q - \sqrt{\mu} \Delta l) \Psi_v(Q) dQ. \tag{C.15}
\]

Their solution is given in equation (3.38).

---

¹ \( H_0(z) = 1, H_1(z) = 2z, H_2(z) = 4z^2 - 2, \ldots \)
C.2 Linear triatomic molecule

C.2.1 Normal modes

For a linear triatomic molecule with parameters shown in Figure C.2(a), the potential energy in mass-weighted coordinates is given by [258]

\[ V = \frac{1}{2} k \left( \frac{q_2}{\sqrt{M}} - \frac{q_1}{\sqrt{m}} \right)^2 + \frac{1}{2} k \left( \frac{q_3}{\sqrt{m}} - \frac{q_2}{\sqrt{M}} \right)^2. \]  

(C.17)

Besides the direct solution of the integrals, there is also an operator approach to solve the FC integrals. The wave function of a vibrational state with \( \nu = 0 \) and origin displaced by \( \Delta Q = \alpha \cdot \Delta Q_{zpm} \) can be written as a coherent state \( |\alpha\rangle = \hat{D}(\sqrt{2}\alpha)|0\rangle = e^{\alpha(\hat{a} - \hat{a}^\dagger)}|0\rangle \) [99, 101]. The FC integrals of the transitions between \( |S_1, \nu' = 0\rangle \) and \( |S_0, \nu = n\rangle \) then correspond to the overlap between the coherent state \( |\alpha\rangle \) and the Fock states \( |n\rangle \):

\[ I(0', \nu) = \langle \alpha | \nu \rangle = \frac{\alpha^\nu}{\sqrt{\nu!}} e^{-\frac{1}{2} \alpha^2}. \]  

(C.16)

A similar procedure can also be applied to initial states with \( \nu' > 0 \) [99, 101].

C.2 Linear triatomic molecule
Its Hessian matrix is

\[ V^{(2)} = \frac{k}{\sqrt{mM}} \begin{pmatrix} (M/m)^{1/2} & -1 & 0 \\ -1 & 2(m/M)^{1/2} & -1 \\ 0 & -1 & (M/m)^{1/2} \end{pmatrix} \]  

(C.18)

and has the following eigenvalues and eigenvectors

\[ \lambda_1 = \frac{k}{m}, \quad \vec{A}_1 \propto (-1, 0, 1)^t \]  

(C.19)

\[ \lambda_2 = k\left(\frac{1}{m} + \frac{2}{M}\right), \quad \vec{A}_2 \propto (1, -2\sqrt{m/M}, 1)^t \]  

(C.20)

\[ \lambda_3 = 0, \quad \vec{A}_3 \propto (1, \sqrt{M/m}, 1)^t. \]  

(C.21)

Leaving out the third result, which corresponds to translation of the molecule, yields the matrix

\[ I_{\text{mwc}} = (\vec{l}_{\text{mwc,1}}, \vec{l}_{\text{mwc,2}}) = \frac{1}{\sqrt{2}} \begin{pmatrix} -1 & a \\ 0 & -2a\sqrt{m/M} \\ 1 & a \end{pmatrix} \]  

(C.22)

with \( a = (1 + 2m/M)^{-1/2} \). The transformation between Cartesian displacements and normal coordinates, \( \dot{\xi} = \vec{l}_{\text{cart}} \cdot \dot{Q} \), is given by the following matrix

\[ \vec{l}_{\text{cart}} = \frac{1}{\sqrt{2m}} \begin{pmatrix} -1 & a \\ 0 & -2am/M \\ 1 & a \end{pmatrix}. \]  

(C.23)

Using \( \vec{l}_{\text{cart}}^{-1} = I_{\text{mwc}}^* M^{1/2} \), the two normal coordinates of the linear triatomic molecule can be written in terms of the Cartesian displacements as:

\[ Q_1 = \sqrt{\frac{m}{2}}(\xi_3 - \xi_1) \quad \text{symmetric stretch,} \]  

(C.24)

\[ Q_2 = \sqrt{\frac{m}{2}}a(\xi_1 + \xi_3 - 2\xi_2) \quad \text{antisymmetric stretch.} \]  

(C.25)

In the symmetric stretch mode, the central atom is at rest while the outer atoms perform synchronous oscillations in opposite directions. In the antisymmetric stretch mode, the outer atoms move in the same direction while the central atom oscillates in the opposite direction. The frequency of the
antisymmetric stretch mode is higher than the frequency of the symmetric stretch mode, because the displacement of the central atom increases the maximum attractive and repulsive forces mediated by the springs. In the normal coordinate basis, the vibrational wave function of a polyatomic molecule can be written as a product of harmonic oscillator wave functions. The corresponding vibrational wave function of the triatomic molecule with vibrational quantum numbers \( (v_1 = 1, v_2 = 0) \) is shown in Figure C.2(d).

By solving the equations of motion along the transverse direction of the axis of the triatomic molecule, one finds two additional, degenerate normal modes [259] (see Figure 3.1(a)).

### C.2.2 Franck-Condon factors

In this section, we illustrate the principle of vibronic selection rules using a calculation for the triatomic molecule. Under the assumption that the molecule has the same symmetry in \( S_0 \) and \( S_1 \) and that the vibrational frequency is identical in both states, one can show that only the totally symmetric mode is FC active.

A displacement of the nuclei of the linear molecule that preserves its symmetry during the transition between \( S_0 \) and \( S_1 \) is necessarily proportional to

\[
\Delta \vec{R} = (−\Delta x, 0, \Delta x)^t. \tag{C.26}
\]

Projecting this displacement to the normal mode basis yields

\[
(\Delta Q_1, \Delta Q_2) = (\sqrt{2m\Delta x}, 0). \tag{C.27}
\]

Hence, as mentioned for the more general case in section 3.2.3, only the totally symmetric normal coordinate changes if the atoms move in such a way that the symmetry of the molecule is preserved [103].

The FC integral for the case of a symmetry-preserving electronic transition from the vibrational ground state \(|\vec{v}'\rangle = |(0, 0)\rangle\) in one electronic state to an
arbitrary vibrational state $|\vec{v}\rangle = |(v_1, v_2)\rangle$ in the other electronic state can be simplified as follows:

\[
I((v_1' = 0, v_2' = 0), (v_1, v_2))
\]

\[
= \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \Psi_{0,0}(Q_1', Q_2') \Psi_{v_1,v_2}(Q_1, Q_2) dQ_1 dQ_2
\]

\[
= \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \Psi_0(Q_1 + \Delta Q_1) \Psi_0(Q_2 + \Delta Q_2) \Psi_{v_1}(Q_1) \Psi_{v_2}(Q_2) dQ_1 dQ_2
\]

\[
= \int_{-\infty}^{\infty} \Psi_0(Q_1 + \Delta Q_1) \Psi_{v_1}(Q_1) dQ_1 \int_{-\infty}^{\infty} \Psi_0(Q_2) \Psi_{v_2}(Q_2) dQ_2
\]

\[
= \begin{cases} 
I(0,v_1) \int_{-\infty}^{\infty} \Psi_0(Q_2) \Psi_{v_2}(Q_2) dQ_2 & \omega_{v_1} = \omega_{v_2} \\
0, & v_2 \in 2\mathbb{N}_0 + 1 
\end{cases}
\]

where $I(0, v)$ of the last line corresponds to the FC integral defined in equation (3.34) for the one-dimensional case. The result of the above calculation shows that the decay from the vibrational ground state $|\vec{v}'\rangle = |(0,0)\rangle$ will not lead to the excitation of a mode with an odd number of excitations in the antisymmetric stretch mode. The overlap integral does not vanish for even, non-zero numbers of vibrational quantum numbers of the antisymmetric stretch if the vibrational frequencies of this mode differ between $S_0$ and $S_1$ [36].
Various formulas and calculations

Rotating wave approximation and rotating frame

The rotating wave approximation and the transformation to a suitable rotating frame, in which the Hamilton operator contains no time-dependent terms, are standard methods in quantum optics.

The rotation wave approximation consists in the elimination of doubly-rotating terms in the Hamiltonian $\hat{H}_{mf}$ in equation (2.3). For this purpose, one can transform this Hamiltonian to the interaction picture: $\hat{H}_I = \hat{U} \hat{H}_{mf} \hat{U}^\dagger$, using $\hat{U} = \exp(i\hat{H}_{m}t/\hbar)$ and the molecular Hamilton operator $\hat{H}_m$ from equation (2.5). This results in

$$\hat{H}_I = -\frac{1}{2} \vec{d}_{ge} \cdot \vec{E}_0 \begin{pmatrix} 0 & e^{-i\omega_{ge}t}(e^{i\omega t} + e^{-i\omega t}) \\ e^{i\omega_{ge}t}(e^{i\omega t} + e^{-i\omega t}) & 0 \end{pmatrix}. \quad (D.1)$$

Applying the rotating wave approximation leads to

$$\hat{H}_{I,RWA} = -\frac{1}{2} \vec{d}_{ge} \cdot \vec{E}_0 \begin{pmatrix} 0 & e^{-i(\omega_{ge}-\omega)t} \\ e^{i(\omega_{ge}-\omega)t} & 0 \end{pmatrix} \quad (D.2)$$

and

$$\hat{H}_{RWA} = \hat{U}^\dagger \hat{H}_{I,RWA} \hat{U} = \frac{1}{2} \hbar \Omega \begin{pmatrix} 0 & e^{i\omega t} \\ e^{-i\omega t} & 0 \end{pmatrix}, \quad (D.3)$$

back in the Schrödinger picture with $\hbar \Omega = -\vec{d}_{ge} \cdot \vec{E}_0$.

To eliminate the time-dependencies, one can transform the total Hamiltonian $\hat{H}_m + \hat{H}_{RWA}$ to a rotating frame using

$$\tilde{H} = \exp(-i\tilde{R})(\hat{H}_m + \hat{H}_{RWA}) \exp(i\tilde{R}) + \hbar \partial_t \tilde{R} \quad (D.4)$$

and

$$\tilde{R} = \frac{1}{2} \omega t \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}. \quad (D.5)$$
This transformation and an energy shift \((-\hbar/2(2\omega_g + \omega)\) on the diagonal) leads to the Hamilton operator of equation (2.6).

**D.2 Born-Oppenheimer approximation**

There is not a single molecule for which the rovibronic Schrödinger equation can be solved analytically [37]. For an analytical treatment one makes use of the fact that the motion of the electrons is a lot faster than the motion of the nuclei. On the timescale of the electronic motion, the nuclei are almost at rest; from the perspective of the nuclei the electrons move so fast that describing their motion via their average (orbital) density instead of their instantaneous positions is justified (BO approximation [260]). This approximation allows separation of the Schrödinger equation into the two independent problems of finding the electronic orbitals and then calculating the nuclear motion. Mathematically, the BO approximation implies that the rovibronic wave function can be separated into a product of electronic and nuclear wavefunctions:

\[
\Phi_{\text{rve}}(\vec{R}_N, \vec{r}_e) = \Phi_e(\vec{R}_N, \vec{r}_e)\Phi_N(\vec{R}_N),
\]

where the electronic wave function \(\Phi_e(\vec{R}_N, \vec{r}_e)\) depends only on the instantaneous positions, but not the motion of the nuclei. The rovibronic Schrödinger equation can then be simplified as follows:

\[
[\hat{T}_e + \hat{T}_N + V(\vec{R}_N, \vec{r}_e) - E_{\text{rve}}]\Phi_{\text{rve}}(\vec{R}_N, \vec{r}_e) \approx [\hat{T}_e^0 + \hat{T}_N + V_{\text{nn}}(\vec{R}_N) + (V(\vec{R}_N, \vec{r}_e) - V_{\text{nn}}(\vec{R}_N)) - E_{\text{rve}}^0] \Phi_e(\vec{R}_N, \vec{r}_e)\Phi_N(\vec{R}_N),
\]

where the (fast) electron dynamics are assumed to fulfill the equation

\[
(\hat{T}_e + V(\vec{R}_N, \vec{r}_e) - V_{\text{nn}}(\vec{R}_N))\Phi_e(\vec{R}_N, \vec{r}_e) = V_e(\vec{R}_N)\Phi_e(\vec{R}_N, \vec{r}_e),
\]

with the internuclear potential

\[
V_{\text{nn}}(\vec{R}_N) = \sum_{\alpha<\alpha'} \frac{C_{\alpha}C_{\alpha'}e^2}{4\pi\varepsilon_0 R_{\alpha\alpha'}},
\]

where \(\alpha\) and \(\alpha'\) run over the indices of the nuclei [37]. In the step from equation (D.6) to (D.7) it is additionally assumed that the (small) term \(\hat{T}_e^0\) can be ignored. \(E_{\text{rve}}^0\) is the rovibronic energy of the molecule in the BO approximation. Equation (D.8) shows how the energy of the electronic state contributes to the potential energy landscape of the nuclear motion. The
equilibrium positions of the nuclei are thus a consequence of the repulsion between the nuclei and the effect of the electrons. Different electronic states are associated with different energy terms $V_e(\vec{R}_N)$ and will consequently lead to different equilibrium positions of the nuclei and a different set of normal modes.

Once the electronic wave function $\Phi_e$ and the energies $V_e(\vec{R}_N)$ have been determined, we are left with the rotation-vibration Schrödinger equation for the motion of the nuclei [37]:

$$[\hat{T}_N + V_N(\vec{R}_N)]\Phi_N(\vec{R}_N) = E_{\text{rve}}^0 \Phi_N(\vec{R}_N),$$

with $V_N = V_{nn} + V_e$.

### D.3 Recursion formula for multi-dimensional FC factors

Barone et al. [87] describe the recursion formulas used by the analysis script in Gaussian 16 to obtain the FC factors of vibronic transitions. Their approach is based on a paper by Ruhoff et al. [111]. For a transition starting in the vibrational ground state $|\vec{0}'\rangle$ and ending in the state $|\vec{v}\rangle = |(v_1, v_2, ..., v_i, ..., v_{N_{\text{vib}}})\rangle$,

$$|\vec{v}\rangle = |(v_1, v_2, ..., v_i, ..., v_{N_{\text{vib}}})\rangle,$$

the recursion relation requires the overlap integrals

$$\langle \vec{0}' | \vec{v} - 1_i \rangle = \langle \vec{0}' | (v_1, v_2, ..., v_i - 1, ..., v_{N_{\text{vib}}}) \rangle,$$

$$\langle \vec{0}' | \vec{v} - 2_i \rangle = \langle \vec{0}' | (v_1, v_2, ..., v_i - 2, ..., v_{N_{\text{vib}}}) \rangle,$$

and

$$\langle \vec{0}' | \vec{v} - 1_i - 1_j \rangle = \langle \vec{0}' | (v_1, v_2, ..., v_i - 1, ..., v_j - 1, ..., v_{N_{\text{vib}}}) \rangle$$

to be known. Based on these, one can calculate the overlap

$$I(\vec{0}', \vec{v}) = \frac{1}{\sqrt{2v_i}} [D_i \langle \vec{0}' | \vec{v} - 1_i \rangle \sqrt{2(v_i - 1)}C_{ii}(\vec{0}' | \vec{v} - 2_i)$$

$$+ \sum_{j \neq i}^{N_{\text{vib}}} \sqrt{2v_j} C_{ij}(\vec{0}' | \vec{v} - 1_i - 1_j) ].$$

In this formula, the $C_{ij}$ refer to the entries of the matrix

$$C = 2\bar{\Gamma}^{1/2}(J^T \Gamma^0 J + \bar{\Gamma})^{-1}\bar{\Gamma}^{1/2} - I$$

(D.17)
and \( D_i \) to the entries of the vector

\[
\vec{D} = -2 \tilde{\Gamma}^{1/2}(J^T \tilde{\Gamma} J + \tilde{\Gamma})^{-1} J^T \tilde{\Gamma} \vec{K},
\]

(D.18)

with the Duschinsky matrix \( J \) and shift vector \( \vec{K} \) defined in equation (3.42) and the matrix of reduced frequencies \( \tilde{\Gamma}_{ii} = \omega_i / \hbar \). Following equation (D.16), the formula for the FC overlap integrals of the fundamentals \(|1_i\rangle\) is given by the relation:

\[
I(\vec{0}', 1_i) = \langle \vec{0}'|1_i \rangle = \frac{D_i}{\sqrt{2}} I(\vec{0}', \vec{0}).
\]

(D.19)

The FC overlap between the vibrational ground states \( I(\vec{0}', \vec{0}) \) can be calculated using equation (3.43). Based on these overlap integrals, the overlap integrals for the first overtones \(|2_i\rangle\) (see equation (3.23)) can be calculated via

\[
I(\vec{0}', 2_i) = \langle \vec{0}'|2_i \rangle = \frac{D_i}{2} I(\vec{0}', 1_i) + \frac{C_{ii}}{\sqrt{2}} I(\vec{0}', \vec{0}).
\]

(D.20)

Overlap integrals with modes that combine two fundamental excitations,

\[|1_i + 1_j\rangle = |(0, 0, ..., v_i = 1, ..., v_j = 1, ..., 0)\rangle\]

(D.21)

follow from

\[
I(\vec{0}', 1_i + 1_j) = \langle \vec{0}'|1_i + 1_j \rangle = \frac{D_i}{\sqrt{2}} I(\vec{0}', 1_j) + C_{ij} I(\vec{0}', \vec{0}).
\]

(D.22)

### D.4 Vibrational relaxation cascade

By summing equation (4.2) in the steady-state condition over all vibrational states, we obtain:

\[
0 = \sum_{j=1}^{V_{tot}} \Gamma_{e\tilde{v}_j} N_e + \sum_{j=1}^{V_{tot}} \left( \sum_{k=j+1}^{V_{tot}} \Gamma_{\tilde{v}_k\tilde{v}_j} N_{\tilde{v}_k} \right) - \sum_{j=1}^{V_{tot}} \Gamma_{\tilde{v}_j} N_{\tilde{v}_j}
\]

\[= \Gamma_{e\tilde{v}_j} N_e + \sum_{j=1}^{V_{tot}} \left( \sum_{k=j}^{V_{tot}} \Gamma_{\tilde{v}_k\tilde{v}_j} N_{\tilde{v}_k} \right) - \sum_{j=1}^{V_{tot}} \left( \sum_{k=1}^{j-1} \Gamma_{\tilde{v}_j\tilde{v}_k} + \sum_{k=1}^{j-1} \Gamma_{\tilde{v}_j\tilde{v}_k} N_{\tilde{v}_j} \right)
\]

\[
0 = \Gamma_{e\tilde{v}_j} N_e + \sum_{j=1}^{V_{tot}} \left( \sum_{k=j+1}^{V_{tot}} \Gamma_{\tilde{v}_k\tilde{v}_j} N_{\tilde{v}_k} \right) - \sum_{j=1}^{V_{tot}} \Gamma_{\tilde{v}_j} N_{\tilde{v}_j} - \sum_{j=1}^{V_{tot}} \sum_{k=1}^{j-1} \Gamma_{\tilde{v}_j\tilde{v}_k} N_{\tilde{v}_j}
\]

\[= \Gamma_{e\tilde{v}_j} N_e - \Gamma_{\tilde{v}_j} N_{\tilde{v}_j}.
\]

(D.26)
The two double-sum terms in equation (D.25) cancel out. This can be demonstrated by defining $\Gamma_{\vec{v}_j \vec{v}_k} = 0$ if $j \leq k$. Using this definition one can write:

$$
\sum_{j=1}^{V_{\text{tot}}} \left( \sum_{k=j+1}^{V_{\text{tot}}} \Gamma_{\vec{v}_k \vec{v}_j} N_{\vec{v}_k} \right) - \sum_{j=1}^{V_{\text{tot}}} \sum_{k=1}^{j-1} \Gamma_{\vec{v}_j \vec{v}_k} N_{\vec{v}_j} = 0.
$$

(D.27)

D.5 Bunching behavior under vibronic excitation

The model of Bernard et al. [179] describes the mono-exponential bunching behavior of the autocorrelation function of a molecule that is excited via its 00-ZPL. Under the assumption of a three-level system ($|g\rangle$, $|t\rangle$ and $|e\rangle$) with low ISC rates, the authors derive the formulas

$$
\lambda = \Gamma_{tg} + \Gamma_{et} \frac{1}{2} \frac{S}{1 + S} 
$$

(D.28)

$$
C = \frac{\Gamma_{et}}{\Gamma_{tg}} \frac{1}{2} \frac{S}{1 + S}. 
$$

(D.29)

with the saturation parameter $S = 2\Omega^2/\Gamma_e^2$ of a two-level system. These formulas cannot be applied directly to the ISC rate measurements in section 4.1.4, because we excited the molecule via a vibronic state. Since the factors $1/2$ in equations (D.28) and (D.29) are related to the maximum excited state population in a two-level system, we expect to obtain an equation that is valid under vibronic excitation by replacing $1/2 \rightarrow 1$. Additionally, we replace $S \rightarrow S_p$ with $S_p$ as defined in equation (4.11) to account for the change in required excitation power as a vibronic level is addressed. Based on these considerations, we assume that the saturation behavior of the bunching peak amplitude recorded in our experiments can be approximated by

$$
\lambda = \Gamma_{tg} + \Gamma_{et} \frac{S_p}{1 + S_p} 
$$

(D.30)

$$
C = \frac{\Gamma_{et}}{\Gamma_{tg}} \frac{S_p}{1 + S_p}. 
$$

(D.31)

Figure D.1(b) shows the bunching behavior of a molecule that is pumped via a vibronic level and via the oo-ZPL as obtained from QuTiP simulations (see Figure D.1(a) for the corresponding level scheme). These simulations
show that pumping a molecule via a vibronic level leads to stronger bunching amplitudes. In Figure D.1(c,d), we compare the results from fits of the function (4.22) to the simulated data. The close agreement justifies the assumption that $C_\infty = \Gamma_{et}/\Gamma_{tg}$ in section 4.1.4.

The parameters of the QuTiP simulations for Figure D.1 were chosen similar to the ones of DBT:pDCB, but assuming no population in the vibrational cascade. We used the Hamiltonian $\hat{H} = \Omega_i/2(\sigma_{gi} + \sigma_{gi}^\dagger)$ with $i = e$ or $i = w$ depending on which level was pumped. Spontaneous decay was modeled using Lindblad jump operators with associated decay rates: $\Gamma_{we} = 10 \cdot (2\pi) \cdot 10^9 1/s$, $\Gamma_{et} = 0.5 \cdot 10^3 1/s$, $\Gamma_{tg} = 150 \cdot 10^3 1/s$, $\Gamma_{ec} = 0$, $\Gamma_{eg} = 1/150 ps$ $\Gamma_{et} = 1/(7 \text{ ns}) - \Gamma_{et} - \Gamma_{ec}$. Setting $\Gamma_{ec} = 0.7 \cdot 1/(7 \text{ ns})$ to include the vibrational levels of the electronic ground state in the simulation reduces the value of $C_\infty$ by less than 2%.

### D.6 Lindblad master equation for fluorescence excitation

In analogy to the optical Bloch equations for a two-level system (see section 2.5), one can use the Lindblad master equation (2.3) to describe the excitation of a vibronic transition by a laser and the associated distribution of population in the level scheme shown in Figure 4.1(b). The pump rate $W_p$ is assumed to be induced by an electrical field $\vec{E}(t) = \vec{E}_p \cos(\omega_p t)$ at the position of the
molecule that oscillates at a similar frequency as the resonance frequency of the transition $|g⟩ \leftrightarrow |w⟩$ (i.e. $\omega_p \approx \omega_{gw} = \omega_w - \omega_g$).

In the following, we apply the steps described for a two-level system in section 2.5 and appendix D.1 to the level scheme displayed in Figure 4.1(b). In the basis $I = \{|g⟩, |c⟩, |t⟩, |e⟩, |w⟩ \}$, the Hamiltonian of the molecule can be written as

$$
\hat{H}_m = \begin{pmatrix}
\hbar \omega_g & 0 & 0 & 0 & 0 \\
0 & \hbar \omega_c & 0 & 0 & 0 \\
0 & 0 & \hbar \omega_t & 0 & 0 \\
0 & 0 & 0 & \hbar \omega_e & 0 \\
0 & 0 & 0 & 0 & \hbar \omega_w
\end{pmatrix}.
$$

(D.32)

The dipole operator of the model shown in Figure 4.1(b) can be approximated by

$$
\hat{d} = \sum_{i,j \in I} |i⟩⟨i| \hat{\vec{d}}|j⟩⟨j| = \begin{pmatrix}
0 & 0 & 0 & \tilde{d}_{ge} & \tilde{d}_{gw} \\
0 & 0 & 0 & \tilde{d}_{ce} & \tilde{d}_{vw} \\
0 & 0 & 0 & 0 & 0 \\
0 & 0 & \tilde{d}_{ge} & \tilde{d}_{ce} & 0 & 0 \\
\tilde{d}_{gw} & \tilde{d}_{vw} & 0 & 0 & 0
\end{pmatrix},
$$

(D.33)

where we assume that the transition dipole elements between the triplet state and the singlet state can be neglected and that the vibronic modes are not infrared active. We apply the rotating-wave approximation by transforming $\hat{H}_{mf} = -\hat{\vec{d}} \cdot \hat{\vec{E}}$ to the interaction picture using $\hat{H}_I = \hat{U} \hat{H}_{mf} \hat{U}^\dagger$ with $\hat{U} = e^{i\hat{H}_m t/\hbar}$.

Keeping only those (slowly varying) terms that include the frequency difference $\omega_p - \omega_{gw}$ in the interaction picture, and transforming the result back to the Schrödinger picture yields

$$
\hat{H}_{RWA} = \frac{\hbar}{2} \begin{pmatrix}
0 & 0 & 0 & 0 & \Omega_p e^{i \omega_p t} \\
0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0
\end{pmatrix},
$$

(D.34)

with the Rabi frequency $\Omega_p = -\tilde{d}_{gw} \cdot \hat{\vec{E}}_p/\hbar$ of the (pump) laser.
Using the operator $\hat{R} = \omega_p t/2(|g⟩⟨g| − |w⟩⟨w|)$ and equation (D.4), one can transform the Hamiltonian $\hat{H}_m + \hat{H}_{\text{RWA}}$ to a rotating frame without explicit time-dependence. Subtracting $\hbar/2(2\omega_g + \omega_p)$ from the diagonal of the resulting Hamiltonian in the rotating frame yields the final Hamiltonian:

$$\hat{H} = \frac{\omega_g - \omega_p/2}{ω_g - \omega_p/2} 0 0 0 0 \Omega_p/2$$

with detuning $\Delta_p = \omega_p - \omega_{gw}$.

Each decay process illustrated in Figure 4.1(b) corresponds to one Lindblad jump operator $\hat{L}_i$ of the system. Plugging the jump operators, the corresponding decay rates, and the Hamiltonian in equation (D.35) into the Lindblad master equation (2.3) leads to the following equations of motion for the relevant elements of the molecular density matrix:

$$\partial_t \rho_{gg} = -i\Omega_p/2(\rho_{wg} - \rho_{gw}) + \Gamma_{eg}\rho_{ee} + \Gamma_{tg}\rho_{tt} + \Gamma_{cg}\rho_{cc}$$

$$\partial_t \rho_{cc} = \Gamma_{ec}\rho_{ee} - \Gamma_{cg}\rho_{cc}$$

$$\partial_t \rho_{tt} = \Gamma_{et}\rho_{ee} - \Gamma_{tg}\rho_{tt}$$

$$\partial_t \rho_{ee} = \Gamma_{we}\rho_{ww} - \Gamma_{ee}\rho_{ee}$$

$$\partial_t \rho_{ww} = i\Omega_p/2(\rho_{wg} - \rho_{gw}) - \Gamma_{we}\rho_{ww}$$

$$\partial_t \rho_{gw} = -i\Omega_p/2(\rho_{ww} - \rho_{gg}) - \rho_{gw}(i\Delta_p + \Gamma_{we}/2)$$

$$1 = \rho_{gg} + \rho_{cc} + \rho_{tt} + \rho_{ee} + \rho_{ww}.$$  

In the steady-state, one can eliminate the coherences $\rho_{gw}$ from these equations and write equations (D.36) and (D.40) as

$$0 = W_p(\rho_{ww} - \rho_{gg}) + \Gamma_{eg}\rho_{ee} + \Gamma_{tg}\rho_{tt} + \Gamma_{cg}\rho_{cc}$$

and

$$0 = W_p(\rho_{gg} - \rho_{ww}) - \Gamma_{we}\rho_{ww},$$

respectively, with the laser-induced pump rate $W_p$ defined in equation (4.25). The system of equations (D.37)–(D.39) and (D.42)–(D.44) is analogous to the rate equations (4.9) if one identifies $\rho_{ii} \rightarrow N_i$. 

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In the following, we present several steps of a Lindblad master equation treatment of the STED spectroscopy scheme displayed in Figure 4.6(a). These steps are similar to the ones described in the context of a two-level system (see section 2.5 and appendix D.1) and of fluorescence excitation spectroscopy (see appendix D.6). We assume that the electric field at the position of the molecule can be written as \( \vec{E}(t) = \vec{E}_p \cos(\omega_p t) + \vec{E}_d \cos(\omega_d t) \) with \( |\omega_p - \omega_{we}|/\Gamma_{we} \sim 1 \) and \( |\omega_d - \omega_{ve}|/\Gamma_{we} \sim 1 \) while \( |\omega_p - \omega_d|/\Gamma_{we} \gg 1 \).

In the basis \( I = \{|g\}, |v\}, |e\}, |w\} \), the Hamiltonian of the molecule can be written as

\[
\hat{H}_m = \begin{pmatrix}
\hbar \omega_g & 0 & 0 & 0 \\
0 & \hbar \omega_v & 0 & 0 \\
0 & 0 & \hbar \omega_e & 0 \\
0 & 0 & 0 & \hbar \omega_w
\end{pmatrix}.
\] (D.45)

Under the assumption that \( |v\)\) is not infrared active, one can write the dipole operator of the model shown in Figure 4.6(a) as

\[
\hat{d} = \begin{pmatrix}
0 & 0 & \hat{d}_{ge} & \hat{d}_{gw} \\
0 & 0 & \hat{d}_{ve} & \hat{d}_{vw} \\
\hat{d}^{\dagger}_{ge} & \hat{d}^{\dagger}_{ve} & 0 & 0 \\
\hat{d}^{\dagger}_{gw} & \hat{d}^{\dagger}_{vw} & 0 & 0
\end{pmatrix}.
\] (D.46)

We apply the rotating-wave approximation by only keeping the terms that oscillate at \( \omega_p - \omega_{gw} \) and \( \omega_d - \omega_{ge} \) in the interaction picture (analogous to the steps in the appendices D.1 and D.6). The part of the Hamiltonian describing the interaction of the molecule with light (\( \hat{H}_{mf} \)) can be expressed as

\[
\hat{H}_{RWA} = \frac{\hbar}{2} \begin{pmatrix}
0 & 0 & 0 & \Omega_p e^{i\omega_p t} \\
0 & 0 & \Omega_d e^{i\omega_d t} & 0 \\
0 & \Omega_d e^{-i\omega_d t} & 0 & 0 \\
\Omega_p e^{-i\omega_p t} & 0 & 0 & 0
\end{pmatrix}
\] (D.47)

in the Schrödinger picture, with the Rabi frequencies \( \Omega_p = -\hat{d}_{gw} \cdot \vec{E}_p / \hbar \) and \( \Omega_d = -\hat{d}_{ve} \cdot \vec{E}_d / \hbar \) of the pump and depletion laser, respectively.
To transform the Hamiltonian $\hat{H}_m + \hat{H}_{\text{RWA}}$ to a rotating frame without time-dependent terms, we use equation (D.4) and the operator

$$\hat{R} = \frac{1}{2} \left( \omega_p t (|g\rangle\langle g| - |w\rangle\langle w|) + \omega_d t (|v\rangle\langle v| - |e\rangle\langle e|) \right).$$

(D.48)

Adding $\hbar/2 (2\omega_g + \omega_p)$ to the diagonal of the resulting Hamiltonian in the rotating frame yields the Hamiltonian

$$\hat{\tilde{H}} = \hbar \begin{pmatrix} 0 & 0 & 0 & \Omega_p/2 \\ 0 & (2\omega_{vg} + \omega_d - \omega_p)/2 & \Omega_d/2 & 0 \\ 0 & \Omega_d/2 & (2\omega_{we} - \omega_d - \omega_p)/2 & 0 \\ \Omega_p/2 & 0 & 0 & -\Delta_p \end{pmatrix}$$

(D.49)

with detuning $\Delta_p = \omega_p - \omega_{gw}$.

Using the Hamilton operator (D.49) and the Lindblad decay terms corresponding to the decay processes indicated in the level scheme in Figure 4.6(a) yields the following equations of motion of the density matrix elements:

$$\partial_t \rho_{gg} = -i \Omega_p/2 (\tilde{\rho}_{wg} - \tilde{\rho}_{gw}) + \Gamma_e \rho_{ee} + \Gamma_{vg} \rho_{vv}$$

(D.50)

$$\partial_t \rho_{vv} = -i \Omega_d/2 (\tilde{\rho}_{ev} - \tilde{\rho}_{ve}) - \Gamma_{vg} \rho_{vv}$$

(D.51)

$$\partial_t \rho_{ee} = i \Omega_d/2 (\tilde{\rho}_{ev} - \tilde{\rho}_{ve}) + \Gamma_{we} \rho_{ww} - \Gamma_e \rho_{ee}$$

(D.52)

$$\partial_t \rho_{ww} = i \Omega_p/2 (\tilde{\rho}_{wg} - \tilde{\rho}_{gw}) - \Gamma_{we} \rho_{ww}$$

(D.53)

$$\partial_t \tilde{\rho}_{gw} = -i \Omega_p/2 (\rho_{ww} - \rho_{gg}) - \tilde{\rho}_{gw} (i\Delta_p + \Gamma_{we}/2)$$

(D.54)

$$\partial_t \tilde{\rho}_{ve} = -i \Omega_d/2 (\rho_{ee} - \rho_{vv}) - \tilde{\rho}_{ve} (i\Delta_d + (\Gamma_e + \Gamma_{vg})/2)$$

(D.55)

$$1 = \rho_{gg} + \rho_{vv} + \rho_{ee} + \rho_{ww},$$

(D.56)

with detuning of the depletion laser $\Delta_d = \omega_d - \omega_{ve}$.

In the steady-state, we can relate the depletion Rabi frequency to an effective depletion rate by eliminating the coherences:

$$W_d = \frac{\Omega_d^2 (\Gamma_e + \Gamma_{vg})}{4(\Delta_d^2 + (\Gamma_e + \Gamma_{vg})^2 / 4)}.$$  

(D.57)

The pump Rabi frequency can be expressed via the pump rate $W_p$ defined in equation (4.25). The system of equations (D.50)–(D.53), (D.42), (D.57), and (4.25) is analogous to the rate equations (4.36) if one identifies $\rho_{ii} \rightarrow N_i$. 

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D.8 STED spectroscopy of overlapping vibronic dips

The model presented in section 4.3.2 only works for a single, isolated vibronic transition and does not take into account additional transitions at similar laser frequencies and spectrally broad ‘baseline’ depletion that we observe in our data (see section 6.2.2). To account for these effects in a model that can be fitted to the data, we introduce a more general model in the current section.

In Figure D.2(a), we show the level scheme of a molecule that is pumped via a vibronic state $|w\rangle$ and has two defined vibronic states $|v\rangle = |S_0, \vec{v}_v\rangle$ and $|u\rangle = |S_0, \vec{v}_u\rangle$ in $S_0$ that are simultaneously addressed by the (single) depletion laser. Additionally, there is a spectrally flat ‘level’ $|G\rangle$ that represents depletion via weak additional channels. We assume that $|G\rangle$ relaxes at the same rate as $|v\rangle$, i.e. $\Gamma_{gg} = \Gamma_{vg}$. The laser detuning is defined with respect to the state $|v\rangle$, i.e. $\Delta_d = \omega_d - \omega_{gv}$. As such, the depletion rates $W_{di}$ from $|e\rangle$ to the the states $|i\rangle$ are given by:

$$W_{d,v}(\Delta_d) = \frac{\Omega_d^2(\Gamma_{vg} + \Gamma_{eg})}{4(\Delta_d^2 + (\Gamma_{vg} + \Gamma_{eg})^2/4)}$$  \hspace{1cm} (D.58)

$$W_{d,u}(\Delta_d) = \frac{\beta_u^2\Omega_d^2(\Gamma_{ug} + \Gamma_{eg})}{4(\left((\Delta_d - \delta_{gu,gv})^2 + (\Gamma_{ug} + \Gamma_{eg})^2/4)$$ \hspace{1cm} (D.59)

$$W_{d,G}(\Delta_d) = \frac{\beta_G^2\Omega_d^2}{\Gamma_{GG} + \Gamma_{eg}}$$ \hspace{1cm} (D.60)

---

Figure D.2: Depletion of the population in $|e\rangle$ via simultaneous resonance of the depletion laser with several vibronic states in $S_0$. (a) Level scheme used to describe the simultaneous depletion of $|e\rangle$ via two vibronic states $|v\rangle$ and $|u\rangle$ as well as a spectrally flat feature $|G\rangle$. (b) Population of $|e\rangle$ for a (squared) pump Rabi frequency $\Omega_p^2 = \Gamma_{eg}\Gamma_{we}$ and various values of the depletion Rabi frequency. (c) Saturation behavior of the depletion of $|e\rangle$ at the three detunings of the depletion laser indicated in (b). Black lines are fits of the function $D_{\text{max}} \cdot \Omega_d^2/c/(1 + \Omega_d^2/c)$ to the data.
Various formulas and calculations

with \( \delta_{g_u,g_v} = \omega_{g_u} - \omega_{g_v} \), the difference between the vibrational frequencies of the states \(|v\rangle\) and \(|u\rangle\). The factors \( \beta_u \) and \( \beta_G \) describe the FC overlaps of the levels \(|u\rangle\) and \(|G\rangle\) with the level \(|e\rangle\) relative to the FC overlap \( \langle v|e \rangle \).

We use rate equations analogous to the set of equations (4.36) but adapted to the level scheme shown in Figure D.2(a) to describe the steady-state distribution of population in this model. These rate equations are given by:

\[
\begin{pmatrix}
N_g \\
N_v \\
N_u \\
N_G \\
N_e \\
N_w
\end{pmatrix} =
\begin{pmatrix}
0 & \Gamma_{vg} & \Gamma_{ug} & \Gamma_{Gg} & \Gamma_{eg} & 0 \\
0 & -\Gamma_{vg} & 0 & 0 & 0 & 0 \\
0 & 0 & -\Gamma_{ug} & 0 & 0 & 0 \\
0 & 0 & 0 & -\Gamma_{Gg} & 0 & 0 \\
0 & 0 & 0 & 0 & -\Gamma_{eg} & \Gamma_{we} \\
0 & 0 & 0 & 0 & 0 & -\Gamma_{we}
\end{pmatrix}
\begin{pmatrix}
N_g \\
N_v \\
N_u \\
N_G \\
N_e \\
N_w
\end{pmatrix}
\]

(D.61)

\[
+ \begin{pmatrix}
W_p(N_w - N_g) \\
W_{d,v}(N_e - N_v) \\
W_{d,u}(N_e - N_u) \\
W_{d,G}(N_e - N_G) \\
W_{d,v}(N_v - N_e) + W_{d,u}(N_u - N_e) + W_{d,G}(N_G - N_e) \\
W_p(N_g - N_w)
\end{pmatrix}
\]

and

\[
N_g + N_v + N_u + N_G + N_e + N_w = 1,
\]

(D.62)

with the depletion rates \( W_{d,i} \) as defined in equations (D.58)–(D.60). We ignore the spontaneous transitions from \(|e\rangle\) to the vibronic states of \( S_0 \) because they do not lead to appreciable accumulation of population in these states. To fit data sets containing more than two vibronic features one can add more vibrational states to \( S_0 \) in the same pattern. We then solved the corresponding set of rate equations analytically and fitted the result for the depletion of \(|e\rangle\) to the data.

The population \( N_e \) of the level \(|e\rangle\) is shown in Figure D.2(b) for a pump rate \( W_p = \Gamma_e \) at various values of the depletion Rabi frequency \( \Omega_d \). Increasing the depletion Rabi frequency leads to stronger stimulated emission. The parameters used for the plots in this figure are listed in Table 4.1 in the column \( M_{vu} \) and are chosen to resemble the data from Figure 6.12(a). Figure D.2(c)
shows the saturation behavior of the spectral profile at the three detunings indicated in Figure D.2(b).

Spectral profiles like the one shown in Figure D.2(a) cannot be described by a sum of several independent depletion processes as described by equation (4.38). Instead, all three depletion processes are coupled via the saturation of the molecule. This generally leads to non-Lorentzian profiles. The Lorentzian model only works if vibronic features do not overlap much and the saturation parameter is low. In this thesis, we fit STED spectra using rate equation models such as the one shown in D.2(a). Depending on the number of discernible vibronic features in the data, we adjust the number of levels in the model before fitting. We then fit the analytical solutions of the rate equations for the depletion factor \( \left( N_e(\Omega_d = 0) - N_e(\Delta p, \Omega_d \neq 0) \right) / N_e(\Omega_d = 0) \) to the depletion factor estimated from the data: \( \left( R(P_d = 0) - R(\Delta p, P_d \neq 0) \right) / R(P_d = 0) \). Sections 6.2.2 and 6.2.3 show examples of data from STED experiments together with fits of the rate equation model.

D.9 Seven-level model for vibronic line splitting

The derivation of the Hamilton operator of the seven-level model shown in Figure 7.3(a) follows the same steps as the derivation shown for the four-level model of section 4.4.2. In this section, we show some steps of the derivation.

We ignore several elements of the dipole operator because they are associated with transitions with low FC overlap or because no laser frequency is close to their resonance frequency. This leads to the following matrix of the transition dipole operator:

\[
\hat{d} = \sum_{i,j \in I} |i\rangle \langle i| \hat{d}|j\rangle \langle j| = \begin{pmatrix}
0 & 0 & 0 & \hat{d}_{ge} & \hat{d}_{gE} & \hat{d}_{gw} & \hat{d}_{gx} \\
0 & 0 & 0 & \hat{d}_{Ge} & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & \hat{d}_{vw} & 0 \\
\hat{d}_{ge} & \hat{d}_{Ge} & 0 & 0 & 0 & 0 & 0 \\
\hat{d}_{gE} & 0 & 0 & 0 & 0 & 0 & 0 \\
\hat{d}_{gw} & 0 & \hat{d}_{vw} & 0 & 0 & 0 & 0 \\
\hat{d}_{gx} & 0 & 0 & 0 & 0 & 0 & 0 
\end{pmatrix},
\] (D.63)

with \( I = \{ |g\rangle, |G\rangle, |v\rangle, |e\rangle, |E\rangle, |x\rangle, |w\rangle \} \).
The interaction Hamiltonian in the Schrödinger picture after application of the rotating wave approximation in the interaction picture reads

\[
\hat{H}_{\text{RWA}} = \frac{\hbar}{2} \begin{pmatrix}
0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 \\
\beta_g \Omega_p e^{-i\omega_c t} & \beta_G \Omega_c e^{-i\omega_c t} & 0 & 0 & 0 & 0 & 0 \\
\beta_E \Omega_p e^{-i\omega_p t} & 0 & 0 & 0 & 0 & 0 & 0 \\
\Omega_p e^{-i\omega_p t} & 0 & \Omega_c e^{-i\omega_c t} & 0 & 0 & 0 & 0 \\
\beta_x \Omega_p e^{-i\omega_p t} & 0 & 0 & 0 & 0 & 0 & 0 \\
\end{pmatrix} + \text{h.c.} \quad (D.64)
\]

with the Rabi frequencies \( \Omega_p = -\vec{d}_{gw} \cdot \vec{E}_p / \hbar, \beta_E \Omega_p = -\vec{d}_{E} \cdot \vec{E}_p / \hbar, \beta_x \Omega_p = -\vec{d}_{gx} \cdot \vec{E}_p / \hbar, \Omega_c = -\vec{d}_{vw} \cdot \vec{E}_c / \hbar, \beta_G \Omega_c = -\vec{d}_{Ge} \cdot \vec{E}_c / \hbar, \) and \( \beta_g \Omega_c = -\vec{d}_{ge} \cdot \vec{E}_c / \hbar \) as indicated in Figure 7.3(a).

To find a suitable rotation matrix for the transformation to a frame in which the time-dependencies disappear, we use the same method as in section 4.4.2. Here, we need to solve the six equations

\[
[\hat{R}, \hat{\sigma}_n^{x}] = i \omega_k t \hat{\sigma}_n^{y} 
\]

for all \((nn') \in S_k\) and \(k \in \{p, c\}\) where \(S_p = \{(gE), (gw), (gx)\}\) and \(S_c = \{(ge), (Ge), (vw)\}\) with the ansatz

\[
\hat{R} = \sum_{(nn') \in S_p \cup S_c} c_{nn'} \hat{\sigma}^{z}_{nn'} \quad (D.66)
\]

In the basis of the molecular states we then obtain:

\[
\hat{R} = \frac{1}{7} \begin{pmatrix}
4\omega_p t & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 4\omega_p t & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & (7\omega_c - 3\omega_p) t & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & (-7\omega_c + 4\omega_p) t & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & -3\omega_p t & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & -3\omega_p t & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & -3\omega_p t \\
\end{pmatrix} \quad (D.67)
\]

Using equation (4.66) and adjusting the zero of energy leads to the final Hamiltonian shown in section 7.2.
D.10 Background induced by the intense control laser

The data in Figure 7.5(a) result from background-correction and normalization via

$$\rho_{ee} = \frac{R - R_c}{R_\infty}. \quad (D.68)$$

The raw APD count rate $R$ used in this formula is shown in Figure D.3(a). Figure D.3(b) displays the APD count rate $R_c$ obtained in a configuration in which the probe laser was blocked and the control laser was tuned to the same frequency as for the measurements of Figure D.3(a). The APD count rate used for normalization was obtained from a saturation measurement in which the molecule was pumped via the vibronic transition at 291 cm$^{-1}$ and the alignment of the detection bandpass window was identical to that for the scans in Figure D.3(a).

The origin of the background rate $R_c$ is not clear to us. It might partly be due to red-shifted light created by the intense control laser in the optical fiber. This contribution is, however, expected to depend linearly on the power of the control laser. The super-linear behavior of $R_c$ suggests that additional processes are involved, for example two-photon absorption by the molecule or the matrix, or transitions from thermally activated phonon states in the PSB of $S_0$ to $|e\rangle$, excited by the control laser.

By calculating the excited state population via equation (D.68), we ignore the possible excitation processes of the molecule via the control laser. This
serves as a simplification to avoid the need to include further laser-induced processes in the seven-level model of section 7.2. Since we are close to the linear regime with $S_p \lesssim 1$ and $R_c < 0.1 \cdot R_\infty$, subtracting the result of an incoherent pump process from the data and neglecting this process in the model should be justified. To clarify the origin of $R_c$ in future experiments, the control laser-induced background could be measured with a spectrometer to determine how much of it is related to fluorescence of the molecule. Using detuning-dependent measurements of the control laser as in Figure 7.6(b) could additionally give insights into the range and magnitude of transitions involving thermally activated phonons.

### D.11 Overlap of fundamental excitations of vibrational modes

In this section, we estimate the overlap of the vibrational states $|1_v\rangle$ and $|1_w\rangle$ associated with the two vibronic states $|v\rangle = |S_0, 1_v\rangle$ and $|w\rangle = |S_1, 1_w\rangle$ using a calculation in the displaced harmonic oscillator approximation of non-mixing normal modes. This calculation shows that for molecules such as DBT with $\alpha_i \lesssim 0.4$, the FC overlap between equivalent normal modes is considerably higher than between different normal modes. We note, however, that while the non-mixing displaced harmonic oscillator approximation is useful to illustrate the qualitative behavior, it is not expected to yield accurate numerical values of the overlap integrals.

In the non-mixing displaced harmonic oscillator approximation, we obtain:

$$
\langle 1_v | 1_w \rangle = \begin{cases} 
(\langle \vec{0}|\vec{0} \rangle \cdot (1 - \alpha_v^2), & \text{for equivalent modes } (s(v) = w) \\
(\langle \vec{0}|\vec{0} \rangle \cdot \alpha_v \alpha_w, & \text{for different modes } (s(v) \neq w). 
\end{cases}
$$

(D.69)

With $\Omega_c = -\langle v | \hat{d} | w \rangle \cdot \vec{E}_c / \hbar = \Omega_{c,0} \langle 1_v | 1_w \rangle$, where $\Omega_{c,0} = -\langle S_0 | \hat{d} | S_1 \rangle \cdot \vec{E}_c / \hbar$, the ratio of the control laser Rabi frequencies under resonance between equivalent normal modes to resonance between different normal modes is given by the ratio of the corresponding FC overlaps:

$$
\frac{\Omega_c(s(v) = w)}{\Omega_c(s(v) \neq w)} = \frac{1 - \alpha_v^2}{\alpha_v \alpha_w}.
$$

(D.70)

Inserting a typical value of $\alpha_i = 0.2$ for both modes corresponds to a 24-fold higher Rabi frequency if the control laser is resonant between two equivalent modes. To achieve the same value of $\Omega_c$ for two modes with $s(v) \neq w$ would require raising the control laser power by a factor of $24^2$. 

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Based on saturation measurements of vibronic transitions, we can estimate the power required to induce control laser Rabi frequencies in the order of \( \Omega_c^2 \approx \Gamma_v \Gamma_w \), the value required to induce a prominent splitting dip in the vibronic line profile. Under the assumption of equal fields at the position of the molecule, i.e. \( \vec{E}_c = \vec{E}_p \) (where \( \vec{E}_p \) stands for the field used to pump a vibronic state), we can relate \( \Omega_c \) to the power \( P_p \) required to excite a vibronic transition:

\[
\Omega_c^2 = \frac{|\langle 1 | 1 \rangle|^2}{|\langle 0 | 1 \rangle|^2} \Omega_p^2 \approx \frac{(1 - \alpha_w^2)^2}{\alpha_v^2} \Gamma_{eg} \Gamma_{we} S_p, \tag{D.71}
\]

and thus

\[
\frac{\Omega_c^2}{\Gamma_v \Gamma_w} \approx \frac{(1 - \alpha_w^2)^2}{\alpha_v^2} \frac{\Gamma_{eg}}{\Gamma_{vg}} \frac{P_p}{P_{sat}}. \tag{D.72}
\]

According to this calculation, the laser power required to induce splitting in a scheme with \( \alpha_w = 0.1 \), \( \Gamma_{eg}/(2\pi) = 23 \text{MHz} \), \( \Gamma_{vg}/(2\pi) = 13.5 \text{GHz} \), \( P_{sat} = 360 \mu\text{W} \) (see Figure 7.1 and section 7.1) to reach \( \Omega_c^2/(\Gamma_v \Gamma_w) = 1 \) is \( P_p \approx 2.2 \text{mW} \). This value agrees closely with our experimental observations shown in Figure 7.5. The value \( \alpha_w = 0.1 \) (for the mode used in the splitting experiments) results from our estimation that \( \alpha_{17} \approx 0.3 \) (see section 6.2.3) and the observation that the Franck-Condon factor of mode 17 is approximately five times larger than the FC factor of the mode around 400 cm\(^{-1}\) (see Figure 6.23(a)).
E Peer-reviewed publications

The following peer-reviewed articles were published in the context of this thesis:


This study is reprinted below but not discussed in the thesis.
Partial Cloaking of a Gold Particle by a Single Molecule

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Extinction of light by material particles stems from losses incurred by absorption or scattering. The extinction cross section is usually treated as an additive quantity, leading to the exponential laws that govern the macroscopic attenuation of light. In this Letter, we demonstrate that the extinction cross section of a large gold nanoparticle can be substantially reduced—i.e., the particle becomes more transparent—if a single molecule is placed in its near field. This partial cloaking effect results from a coherent plasmonic interaction between the molecule and the nanoparticle, whereby each of them acts as a nanoantenna to modify the radiative properties of the other.

Macroscopic objects cast a shadow in a beam of light, and the shadow becomes darker if the medium is made optically thicker. This scenario also persists in the nanoscopic domain when the object is smaller than the wavelength of light. For instance, a gold nanoparticle (GNP) of diameter less than 100 nm can extinguish more than half the power of a laser beam if placed in its focus [1,2]. According to the Beer-Lambert law, this shadow becomes exponentially darker as more particles are added [3]. However, it turns out that one can make a GNP transparent to light by adding a single atom [4–6]. The underlying mechanism of this intriguing phenomenon is the interference between the fields scattered by two near-field coupled oscillators [6–9]. Here, it is helpful to recall that the cross section of a two-level atom with transition at wavelength λ can be as large as σ0 = 3λ2/2π [10], which can be comparable to the extinction cross section and the physical size of a nanoparticle [3]. In other words, although both an atom and a GNP can individually extinguish a laser beam, their composite entity becomes transparent due to a coherent interference effect [6].

Over the past fifteen years, plasmonic platforms have been employed in a wide range of studies [11,12]. One of the main thrusts of these works has been in the incoherent enhancement of excitation or fluorescence rates, where a metallic nanostructure acts as an optical antenna for ameliorating the efficiency of interaction between the emitter and propagating photonic modes [12]. Coupling of plasmonic nanoparticles to emitters has also been theoretically proposed for enhancing light absorption or transmission [4–6,13,14]. Furthermore, there have been the first reports of coherent plasmonic interactions, reaching the strong coupling regime of cavity quantum electrodynamics (CQED) [15–20]. The degree of coherence achieved in these experiments, however, has been very limited because they were performed at room temperature. Recent impressive experiments at cryogenic temperatures have not reached the intrinsic degree of coherence given by the radiative lifetime of the excited state either [21].

Several factors make a laboratory demonstration of plasmonic interactions with long coherence times challenging. First, an emitter and a GNP would have to be placed at separations much smaller than a wavelength. Second, the orientation of the emitter dipole moment has to suit the geometrical features of the nanostructure. Despite decades of nanotechnology experience, these challenges are still not easy to tackle. Third, σ0 is lowered and the homogeneous spectra are broadened by about five orders of magnitude for solid-state emitters at room temperature. In this Letter, we use dye molecules at a temperature of T = 1.5 K to essentially reach their natural linewidth limit [22]. We discuss how we overcome various experimental difficulties to achieve a successful realization of emitter-induced transparency of a GNP, analogous to its CQED equivalent using cavities [23,24], and validate our measurements using a theoretical model.

Figure 1(a) illustrates the schematics of the core of our experimental arrangement, where a laser beam is tightly
focused onto a sample carrying GNPs and dibenzoterrylene (DBT) molecules. These are placed inside a channel of width 250 nm and depth 245 nm fabricated in a glass chip (see text for details). SIL: solid-immersion lens, GNP: gold nanoparticle. Arrows at the bottom show the translational degrees of freedom. (b) Scanning electron microscope image of the GNP array. Inset: enlargement of a single GNP. (c) Optical transmission image of two GNPs at $\lambda = 740$ nm. Upper panel shows a normalized cross section along the dashed line. (d) Fluorescence spectrum of DBT recorded upon excitation via transition from $|g, v = 0\rangle$ to $|e, v \neq 0\rangle$. The strong emission line at $\lambda = 740.3$ nm represents the 00ZPL. Inset: molecular structure and Jablonski diagram of DBT. (e) Plasmon resonance of a GNP measured in transmission (dots) fitted by a Lorentzian profile (black curve). (f) Predicted reduction of the GNP extinction at the resonance of a single molecule that is coupled to it in the near field.

FIG. 1. (a) Schematics of the experimental arrangement. The sample consists of DBT molecules in a pDCB crystal surrounding an array of gold nanoparticles prepared in a nanochannel (see text for details). SIL: solid-immersion lens, GNP: gold nanoparticle. Arrows at the bottom show the translational degrees of freedom. (b) Scanning electron microscope image of the GNP array. Inset: enlargement of a single GNP. (c) Optical transmission image of two GNPs at $\lambda = 740$ nm. Upper panel shows a normalized cross section along the dashed line. (d) Fluorescence spectrum of DBT recorded upon excitation via transition from $|g, v = 0\rangle$ to $|e, v \neq 0\rangle$. The strong emission line at $\lambda = 740.3$ nm represents the 00ZPL. Inset: molecular structure and Jablonski diagram of DBT. (e) Plasmon resonance of a GNP measured in transmission (dots) fitted by a Lorentzian profile (black curve). (f) Predicted reduction of the GNP extinction at the resonance of a single molecule that is coupled to it in the near field.

and the gold to avoid strong quenching. The sample is then placed in a cryostat and cooled to $T = 1.5$ K.

A beam from a Ti:sapphire laser is coupled to the sample via an aspheric lens and the SIL, reaching a focus spot with a full width at half-maximum (FWHM) of 270 nm assessed by mapping the fluorescence of a single molecule. A second aspheric lens is used to recollimate the laser beam in transmission. Figure 1(c) displays a transmission image recorded by scanning the focus of the incident laser beam across two GNPs. A cut through the image (see upper panel) reveals an extinction dip of about 50% from each GNP. In Fig. 1(e), we plot the extinction plasmon spectrum of a single GNP (see the Supplemental Material [25]).

The inset in Fig. 1(d) displays the structure of DBT and its Jablonski diagram. DBT is a member of the polycyclic aromatic hydrocarbon family and possess a strong zero-phonon line (00ZPL) between $|g, v = 0\rangle$ (ground electronic and vibrational state) and $|e, v = 0\rangle$ (ground vibrational and electronic excited state) when placed in an appropriate crystal. Figure 1(d) presents the emission spectrum of a single DBT molecule upon excitation to a $|e, v \neq 0\rangle$ state, followed by a fast nonradiative decay to $|e, v = 0\rangle$ with a radiative lifetime of a few nanoseconds. The spectrum shows that a large fraction of the decay from $|e, v = 0\rangle$ takes place via the 00ZPL, leading to a branching ratio of about 44% [36].

In our sample, DBT molecules are stochastically distributed in the pDCB matrix, but we can identify and interrogate each molecule individually with very high spatial and spectral resolution. Here, we first scan the wavelength of the narrow-band laser across the inhomogeneous band of DBT:pDCB around $\lambda = 740$ nm [35,36]. The exquisitely narrow 00ZPL resonances (20–40 MHz) associated with the molecules do not overlap so that each can be selectively addressed by tuning the laser frequency. The spectral selection of a single molecule also allows us to image it and, thus, determine the center of its point-spread function beyond the diffraction limit.

Our goal in this Letter is to show that a single molecule can counteract the extinction effect of a single GNP. Our strategy is first, to locate a DBT molecule close to a GNP and examine its near-field coupling via incoherent fluorescence measurements. We then explore the coherent effect of the composite system of a molecule and a GNP. As depicted in Fig. 1(f), we expect the resonant transmission signal to experience a substantial increase.

To identify molecules that are located in the near field of a GNP, we first centered the focus of the laser beam on the GNP and scanned the laser frequency. Figure 2(a) presents an example of the ZPLs obtained at this position by recording the red-shifted fluorescence as the laser frequency was scanned through the inhomogeneous band of about 1 THz. The differences in the observed signal stem mostly from variations in the positions of the molecules within the laser intensity profile. The inset in Fig. 2(a)
FIG. 2. (a) Fluorescence of DBT molecules located within a focal spot of one GNP as a function of the excitation laser frequency. The applied laser power of 79 nW corresponds to an excitation intensity above saturation. Inset: an enlargement of the spectrum of M0 recorded at low excitation power. (b) An extinction image of a single GNP recorded in transmission overlaid with the locations of the GNP obtained from its fluorescence image (yellow), M0 (magenta), and M1 (blue). The arrows depict the in-plane orientations of the molecular dipole moments. (c) 240 spectra recorded at 20 GHz/s over one minute well below saturation (excitation power 0.04 nW). (d) Sum of the aligned spectra shown in (c) (symbols) and a Lorentzian fit (solid curve).

Molecules that experience a significant degree of plasmonic enhancement are expected to display shorter fluorescence lifetimes, broader 00ZPLs and higher emission rates upon saturation. The channel depth of 245 nm limits the axial distance variations and greatly limits the axial distance variations and greatly.

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and a higher vibrational level of the electronic excited state \( |e, v \neq 0 \rangle \), respectively. Pronounced antibunching effects at zero delay time assure us that the signals stem from single molecules. A fit to the measured data lets us extract an excited state lifetime of \( T_1 = 8.1 \pm 0.4 \text{ ns} \) for \( M0 \) and \( T_1 = 1.4 \pm 0.1 \text{ ns} \) for \( M1 \) (see the Supplemental Material [25]).

The resulting sixfold lifetime shortening could be caused by an increase in the nonradiative rate \( (\Gamma_{nr}) \) or the enhancement of the radiative rate \( (\Gamma_{\text{rad}}) \), i.e., a plasmonic Purcell effect [12,43]. To inquire about the relative weights of these effects, we excited \( M0 \) and \( M1 \) via their 00ZPLs at different incident powers. The fluorescence signals presented in Fig. 3(b) show that at saturation, the power radiated by \( M1 \) is about five times larger than that of \( M0 \) if we assume similar collection efficiencies [44]. This confirms a substantial Purcell enhancement of the radiative decay. Figure 3(c) also presents the evolution of the molecular linewidths as a function of the laser power.

Our findings verify that a GNP acts as a plasmonic nanoantenna to enhance the radiative properties of \( M1 \). However, as in the case of the great majority of previous reports on plasmonic antennas [11,12,43,45], our abovementioned studies were solely based on the behavior of the excited-state population observed via the red-shifted fluorescence. Resonant scattering, however, depends sensitively on the degree of coherence in the molecular dipole moment. Indeed, the measured fluorescence lifetime of 1.4 ns lets us deduce a homogeneous linewidth \( (\Gamma_1/2\pi) \) of 114 ± 8 MHz for the 00ZPL of \( M1 \), which is notably less than the directly measured FWHM of 290 MHz. Thus, we expect a contribution from pure dephasing.

To extract additional information about the fast dynamics that might contribute to dephasing, we analyzed \( g^{(2)}(\tau) \) as a function of excitation power. Figure 3(d) plots two examples of such measurements for \( M0 \) (magenta) and \( M1 \) (blue) under strong excitation. A simultaneous fit of the data let us extract a pure dephasing rate of \( \Gamma_{\text{det}}/2\pi = 87 \pm 35 \text{ MHz} \) for \( M1 \), corresponding to \( T_2^\ast \sim 1.8 \text{ ns} \) (see the Supplemental Material [25] for a detailed discussion). This implies FWHM = \( (\Gamma_1 + 2\Gamma_{\text{det}})/2\pi = (114 + 2 \times 87) \text{ MHz} = 288 \text{ MHz} \), which is in good agreement with the directly measured value of 290 MHz.

Having established a good understanding of the degree of coherence in our molecular system, we now present our results on resonant extinction spectra. The magenta data points in Fig. 4(a) display the transmitted power of the incident laser beam as its frequency was scanned through the 00ZPL of \( M0 \), whereby the data are normalized to the GNP extinction signal [see Figs. 1(c), 1(e), and 1(f) and the Supplemental Material [25]]. The observed extinction dip of 4% is in the range of previous measurements on single polycyclic aromatic hydrocarbon molecules [46,47]. However, the blue symbols in Fig. 4(a) show that in the case of \( M1 \), in addition to a larger linewidth, the transmitted power is increased by 10%. In other words, by adding a single molecule, we have indeed turned a gold nanoparticle more transparent.

Because extinction is intrinsically an interferometric phenomenon [10], the laser intensity observed in the far field depends on the relative phase and amplitude of the excitation and scattered fields at the detector. Thus, considering the characteristic dependence of the Gouy phase around the focal plane, one expects a clear change in the resonance profile upon axial scan of the sample [48]. The Fano-type spectra in Figs. 4(b) and 4(c) show this effect for both \( M0 \) (magenta) and \( M1 \) (blue) at two positions of the sample-SIL assembly across the focal plane of the aspherical lens [see Fig. 1(a)]. In Fig. 4(d) we plot the extinction spectra of \( M1 \) for an extended axial sweep. A more detailed discussion and the equivalent data for \( M0 \) can be found in the Supplemental Material [25].

The quantitative details of the plasmonic coupling of \( M1 \) crucially depend on the geometrical features of the GNP as well as the exact position and orientation of the molecule. Considering that we do not have access to these parameters, we cannot use rigorous numerical simulations to fit our experimental data. However, the underlying physics can be captured by employing a model based on driven coupled oscillators [8,9,49] (see the Supplemental Material [25] for details). Figure 4(e) presents the outcome of such
calculations fitted to the corresponding measurements shown in Fig. 4(d). The solid curves in Figs. 4(a)–4(c) through the measured data of M1 represent the cuts marked by the dashed lines in Fig. 4(e). The consistent agreement between the experimental data and the theoretical model provides assurance that the resonance profiles follow the phase behavior expected from the coherent interaction between the laser beam, GNP and M1. This analysis lets us deduce a coupling constant of $\kappa g=53\text{ GHz}$ and a cooperativity of $C=(4g^2/\kappa \gamma)=0.23$, as commonly stated in the CQED formalism. It is worth emphasizing that the reason for $C$ reaching the order of unity in our arrangement is the high degree of emitter coherence (i.e., small $\gamma$), but we remain deep in the weak coupling regime since $4g<\kappa+\gamma$ [20] (see the Supplemental Material [25]). We also note that our model also predicts a “Lamb shift” of 12 MHz in the resonance of M1 induced by coupling to the GNP. While this small frequency shift is accessible to our high-resolution spectroscopic studies, we did not verify it because we could not examine M1 in the absence of GNP as is done in scanning-probe arrangements [15,16,18,43,45].

Two main advantages of plasmonic antennas over conventional microresonators regard their nanoscopic compactness and broad bandwidth. These features provide important opportunities for the realization of subwavelength building blocks of quantum photonic circuits for operations such as switching and phase modulation. In future, stronger near-field couplings through more advanced antenna designs [12,19,45] will enhance the system performance well beyond the first demonstration presented in this Letter.

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[22] Decisive advantages of dye molecules in organic matrices are as follows: small size of about one nanometer, availability at many different wavelengths, and strong Fourier-limited zero-phonon lines in the order of 10–50 MHz. This is to compare with the typical room-temperature linewidth of a solid-state emitter at our wavelength, which is about 10 THz.
[25] See the Supplemental Material at http://link.aps.org/supplemental/10.1103/PhysRevLett.125.103603 for more details about the sample, the experimental setup, the models used to fit the autocorrelation measurements, the coupled oscillator model, and the axial scan of the sample, which includes Refs. [26–34].
[44] This is a reasonable assumption because the two molecules are very close to each other and the numerical aperture of our collection optics is very high.
[47] We observed extinction dips as large as 10% for other molecules in our sample. The lower extinction effect is because the GNP in this study did not lie on the SIL axis.
Acknowledgments

The last five years were an exciting and intense journey into a deeper understanding of physics and the scientific method. Besides acquiring the experimental skills and developing a theoretical understanding of the relevant processes, I found the combination of both aspects particularly fascinating: a model needs to capture all relevant physical processes, otherwise it is not possible to yield a close quantitative agreement between model and experimental data. The moments in which I discovered missing pieces in the theoretical description that led to a quantitative description of the experimental data are among my personal highlights of the time as a PhD student.

The experiments in this thesis were performed at the Max Planck Institute for the Science of Light. I am very grateful that I could work on my PhD thesis in the excellent scientific framework provided by the Max Planck Society. This includes access to the best experimental instrumentation, many talks by renowned speakers, discussions with smart and highly motivated colleagues, and a good working atmosphere in a modern building with a stunning architecture.

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Finally, I thank the people closest to me: my friends and my family. Thanks so much for your love and support!
Dye molecules in organic crystals are excellent single-photon sources and can act as non-linear elements in optical circuits. Since these molecules lack a long-lived spin state, they have previously not been considered for applications that require a quantum memory. In principle, the vibrational modes of single dye molecules in organic crystals could serve that purpose and act as qubits. Due to their coupling to the crystal lattice, the lifetimes of molecular vibrations are often limited to around 10 ps. In the field of cryogenic single molecule spectroscopy, however, the decay constants of vibrational modes have never been studied systematically. This leaves open the possibility that some modes exhibit considerably longer lifetimes.

In this work, we study the linewidths of vibrational modes of single dibenzoterrylene (DBT) molecules in paradichlorobenzene (pDCB) and anthracene (AC) crystals at cryogenic temperatures using their vibronic spectra. To identify long-lived modes, these spectra are measured at a high spectral resolution via fluorescence excitation spectroscopy and stimulated emission depletion (STED) spectroscopy with narrowband tunable lasers. We show that the linewidths of some vibrational modes of DBT in pDCB reach values around 2 GHz. This corresponds to a lifetime of 80 ps and is, thus, significantly longer than the typical lifetimes of vibrational modes in the solid state.

We also observe indications of the coherent excitation of a vibronic mode in the electronic ground state of DBT in pDCB. The associated splitting of the absorption profile of a vibronic transition is achieved by tuning an intense control laser on resonance with a transition between two vibronic states with a high Franck-Condon overlap. According to our model calculation, 80 % of the population that is transferred to the vibronic state of the electronic ground state is coherent in this process. If the vibrational lifetimes of certain modes can be extended by decoupling them from crystal phonons, similar schemes may be exploited in future for the coherent transfer of a flying qubit state to a vibrational state of a single molecule.