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Citation: *J. Chem. Phys.* **135**, 144301 (2011); doi: 10.1063/1.3646732

View online: <http://dx.doi.org/10.1063/1.3646732>

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Electron-vibron coupling in halogenated acenaphthenequinone upon O *K*-edge soft x-ray absorption

Norman Schmidt,¹ Tim Clark,² Stephen G. Urquhart,³ and Rainer H. Fink^{1,a)}

¹*Interdisciplinary Center of Molecular Materials (ICMM) and Interdisciplinary Center for Interface-Controlled Processes (IC-ICP), Universität Erlangen, Egerlandstraße 3, D-91058 Erlangen, Germany*

²*Computer-Chemie-Centrum (CCC), Universität Erlangen, Nögelsbachstraße 25, D-91052 Erlangen, Germany*

³*Department of Chemistry, University of Saskatchewan, 110 Science Pl., Saskatoon, Saskatchewan S7N 5C9, Canada*

(Received 19 June 2011; accepted 16 September 2011; published online 10 October 2011)

We present high resolution oxygen *K* near-edge x-ray absorption spectra of the acenaphthenequinone (ANQ) derivative 3,8-dibromo-5,6-dichloro-ANQ (Br₂Cl₂-ANQ). The spectral features exhibit an almost identical vibronic fine structure compared to that shown by ANQ. The unequal distances of the vibronic levels as derived from the least-squares fit analysis of the vibronic progressions allows us to determine the anharmonicity of the excited state potentials involved. We conclude that a single vibrational progression couples to the resonant excitation of O 1s core electrons preferentially. Comparison of the two ANQ derivatives gives a clear indication that the vibronic mode corresponds to a C=O stretching mode, rather than coupling to a C–H mode as suggested previously. These conclusions are supported by density functional theory calculations. © 2011 American Institute of Physics. [doi:10.1063/1.3646732]

I. INTRODUCTION

Spectral resolution in the soft x-ray regime has improved significantly with the advance of third-generation synchrotrons and thus, the vibronic fine structure in near-edge x-ray absorption fine structure (NEXAFS) spectra can be observed, even for large molecules.^{1,2} In the case of oxygen *K*-edge spectroscopy the coupling of vibronic excitations to electronic transitions has usually only been reported for small molecules (e.g., O₂ (Ref. 3) and CO^{3–5}). Small organic aldehydes, ketones, or acids were investigated only recently.^{6,7} The hydrogen-bond networks in water were also recently investigated using time-resolved NEXAFS.^{8,9} Vibrational resolution in NEXAFS C *K*-edge investigations of polystyrene exhibit vibrational resolution due to an isotope effect in the C–H stretch modes of h-polystyrene/d-polystyrene.¹⁰ Both an increasing number of electronic transitions and molecular vibrations ((3*N*–6) normal modes, where *N* is the number of atoms) will contribute to the spectrum with increasing molecular size, leading to overlapping electronic transitions and a large number of vibrational modes. Therefore, only in cases where the electronic transition couples preferentially to only one or few vibrational modes can the fine structure be resolved experimentally and thus be analyzed in detail. In special cases, such as naphthalenetetracarboxylic dianhydride (NTCDA) in the condensed phase (i.e., highly ordered multilayer films), detailed analysis of vibronic fine structures in the C 1s absorption spectra gave first evidence of a Davydov-splitting observed in core excitation spectra.¹ For condensed acenaphthenequinone (ANQ, 182 amu), vibronic progressions were detected in O *K*-edge NEXAFS.¹¹

In Ref. 11, it was concluded that the excitation of O 1s electrons couples to a C–H stretching mode since the derived vibrational energy corresponds well to that of C–H stretching modes known from IR spectroscopy.¹² However, such a long-range coupling would require a strong interaction via the delocalized electronic system of the aromatic core, and a more likely coupling to a C=O stretching mode would have to be suppressed, which both seem rather unlikely.

In order to reconsider the previous interpretations, we used an ANQ derivative where most of the hydrogen atoms were replaced by electronegative halogen atoms. Here we report a high-resolution O *K*-edge NEXAFS study of 3,8-dibromo-5,6-dichloro-acenaphthenequinone (C₁₂H₂Br₂Cl₂O₂, 409 amu, hereinafter Br₂Cl₂-ANQ, structural formula see inset in Fig. 1). In carefully examining the data, we can unambiguously identify the origin of the observed vibrational mode in ANQ discussed previously in Ref. 11. The vibrationally resolved C *K*-edge spectra will be discussed and compared to other related heteroaromatics elsewhere with emphasis on the intermolecular interactions.¹³

II. EXPERIMENTAL DETAILS

Br₂Cl₂-ANQ was provided by Professor J. Siegel (ETH Zürich, Switzerland)¹⁴ and was used without further purification. The material was carefully outgassed in a separate vacuum chamber to evaporate potential fragments or solvent molecules prior to sublimation in the preparation chamber. Br₂Cl₂-ANQ multilayer films (thickness: 10–20 layers) were prepared by vacuum sublimation under UHV conditions on a well-defined Ag(111) surface. The organic material was evaporated from a home-made Knudsen cell in a separate ultrahigh-vacuum preparation chamber. The pressure during

^{a)}Electronic mail: fink@chemie.uni-erlangen.de.

FIG. 1. Comparison of the normalized O *K*-edge NEXAFS spectra of condensed multilayer films of Br₂Cl₂-ANQ (a) and ANQ (b). In order to visualize the spectral differences, spectrum (a) is plotted in grey behind the ANQ spectrum (b) as direct reference. The inset shows the structural formula of Br₂Cl₂-ANQ.

evaporation did not exceed 5×10^{-9} mbar, while the Ag substrate was kept at room temperature. X-ray photoemission (XPS) of thus prepared films only showed very weak Ag *3d* intensity, which proves the homogeneity and thickness in the multilayer regime of the organic films.

O *K*-edge absorption spectra of the condensed materials were recorded at the UE52-PGM undulator beamline¹⁵ at the high-brilliance synchrotron radiation source BESSY-II (Berlin, Germany). The spectral width at 530 eV is 56 meV, yielding a resolving power $E/\Delta E$ of about 10 000. We used the Ag *3d* substrate lines in photoemission with an excitation energy of 550 eV for photon energy calibration, which results in reproducible accuracies of 0.1 eV. Normalization of the NEXAFS spectra of the organic films was performed with respect to I_0 spectra taken from sputter-cleaned Ag(111) surfaces according to Ref. 16.

The fine structure of the O *K*-edge NEXAFS spectra was analyzed by fitting a series of pseudo-Voigt peaks as described in Ref. 17 to the experimental data. The energy position and intensity of each pseudo-Voigt peak were fitted independently and without restriction. The overall peak width and the Gaussian fraction were assumed to be valid for a whole progression, i.e., the same for all peaks, which is justified since the determining core-hole lifetime should be identical in all cases. The resulting fit values have been converted to the Gaussian and Lorentzian widths of the corresponding Voigt profile according to Ref. 17.

The presented theoretical results were performed with the program SPARTAN '08. Optimized geometries for ANQ and halogenated ANQ, energies of the vibrational modes in the ground and core-excited state, and singly occupied molecular orbital (SOMO, the MO that contains the excited electron) electron densities were acquired with density functional theory (DFT) at the BP 6-31G* level. Vibrations were treated within the harmonic approximation. The O *1s* core-ionized state was simulated via the equivalent ionic core virtual orbital model (EICVOM or Z+1 model).¹⁸ In this model, one

carbonyl oxygen atom is replaced by its Z+1 atom (i.e., fluorine), maintaining the previous geometry. The resulting vibrational energies were corrected for the increased atomic mass of the equivalent core fluorine. Normally, in the Z+1 model, a charge of +1 is placed on the molecule to preserve the electron count. In this case, the molecule was left with a neutral charge, which leads to a single occupancy of the SOMO, with a doublet state to account for the unpaired electron. This provides for an approximate description of the core hole and the NEXAFS final state with a single occupancy of the antibonding π^* MO and its influence on the molecular vibrations.

III. EXPERIMENTAL RESULTS AND DATA ANALYSIS

Normalized and energy-calibrated high-resolution O *K*-edge NEXAFS spectra of condensed multilayer films of Br₂Cl₂-ANQ (a, black squares) and ANQ (b, red open circles) are directly compared in Fig. 1. Both show quite similar broad (full width at half maximum ≈ 1 eV) resonances. Both compounds show pronounced shoulders at the leading edge of the resonance. The shoulders are more distinct for ANQ, also on the high-energy side of the resonance. Notably, the maxima of the resonances are located at almost identical energies. The calibration of the photon energy scale has been checked carefully.

The brighter (grey) data points plotted behind the ANQ spectrum (black) repeat the experimental spectrum of Br₂Cl₂-ANQ and visualize the major spectral differences between the two substances. The spectra mainly differ in the relative intensities of some shoulders of the progression, most obviously at 529.9 and 530.2 eV. The slight deviation in the slope of the high-energy side of the progression may be attributed to background normalization effects. The apparent similarity of the spectra allows us to treat them in the same way for the following detailed data evaluation.

Ab initio calculations using the GSFC3-code^{19,20} were previously discussed in Ref. 11 and predict only one electronic transition for ANQ for O *K*-edge excitation. There is no plausible reason to consider additional electronic transitions for Br₂Cl₂-ANQ. Therefore, the fine structure of this resonance must be attributed to other excitations than pure electronic transitions. Because of the magnitude of the energy separations of the single peaks of about 150 meV, only vibronic excitations are plausible for describing the present spectra.

The least-squares peak-fitting analysis of the vibronic progressions in O *1s* NEXAFS of Br₂Cl₂-ANQ is shown in Fig. 2. In the present study, we compare two different fitting approaches. Both use a sum of pseudo-Voigt profiles for the vibronic levels involved; the resulting residuals (multiplied by a factor 5) are shown in the bottom part of Fig. 2.

The first fitting approach (solid lines in Fig. 2) considers an anharmonic potential for the electronically excited state as in the previous study for ANQ.¹¹ The potential is given by a Morse-type²¹ function

$$E(r) = D_e[1 - e^{-a(r-r_e)}]^2, \quad (1)$$

FIG. 2. (a) Spectral analysis of the O K -edge excitation spectrum recorded for condensed Br_2Cl_2 -ANQ. Two different sets of progressions of pseudo-Voigt profiles were tested. Solid lines: Resonance positions were fitted according to Eq. (2). Dotted lines: Resonances fitted on the basis of 15 unrestricted pseudo-Voigt peaks. (b and c) Residuals (scaling factor 5) comparing the experimental data points with the fits of the sum of resonances with solid (b) or dashed lines (c). Spectrum (d) shows the differences of the two fitting procedures (scaling factor 5).

with the atomic distance r , the equilibrium bond distance r_e , the dissociation energy D_e , and a constant a describing the width of the potential well.

The corresponding energy eigenvalues are given by

$$E_{n'} = -D + hv'(n' + 0.5) - \chi hv'(n' + 0.5)^2, \quad (2)$$

with the anharmonicity factor χ , the vibrational energy hv' , the energy of the vibrational ground state $-D$, and the vibrational level n' . Equation (2) can also be considered as a second-order expansion of the harmonic solution (hence “second order” fit). This polynomial restricts the energy positions (small filled squares in Fig. 3) in the least-squares fit, which results in the parameters $-D$, hv' , and $\chi hv'$ (listed in Table I, first data row).

To ensure that Eq. (2) does not constrain the fit, a second fit analysis (resonances plotted as dotted lines in Fig. 2) was carried out. We fitted the experimental spectrum with a set of 15 pseudo-Voigt profiles with completely free intensities and energy positions (hence “free fit”). The peak widths and Gaussian fractions were free but identical for all components.

A comparison shows that in the low-energy regime (up to peak $n' = 5$), the energy positions of the two fits coincide. In

this energy region, the spectral features are well pronounced and allow reliable determination of the peak positions. From resonance $n' = 6$ onwards, the energy positions resulting from the “free fit” are slightly redshifted. Increasing the number of pseudo-Voigt profiles results in a marginally higher redshift. We should note that the experimental data do not show distinct spectral features in this region and therefore this part of the spectrum should not be over-interpreted. The resulting “second order” fit energies are restricted by Eq. (2), but the impact of such uncertainties should be small because of the relatively low peak intensities. The difference spectrum of the residuals (d) in Fig. 2 compares the two fitting procedures and reflects the major differences in the two sets of residuals.

In order to compare the present data and fit analysis for Br_2Cl_2 -ANQ with the previously reported data on ANQ, we refitted the ANQ data sets with the second order fit routine discussed above. The resulting fit parameters are listed in Table I for direct comparison. By and large, the second order fits for the two substances result in the same values for the adiabatic and vertical transition energies. The vibration energy hv' for Br_2Cl_2 -ANQ is slightly lower; the anharmonicity χ is almost identical compared to ANQ. The difference in line widths is due to the different experimental circumstances (beamline setup), also structural imperfections may play a role. We should note that the data evaluation in Ref. 11 has some drawbacks in the sense that there, the adiabatic transition (E_A) has vanishing intensity. Our re-evaluation does not confirm the existence of the two peaks lowest in energy. Consequently, the presently derived values for E_A , and also to a lesser extent the other parameters, deviate from the values stated in Ref. 11.

For better visualization, we have plotted the energy positions of the fitted pseudo-Voigt profiles in Fig. 3. In the present plot, the variation of the resonance positions for the free fit (small dots) and resonance positions based on an anharmonic potential according to Eq. (2) (open squares, solid line) is negligible up to $n' = 6$. We may therefore conclude that the deviation from linear behavior (dotted line, as deduced from the linear part in Eq. (2)) clearly indicates an anharmonic potential in the electronically excited state.

Since the vibronic energies resulting from the fit ($hv' \approx 190$ meV) are valid for a vibration of the O $1s$ core-excited molecular state, they cannot directly be compared to electronic ground state data, e.g., from IR spectroscopy. For ultraviolet photoemission spectroscopy, an empirical formula

$$hv_0 = hv'(\Delta E_{FC}/1.2 + 1), \quad (3)$$

TABLE I. Comparison of peak fitting results for the O $1s \rightarrow$ LUMO resonance for Br_2Cl_2 -ANQ and ANQ, in detail: Lorentzian (Γ_L) and Gaussian (Γ_G) line width of the pseudo-Voigt profiles (converted according to Ref. 17), energy of the adiabatic (E_A) and vertical (E_V) transitions, Franck-Condon shift ($\Delta E_{FC} = E_V - E_A$), vibrational ground state energy ($-D$), vibronic energy in the core-excited state (hv') and anharmonicity ($\chi hv'$).

	Γ_L (meV)	Γ_G (meV)	$E_A = E_0$ (eV)	E_V (eV)	$\Delta E_{FC} = E_V - E_A$ (eV)	$-D$ (eV)	hv' (meV)	$\chi hv'$ (meV)
Br_2Cl_2 -ANQ (second order fit)	70	239	529.39	530.08	0.69	529.29	186	2.4
Br_2Cl_2 -ANQ (free fit)	72	234	529.40	530.08	0.68	n/a	n/a	n/a
ANQ (second order fit)	99	218	529.35	530.07	0.72	529.26	193	2.5
ANQ (Ref. 11, second order fit)	97	156	528.98	530.08	1.10	528.88	200	2.6

FIG. 3. Energy positions of the fitted resonances (compare Fig. 2) plotted versus the term value n of the fitted progressions. The solid curve corresponds to resonances fitted to $E_n = -Dh\nu' \cdot (n'+0.5) - h\nu' \cdot (n'+0.5)^2$, from which the parameters $-D$, $h\nu'$, and $\chi h\nu'$ were deduced. The dashed line corresponds to linear behavior, i.e., a harmonic excited state potential.

has been derived and has been used to estimate the ground state vibronic excitations.²² Based on this formula, a value $h\nu_0 = 390$ meV for ANQ was reported in Ref. 11. Since this value fits best to C–H stretching modes found between 376 and 381 meV in FTIR,¹² a very efficient coupling of the O 1s excitation to C–H stretching modes and at the same time a suppressed coupling to C=O stretching modes was deduced.

Using our present data evaluation, the lowest vibrational level ($n' = 0$) of the excited state is found at $E_A = 529.4$ eV for Br₂Cl₂-ANQ, and the vibronic energy in the electronically excited state is 186 meV. The energy of the so-called vertical transition (i.e., the maximum of the measured envelope of the vibronic progression) is $E_V = 530.08$ eV. From $\Delta E_{FC} = E_V - E_A$, we derive a Franck-Condon shift ΔE_{FC} of 0.69 eV. Applying our present values to the above-mentioned empirical formula, the energy of the vibronic ground state for Br₂Cl₂-ANQ would be estimated to 293 meV. This value significantly deviates from that of 390 meV for ANQ reported in Ref. 11. On the other hand, the present re-evaluation of the ANQ data leads to almost identical fit parameters for Br₂Cl₂-ANQ and ANQ, i.e., $E_A = 529.4$ eV, $\Delta E_{FC} = 0.68$ eV and a resulting ground state vibronic energy of 309 meV for ANQ.

The two compounds investigated differ with respect to the substituents of the naphthalene core insofar that four of six hydrogen atoms have been replaced by two bromine and two chlorine atoms. At the same time, we find a strong similarity in fit parameters for the two compounds. This would be quite astonishing if the conclusions of Ref. 11, namely, the origin of the vibronic progression being a coupling of the O 1s excitation to a C–H stretching mode, were correct. We may thus conclude that our present findings contradict the previous interpretation. The following discussion will address these aspects in more detail.

IV. DISCUSSION AND CONCLUSIONS

Since NEXAFS probes the electronic coupling to vibronic excitations in the electronically excited state, it is

difficult to compare the derived results with those from ground state vibrational spectroscopy (e.g., IR spectroscopy or high-resolution electron energy loss spectroscopy). In an attempt to overcome this, the empirical formula given above (Eq. (3)) has been derived based on valence photoionization and ground state vibrational data of small molecules, such as O₂, C₂H₂, CH₃CN, CO, and NO.²² In favorable cases, the formula has been found to yield relatively good accuracies, albeit some given examples deviate significantly. Nonetheless, it seemed encouraging enough to apply the above formula to larger molecules as well. With our present evaluation, the formula estimates the ground state vibrational energy to 309 meV for ANQ, while FTIR spectroscopy yields C=O stretch vibrations at 214–221 meV and C–H at 376–381 meV, respectively.¹² Thus, the calculated value is off these experimental values by 20% in both directions.

No experimental IR data have been reported for Br₂Cl₂-ANQ. We have carried out gas-phase DFT calculations for ANQ and Br₂Cl₂-ANQ. For the former molecule, these result in vibrational energies for the C–H stretching modes ranging from 384 to 386 meV, while for C=O stretching modes, energies of 215 (antisymmetric) and 219 meV (symmetric) were found. For Br₂Cl₂-ANQ, the values are slightly higher of 391 meV for C–H and again 215 (antisymmetric) and 219 meV (symmetric) for C=O stretching modes. The slight discrepancies between experimental and theoretical IR data can be attributed to systematic scaling errors and the fact that the calculation does not account for anharmonicity.

The small energy splitting between the symmetric and antisymmetric modes may also be a reason for the missing features in the high-energy regions of the O 1s NEXAFS spectra. If the vibrational series found were in fact a superposition of two series with similar, but not identical parameters, the difference might add up to 30–50 meV for the higher vibronic levels.

In summary, the two molecules show very similar ground state vibration energies. Equation (3) estimates a ground state vibrational energy of 293 meV, which is again far off any ground state vibration. Therefore, our present data analysis does not support the applicability of the empirical formula in Ref. 22 to molecules such as ANQ. The formula neglects too many effects such as symmetry reduction in the core-excited state and in hindsight, its application to vibrationally resolved NEXAFS of large molecules seems too simplistic. Thus, it cannot support conclusions on the nature of the vibronic fine structure, either a coupling to C–H or C=O modes.

A direct comparison with the high-resolution O 1s NEXAFS spectra of carbon monoxide and formaldehyde shows vibronic series that are very similar to that in the O 1s NEXAFS spectra of ANQ and Br₂Cl₂-ANQ. In CO, the fine structure of the O 1s $\rightarrow \pi^*_{C=O}$ transition unambiguously originates from a coupling to the carbonyl stretch vibration.^{3,5} The spectral analysis shows the vibrational energy for the core-excited state (O 1s⁻¹; $\pi^*_{C=O}$) to be 166 meV, which is smaller than the ground state value of 269 meV measured by IR spectroscopy.²³ The smallest organic molecule containing a carbonyl group, formaldehyde, shows a vibrational energy for the core-excited state (O 1s⁻¹; $\pi^*_{C=O}$) of 136 meV,⁷

FIG. 4. Electron density distributions for the SOMO of ANQ (left) and $\text{Br}_2\text{Cl}_2\text{-ANQ}$ (right) as derived from DFT calculations using SPARTAN '08. The Z+1 approximation was applied to simulate an oxygen 1s core hole (sites indicated by an arrow), and a neutral molecule provides for single occupation of the SOMO.

which is again smaller than the ground state value of 217 meV measured by IR spectroscopy.²⁴ CO, formaldehyde, ANQ, and $\text{Br}_2\text{Cl}_2\text{-ANQ}$ all exhibit a decrease in vibrational energy for the core-excited states with respect to the ground state IR data. The reason is the destabilization of the $\text{C}=\text{O}$ bond upon O 1s core hole creation (e.g., XPS data of Kempgens *et al.*²⁵) and upon occupation of an antibonding molecular orbital by the excited electron. Moreover, the vibrational energies and also the experimental O 1s NEXAFS intensities for ANQ and $\text{Br}_2\text{Cl}_2\text{-ANQ}$ are almost identical. This should not be the case if the vibrational coupling were to a C–H mode, since $\text{Br}_2\text{Cl}_2\text{-ANQ}$ has only two hydrogen substituents, while ANQ has six.

Obviously $\text{Br}_2\text{Cl}_2\text{-ANQ}$ and its parent compound ANQ are not directly comparable to the much simpler formaldehyde or CO, at least not quantitatively. The difference between the ($\text{O } 1s^{-1}$; $\pi^*_{\text{C}=\text{O}}$) and the ground state vibrational energies is lower in ANQ than in CO or formaldehyde. The C–C–C angle at the carbonyl C atom of ANQ is 107° ,²⁶ much less than in formaldehyde (118°),²⁷ resulting in some angular strain. In the acenaphthenequinones, two neighboring carbonyl functions are conjugated with the aromatic system. Furthermore, the delocalization of the $\pi^*_{\text{C}=\text{O}}$ level, which is only possible in larger molecules, will distribute the antibonding character over the two carbonyl groups and the rest of the molecule. This is evident in the density plots of the SOMOs of both ANQ and $\text{Br}_2\text{Cl}_2\text{-ANQ}$ (Fig. 4). These effects may explain the smaller effect in the case of the molecules investigated in this work. Nonetheless, the similarities suggest a *common source* to these common features, i.e., a $\text{C}=\text{O}$ stretch.

The creation of the localized core hole in the NEXAFS process leads to a reduction of the molecular symmetry.^{28,29} Core-excited-state calculations based on the Z+1 approach account for this. Only final states with density at the excited oxygen atom, i.e., at the site of the core hole, will have a significant overlap with the initial state and result in a significant transition probability.

The calculated SOMO electron densities shown in Fig. 4 clearly have a considerable coefficient on the site of the core hole. Additionally, the effect of symmetry reduction can clearly be recognized. The SOMOs are delocalized over both carbonyl functions (asymmetrically) and one of the two fused rings of the naphthalene fragment. This symmetry re-

duction is probably also responsible for the greater spread in the calculated energies of the $\text{C}=\text{O}$ vibrations (223 and 233 meV) with respect to the ground state values in both investigated molecules. The core hole also greatly influences the localization of the vibrations. In the Z+1 SOMO calculation, the vibration with higher energy is almost entirely localized on the carbonyl group with the O 1s core hole, the vibration with lower energy is localized on the other carbonyl group. The symmetry reduction effects can also be studied by comparing to ground state HOMOs and LUMOs (see the supplemental material³⁰).

A further inspection of the SOMO of ANQ and its halogenated derivative provides another argument in favor of the $\text{C}=\text{O}$ origin of the O 1s absorption fine structure. As can be seen in Fig. 4, the C–H bonds are electronically not involved in the SOMO. Therefore, an efficient electronic coupling of the C–H bonds to the site of the core hole seems very unlikely. The halogen atoms in $\text{Br}_2\text{Cl}_2\text{-ANQ}$, however, are involved in the delocalization of the excited electron, which is a potential reason for the slightly lower vibrational energy (see Table I).

Furthermore, a detailed analysis of the calculated normal modes of $\text{Br}_2\text{Cl}_2\text{-ANQ}$ indicates that there is essentially no displacement in the $\text{C}=\text{O}$ bond for C–H stretch modes and only a very small participation in the C–Hal stretches. Small movements corresponding to C–H stretches are found in the $\text{C}=\text{O}$ stretch vibrations, but this is expected because of the small mass of the hydrogen atoms. Thus the involvement of the C–H and C–Hal bonds in the vibrational fine structure by a vibrational coupling is not significant.

From the above arguments and from the conspicuous similarity of the experimental data of ANQ and its halogenated derivative $\text{Br}_2\text{Cl}_2\text{-ANQ}$, we can conclude that the observed vibronic fine structure is due to the coupling of the excited O 1s electron to a $\text{C}=\text{O}$ stretching mode rather than to C–H modes. Therefore, the previous assignment of the vibronic fine structure is no longer maintainable. Our results furthermore raise concerns about the application of Turner's empirical formula to the NEXAFS spectra of more complex organic molecules such as ANQ or $\text{Br}_2\text{Cl}_2\text{-ANQ}$.

ACKNOWLEDGMENTS

We acknowledge experimental support by the BESSY staff. In particular, we thank D. Batchelor and R. Follath. We also thank B. Graf and G. Tzvetkov for their assistance during the experiments. The ANQ derivative was synthesized and supplied by the group of Professor J. Siegel (ETH Zürich, Switzerland). This work is financed by the BMBF under Contract Nos. 05 KS7 WE1 and 05 K10 WEA. Travel support was provided by BESSY within the BMBF Project 05 ES3XBA/5. T.C. gratefully acknowledges the support of the Cluster of Excellence “Engineering of Advanced Materials” at the University of Erlangen-Nuremberg, which is funded by the German Research Foundation (DFG) within the framework of its “Excellence Initiative.”

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