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Photogenerated cumulenic structure of adamantyl endcapped linear carbon chains: An experimental and computational investigation based on infrared spectroscopy

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The infrared (IR) spectrum of an adamantyl endcapped α , ω -polyyne (the hexayne, Ad-C₁₂-Ad) is investigated both experimentally and computationally. A new IR band is observed upon UV photoexcitation of the compound (embedded in a poly methyl methacrylate matrix at 78 K), thus, revealing the existence of new photogenerated molecular structure trapped at low temperature. Complete reversibility is found, thus, demonstrating that the photoexcitation is responsible for the generation of metastable excited states of the molecule. Density functional theory and time dependent density functional theory calculations indicate that these metastable states result from the forbidden singlet (S₁) or triplet (T₁) excited states, and geometry optimizations of the polyyne trapped in either S₁ and/or T₁ states demonstrate that the carbon chain takes on a *cumulenic structure*. Comparison of the experimental and the computed IR spectra for the molecule trapped in the forbidden states confirms that the new IR features are clear markers of cumulenic species. The temperature and time dependent behavior of the new IR band is analyzed, while the experimentally determined value of the activation energy highlights the low stability of these molecular structures. © 2011 American Institute of Physics. [doi:10.1063/1.3571451]

I. INTRODUCTION

Linear carbon chains are interesting molecular systems because of their unique electronic, optical, and physico-chemical properties. In the large family of carbon nanostructured materials, *sp*-carbon systems attract great interest because of their inherent structural simplicity, as well as their peculiar properties, as analyzed both theoretically and experimentally in several papers.^{1–14} Linear carbon chains can exist in two isomeric forms, namely, one consisting of alternating single and triple carbon bonds (C–C≡C, polyynes) and the other one consisting of only double bonds (C=C=C, cumulenes).¹⁴ The polyyne structure is predicted to be more stable and indeed endcapped polyynes with up to 44 carbon atoms in the chain have been synthesized and characterized that support this premise.¹⁴

The *sp*-hybridized carbon chains composed of alternating single and triple bonds are found in interstellar space, plants, fungi, and marine organisms.¹² Polyynes are extensively used as building blocks for nanostructured carbon based materials and in supramolecular chemistry.³ Recent experimental and theoretical predictions, describing both linear and nonlinear optical responses of polyynes, support the fact that *sp*-hybridized carbon chains show the behavior expected

for true one-dimensional (1D) conjugated systems showing large second order hyperpolarizability values,^{3,4} thus, paving the way for their possible use in nonlinear optical applications.

In order to investigate the basic physico-chemical properties of such 1D π -electron systems, IR and Raman vibrational spectroscopies turn out to be powerful tools. The relevance of vibrational spectroscopy does not rely exclusively on its capability to give information on the molecular structure and symmetry of the systems investigated, but also can provide information on the electronic properties of π -electron conjugated systems.¹⁵ This is indeed due to the strong electron–phonon coupling that characterizes organic conjugated compounds.^{9,15,16} In this framework, vibrational spectroscopy is used to obtain insight on the question of bond length alternation in rather long *sp*-carbon chains,^{6,9–12,17} and polyynes have been investigated in detail as an experimentally available prototype of a 1D conjugated and Peierls distorted system.⁶ Furthermore, polyne Raman spectra and phonon dispersion branches have been analyzed both by Density Functional Theory (DFT) calculations and semiempirical analytical models, thus, providing a sound assignment of the main vibrational transitions.^{6–9,18}

Structure–property relationships have been derived in order to correlate specific vibrational signatures (in terms of frequency and/or intensity of the vibrational transitions) with

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SCHEME 1. Structures discussed in this study.

specific molecular geometries. An interesting example of how spectroscopy can be used for obtaining molecular structure information is given by the observed violation of the mutual-exclusion principle between IR and Raman signals for centrosymmetric endcapped polyynes.¹⁸ This observation has been used to document the nonlinear (bent) shape that *sp*-carbon chains present, not only in the solid state (due to packing effects), but also in solution. The vibrational analysis has shown that the bent molecular shape is due to a dynamical deviation from linearity (resulting from low-frequency skeletal bending vibrations) and/or to the existence of low-energy bent structures.¹⁸

In the present work, we discuss the results obtained in a combined experimental and theoretical study, based on IR spectral analysis, to investigate the nature and temperature dependent behavior of photogenerated (UV light) species of an adamantyl (Ad) endcapped polyyne, the hexayne Ad-C₁₂-Ad (Scheme 1). Indeed, by analyzing the IR spectral data of Ad-C₁₂-Ad microcrystals embedded in a polymethyl methacrylate (PMMA) matrix before and after UV photoirradiation at low temperature (78 K), new vibrational IR transitions appear in the region of the C≡C stretching (i.e., 2200–2100 cm⁻¹), thus, revealing the presence of photogenerated species that show unusual structural and vibrational properties.

The DFT calculations indicate that the new IR band can be due to the presence of molecules excited, as a consequence of photoirradiation, in a low-lying forbidden excited state. The equilibrium molecular structure of both the first triplet state (T₁) and the first forbidden excited singlet state (S₁) are predicted by calculations to have a strong *cumulenenic character* in the inner part of the molecular chain and the calculated IR spectrum of T₁ species seems to be in better agreement than that of the S₁, with the new redshifted IR band observed experimentally. The assignment of this photoexcited state of Ad-C₁₂-Ad to either the S₁ or T₁ state is, however, neither straightforward nor unambiguous.

II. MATERIALS AND METHODS

A. Experimental details

The synthesis of Ad-C₁₂-Ad has been reported.¹⁸ The sample, in the form of a microcrystalline powder, was used without further purification. Spectroscopic grade tetrahydrofuran (THF) and PMMA were purchased from Sigma Aldrich.

Infrared spectra have been recorded on thin film samples of Ad-C₁₂-Ad dispersed in PMMA as a matrix obtained as follows: PMMA (80 mg) was dissolved in THF (1.6 ml) and

a few drops of this solution were then added to Ad-C₁₂-Ad (0.5 mg). Thin films were obtained by spin coating this solution directly onto Indium Thin Oxide (ITO) coated glass substrates. In the films, the Ad-C₁₂-Ad sample was stable to UV illumination under the experimental conditions.

Microinfrared spectra of thin film samples were recorded with a Thermo Nexus FT-IR spectrometer coupled with continuum microscope on a sample placed in a Linkam FTIR 600 temperature controlled cell in a double transmission geometry: the IR beam focused on the surface of the samples reaches the conductive layer of ITO, and it is reflected back toward the objective, passing twice through the sample.

The laser line at 325 nm of a 60 mW He-Cd Kymmon laser was used as the excitation source. The laser light was guided to the sample with an optical fiber (200 μm fiber core) inserted into the cell and placed under the ITO glass. The UV light was transmitted through the glass substrate and the ITO layer before reaching the sample. The power of the UV light reaching the sample was measured as 5–6 mW. As reported in the literature,¹⁹ photoexcitation experiments need (i) low temperature to stabilize the photogenerated species and (ii) a large number of acquisitions (typically a few thousands) to increase the signal-to-noise ratio because of the very weak signals of the photoexcited species. To meet these requirements, the sample was kept at 78 K in a nitrogen atmosphere and, in order to avoid instrumental instability due to the long time required for the spectral acquisition, hundreds of spectra, each consisting of 16 scans (roughly 1 s per scan) under UV irradiation (sample) and 16 scans without UV irradiation (background), have been recorded and then averaged.

In Fig. 1 we report the UV-Vis absorption spectra of the Ad-C₁₂-Ad microcrystals dispersed in PMMA matrix by using a spectrophotometer UV-Vis-NIR Jasco V570. It can be seen that the laser line at 325 nm used as exciting source is in

FIG. 1. UV-Vis absorption spectra of Ad-C₁₂-Ad microcrystals dispersed in PMMA matrix.

near resonance with respect to the lowest energy Ad-C₁₂-Ad electronic absorption at $\lambda_{\text{max}} = 300$ nm.

B. Computational details

The DFT calculations have been carried out on Ad-C₁₂-Ad, by using the GAUSSIAN09 code.²⁰ The optimized molecular structure and IR spectra of Ad-C₁₂-Ad (as sketched in the inset of Fig. 2) have been obtained by using the PBE1PBE hybrid functional²¹ combined with cc-pVTZ basis set. In previous papers,⁸ it has been proven that this combination can give a very good description of the vibrational properties of *sp*-carbon chains. Both singlet (*S*₀, RPBE1PBE) and triplet states (*T*₁, UPBE1PBE) need to be investigated, as discussed in Sec. III. The stability of the ground state *S*₀ wavefunction has been checked in order to rule out the presence of more stable broken symmetry wavefunction biradicaloid states, as has been calculated in high π -electron correlated systems.¹⁶ Furthermore, an investigation on the excited states of the molecule has been carried out with TD-(U)PBE1PBE approach; both singlet and triplet vertical excitation energies have been evaluated to explore the dipole-allowed states and their energy levels. In the case of triplet-triplet transitions, the value of the oscillator strength, *f*, ranges from 0 to a maximum of 5.4; in the case of singlet-singlet transition the values of *f* are reported in Fig. 5.

Due to the very large computational demands, the study of the equilibrium molecular structure of Ad-C₁₂-Ad polyne in the dipole forbidden (dark) singlet excited state *S*₁ has been restricted to calculations of a *model molecule* [namely tBu-C₁₂-tBu, thus replacing each adamantyl endcapping group with a *tert*-butyl (tBu) group]. Both the ground and the excited states' calculations on tBu-C₁₂-tBu have been carried out at the same level of theory (PBE1PBE/cc-pVTZ). For the

model molecule, we have verified that neither the molecular structure (in terms of bond length alternation) nor the vertical excited state energy is altered significantly by replacing the adamantyl groups with *tert*-butyl groups.

Structural and vibrational properties of Ad-C₁₂-Ad have also been compared to those of the C₈ cumulenlic structure (see Scheme 1), showing a comparable trend in bond length alternation: this comparison has been possible using published data,¹¹ where the vibrational spectra of linear cumulenlic C_{*n*} chains have been studied. In the case of C₈, the ground state electronic configuration corresponds to a triplet state, as is true for all the C_{*n*} chains with even *n* value. The comparison between DFT calculations carried out on C₁₂ polyne in both the *S*₁ and *T*₁ forbidden states and on the C₈ cumulenlic chain show that similar results, both in terms of molecular structure and IR spectra, are obtained.

III. RESULTS AND DISCUSSION

In the following, we focus the discussion on the vibrational analysis of the acetylenic/cumulenlic CC bond stretching region (2300–1700 cm^{−1}). This is the most interesting part of the spectrum for studying carbon chains and it has previously been widely investigated by Raman spectroscopy with the purpose of obtaining better insight on both structural and electronic properties of polyne systems.^{6–11} Most of the bands in other spectral regions are primarily due to vibrations arising from either the adamantyl endcapping groups or the PMMA matrix, and these will be omitted in the following discussion (it should be noted that in the region of 2300–1700 cm^{−1}, no spurious bands of PMMA are found). Figure 2 compares the IR absorption spectrum of Ad-C₁₂-Ad microcrystals embedded in PMMA matrix at low temperature (red line) and the photoexcited spectrum (blue line) obtained as the ratio between the IR spectra during (UV on) and before (UV off) photoexcitation. Before photoirradiation, Ad-C₁₂-Ad shows two strong IR bands near 2200 cm^{−1}. The DFT calculations assign these bands to a collective CC stretching mode (i.e., C≡C lengthening and C–C shrinking), as discussed below. Hereafter, the IR spectrum before UV irradiation is referred to as that of Ad-C₁₂-Ad in its ground state (*S*₀). Under UV irradiation (blue line), the recorded IR spectrum is plausibly associated to the vibrational modes related to the molecules in the bright singlet excited state (*S*₇, see Fig. 5 for details). The recorded sigmoidal profile suggests that only a minimal softening of the CC stretching frequency (redshift of 5 cm^{−1}) takes place in the excited state. Time dependent density functional theory (TDDFT) optimization of the bright (dipole-allowed) excited state (i.e., *S*₇, see the scheme in Fig. 5 for Ad-C₁₂-Ad), confirms a decrease of the bond length alternation of carbon atoms in the chain; triple bonds become longer and single bonds become shorter. While the molecular structure in the bright state *S*₇ is more equalized with respect to that in the ground state *S*₀, a significant bond length alternation is nevertheless retained. Thus, the slight softening of the experimental recorded IR active bands shown in Fig. 2, is consistent with the bond length equalization in the polyne chain predicted by TDDFT calculations.

FIG. 2. IR absorption spectrum of Ad-C₁₂-Ad in a PMMA matrix at 78 K before (red line) and during excitation (blue line), in the wavenumber range of cumulenlic/acetylenic bond stretching. The calculated molecular structure (PBE1PBE/cc-pVTZ) of Ad-C₁₂-Ad in the *S*₀ state is also shown in the inset.

FIG. 3. IR spectra of Ad-C₁₂-Ad embedded in a PMMA matrix: before (red line) and after 40 min UV irradiation with a 325 nm line (black line) recorded at 78 K.

In Fig. 3, the IR spectrum of Ad-C₁₂-Ad microcrystals embedded in PMMA matrix before the photoexcitation experiment (black line) is compared with that recorded at 78 K after the photoexcitation experiment (red line). The IR spectrum after UV irradiation (total exposure time 40 min) shows a new band near 2130 cm⁻¹: since no bands were present in this region before irradiation, it is likely that this new band may be associated to a *new* molecular structure, photogenerated during the exposure to the UV light. Temperature dependent experiments demonstrate that the phenomenon is reversible, and upon bringing the sample to room temperature, the IR active band at 2130 cm⁻¹ gradually disappears; thus, ruling out the possibility of sample degradation.

The aim of the present work is to provide an interpretation of these experimental results and to explore the nature of the new state observed experimentally. For this purpose, we rely on the comparison of the experimental data with the theoretical results. Before discussing these results, however, the reliability of the level of calculation used to assist in the interpretation is assessed.

In Fig. 4, the experimental IR absorption spectrum of Ad-C₁₂-Ad is compared to that calculated by DFT. The agreement is good; the two active IR transitions at 2200 and 2170 cm⁻¹ are related to CC stretching modes of carbon atoms in the chain as reported in the insets of Fig. 4 where the CC displacements for each CC bond in the chain have been sketched. At this level of theory the vibrational features of the ground S₀ state of Ad-C₁₂-Ad are satisfactorily reproduced and assigned.

According to the DFT calculations, the IR band at 2130 cm⁻¹ shown in Fig. 3 cannot be explained as a vibrational mode of the molecule either in its ground state S₀ or in the bright dipole-allowed excited state S₇. PBE1PBE/cc-pVTZ simulations in both the S₀ and S₇ states do not reproduce this lower frequency stretching mode and the decrease in bond length alternation predicted for S₇ is not enough to justify

FIG. 4. Black line: calculated IR spectrum (PBE1PBE/cc-pVTZ) of Ad-C₁₂-Ad in its ground S₀ state; frequencies have been scaled by a common scale factor (0.96) for a better comparison. Red line: experimental IR spectrum of Ad-C₁₂-Ad embedded in PMMA matrix before UV-Vis light irradiation. The insets show the normal modes of vibration associated to the bands indicated by the arrows; bars are proportional to the CC bond length changes.

such a large frequency shift. In order to identify the nature of the photogenerated species giving rise to this new feature in the IR spectrum, the possible existence of some forbidden intermediate state (within the optical gap S₀-S₇) should be investigated, which, if populated, may have a sufficiently long lifetime to allow the measurement of the vibrational spectrum of the molecule in this *new* excited state.

To this aim, starting from the optimized singlet ground state S₀ structure, we have computed the manifold of both singlet and triplet excited states of Ad-C₁₂-Ad, by using the time

FIG. 5. Scheme of the energy levels of Ad-C₁₂-Ad for both singlet (left, red lines) and triplet (right, blue lines) excited states, as calculated at the TD-(U)PBE1PBE/cc-pVTZ level of theory, with respect to the ground state S₀ level. The symmetry species (C_{2v} point group) are also reported for singlet excited states and the relative oscillator strength (*f*) for S₀ → S_{*n*} transitions.

FIG. 6. CC bond lengths along the Ad-C₁₂-Ad carbon chain of S₀, S₁ (*model molecule* tBu-C₁₂-tBu), and T₁ states. For comparison, the CC bond lengths of cumulene C₈ (triplet ground state electronic configuration) are also reported.

dependent unrestricted approach. The unrestricted condition is necessary in order to calculate triplet states. In Fig. 5 we report the energies of both singlet and triplet excited states with respect to the ground state S₀ energy. In particular we focus our attention at three states: the first dipole forbidden excited state S₁, the dipole-allowed state S₇ (as discussed above), and the low-lying triplet state T₁.

The reasons for considering triplet states derive from the fact that triplet states have long lifetimes and are generally believed to play an important role both as reaction intermediates and in charge/excitation transport phenomena.²² It can be noticed that T₁ is lower in energy than S₁ by ~0.9 eV and it, thus, deserves careful consideration. As well, experimental indications of the activated, albeit dipole forbidden, states in the optical gap can be found in the literature²³ and should also be taken into account. For these reasons we decided to investigate both S₁ and T₁ states.

Starting from the analysis of the molecular structure, we first explored the optimized geometry of both the T₁ and S₁ states. The CC bond lengths along the carbon chain for the S₀, S₁ (*model molecule*), and T₁ states are reported in Fig. 6. For sake of comparison, we also report the bond length alternation previously calculated¹¹ for the cumulene C₈ ($n = \text{even}$ number, i.e., triplet ground state) linear carbon chain, and this molecule can be used as a model since it has a cumulenic structure with an extremely low bond length alternation.²⁴

Most notable from this comparison is that the optimized geometries of both the S₁ and T₁ states yield a *cumulenic structure*, at least in the central part of the molecule (far from end group effects), very similar to that obtained for the pure cumulene C₈ molecule. Given the importance of the *cumulenic versus polyynic* structure in linear carbon systems, as discussed in the introduction, attempts to identify the

metastable photogenerated state as a cumulenic state is very appealing and may give further insight into the photophysics of polyynes.

The calculation of the IR spectrum has been carried out for tBu-C₁₂-tBu in the S₁ state and for the Ad-C₁₂-Ad in the T₁ state. It has been verified in previous papers^{6,9} that the bond length alternation in linear carbon chain is directly correlated to the observed vibrational frequency. Thus, due to the very similar cumulenic geometry, similar spectra are expected for both S₁ and T₁ states. For these systems in particular, we analyzed the frequency of the CC stretching modes: since in both the S₁ and T₁ states CC bonds are equalized to a large extent (C=C=C) and we expect that the average force constants between carbon atoms should decrease (with respect to the more alternated C-C≡C structure); thus, lowering the active IR vibrational frequencies. The calculated IR spectra of the molecules in the S₁ and T₁ states are reported in Fig. 7 together with the IR spectrum of Ad-C₁₂-Ad in the S₀ state. For both S₁ and T₁ states, we observe the appearance of an IR band that shows CC stretching character at a lower frequency with respect to that measured in the S₀ state, which satisfactorily compares with the experimentally observed photogenerated band at 2130 cm⁻¹. These bands are associated to a longitudinal CC stretching mode as reported in Fig. 7.²⁵

In Fig. 8 the calculated IR spectra are further compared with those of the cumulene C₈: a good agreement is found between the T₁ state of Ad-C₁₂-Ad and C₈ (triplet ground state), and this observation, once again, strongly supports the assignment of the new band observed in the IR spectrum to the photogenerated species trapped in a metastable excited state (singlet S₁ or triplet T₁) related to a cumulenic molecular structure. Moreover, the calculated T₁ spectrum shows an absorption near 1800 cm⁻¹, which is also observed as a

FIG. 7. Left: Experimental IR spectra of Ad-C₁₂-Ad before UV irradiation (red) and after 40 min of irradiation (laser line 325 nm) recorded at 78 K (black); PBE1PBE/cc-pVTZ IR calculated spectra of S₀ state of Ad-C₁₂-Ad (black), TD-PBE1PBE/cc-pVTZ calculated S₁ state of tBu-C₁₂-tBu (blue), and UPBE1PBE/cc-pVTZ calculated T₁ state of Ad-C₁₂-Ad (pink). Frequencies have been scaled by a common scale factor (0.96) for a better comparison. Right: The normal mode of vibration associated to the S₁ and T₁ IR active bands are reported; bars are proportional to the CC bond length changes.

weak band in the experimental spectrum (shown in Fig. S11 of the supplementary information), favoring the assignment of the intermediate as the photogenerated T₁ state.

As further experimental evidence of the existence of a photogenerated species, temperature dependent IR spectra of the photoexcited sample were recorded. Figure 9 shows that by increasing the temperature, the signature of the photogenerated species disappears, namely, the IR band assigned to the photogenerated species (2130 cm⁻¹) loses intensity and the IR band assigned to the S₀ species (2200 and 2170 cm⁻¹)

FIG. 8. Calculated PBE1PBE/cc-pVTZ IR spectra of Ad-C₁₂-Ad in the S₀ state (black), tBu-C₁₂-tBu in the S₁ state (TDDFT, blue), and Ad-C₁₂-Ad in the T₁ state (UPBE1PBE, pink). UPBE1PBE/cc-pVTZ IR spectra of C₈ cumulene (triplet ground state, green) is also reported. In the inset, the normal mode of vibration associated to the band indicated by the arrow, is reported; the length of the bars is proportional to the CC bond length changes.

FIG. 9. Temperature dependence (78–223 K) of the IR spectra of Ad-C₁₂-Ad embedded in PMMA matrix, after the photoirradiation process. The spectra at increasing temperature are superimposed and shifted vertically for the sake of clarity. The low temperature activated IR band, ascribed to an excited state with a strong cumulenenic structure, is indicated by an arrow.

gains intensity. Since the *cumulenenic-like* species (as the structures predicted in the T₁ or S₁ states for C₁₂) are known to be particularly unstable and reactive, the observed trends can be rationalized by considering that by increasing the temperature we destabilize the cumulene structure (C=C=C) and the molecule can relax back to the S₀ ground state, recovering the more alternated (C-C≡C) polyyenic structure.

The temperature dependent behavior of the IR intensity of polyyenic species in the ground S₀ state and the cumulenenic band are shown in Fig. 10. From this data, the activation energy (E_a) necessary for the thermal conversion from the cumulenenic (S₁ or T₁) excited state to the polyyenic ground state can be estimated as approximately $E_a = 0.3$ kcal/mol, in

FIG. 10. Evolution of the IR intensities of Ad-C₁₂-Ad in the polyyenic ground state S₀ structure and cumulenenic (S₁ or T₁) excited state as a function of temperature. The dotted line is reported as a guide to the eye.

FIG. 11. Raman spectra (excited at 785 nm) of UV degraded (red) and undegraded (green) Ad-C₁₂-Ad samples.

agreement with the low stability predicted for the cumulenenic state.

Furthermore, from the time evolution of the two IR bands associated to the polyene and cumulene structures and using the first order kinetic model, it becomes possible to calculate both (i) the rate of intensity decrease of the C≡C stretching bands and (ii) the rate of intensity increase of the new component. The k -values obtained are: -8.2×10^{-3} and -1.06×10^{-2} for the polyene bands and 2.71×10^{-2} for the cumulene band. These values are in agreement with the values reported by Cataldo *et al.* for similar systems.²⁶

In combination, these observations are consistent with the idea that the new photogenerated structure corresponds to the molecule being excited in a low-energy metastable state that possesses *cumulenenic character*, which has been populated after the photoexcitation event and is stabilized at low temperatures (i.e., $T = 78$ K). Currently, it is not possible to definitely assign the multiplicity (singlet S_1 or triplet T_1) of this state, although there is some support for a T_1 state.

IV. CONCLUSIONS

The photoexcitation of polyene molecules produces the population of a new molecular species that can be tentatively assigned to a low-lying forbidden state. Most interesting is that this new state has a cumulenenic structure, it is low in energy and it shows a temperature dependent evolution. This seemingly reactive state, which can be easily populated because of its low energy, can play a fundamental role as an intermediate in some of the photoinduced degradation processes which make certain polyene and carbyne systems extremely unstable. An example is shown in Fig. 11 where the Raman spectrum of photodegraded Ad-C₁₂-Ad shows the disappearance of the sp -carbon bands and the appearance of a broad feature associated to disordered sp^2 carbon structures. The very broad scattering observed in Fig. 11 shows meaningful features, which have been abundantly reported and discussed in the recent literature related to graphite and graphenes (i.e., cross-linked carbon atoms with sp^2 hybridization). Indeed, qualitatively, the maximum near 1500 cm^{-1} and the plateau extending to 1000 cm^{-1} may be taken as a convolution of the

so-called G and very broad D Raman peaks which are the ubiquitous fingerprints of “graphitic-like” or “graphene-like” systems.^{27,28} The Raman spectrum of amorphous carbon is also similar to the spectrum of Fig. 11. The broad feature near 500 cm^{-1} may be considered as the convolution (i.e., mapping of the density of vibrational states) originating from the many skeletal bending modes of graphite.²⁸

These findings might also be of some help in trying to elucidate the evolution of carbon structures, from linear chains to rings, cross-linked planar (e.g., polycyclic aromatic hydrocarbon (PAH)-like) or clusterlike (e.g., spherical cages, nanotubes) architectures, that take place in hot carbon plasmas, in the chemistry of carbon stars, comets and interstellar molecular clouds. This represents a major scientific challenge that requires the interplay of new and sophisticated experimental and theoretical techniques.¹²

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