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Raman phonon spectra of pentacene polymorphs

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Abstract

We report for the first time lattice phonon Raman spectra of pentacene measured by means of a Raman microprobe technique. We experimentally prove the existence of two polymorphs, as expected from recent structural studies. A comparison with Quasi Harmonic Lattice Dynamics calculations, previously performed starting from the available X-ray data, help us in identifying the phase to which each crystal belongs. © 2002 Elsevier Science B.V. All rights reserved.

1. Introduction

Pentacene is a well-known organic semiconductor, which is currently subject of renewed interest after the recent discovery of its high carrier mobilities, yielding a wealth of new and extraordinary phenomena [1]. The hints that its interesting transport properties can somehow be related to preparation, purity and crystal structure of the material [2,3] have prompted several studies to revisit growing techniques and structural investigations. On the basis of the five structural analyses so far reported on single crystals of pentacene [4–7] and of our recent theoretical work [8,9], it is clear that pentacene

shows *at least* two polymorphic structures in the bulk phase. These two structures are found to correspond unambiguously to the two ‘inherent structures’ of minimum energy [8,9]. We have named the two polymorphs as phase **C**, after the structure of Campbell et al. [4] and as phase **H**, after the structure which results from the more recent crystallographic investigations [5–7].

In the present Letter we tackle the problem from a different point of view, that is, we focus our attention on the dynamical, rather than on the structural, properties of the lattice, as a means to discriminate between different crystal phases. This also provides a further check of theoretical predictions advanced in [8,9]. Among the possible spectroscopic techniques to help the phase assignment, we have chosen Raman scattering in the lattice phonon region (10–150 cm^{−1}) which represents the fingerprint of the individual crystal

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lattice. This choice is also supported by the possibility to interface optical microscopy to Raman spectroscopy, achieving a spatial resolution of about 1 μm , which enables a careful mapping of the physical features of each crystal sample. The experimental results provide a phonon assignment consistent with the available Quasi Harmonic Lattice Dynamics (QHLD) computations [8], again identifying phase **H** and **C** as the only ones so far related to the available structural data.

2. Experimental

Different commercial sources were used as samples for Raman experiments without further purification: selected metal-like bluish platelets from Koch & Light (KL), Fluka purum (F) and Aldrich (A). A different morphology, i.e., tiny blue microcrystals, was obtained for samples vapor-grown by fast sublimation, in an atmosphere of 2.5–10 kPa (25–100 mbar) of nitrogen or argon, at a temperature of about 500 K. These crystals will be referred to as (B). Raman spectra in the region of the lattice phonons and of the low energy intramolecular modes were recorded with the spectrometer Jobin Yvon T64000. Care must be taken in selecting the excitation wavelength. A strong fluorescence, exciton-like or from impurities, whose profile depends upon sample history and laser excitation energy, produces a strong background which prevents the collection of the Raman scattering. To avoid this we have used low energy excitation from a krypton laser tuned at 752.5 nm. The spectra have been recorded with the single crystal placed on the stage of a microscope (Olympus BX40) interfaced to the spectrometer, with 50 \times or 100 \times objectives, reaching a spatial resolution of about 1 μm . With this procedure we could carefully test the spatial variation of the Raman profile which, in the lattice phonon region, is a powerful probe of the physical purity of the crystal lattice. Chemical purity of the crystals was checked by mass spectrometry, elemental analysis and ir spectroscopy. These methods have revealed a low quantity of 6,13-pentacenequinone after keeping the samples in air for prolonged time.

3. Raman phonon spectra

It is very surprising that, despite the growing importance that intermolecular phonons are found to have in the pentacene peculiar transport properties [10,11], a Raman spectrum is still missing in the literature. To our knowledge and with the exception of our recent computational investigation of [8], the only estimate of lattice vibrations of pentacene was given by a calculation of several years ago [12] without any possibility of a comparison to experiments. We have then measured the Raman spectrum by using the different crystal samples described in the previous section and checked their ‘physical purity’ by mapping their phonon spectra in several spots of the single crystals. In Fig. 1 we report typical Raman profiles in the region 20–250 cm^{-1} , where all the intermolecular, as well as a number of low frequency intramolecular modes, are present. Indeed, in such a flexible molecule as pentacene, some intramolecular modes are expected to overlap in energy and be therefore strongly coupled with lattice phonons [9]. The spectra in the figure show that, whatever crystal did we measure, only two distinct lattice phonon profiles (spectra **I** and **II**) are essentially found. Spectrum **I** originates from single crystals selected from platelets of the kind: (KL), (F) and (A); spectrum **II** is the one resulting from the microcrystals (B) grown by the sublimation method described in the experimental section. We thus believe that two different pentacene polymorphs, **I** and **II**, are found in our samples. In order to interpret the low frequency region of the spectra, we recall that in all crystal structures so far reported [4–7] pentacene belongs to a triclinic space group, $P\bar{1}$ with two inequivalent molecules per unit cell, located in the symmetry center of the crystal lattice. The factor group analysis of $k = 0$ phonons predicts nine optically active intermolecular vibrational modes: $6A_g$ (Raman-active) and $3A_u$ (IR-active). It is then plausible to assign the lowest energy bands in spectra **I** and **II** to the expected A_g intermolecular vibrations, although above $\sim 100 \text{ cm}^{-1}$ the strong coupling to low frequency intramolecular vibrations should result in a mixed character of the A_g modes [9,12]. A

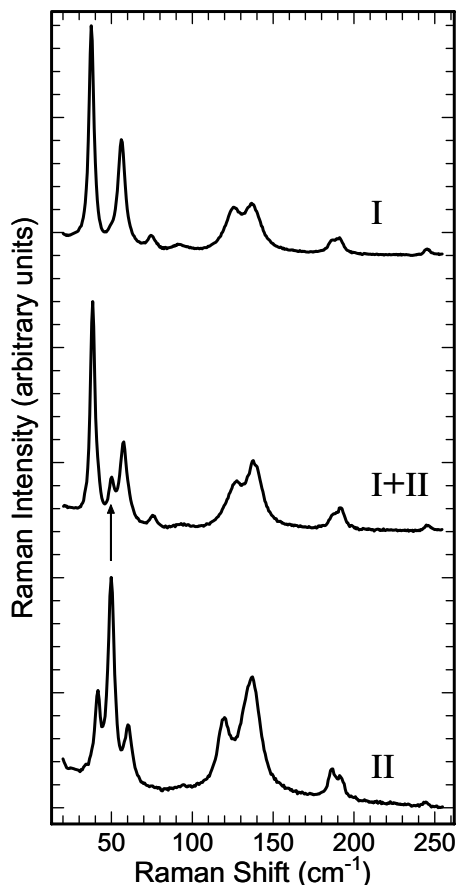


Fig. 1. Raman (single crystal) spectra of pentacene polymorphs: (I) samples (KL), (F) and (A); (II) microcrystals obtained by sublimation (see text for details).

further remark should be made in Fig. 1: the spectra originating from commercial samples (polymorph I, morphologically *platelets*) evidence in some cases an additional feature at $\sim 50\text{ cm}^{-1}$, as shown by the arrow in the spectrum (I+II) of the same figure. This band is clearly due to a physical residual impurity of polymorph II (morphologically *microcrystals*), that can be monitored in regions of the commercial specimens extended only few microns, as indicated by the decreasing intensity of the band on increasing the laser spot size and therefore the crystal area sampled. The fact that a residual presence of polymorph II can be found in different amount on the measured crystals ($A > F > \text{KL}$) is cer-

tainly related to the different degree of purity of the commercial products used: it is plausible that physical defects can be triggered by chemical impurities. To eliminate any possible source of misinterpretation of the experiments, we have also measured lattice phonons of single crystals of 6,13-pentacenequinone, as the most likely impurity due to sample degradation, and definitely found no overlap with the phonon bands of Fig. 1. Finally, we have extended the Raman investigation to the intramolecular region up to 1700 cm^{-1} , in order to see whether any other spectral difference between the polymorphs could be recorded. The full spectrum, with details of selected spectral regions, is reported in Fig. 2. Above 200 cm^{-1} the Raman bands of the two polymorphs are essentially the same with the only exception of the region $1150\text{--}1200\text{ cm}^{-1}$, corresponding to the CH bending region, where the spectral contours differ in shape and resolution. We avoid here tentative explanations of the observed spectral differences in this high frequency part of the spectrum. Such a difference certainly requires further investigations to be exploited also by checking sample phase homogeneity through commercial Raman imaging systems.

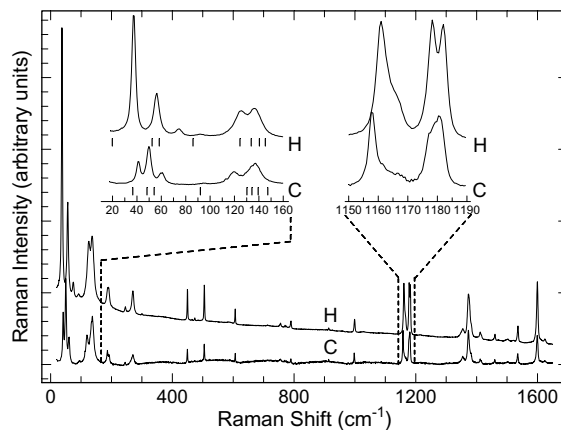


Fig. 2. Raman spectra of pentacene. In the upper part, two enlarged frequency regions, where polymorphs I and II mostly differ, are reported. The vertical bars indicate QHLD frequencies computed at the minimum Gibbs energy G_{\min} at 298K for phases H and C [9].

4. Discussion and conclusions

In previous theoretical works [8,9] we investigated the relationships among the five X-ray structures known for bulk pentacene and reported by Campbell et al. [4] (structure **C**₂₉₅), Holmes et al. [5] (structure **H**₁₈₀), Siegrist et al. [6] (structure **S**₂₉₃) and Mattheus et al. [7] (structures **M**₂₉₃ and **M**₉₀). The subscripts indicate the temperature of the experiment. Structures **H**₁₈₀, **S**₂₉₃, **M**₂₉₃ and **M**₉₀ were shown to belong to the same phase, which we named phase **H**, unlike structure **C**₂₉₅ (phase **C**). Since the differences of energies and structural parameters calculated for the two phases **H** and **C** appeared to be quite subtle, the analysis of the computed lattice phonon frequencies was indispensable to discriminate between them. Indeed, the calculations showed that the lattice phonon frequencies significantly differ in the two phases, revealing distinct patterns especially for the low wavenumber lattice phonons. These calculations were performed adopting the rigid molecule approximation (RMA), disregarding the mixing between lattice and molecular vibrations, and at the minimum of the potential energy Φ_0 , that is, neglecting any temperature effect [8]. In Table 1 we list the experimental peak wavenumbers of polymorphs **I** and **II**, along with the wavenumbers calculated for phases **H** and **C** at the temperature of our experiments (298 K). The latter values anticipate the results of a novel QHLD

calculation [9] aimed to reproduce structures and phonons as a function of T (minimum Gibbs energy G_{\min} values). These calculations represent a significant improvement of our previous model [8] as we relaxed the RMA constraint and also accounted for electrostatic interactions within the potential model. It is worth remarking that only the first four computed lattice phonons have full intermolecular character [9], whereas at higher energies the mixing with the internal modes is very strong. Therefore, for a correct comparison, we list in Table 1 all the experimental peaks of each polymorph, together with the computed values for **H** and **C** structures, up to 200 cm^{-1} . The complete vibrational assignment, also accounting for the additional features appearing at low temperatures, will be given in a future work. For completeness we also report in the table the six lattice phonons originally calculated in [8] for phases **H** and **C** at the minima of the potential energy Φ_0 .

In the present Letter our aim is to check whether the phonons measured for polymorphs **I** and **II** match those calculated for either phase **H** or **C**. The general agreement between experiments and calculations is reasonable and well within the limits of the method. Besides, we notice that the most important feature is that the calculations reproduce the distinctive patterns of the experimental Raman profiles, particularly in the low frequency region of polymorph **II**, whose spectrum shows a cluster of three closely spaced phonons

Table 1

Experimental wavenumbers (cm^{-1}) of the six Raman-active lattice phonons and of the lowest intramolecular modes of the polymorphs **I** and **II** of pentacene

Exp. (I)	Calc. G_{\min} (H) [9]	Calc. Φ_0 (H) [8]	Exp. (II)	Calc. G_{\min} (C) [9]	Calc. Φ_0 (C) [8]
37.6	19.8	33.5	41.5	36.6	46.7
56.2	52.4	64.1	49.9	48.2	57.2
74.8	58.3	76.9	60.5	54.1	72.5
92.0	86.0	110.2	94.4	92.0	115.0
125.2	124.5	157.9	119.5	130.2	155.8
137.4	133.7	164.1	136.4	134.3	164.8
—	140.4	—	—	139.4	—
—	145.3	—	—	147.3	—
186.4	191.7	—	186.3	194.2	—
191.3	193.9	—	191.9	194.4	—

Comparison with calculated values (QHLD) at the minimum of the potential energy Φ_0 [8] and at the minimum Gibbs energy G_{\min} at 298 K for phases **H** and **C** [9].

characterizing the range between 40 and 60 cm^{-1} . A comparison with the calculated frequencies for phase **C**, and even more clearly, with the plot of these values by means of vertical bars in the low energy region of Fig. 2, enables us to identify unambiguously polymorph **II** with phase **C**. On the other hand, the same kind of comparison, carried out between the first more evenly spread four phonons of spectrum **I** and the corresponding frequencies calculated for phase **H**, leads us to match this structure to polymorph **I**. It is also worth mentioning that on increasing energy, i.e., with increasing weight of intramolecular character of the modes, the two polymorphs exhibit more similar spectral profiles and also this feature is well represented by the calculations [9].

In conclusion, Raman phonon spectroscopy turns out to be a very suitable technique to probe the structure of pentacene polymorphs, with the advantage to be fast, reliable and capable to monitor physical modifications in the micron range. In no way we want to claim which growing technique can be used to reproduce crystals of either structure, as this is beyond the scope of this spectroscopic investigation.

We are currently engaged in refining the calculations of structural and dynamical properties of both pentacene polymorphs including the temperature and pressure dependence of Raman-active lattice vibrations. It is interesting to remark that the experiments have identified the very same two polymorphs that a systematic scanning of the potential hypersurface has found to correspond to its two deepest minima [13]. The same calculation has also allowed us to determine that no deeper

global minima can be found. Thus, phases **H** and **C** are proved to be the most thermodynamically stable structures.

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