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Iodine insertion in pentacene thin films investigated by infrared and Raman spectroscopy

M. Cazayous* and A. Sacuto
Laboratoire de Physique des Solides (UPR5 CNRS), ESPCI, 10 rue Vauquelin, 75231 Paris, France and Laboratoire Matériaux et Phénomènes Quantiques (FDR 2437), Université Denis-Diderot (Paris 7), 2 place Jussieu, 75251 Paris, France

G. Horowitz and Ph. Lang
ITODYS, CNRS, Université Denis-Diderot (Paris 7), 1 rue Guy-de-la Brosse, 75251 Paris, France

A. Zimmers and R. P. S. M. Lobo
Laboratoire de Physique des Solides (UPR5 CNRS), Ecole Superieure de Physique et de Chimie Industrielle, 10 rue Vauquelin, 75231 Paris, France

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Vibrational and electronic properties of iodine doped pentacene thin films were studied by Raman and infrared measurements. The observation of the polaronic transition in charged pentacene gives access to the reorganization energy of the pentacene molecules. Iodine insertion induces a modification of the CH vibrational modes located at the end and along the pentacene molecules. At low doping level, iodide ions are intercalated between the two-dimensional pentacene layers. At high doping level, iodine is inserted inside the layers of pentacene in an irreversible way, which is expected to decrease charge transport performance.

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Organic semiconductors are promising compounds for electronic and opto-electronic applications. The high charge carrier mobility of pentacene, a rigid molecule made of five fused benzene rings, has fostered investigations aimed at elaborating thin-film transistors and designing more complex electronic circuits based on this material.[1] It is now well established that the electrical conductivity of molecular semiconductors can be increased by chemical doping, i.e., exposing the molecular solid to vapors of an electron withdrawing agent. For instance, iodine is an efficient electron acceptor for doping oligothiophenes and pentacene.[2] The redox reaction involved between iodine and pentacene leads to the formation of positively charged pentacene on the one hand, and negatively charged iodide counter anions (I_3^-, I_5^-, …) on the other hand. Pentacene thin films present a layered structure with an interlayer spacing slightly lower than the length of the molecule because molecules are slightly tilted to the substrate plane (see Fig. 1). Structural characterization based on x-ray and electron diffraction measurements indicated that the iodide counter-anions tend to intercalate between pentacene layers.[2] However, a deeper knowledge of the mechanism of doping, and in particular its effect on the molecular configuration of the pentacene solid, is needed for a better control of charge transport efficiency. In the present work we measured the effect of the additional charge on the free excitonic transition. We focus on the modification of the C-H vibrational modes of the carbon atoms located at both ends and alongside the pentacene molecule during the iodine doping. Raman and infrared (IR) measurements were used to probe the geometric distortion of the doped molecules, and allowed us to precisely identify two different sites occupied by iodide ions depending on the doping level.

Pentacene films were deposited on glass substrates by heating the solid material in a molybdenum boat in a vacuum chamber at a base pressure of 10^{-7} Torr. The deposition rate was fixed to 0.6 nm/min, with a typical thickness of around 100 nm. Doping was carried out by exposing the film to iodine vapor. The film was placed in a sealed tube filled with argon together with a small amount of iodine powder. The doping time ranged from a few minutes to several hours. The iodine desorption process occurs under room conditions. The micro-Raman measurements were performed with an optical microscope coupled to a Jobin-Yvon T64000 triple spectrometer equipped with a nitrogen cold CCD detector. The lateral size of the laser spot was about 1 μm^2, which allowed us to analyze the homogeneity of the doped phase at the micron scale. We used the 488 and 647 nm excitation lines from an Ar^+-Kr^+ mixed gas laser. The laser power on the sample was

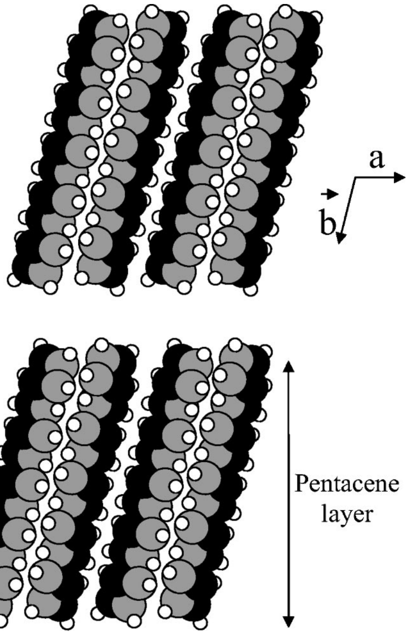

FIG. 1. Pentacene thin film with a layered structure.

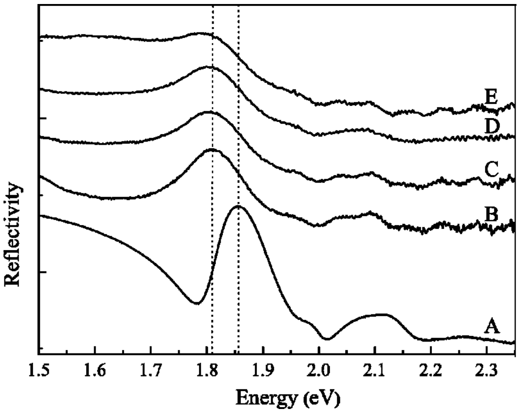

FIG. 2. Reflectivity spectra of the pentacene electronic bands. Spectrum A corresponds to the neutral pentacene film. Spectra B, C, D and E were, respectively, recorded increasing the iodine content.

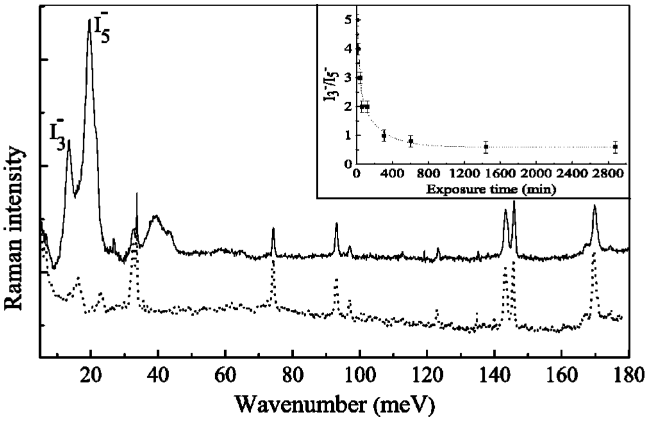

FIG. 3. Raman spectrum of pure (dashed line) and iodine doped (solid line) pentacene thin films. The inset shows the ratio of I_3^- and I_5^- peak intensity vs exposure time based on Raman spectra recorded out of resonance of the iodide ions.

kept around 10^{-5} μW/cm^2 to prevent thermal damage of the pentacene thin film. The spectrometer resolution was down to 0.07 meV. Infrared and visible reflectance measurements were conducted using a Bruker IFS 66v interferometer. The apparatus was equipped with a DTGS pyroelectric detector associated with a globar source and a Si photodiode detector coupled with a tungsten halogen lamp for the near infrared and the visible range, respectively. The spectral resolution was 0.05 meV.

Optical reflectivity spectra in the electronic transition region of neutral and doped pentacene films are shown in Fig. 2. The neutral pentacene spectrum exhibits the free excitonic band at 1.86 eV. The second peak centered at 2.1 eV is related to the Davydov splitting. The splitting level is induced by the presence of two translationally inequivalent pentacene molecules in the unit cell.[3] As soon as iodine is inserted, the doped pentacene spectra present a new band at 1.81 eV. This band is assigned to the polaronic transition. The charged pentacene film spectra reveal a redshift of about 50 meV of the polaron band with respect to the free exciton absorption band. This energy shift corresponds to the relaxation energy from the neutral to the charged state geometry of pentacene molecules. The hole doping removes an electron from a binding orbital and reduces the original free exciton gap. The relaxation energy is interpreted as the formation of polaron resulting from the strong coupling between the additional positive charge and pentacene vibrations.[4] The measured relaxation energy is in agreement with experimental and theoretical studies by high-resolution gas-phase photo-electron spectroscopy.[5] When increasing the iodine content, the full width at half maximum of the polaronic band in the IR reflectivity spectra first increases with the eventually vanishing of the polaronic band. This suggests that the pentacene molecular conformation, which defines the electronic transitions, is strongly altered by the iodine doping level at saturation. In order to localize the iodide ions inserted into the pentacene structure, we have tracked the pentacene bond changes by vibrational Raman and IR measurements.

Several spectroscopic studies have already assigned the Raman active modes of iodine.[6–8] Figure 3 shows the Raman spectrum of an iodine doped pentacene film in the range 10–180 meV obtained with an excitation at 488 nm. We observed Raman peaks located at 13.6 and 19.7 meV. These peaks are associated with the stretching frequencies of I_3^- and I_5^- ions, respectively. The broad bands centered at 40 and 60 meV are related to the second and third order combination scattering of I_3^- and I_5^- modes due to the resonant Raman condition at 488 nm.[7] No peak at 22.3 meV attributed to I_2 has been detected showing the absence of unreacted iodine. Therefore, all the iodine is inserted inside pentacene films as I_3^- and I_5^- ions. According to the inset of Fig. 3, the ratio of I_3^- and I_5^- peak intensity decreases as a function of the exposure time. After about 300 min, this ratio is reversed. As expected, the first doping steps correspond to the formation of I_3^- the smaller iodide ions. At higher doping level, the I_5^- ion is mainly formed. The x-ray and electron diffraction structural analysis of iodine doped pentacene have shown an increase of the long lattice parameter suggesting the intercalation of iodide ions between the two dimensional layers of pentacene.[2] Let us concentrate first on the C-H bending

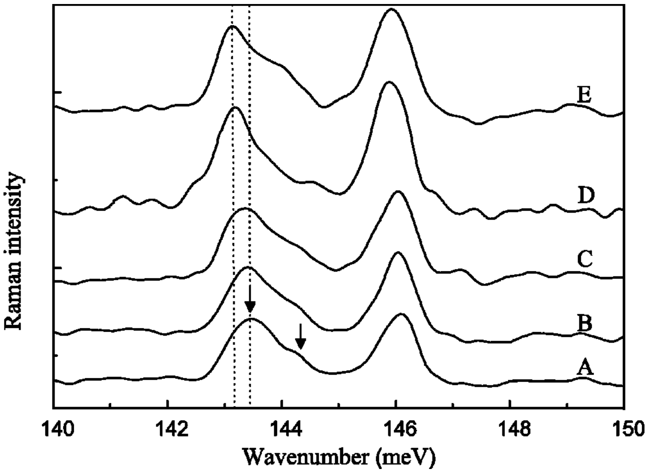

FIG. 4. Raman spectra of C-H in plane bending modes as a function of iodine content from neutral pentacene (spectrum A) to over doped pentacene (spectrum E). We used crossed polarization. Dashed lines are guides for the eye.

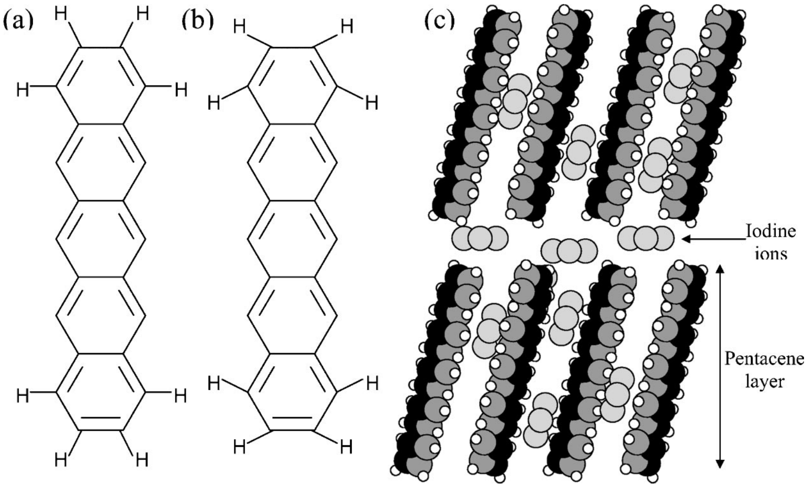

FIG. 5. CH in plane vibrational mode located at the end of the pentacene molecule in the low doping regime: (a) before and (b) after doping. (c) Iodide ions are inserted between and inside pentacene layers at low and high doping, respectively.

modes of pentacene molecules. Figure 4 shows Raman spectra in the energy range 140–150 meV. Both vibration bands around 144 meV and 146 meV are related to C-H bending modes in the plane of the pentacene molecule. The band at 143.8 meV is made of two peaks at 143.5 and 144.3 meV with an intensity ratio that depends on the polarization. These C-H in-plane bending modes are assigned to the motion of atoms located at the end of the pentacene molecule [Fig. 5(a)].[9,10] The splitting is due to a different coupling between the pentacene molecules that can assume two different angular positions. We focus here on the peak at 143.5 meV maximized under crossed polarization. The iodine doping induces a maximum frequency down-shift of $\Delta\nu = 0.35$ meV for this mode. Two effects can explain this frequency shift: (i) the coupling between additional charges and the C-H vibration mode, (ii) the deformation of the C-H bond generated by the insertion of iodide ions between pentacene layers. The charge-vibration coupling first modifies the C-C bond lengths when going from the neutral to the charged state. The C-C intra-ring stretching mode is then affected.[5,11] Even in resonance with the polaronic transition of doped pentacene, no frequency shift of the related mode has been detected. The observed frequency shift of the C-H mode can thus be assigned to the squeezing of the pentacene bonds as indicated in Fig. 5(b) as compared to Fig. 5(b). The geometric distortion of this bond is induced by I_3^- and I_5^- iodide ions intercalated between the two dimensional pentacene layers [Fig. 5(b)].

Figure 6(a) presents IR spectra of the out-of-plane C-H bending mode of pentacene molecules. We measured in the low doping regime a maximum red shift of 0.28 meV. No more shift is observed in the high doping regime. This mode is associated with the C-H bond vibration with four neighboring C-H groups and is located at the interface between the pentacene layers.[12,13] The frequency shift confirms the deformation effect pointed out by Raman measurements and the insertion of iodide ions between pentacene layers at low doping. Figure 6(b) shows a frequency shift of about 0.23 meV of the out-of-plane C-H bending modes only observed in the high doping regime. The latter are associated with the vibrations of CH bonds with no neighboring C-H groups.[12,13] They are located alongside the pentacene molecules and probe the local environment between two pentacene molecules inside the two dimensional layers. The deformation of this C-H bond shows that at high doping the iodide ions are inserted inside the two dimensional pentacene layers as displayed in Fig. 5(c). The diffusion process of iodide ions into the pentacene films can be divided in two stages: an intercalation between the two dimensional pentacene layers followed by a diffusion inside the layers.

Figure 7 shows the frequencies of the Raman and IR modes presented, respectively, in Figs. 4 and 6 as a function of the doping time. The Raman and IR frequencies of the C-H mode located at the interface between pentacene layers exhibit the same behavior [Figs. 7(a) and 7(b), respectively]. The down-shift of the frequencies at low doping (below

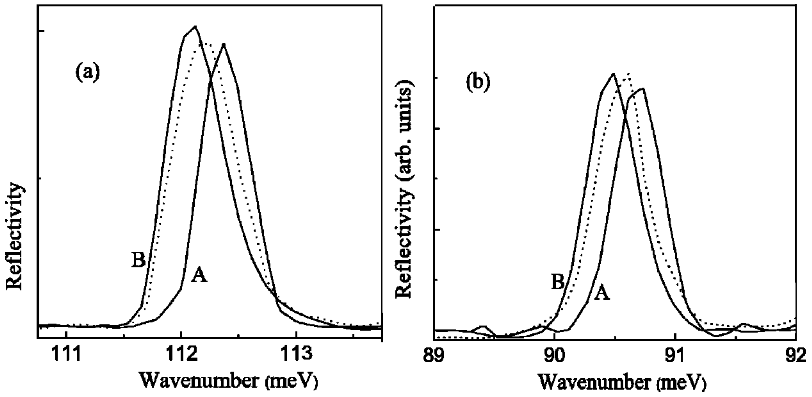

FIG. 6. (a) Out-of-plane CH bending mode with four neighboring CH groups (at the end of the pentacene molecule) recorded at low doping. (b) Out-of-plane CH bending mode with no neighboring CH groups (alongside the molecule) measured at high doping. A and B are, respectively, the IR spectra before and after the frequency shift. The dashed spectra are intermediate ones.

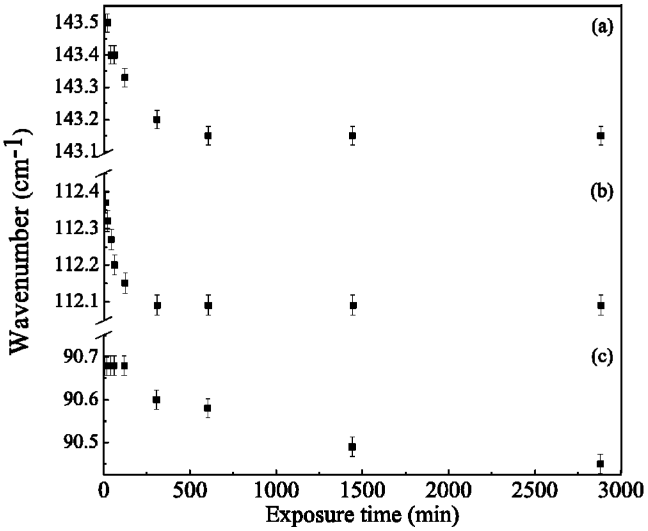

FIG. 7. (a) Raman and (b) IR frequencies of the C-H mode located at the interface between pentacene layers versus the exposure time; (c) IR frequencies of the C-H bond located alongside the pentacene molecule.

300 min) is followed by a saturation in the heavily doped regime (over 600 min). Conversely, the IR frequency of the C-H bond located alongside the pentacene molecule only decreases at high doping (over 600 min). These two different behaviors as the doping exposure time reveal two distinct kinetics for the iodine diffusion between and inside the pentacene layers.

We have also investigated the gradual iodine desorption effect. In both the low and heavily doped regime, the frequency shift of the C-H in plane Raman and IR bending modes tends to vanish with time [modes presented in Figs. 4 and 6(a), respectively]. Thus, the intercalation of iodide counter anions between the inter-layer spacing is reversible. However, the redshift of the C-H bending mode alongside the pentacene molecules is maintained [Fig. 6(b)]. These findings underline the fact that in the saturation regime the iodine diffusion inside the two dimensional pentacene layers is an irreversible process. These changes are crucial for the charge transport properties. The conformation changes from neutral to charged state at the bond scale allow for a reversible and controlled enhancement of the conductivity. By contrast, the saturation regime would lead to irreversible damages to the charge transport properties.

In summary, we have observed in pentacene thin films a transition between the exciton and the polaron bands upon doping. The energy difference is associated with the reorganization energy of the pentacene molecule from neutral to excited state. We have tracked the frequency shifts of CH modes located at the end and along the pentacene molecules. These probes of the pentacene molecular environment reveal that the intercalation of iodide ions may occur between and inside the two dimensional pentacene layers as a function of the iodine doping level. Heavy doping is an irreversible process at the bond scale and is likely to degrade the conductivity of pentacene films. The characterization of the vibrational modes modification is a key for optimizing the enhancement of charge transport in doped organic thin films.

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*Email address: maximilien.cazayous@espci.fr

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