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Electronic states of pyrene single crystal and of its single molecule inserted in a molecular vessel of cyclodextrin

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Abstract

Highly purified single crystals of pyrene were made by a gas phase crystal growth method from 180 times of zone-refined pyrene. The absorption spectra of the single crystal have been transformed from the reflection spectra between 2.5 and 6.5 eV at 2, 77 K and room temperature. The dry powder of β-cyclodextrin including pyrene single molecule were prepared in vacuum to investigate the electronic states of the isolated molecule. The absorption spectra of the single molecule show similar spectra to those of the single crystal. The pyrene molecule keeps its electronic character even in the single crystal.

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Keywords: Pyrene; Single crystal; Single molecule; Cyclodextrin; Optical absorption spectra

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1. Introduction

Although there are many papers on pyrene, the optical absorption spectra of its single crystal at low temperatures have been scarcely reported. Fischer et al. reported direct absorption measurements of its very thin single crystal at low temperatures. It reported that they had cooled the crystals down to 4 K and the shortest wavelength was 360 nm (3.44 eV) in the paper. Only the absorption spectral changes between 117 and 141 K were reported. There is a phase transition temperature at 123 K [1]. The excitation spectra of its free exciton luminescence and the excimer luminescence were reported by other authors [2–7]. The excitation spectra do not show the absorption spectra directly.

It is quite difficult to deal with the single crystal of pyrene at low temperatures, because of its structural phase transition and very weak crystalline bonding forces. It cracks into fragments when it passes the structural phase transition temperature, 123 K in the process of cooling. For this reason, only excitation spectra at low temperatures have been mainly reported instead of direct absorption spectra or the reflection spectra.

The purpose of the present paper is to measure the reflection spectra of a single crystal at low temperatures, 77 and 2 K. The single molecule state of pyrene was also prepared by the same way as anthracene using Gyclodextrin (CyD) capsule to compare the electronic states of the crystal and those of the single molecule [8–10].

The space lattice of a pyrene single crystal is a base-centered monoclinic and the space group is $P2_1/a$ [11]. A couple of pyrene molecules occupy each lattice point. The couple of molecules are arranged in face-to-face of their molecular planes. It is speculated that the

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interaction force between the nearest neighbor couple of molecules is stronger than that between the couples at each lattice point. That would be one of the reason why the crystal easily breaks into fragments when it is cooled under the structural phase transition temperature [1,3]. The melting point is 429 K, which is much lower than that of naphthalene (630 K) and anthracene (489.4 K). The low melting temperature of pyrene suggests that the bonding force is limited between two molecules of the twin and the force is weakened between twins in the crystal.

2. Experiments

2.1. *Single crystal of pyrene*

Single crystals of pyrene were made by the vapor growth method from the zone-refined pyrene. We started powder pyrene of commercial grade of 99%. A cleaned borosilicate glass tube was evacuated and filled with Ar gas. The tube was filled with commercial pyrene powder as much as two thirds of it. It was evacuated with rotary pump and then sealed. The sealed glass tube was set to a zone melting equipment. The zone melting temperature was set to 425 K which is just below the melting temperature of 429 K at atmospheric pressure. Only the part of about 1 cm length of the sample rod was melted in the zone-melting equipment. The sample tube was pulled up at the rate of 2 cm/h. It passed through the heating zone 60 times, then it was cooled to room temperature (RT) and broken. One third of the upper middle part of the sample rod was cut out. The same parts were cut out from other 8 sample tubes which were treated by the same way mentioned above. They were divided into three glass tubes and sealed with the same treatment procedures. They were zone refined by 60 times furthermore. Then the glass tubes were broken and one third of the upper middle part of each sample rod was cut out once again. These three samples were put into a newly prepared glass tube and zone refined 60 times again. Totally 180 times zone-refined sample was prepared. From this zone-refined rod, one third of the upper part was cut out as a very highly purified sample and was used to make single crystals by gas phase crystal growth. Only 0.1% of single crystals were grown from the starting powder of pyrene.

Single crystals were made as follows: The purified sample of pyrene was put into a cleaned glass tube and was filled with Ar gas of 1.7×10^4 Pa and then sealed with gas flame. It was heated to 413 K by putting in another glass tube which was wound with tungsten heater. Both of the sealed sample tube and the heating tube were tilted 7° of angle from horizontal axis. Single crystals grew at the upper and cool part of the glass tube after a week. Single crystals of pyrene were grown to $10 \times 10 \times 0.3\,\mathrm{mm}^3$ size. They are light yellow at RT.

One of them was put into a letter case type of holder which was made of black paper with glue and fixed on the finger of a long sample holding rod. When the crystal was fixed on the holder with both sided adhesive tape or vacuum grease, the crystal was deformed and the different kinds of reflection spectra were obtained for each samples. The rod was put into the entrance tube of a cooling dewar and slowly pushed down to the liquid helium surface and soaked into it. It took 3 h to set the sample dip into the liquid helium surface by pushing down only 15 cm height from the surface of the liquid helium. Then the liquid helium was cooled to 2 K by evacuating it with rotary pump to prevent the bubble noise for optical measurements. When a crystal was quickly cooled down to liquid helium temperature, it cracks into fragments.

The reflection spectra of the pyrene single crystals were measured at near-normal incidence of the light to the surface of the single crystal. The angle between incident light and reflected light was less than 15°. The reflection spectra were measured at RT, 77 K and 2 K. A deuterium lamp (Hamamatsu Photonics L1626, 24 W) was used for the light source to measure the optical spectra in the wavelength region from 190 to 350 nm and a tungsten lamp (Ushio 12 V, 50 W) from 350 to 900 nm. A set of a monochromator (Acton Research Corporation Spectra Pro-500) with CCD photo detector and the photodiode array (Hamamatsu Photonics C4448-11) system were used for the reflection measurements.

2.2. *Single molecule of pyrene in β-CyD*

Single molecule of pyrene was made as follows. A cleaned glass tube was filled with Ar gas. β-CyD powder was put in it and evacuated and heated to 393 K. The tube was cooled to RT and filled with Ar gas. The single crystals of pyrene were put in it with CyD and evacuated to 1.3×10^{-3} Pa, then the glass tube was sealed. It was heated to 408 K for a day and then the sealed edge was pulled out of the heating tube and kept for 3 h to take off the excess pyrene from the CyD powder surface. Excess pyrene were recrystalized at the cooled edge. Then the sample tube was taken out of the heating tube. By these processes, a single pyrene molecule was inserted in β-CyD. The inside diameter of β-CyD is wide enough to encapsule single pyrene molecule but not wide enough to encapsule twin pyrene in it.

3. Experimental results and discussion

The absorption spectra of the single crystal of pyrene are shown in Fig. 1. The exciton absorption band peak is not clearly distinguished at 3.30 eV. A weak absorption structure is seen in the figure only at 2 K around 3.3 eV. It was reported that the very week exciton absorption

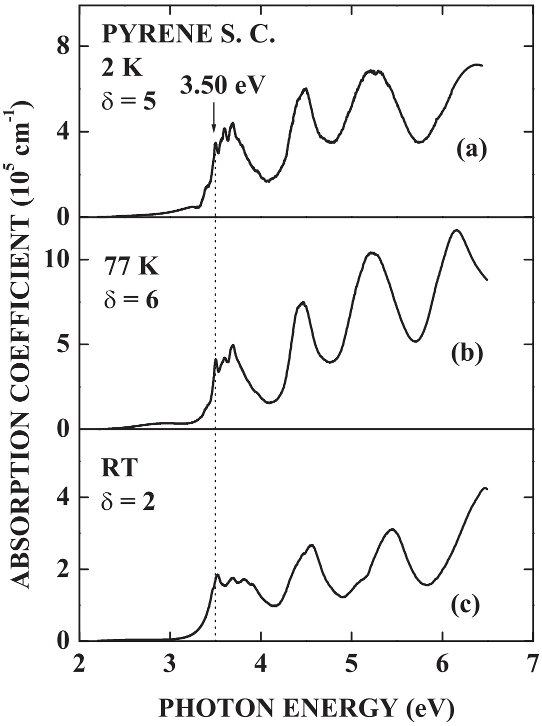

Fig. 1. Absorption spectra of a single crystal of pyrene at 2 K (a), 77 K (b) and RT (c). They were derived from the measured reflectivities by using the Kramers–Kronig formula, with the damping factor of $\delta = 5$, 6 and 2 for 2, 77 K and RT, respectively.

peak and the free exciton luminescence (hot luminescence) was observed at 376 nm (3.30 eV) [7]. The first peak at around 3.5 eV has some fine structures in each spectra at 2 K, 77 K and RT. There are other broad absorption bands observed at higher energy side of the first peak with the energy intervals of about 0.8 eV.

The present paper is the first report of the absorption spectra of the pyrene single crystal in the wide wavelength region from 2 to 6.5 eV and also at low temperatures, 77 and 2 K. There has been only one report of absorption spectra at low temperatures before [1]. It was the direct absorption measurement of very thin single crystal and the measured wavelengths were only from 360 nm (3.44 eV) to 380 nm (3.26 eV). The reported absorption spectra at 117 and 141 K suggested that there was a structural phase transition between these temperatures. The transition temperature was reported as 123 K [1].

The absorption spectra of a pyrene single molecule in β-CyD were derived from the diffusive reflectivity spectra using a Kubelka–Munk formula,

$$A(\lambda) = (1 - R(\lambda))^2/2R(\lambda), \quad (1)$$

where $A(\lambda)$ is the absorbance and $R(\lambda)$ is the measured diffuse reflectivity at each wavelength λ [12]. The absorption spectra of the pyrene single molecule in β-CyD at 2 K are shown in Fig. 2(a). Three main absorption bands are seen at around 3.6, 4.5 and 5.1 eV. They are quite similar to those of the single crystal. From this fact, it became clear that the pyrene molecules do not change their electronic energy levels appreciably even in the single crystal. There are a couple of molecules at each lattice point of the single crystal. The attractive force is strong between the two nearest molecules which are arranged in face-to-face and the energy transfer may be dominant mainly between the twin. Photon energy is absorbed by one of the twin, thus the absorption spectra were similar to those of isolated single molecules. The excited state energy resonates with the other pyrene and relaxes. Thus the energy is scarcely transferred resonantly to another lattice sites of molecules [2,3].

The fine structures of molecular vibrations are more clearly observed in the single molecule spectra as shown in Fig. 2 than those in the single crystal in Fig. 1. The lower energy peaks are sharp in a single crystal (Fig. 1) compared with those in a single molecule (Fig. 2). Although the energy transfer is small in a single crystal, there is still a small rate of energy transfer between a couple of molecules at each lattice sites. It makes the lower energy absorption peaks sharper than those of the single molecule state.

Theoretically calculated spectra are shown with thick vertical lines in Fig. 2(a). These line spectra were calculated with the configuration interaction model

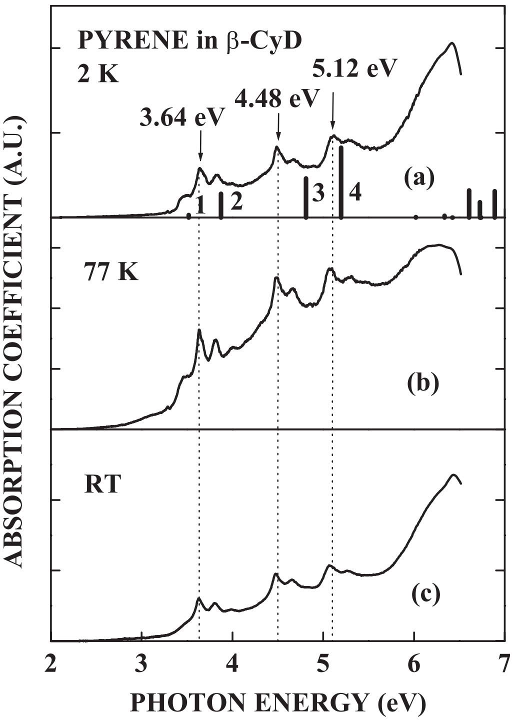

Fig. 2. Absorption spectra of a single molecule of pyrene in β-CyD at 2 K (a), 77 K (b) and RT (c). They were derived from the diffusive reflectivities by using a Kubelka–Munk formula. The vertical thick lines in (a) are the absorption spectra which were calculated by the WinMOPAC program using the configuration interaction model.

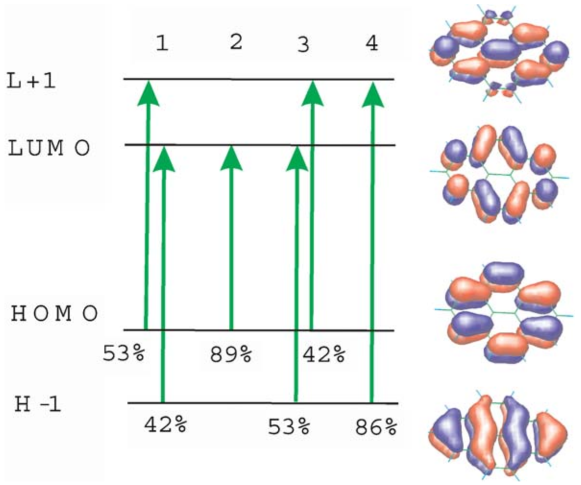

Fig. 3. Energy levels and the electronic transitions which correspond to the absorption bands of Fig. 2(a). The green arrows show electronic transitions. Upper numbers 1, 2, 3 and 4 correspond to the absorption bands shown in Fig. 2(a). Very week absorption band of No. 1 corresponds to the combination of the two different kinds of transitions from HOMO (H) to LUMO +1 (L+1) and from HOMO-1 (H-1) to L. The absorption band of No. 2 corresponds to the transition from H to L. The absorption band of No. 3 corresponds to the combination of the two different kinds of transitions from the second lower occupied level of H-1 to L and from H to L+1. The absorption band of No. 4 corresponds to the transition from H-1 level to L+1 level. The wavefunctions of these molecular orbitals are shown on the right side of each energy level. The red and blue colors show the parity of each π-wavefunctions.

program of WinMOPAC.[2] It is a compact calculation program of a semi-empirical molecular orbital methods. The method of PM5 was used for the calculations. MOS-F and INDO/S methods were also used to calculate the absorption spectra. The agreement is good between the measured spectra and the theoretical line spectra shown in Fig. 2(a). The absorption band line at 3.87 eV which is (indicated as No. 2 in Fig. 2(a)) corresponds to the transition mainly from HOMO (H) to LUMO (L). The higher energy absorption line at 4.81 eV (No. 3 in Fig. 2(a)) is the combination of the two different kinds of transitions from H-1 to L and from H to L+1. The absorption band at 5.20 eV (No. 4 in Fig. 2(a)) corresponds to the transition from H-1 to L+1.

A very weak (short line) absorption at 3.52 eV (No. 1 in Fig. 2(a)) is multiplied 30 times, that is, the absorption intensity is 100 times weaker than that of No. 2. The line of No. 1 corresponds to the combination of two transitions from H to L+1 and from H-1 to L. These transitions of No. 1, 2, 3, and 4 are shown with green arrows in Fig. 3. Numbers at the top of each arrows correspond to those absorption lines in Fig. 2(a). The wavefunctions of the molecular orbitals are shown on the right side of each energy level. Theoretically calculated percentages of each transition are exhibited under the arrows for the transitions, 1, 2, 3, and 4.

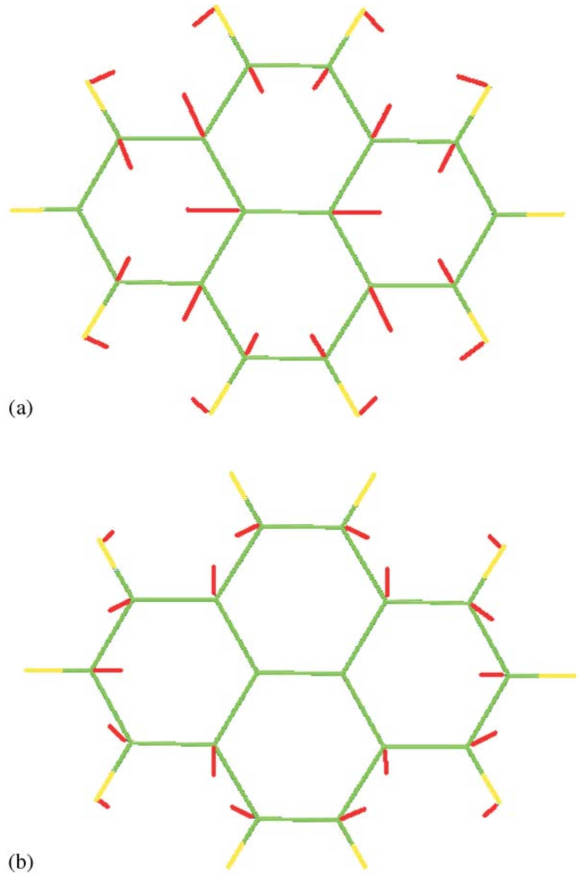

Fig. 4. Molecular vibrations of the breathing mode on the molecular plane. Green lines show the carbon-carbon covalent bonds. Green and yellow lines show the covalent bonds between a carbon atom and a hydrogen atom. Short red bars imply the vibration directions of each atoms of carbon atoms and hydrogen atoms of pyrene. The molecular vibration energy of upper mode (a) is 168 meV (1355 cm^{-1}) and that of the lower mode (b) is 183 eV (1480 cm^{-1}).

In Fig. 2(a), fine structures are seen on each absorption peak. The energy separations of these peaks are nearly 170 meV (1370 cm^{-1}) which is close to the molecular vibration energy of A_g mode. The A_g modes are the breathing modes of pyrene molecular vibrations. There are two different kinds of A_g modes which are close to 170 meV. They are shown in Fig. 4(a) and (b), which were calculated by the WinMOPAC. At the first stage, the calculations of the molecular bases were proceeded. After then the vibration energies were calculated. Vibration directions of these two modes are shown with the short red lines at each atomic site of carbons and hydrogens of a pyrene molecule. The vibration distortion directions of the molecule are on the molecular plane. The theoretical calculations show these two different mode of vibration energies as 168 meV (1355 cm^{-1}) and 183 meV (1480 cm^{-1}). Fig. 4(a) is the

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[2] Compact caluration program of the molecular orbital, MOPAC for personal computer of Fujitsu Company. New version of 3.5 supports the PM5 method.

168 meV vibration mode and the lower one is the 183 meV vibration mode. They are quite close to the observed value of 170 meV (1370 cm^{-1}). The data of infrared absorption spectra show the breathing mode of vibration energy as 174 meV (1407 cm^{-1}) [13]. Raman scattering spectra also show the breathing mode of 174 meV (1407 cm^{-1}) [14,15]. Taking into account these data of theoretical calculations, the Raman data and the infrared absorption data, the observed fine structure of 170 meV (1370 cm^{-1}) separations are assigned as the breathing modes of pyrene molecular vibrations.

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