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Excited states of pyrene excimer observed by photodissociation spectroscopy in a supersonic jet

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ABSTRACT

The absorption spectrum of jet-cooled pyrene excimer was measured using photodissociation spectroscopy. Broad absorption bands were observed in the near-IR and visible regions, which were assigned to the $B_{2u}^{-} \leftarrow B_{3g}^{-}$ and $B_{2u}^{+} \leftarrow B_{3g}^{-}$ transitions of the excimer, respectively. Excitation of these bands results in rapid dissociation of the excimer into monomer fragments, one of which is an electronically excited monomer in the S_2 state. The formation mechanism of the pyrene excimer from the vdW dimer is also discussed.

1. Introduction

Förster and Kasper reported the first observation of broad and red-shifted fluorescence in a concentrated solution of pyrene, which was interpreted as anomalous fluorescence emitted from the bound excimer [1]. The bound state is caused by the association of an electronically excited monomer with a ground-state monomer. The stability of the excimer has been explained as resulting from the configuration interaction of exciton states and charge resonance (CR) states [2–5]. Azumi et al. calculated the configuration interaction, assuming that the pyrene excimer has D_{2h} symmetry [2–4]. They showed that the electronic states of the pyrene excimer are B_{3g}^{-}, B_{2u}^{-}, B_{2u}^{+} and B_{3g}^{+}, in the order of their respective energies.

The measurement of an absorption spectrum of the excimer is required for evaluation of the magnitude of the excitonic interaction. Transient spectroscopy has been conducted to obtain the absorption spectrum of the pyrene excimer in the condensed phase [6–10]. Goldschmidt first reported the appearance of an absorption band at ca. 500 nm [6]. Another absorption band in the near-infrared (IR) was then reported by Post [7]. Katoh et al. assigned the IR band to a transition from the lowest excimer state to a higher state that has an ion-pair character [10].

The absorption spectrum of the excimer under jet conditions provides more important information to explain the excimer formation in an isolated molecule. One method to measure the absorption spectrum of the excimer in a jet is by photodissociation spectroscopy [11–14]. For example, Saigusa and Lim reported the absorption spectrum of a naphthalene excimer using this technique and showed that the naphthalene excimer absorbs light efficiently in the near-IR region [11]. They also reported that excitation of this band leads to rapid dissociation of the excimer into monomer fragments, one of which is an electronically excited monomer. From these results, the mechanism for formation and the photodissociation of the excimer were discussed.

Ever since the first observation of excimer fluorescence in a condensed phase, there have been few reports on the pyrene excimer in the gas phase. In 1993, Suzuka et al. observed the formation of the pyrene excimer in a supersonic jet for the first time [15]. They measured the fluorescence excitation and the dispersed fluorescence spectra by excitation for the S_1 and S_2 states and suggested that the pyrene excimer was produced by excitation of a van der Waals (vdW) cluster to the excimer potential surface. Subsequently, in 1996, Borisevich et al. confirmed the formation of the pyrene excimer in a supersonic jet by measuring the fluorescence-decay time [16]. They also presented a schematic potential energy curve for the formation of the pyrene excimer from the vdW dimer. The direct transition from the vdW dimer to the excimer potential was proposed, as previously predicted by Suzuka et al.

In order to investigate the mechanism for the formation of pyrene excimer in the present study, the absorption spectrum of the pyrene excimer was measured under jet conditions using pho-

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todissociation spectroscopy. We successfully observed absorption bands of the pyrene excimer in the near-IR and visible regions. Excitation of the absorption band of the excimer was also found to lead to dissociation into monomers, one of which is in the S_2 state.

2. Experimental

The apparatus used for generation of the supersonic free jet was similar to that described previously [17,18]. Samples heated to 180–200 °C were seeded in He (3 atm). The pulsed jet of the sample vapor was expanded into a vacuum chamber at 2.0×10^{-6} Torr through a nozzle (General Valve Series 9, 0.8 mm diameter). A frequency-doubled dye laser (Lambda Physik, LPD2002) pumped by the excimer laser (Lambda Physik, Lextra 50) was used as the excitation light source, which has a typical bandwidth of $0.2\,\text{cm}^{-1}$. The laser beam was crossed by the jet 12 mm downstream. The laser intensity was monitored using a pin photodiode after passing through the jet and was kept constant during the scan. During the measurement of the fluorescence excitation spectra, scattered laser light was eliminated using a glass filter. Signals were averaged using a boxcar-integrated averager (Stanford Research SR-250). The dispersed fluorescence spectra were obtained through a 0.75 m monochromator (Nalumi-750). The signals were detected by a Hamamatsu R-928 photomultiplier equipped with a cooling system, and accumulated by the same integrator system as that used for measurement of the fluorescence excitation spectra. Fluorescence lifetimes in the jet were measured by a digital oscilloscope (Lecroy 9400A) triggered by the excitation laser light. The ions produced by one-color two-photon resonance ionization were led to the time-of-flight mass spectrometer and were detected by a micro-channel plate (Hamamatsu Photonics F222-21S). The mass-selected REMPI spectrum was obtained by scanning the laser wavelength while monitoring mass-selected ions.

For the measurement of the photodissociation spectra, the frequency-doubled dye laser (Lambda Physik, LPD2002) pumped by the excimer laser (Lambda Physik, Lextra 50) was used as the pump laser (ν_1) to produce the pyrene excimer, and a parametric laser (Lambda Physik Scanmate OPPO) pumped by the second harmonics of a YAG laser (Continuum Powerlite 8000) was used as the probe laser (ν_2). The signal and idler light of the OPPO parametric laser were used for scanning in the visible and near-IR regions, respectively.

The ν_1 and ν_2 lasers were co-axially introduced into the vacuum chamber, and the two beams were crossed at 12 mm downstream from the jet. The temporal delay of ν_1 and ν_2 was controlled using a digital pulse generator (Stanford Research DG535) and ν_1 was introduced 40 ns prior to ν_2. In order to avoid saturation of the transitions, care was taken to adjust for suitable laser power of ν_2 in the range where the dip depth changed linearly with the laser power. The ν_2 laser power was kept constant while scanning the ν_2 wavelength. In order to remove scattered light, the fluorescence was detected with a photomultiplier through a monochromator. Pyrene (Wako Pure Chemical Industries) was purified several times by column chromatography until it became colorless.

3. Results and discussion

3.1. Formation of pyrene excimer in a supersonic jet

Fig. 1(a) shows the $S_1 \leftarrow S_0$ fluorescence excitation spectrum of jet-cooled pyrene obtained by monitoring >350 nm fluorescence. This spectrum consists of sharp bands and a very broad band like background. The sharp band that appears at the longest wavelength ($27{,}208\,\text{cm}^{-1}$) is assigned to the 0–0 band of the $S_1 \leftarrow S_0$ transition of the pyrene monomer. All sharp bands coincide well with the previous reports of Topp et al. [19], and Ohta et al. [20], so that they were assignable to the pyrene monomer bands. On the other hand, the broad band was assigned to the pyrene cluster band, because its intensity drastically increased with the vapor pressure of pyrene. Fig. 1(b) shows the $S_1 \leftarrow S_0$ fluorescence excitation spectrum of jet-cooled pyrene obtained by monitoring >470 nm fluorescence. All the sharp bands shown in Fig. 1(a) disappeared and only a broad band appeared, which indicates that the pyrene cluster emits at longer wavelength fluorescence than the monomer.

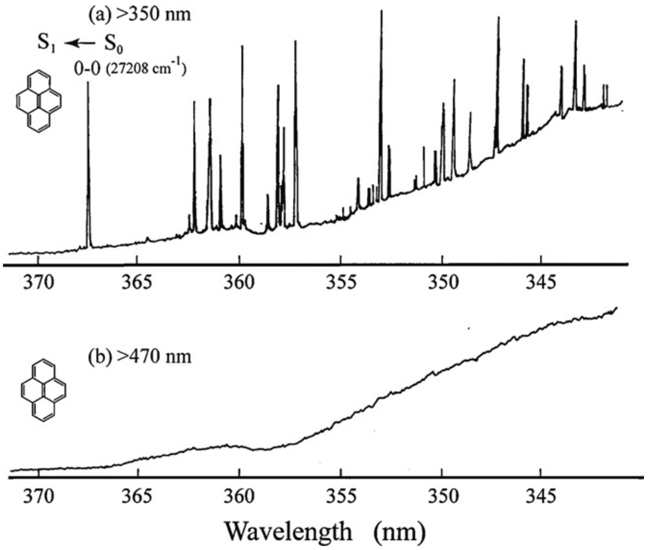

Fig. 1. Fluorescence excitation spectra of jet-cooled pyrene obtained by monitoring (a) resonance fluorescence (>350 nm) and (b) long wavelength fluorescence (>470 nm).

In order to confirm the fluorescence wavelength emitted from the pyrene cluster, the dispersed fluorescence spectrum was measured in a jet. Fig. 2 shows the dispersed fluorescence obtained by excitation at 343 nm. This spectrum exhibits a broad band having a maximum at ca. 470 nm, which is red shifted by $\sim 7000\,\text{cm}^{-1}$ from the excitation point. The feature and the band position of this spectrum is similar to the excimer fluorescence of pyrene in concentrated solution, therefore, we assigned that the broad and red-shifted band in Fig. 2 is the excimer fluorescence. The result confirms that the pyrene excimer is formed by excitation of the pyrene cluster into the S_1 state in the jet.

Excimer formation for several aromatic molecules from the photoexcited vdW cluster band has been reported [21–24]. In the present study, the broad band that appeared in Fig. 1(b) was also assigned to the vdW cluster. To determine the cluster size, the mass-selected resonance enhancement multi-photon ionization (REMPI) spectrum was measured. Fig. 3 shows the $S_2 \leftarrow S_0$ fluorescence excitation spectrum obtained by monitoring (a) >350 nm fluorescence (b) >470 nm fluorescence and (c) the $S_2 \leftarrow S_0$ REMPI spectra obtained by monitoring the dimer$^+$. The REMPI spectrum obtained by monitoring the dimer$^+$ coincides with the fluorescence

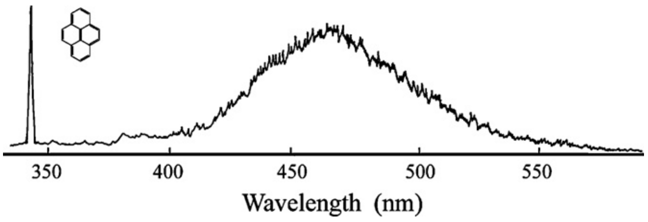

Fig. 2. Dispersed fluorescence spectrum of jet-cooled pyrene obtained by excitation at 343 nm.

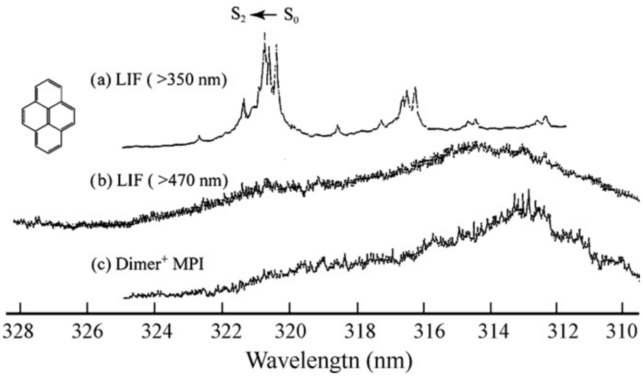

Fig. 3. $S_2 \leftarrow S_0$ fluorescence excitation spectra obtained by monitoring (a) >350 nm and (b) >470 nm and (c) REMPI spectrum obtained by monitoring the dimer ion.

excitation spectrum obtained by monitoring >470 nm fluorescence. The intensity of dimer$^+$ is about six times larger than that of trimer$^+$ in the TOF-mass spectrum obtained by excitation to the broad band. Accordingly, the broad component of the fluorescence excitation spectrum obtained by monitoring >470 nm fluorescence is mainly dimer.

Investigation of the lifetime also supported that the pyrene excimer was formed in a jet. It is widely known that the lifetime of the pyrene excimer becomes shorter than that of the monomer in a condensed phase [25] and in a jet [16]. In this work, the lifetime of the pyrene excimer obtained by excitation at 343 nm was 170 ns and that of the monomer obtained by excitation at the 0–0 band of the $S_1 \leftarrow S_0$ transition was 1400 ns. The shortened lifetime corresponds to the formation of the pyrene excimer in the jet. Therefore, even excitation to the S_1 state leads to the excimer formation. The S_2 lifetime of the jet-cooled pyrene excimer was reported around 200 ns [16], which was almost identical to the lifetime obtained by excitation in the S_1 state. It is considered that after excitation in the S_1 state, the pyrene excimer is produced, which is the same as the S_2 state excitation.

3.2. Photodissociation spectrum of the pyrene excimer

The transition diagram for photodissociation spectroscopy is schematically shown in Fig. 4. The wavelength of the pump laser (ν_1) was fixed at 335 nm, which was the maximum pyrene dimer band, and the induced excimer fluorescence was monitored. The probe laser (ν_2), which was delayed by 40 ns after the ν_1 laser, was scanned in the region of the electronic transition of the pyrene excimer. When the energy of the scanning ν_2 laser is coincident with an excited electronic state of the pyrene excimer, the excimer dissociates immediately into monomers, with the consequential decrease in the intensity of the excimer fluorescence. The photodissociation spectrum was obtained by scanning the ν_2 wavelength while monitoring the excimer fluorescence, and it will correspond to the absorption spectrum of the jet-cooled pyrene excimer.

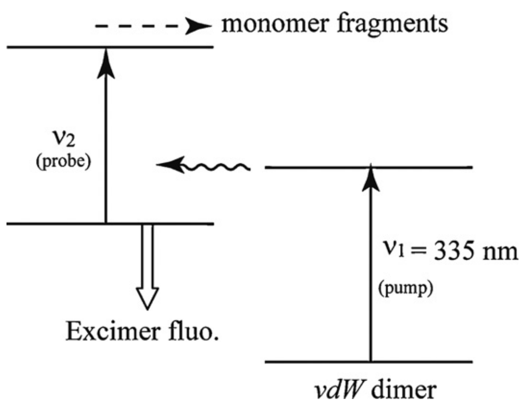

Fig. 4. Schematic diagram of photodissociation spectroscopy.

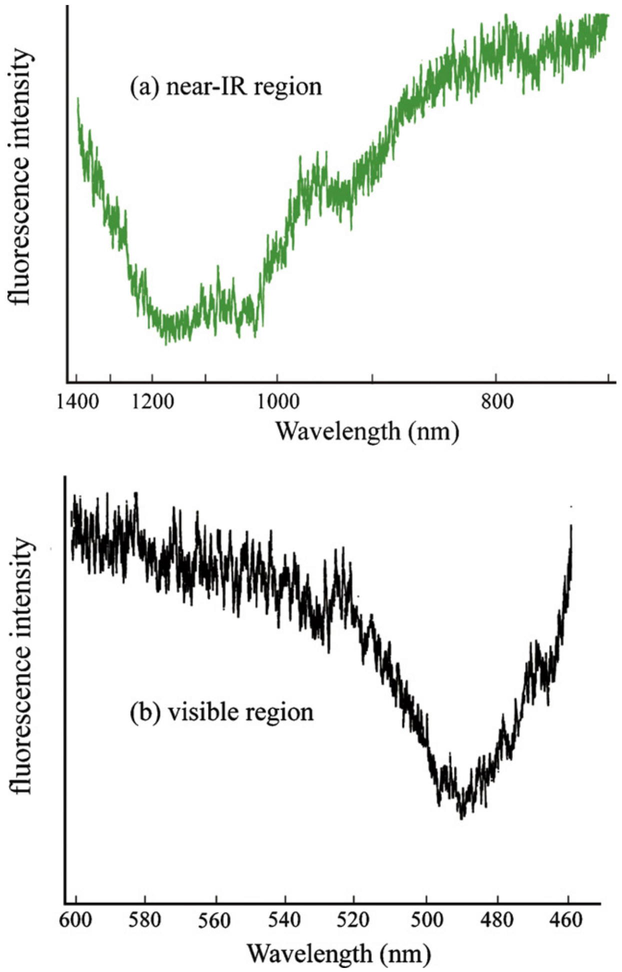

Fig. 5. photodissociation spectra of jet-cooled pyrene excimer (a) in the near-IR and (b) in visible regions.

Fig. 5 shows the photodissociation spectra of the pyrene excimer in (a) the near-IR region and (b) the visible region. Both spectra are very broad with dip intensity maxima at approximately 1150 and 490 nm in Fig. 5(a) and (b), respectively. These spectra closely correspond to the transient absorption spectrum of the pyrene excimer in solution [6–10], except for the bandwidth. Although the transient absorption spectrum in the condensed phase may include the absorption of the excited monomer, such as singlet–singlet or triplet–triplet transitions, the photodissociation spectra in the jet do not include the absorption of the excited monomer in principle, because it is obtained by excitation of the vdW dimer. Accordingly, the photodissociation spectra in Fig. 5 show only the absorption of the pyrene excimer in a jet. As shown in Fig. 5, the bandwidth obtained using photodissociation spectroscopy is around 2000 cm^{-1}, which is half the width of the transient spectrum in the condensed phase [6–10]. It is considered that the dissociation spectrum in a jet is not affected by solvent. Despite the photodissociation spectrum was measured under jet-cooled condition, Fig. 5 shows broad feature. There are two reasons: One is that the excimer produced by photoexcitation of the *vdW* dimer is vibrationally excited. Another reason is that the excited state of the excimer

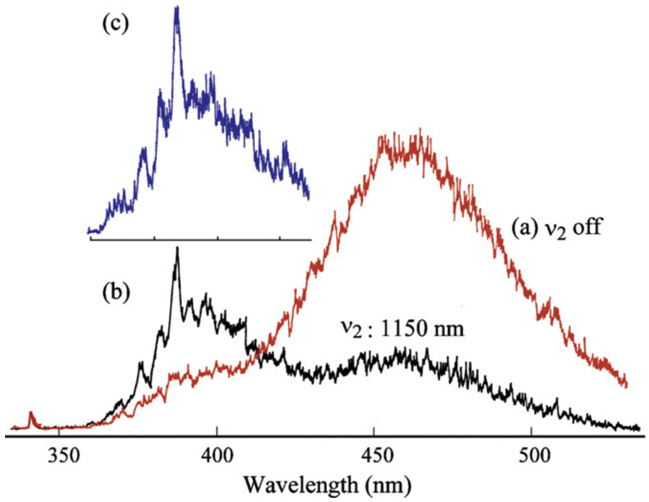

Fig. 6. Dispersed fluorescence spectra of (a) pyrene excimer produced by excitation at 335 nm, (b) the photofragment resulting from the excimer photodissociation at 1150 nm and (c) the monomer excited to the S_2 origin.

has dissociative potential. We will discuss the photodissociation mechanism of the excimer in the next section.

Azumi et al. calculated the configuration interaction between the exciton states and CR states, assuming that the pyrene excimer has D_{2h} symmetry [2–4]. They showed that the electronic states of the pyrene excimer are B_{3g}^-, B_{2u}^-, B_{2u}^+ and B_{3g}^+, in the order of their respective energies. The allowed transitions from the B_{3g}^- state, which is the most stable electronic state of the pyrene excimer, are the $B_{2u}^- \leftarrow B_{3g}^-$ and $B_{2u}^+ \leftarrow B_{3g}^-$. According to the configuration interaction calculation by Azumi et al., it was estimated that the energies of the $B_{2u}^- \leftarrow B_{3g}^-$ and $B_{2u}^+ \leftarrow B_{3g}^-$ transitions were approximately 1 and 2–3 eV, respectively [3]. The photodissociation spectra measured in the present investigation exhibit broad bands with maxima at approximately 1150 nm (1.1 eV) and 490 nm (2.5 eV), as shown in Fig. 5. Therefore, the bands that appeared in the near-IR and visible regions were assigned to the $B_{2u}^- \leftarrow B_{3g}^-$ and $B_{2u}^+ \leftarrow B_{3g}^-$ transitions, respectively.

3.3. Photodissociation mechanism of the pyrene excimer

Saigusa et al. reported that the excitation of aromatic excimers led to rapid dissociation into the monomer fragments. They measured the electronic state of the fragment monomer and discussed the mechanism of excimer formation; for example, they elucidated that the excimer stability of naphthalene [11] and fluorene [12] originates from S_2 and S_1 exciton interactions, respectively. We shall consider the mechanism of pyrene excimer formation. It is well known that the stability of the excimer arises from the exciton states, which are stabilized by configuration interaction with the CR states [2–4]. The stability is dependent on the exciton interaction that is proportional to M^2/R^3, where M is the transition moment and R is the distance between the molecular planes [26]. The S_2 state of pyrene has a larger oscillator strength (f = 0.33) than the S_1 state (f = 0.0014) [27]; therefore, the excimer stability of the pyrene excimer originates from the S_2 exciton interaction. In order to confirm the importance of the S_2 state as the origin of the pyrene excimer, the fluorescence from the monomer fragment produced by photodissociation of the pyrene excimer was measured.

Fig. 6 compares the dispersed fluorescence spectrum of the monomer fragment produced by the photodissociation of the excimer with the spectra of pyrene excimer and the monomer. Fig. 6(a) shows the dispersed fluorescence spectrum obtained by excitation at 335 nm. The spectrum shows excimer fluorescence that is similar with Fig. 2. On the other hand, the fragment fluorescence obtained by photodissociation of the excimer at 1150 nm exhibits that the excimer fluorescence decreases and newly structured bands appear in the ca. 380 nm region as shown in Fig. 6(b). The fluorescence bands correspond to the region for fluorescence from the pyrene monomer. This result proves that excitation of the pyrene excimer leads to photodissociation into the monomers, and that one of the monomers is in an electronically excited state. The new fluorescence shown in Fig. 6(b) exhibits vibrational structures, which indicates that the monomer fragment has less excess vibrational energy. If it has large excess vibrational energy, its fluorescence spectrum may exhibit a broad feature due to intramolecular vibrational redistribution (IVR). The energy to produce the pyrene excimer is ca. 21,000 cm^{-1} and that required to excite the pyrene excimer to the higher electronic state is ca. 9000 cm^{-1}; therefore, the energy of the electronically excited excimer is ca. 30,000 cm^{-1}, which corresponds to the S_2 state of the monomer. The electronic state of the excited monomer produced by photodissociation of the excited pyrene excimer is considered to be the S_2 state. The spectral features of Fig. 6(b) closely resemble the dispersed fluorescence spectrum obtained by excitation to the S_2 state of pyrene monomer (Fig. 6(c)). From these results, the electronic state of the fragment monomer is the S_2 state. Excitation of the pyrene excimer at 490 nm ($B_{2u}^+ \leftarrow B_{3g}^-$ transition) resulted in monomer fluorescence at approximately 380 nm. As expected, the fluorescence is weaker and structureless in comparison with Fig. 6(b), which implies that IVR occurs because the electronically excited monomer in the S_2 state produced by photodissociation has large excess energy. The absorption and dissociation of the pyrene excimer is schematically as follows:

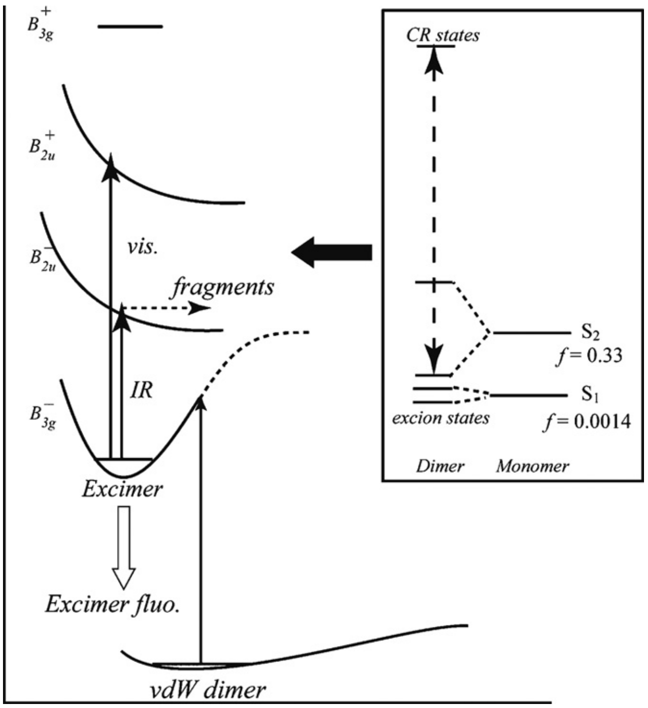

Fig. 7. Schematic potential energy curve illustrating the formation and the dissociation processes of the pyrene excimer. The insert shows the interaction between the exciton and the CR states. The vdW dimer is excited to the excimer potential directly. The excitation of the excimer to the upper state results in the rapid dissociation into monomer fragments, one of which is in the S_2 state.

$$\text{Pyrene excimer}\,(B_{3g}^-) \xrightarrow{\nu_2} \text{pyrene excimer}^*(B_{2u}^-,\ B_{2u}^+)$$

$$\xrightarrow{\text{dissociation}} \text{pyrene monomer}^*(S_2) + \text{pyrene monomer}(S_0)$$

From these results, it was experimentally confirmed that the stability of the pyrene excimer originates from the S_2 exciton interaction. A schematic diagram of the formation and photodissociation processes of the pyrene excimer is shown in Fig. 7. Exciton splitting takes place more remarkably in the S_2 state than in the S_1 state. The exciton states are much more stabilized by the configuration interaction with the CR states, which are the pyrene excimer states. In addition, the depth of the potential-well of the excimer is very large. Subsequently, the fluorescence excitation spectra obtained by monitoring the excimer fluorescence were very broad from the S_1 to the S_2 regions, because the pyrene dimer produced in the jet is directly excited to the excimer potential surface. The excimer absorbs efficiently light in the near-IR (ca. 1150 nm) and visible (ca. 490 nm) regions, as shown in Fig. 5. Excitation to the absorption bands of the excimer leads to fast dissociation into the monomers, which implies that the excited states of the excimer have repulsive potentials. The electronic state of the fragment monomer, which is produced by the photoabsorption, is found to be the S_2 state. This experimental evidence is consistent with the theoretical consideration [2–4] that the pyrene excimer originates from the S_2 exciton interaction.

4. Conclusion

We measured the absorption spectrum of jet-cooled pyrene using photodissociation spectroscopy for the first time. The absorption spectrum of the pyrene excimer is very broad with intensity maxima at 1150 and 490 nm, which are assigned to the $B_{2u}^- \leftarrow B_{3g}^-$ and $B_{2u}^+ \leftarrow B_{3g}^-$ transitions, respectively. It closely corresponds to the transient spectrum in a condensed phase, which indicates that the upper state of the pyrene excimer is a repulsive state. Excitation of the excimer bands leads to rapid photodissociation into monomer fragments, one of which is an electronically excited state, which was found to be the S_2 state by dispersed fluorescence spectroscopy of the monomer fragment. This is direct evidence that the pyrene excimer originates from the exciton interaction from the S_2 state.

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