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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 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 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.

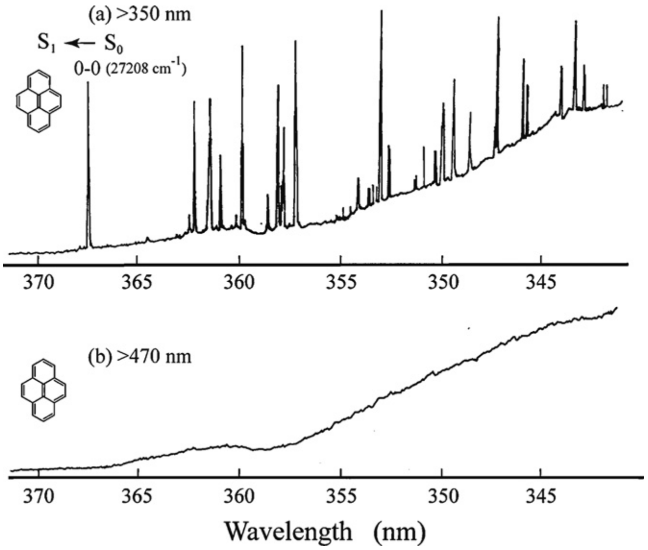

Fig. 1. Fluorescence excitation spectra of jet-cooled pyrene obtained by monitoring (a) resonance fluorescence (>350 nm) and (b) long wavelength fluorescence (>470 nm).

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 ~7000 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

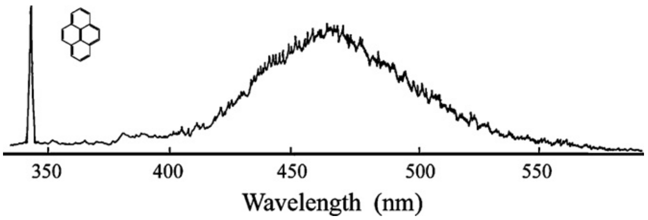

Fig. 2. Dispersed fluorescence spectrum of jet-cooled pyrene obtained by excitation at 343 nm.