

First detection of an ultraviolet transition in an ionized polycyclic aromatic hydrocarbon

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(Received 22 February 1999; accepted 3 May 1999)

We report the first measurement of a polycyclic aromatic hydrocarbon cation electronic transition in the ultraviolet spectral region. The UV excitation spectrum of the D_n-XD_0 transition of the perylene cation ($C_{20}H_{12}^+$) isolated in an argon matrix was pumped with tunable, coherent radiation and monitored using the vibronic bands of the $D_1(^2B_{3g}) \rightarrow (^2A_u)D_0$ system. The two component band peaks at 244 and 250.2 nm, close to the $S_2(^1B_{3u}) \leftarrow (^1A_g)S_0$ transition in neutral perylene.
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I. INTRODUCTION

Polycyclic aromatic hydrocarbon (PAH) ions are promising candidates to account for some of the visible and near-infrared diffuse interstellar absorption bands (DIBs)^{1,2} as well as the interstellar “unidentified” infrared (UIR) emission bands.³ Recently, it has been recognized that some DIBs are also seen in emission⁴ implying that, when excited, the carriers of these bands can relax radiatively. In order to further test the possible connection between PAHs and the DIBs we have developed a laboratory program to measure the electronic spectra of PAH ions under conditions which mimic the interstellar environment where the molecules are in the gas phase and at low temperatures. Matrix isolation provides a good approximation of such conditions.⁵ Part of this program has been devoted to characterizing the visible and near-IR emission of PAH cations, first employing broad band excitation⁶ and, most recently, tunable laser excitation.⁷ Since the ultraviolet properties of ionized PAHs are largely unknown, these excitation studies have now been expanded into the ultraviolet. This information is needed to interpret the UV portion of the interstellar extinction and to understand the molecular mechanism which converts much of the interstellar UV radiation into the ubiquitous IR emission features.

While there has been a great deal of theoretical effort to determine the UV properties of ionized PAHs using molecular orbital theory and related models,^{8–11} very limited experimental information is available due to the complications inherent in measuring the spectra of PAH ions in this region.⁵ In matrix experiments, the cations are formed *in situ* through direct photoionization of the isolated, neutral precursor molecules. Since the ionization yield is generally low in the solid matrix (5%–10%) and the UV absorption bands of the neutral molecule are strong, they screen the much weaker absorptions associated with the ion. In fact, in most experi-

ments, the UV region is saturated by the strong neutral absorption.

Apart from the fundamental interest in the UV properties of PAH ions, there are important astrophysical issues involved as well. For example, since PAHs are widespread throughout the interstellar medium and rather abundant by interstellar standards, the UV properties of ionized PAHs contribute to the radiative balance in many phases of the interstellar medium. The UV spectral properties of PAHs are needed, for example, to analyze the UV-to-IR conversion in such diverse objects as H-II regions, planetary nebulae, galactic nuclei, and the diffuse interstellar medium.^{3,12} In addition, the high quality UV spectral data made available through the Hubble Space Telescope warrants careful experimental studies of PAH properties in the UV range.

Here, we report the first results of this program, the detection of the 244 and 250.2 nm bands of the matrix isolated perylene cation ($C_{20}H_{12}^+$).

II. EXPERIMENT

The experimental setup used for the absorption and fluorescence studies of the perylene cation using matrix isolation techniques is described elsewhere.⁷ Briefly, the experimental procedure consists of: (i) preparing an Ar matrix (10 K) of isolated neutral and ionized perylene; (ii) probing the sample in absorption to check the degree of isolation of the trapped species and the ionization yield, (typically a few percent) and, finally; (iii) measuring the excitation spectrum with tunable coherent radiation. The manually tunable coherent light source is driven by an Alexandrite laser (Light Age Inc., PAL 101). The tunable fundamental of the flash lamp pumped alexandrite laser emits in the 715–800 nm range and a birefringent tuning element (Fabry–Perot interferometer type) narrows the band to approximately $\Delta\nu < 10 \text{ cm}^{-1}$. For the experiment described here, the fundamental is doubled, then mixed with the first harmonic to produce the third harmonic between ~ 235 and 270 nm.

Perylene molecules are vacuum evaporated from an oven at about 110 °C, and are codeposited with argon gas flowing from a separate tube onto the cold (10 K), sapphire

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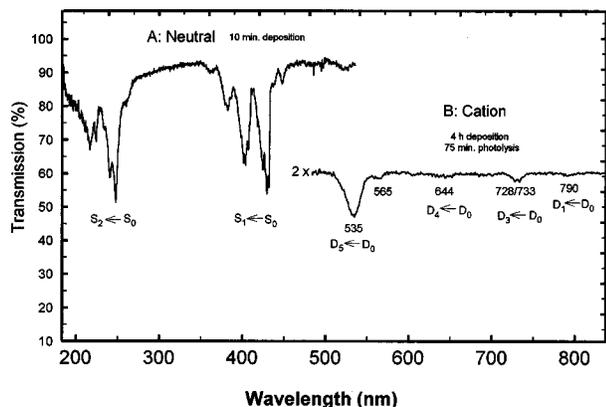


FIG. 1. Absorption spectra of (A) neutral perylene and (B) the perylene cation isolated in an argon matrix. Deposition conditions are 10 min for the neutral and 4 h followed by 75 min photolysis for the cation. In both cases an Ar flow of 10 mmol/h was used.

window cooled with a closed-cycle helium cryostat. Ions are formed, *in situ*, by vacuum ultraviolet (VUV) irradiation (10.2 eV) from a microwave-powered H₂/He (10%) flow lamp. Spectra are then recorded using a spectrograph equipped with a charge-coupled device (CCD) detector (1024×256 pixels) cooled to -10°C . For absorption, the combination of a 60–70 μm entrance slit with a 300 ℓ/mm grating blazed at 400 nm provides a spectral resolution of about 0.3 nm. For emission measurements, the excitation source beam and the detection system light path are at 90° with respect to one another, and the sample window is positioned at about 30° with respect to the laser excitation beam. The entrance slit is typically opened to 100–150 μm for emission and a 200 ℓ/mm grating blazed at 1000 nm is employed, yielding a spectral resolution of about 0.5 nm.

III. RESULTS

The absorption spectra of neutral perylene and its cation isolated in an Ar matrix are shown in Fig. 1. For the neutral molecule, two band systems are observed peaking at 248.0 ± 0.3 nm and 433.0 ± 0.3 nm, corresponding to the $S_2(^1B_{3u}) \leftarrow S_0(^1A_g)$ and $S_1(^1B_{1u}) \leftarrow S_0(^1A_g)$ transitions, respectively.¹³ A short (5–10 min) deposit of perylene with argon at an Ar flow rate of 10 mmol/h produces a matrix (peryene: Ar \sim 1:2000) with a good quality absorption spectrum for the neutral. In contrast, obtaining a similar quality absorption spectrum for the cation is more difficult, requiring 4 h of deposition followed by 75 min of photolysis to record only relatively weak bands. The perylene cation transitions, denoted in Fig. 1, are assigned as discussed in Refs. 6 and 7. The strongest absorption band falls at 535 ± 0.3 nm and is associated with the $D_5(^2B_{3g}) \leftarrow D_0(^2A_u)$ transition. The $D_3(^2B_{2g}) \leftarrow D_0(^2A_u)$ transition, which falls at 730 nm and is considerably weaker, shows substructure (728, 733 and minor features). The lowest energy transition [$D_1(^2B_{3g}) \leftarrow D_0(^2A_u)$] falls at 792 nm and is quite weak. There may also be evidence for the $D_4(^2B_{2g}) \leftarrow D_0(^2A_u)$ transition at 644 nm, just above the background. The difficulty inherent in measuring any UV transition associated with the perylene cation is illustrated in Fig. 1. Screening by the much more

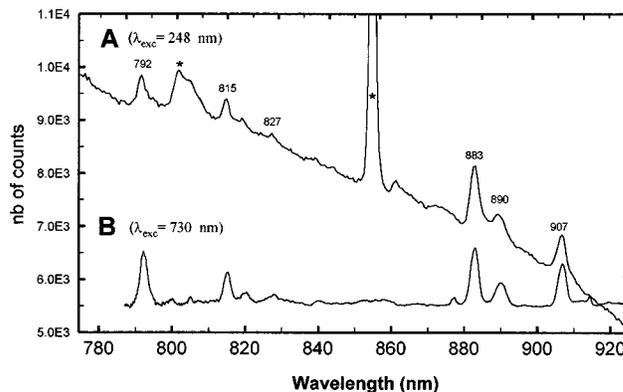


FIG. 2. Laser-induced fluorescence spectrum of the perylene cation isolated in an argon matrix excited at (A) $\lambda_{\text{exc}} = 248$ nm (D_n) and (B) $\lambda_{\text{exc}} = 730$ nm (D_3). The labeled peaks all arise from the perylene cation. (An asterisk designates spectral artifacts resulting from matrix scattering.)

intense bands that arise from neutral perylene makes direct absorption measurements of the cation impossible. To overcome this severe screening of the UV spectral range by unconverted neutral species inherent in matrix studies, we have developed the capability to measure the excitation spectra of ionized PAHs.

Figure 2 shows the dispersed fluorescence spectrum of the perylene cation ($\lambda_{\text{exc}} = 248$ nm) compared to that produced by direct excitation into the D_3 state at 730 nm. In both cases, $D_1 \rightarrow D_0$ perylene cation luminescence is observed. As discussed previously,^{6,7} the emission bands at 792, 815, 883, and 907 nm are associated with the perylene cation isolated in an Ar matrix. The $D_1 \rightarrow D_0$ transitions are associated with the vibrational modes of the ground electronic state. Figure 2 also proves that the perylene cation absorbs at 248 nm, the position where the strongest absorption (for the $S_2 \leftarrow S_0$ transition) of neutral perylene is measured (Fig. 1). This behavior is consistent with previous studies⁹ which conclude that the perylene cation does not undergo a drastic structural change with respect to neutral perylene. Ionized perylene is thus expected to have transitions that fall in the UV, close to its neutral counterpart. In addition to the perylene cation bands shown in Fig. 2, strong emission at 802 and 855 nm are also seen. They are due to scattering induced by the matrix and also appear from a blank matrix.

To probe the characteristics of perylene cation absorption in the 248 nm region, we have measured the excitation spectrum of the $D_n \leftarrow D_0$ band as shown in Fig. 3. This was recorded as follows. The output of the third harmonic of the Alexandrite fundamental was held constant at 1.3 mJ/pulse as the laser was manually scanned to 13 different excitation wavelengths between 238 and 263 nm. The complete dispersed fluorescence spectrum of the perylene cation was measured at each excitation wavelength.

Figure 3 shows the variation in intensity of the five principal perylene cation emission bands 792, 815, 883, and 907 nm as a function of the excitation wavelength. As expected, they show the same profile, indicating that they all arise from the same emitter. In Fig. 4, the UV absorption spectrum of

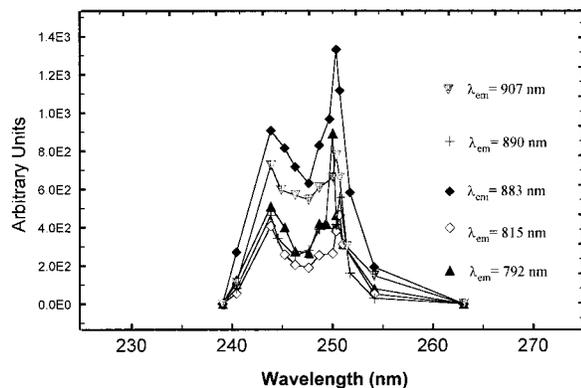


FIG. 3. Excitation spectrum of the perylene cation isolated in an argon matrix monitored at the five wavelengths (792, 815, 883, 890, and 907 nm) associated with the $D_1 \rightarrow D_0$ transition as shown in Fig. 2.

neutral perylene (recorded with a deuterium lamp as a light source) is compared with the laser-induced fluorescence excitation spectrum of the perylene cation. The laser-induced fluorescence excitation spectrum is constructed by summing, at each wavelength position, the intensities of the five emission bands associated with the $D_1 - D_0$ transition shown in Fig. 3. The UV band of the ion presents a doublet structure as does the corresponding transition of the neutral. The maxima are located at 244 ± 0.5 nm and 250.2 ± 0.5 nm with an energy difference of 1016 cm^{-1} which falls in the range of the C-H in-plane bending vibrations.¹⁴ Compared to the neutral band peaks, which fall at 241 ± 0.3 nm and 248 ± 0.3 nm, the ion peaks are redshifted by 510 and 355 cm^{-1} , respectively. This redshift could be an indication that, due to the destabilization of the electronic ground state by removal of an electron, the ground electronic state of the ion (D_0) lies

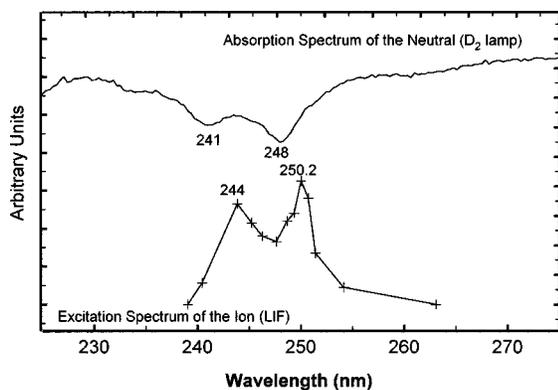


FIG. 4. Comparison between the Ar matrix absorption spectrum of the $S_2(^1B_{3u}) \leftarrow S_0(^1A_g)$ transition of neutral perylene with the excitation spectrum of the cation. The excitation spectrum is the sum of the intensities of the five bands shown separately in Fig. 3.

at higher energy than the corresponding state (S_0) in the neutral. This destabilization may also be interpreted as another indication that the electronic structure of the perylene cation is not a delocalized antiaromatic, 20π electron cloud, but, rather two distinct aromatic, 10π electron clouds (naphthalene moieties) as considered in Ref. 7.

IV. CONCLUSION

We report the first observation of an UV transition of an ionized PAH. The UV excitation spectrum of the $D_n - XD_0$ transition of the perylene cation ($C_{20}H_{12}^+$) isolated in an argon matrix was pumped with tunable, coherent radiation and monitored using the vibronic bands of the $D_1(^2B_{3g}) \rightarrow (^2A_u)D_0$ system. The two component band peaks at 244 and 250.2 nm, close to the $S_2(^1B_{3u}) \leftarrow (^1A_g)S_0$ transition in neutral perylene.

From the astrophysical point of view, this further supports the PAH hypothesis, showing that PAH cations can be excited with UV as well as visible photons and provides the first example of a possible DIB carrier class which converts UV photons into red photons via a classical pump-emission mechanism.

ACKNOWLEDGMENTS

This work was supported by NASA's Laboratory Astrophysics (Grant Nos. 344-02-06-01 and 344-01-57-41) and Long-Term Space Astrophysics Programs (Grant No. 399-20-61). X.D.F.C. thanks the *Swiss National Science Foundation* for his support. B.M.S. acknowledges the Stanford/NASA Ames Research Center/American Association for Engineering Education (ASEE) summer Faculty Fellowship Program for support.

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