LETTERS TO THE EDITOR

COMMUNICATIONS

Photoinduced fluorescence from the perylene cation isolated in Ne and Ar matrices

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The fluorescence and fluorescence excitation spectra of the perylene cation isolated in neon and argon matrices are reported. This is the first report of the fluorescence spectrum of a polycyclic aromatic hydrocarbon ion in any phase. © *1995 American Institute of Physics.*

I. INTRODUCTION

Polycyclic aromatic hydrocarbon (PAH) ions are considered to be plausible candidates to account for the diffuse interstellar bands (DIBs). The DIBs are visible absorption features observed in the spectrum of the interstellar matter. A recent review of the DIB carrier candidates is given in Ref. 1. It has quite recently been recognized that some DIBs are also seen in emission[2] implying that their carriers can relax radiatively. We have developed an experiment to study the electronic luminescence of cold, isolated PAH ions and thereby test their relevance as a class of DIB carrier candidates. With the exception of benzene and some of its derivatives,[3(a),3(b)] and the decacyclene anion,[3(c)] no studies of the luminescence of aromatic ions have been published. We report here the fluorescence of the perylene cation $(C_{20}H_{12}^{+})$ isolated in inert gas matrices (Ne, Ar).

II. EXPERIMENT

The experimental setup used for the study of the absorption of neutral and ionized PAHs using matrix isolation spectroscopy has been described previously.[4] Briefly, the experimental procedure consists of (i) preparing a sample of neutral and ionized perylene molecules isolated in a rare gas matrix, (ii) probing the sample in absorption to check the degree of isolation of the trapped molecular species and their ionization yield, and finally (iii) performing luminescence measurements.

Neon (or argon) gas and perylene, evaporated under vacuum from an oven, are co-deposited on the cold (4.2 K) sapphire window of a continuous flow liquid helium cryostat. Ions are formed by the VUV radiation (10.2 eV) from a microwave-powered H_2 flow lamp. The absorption spectrum of the ions formed *in situ* is measured with a UV-visible near IR spectrograph. For emission studies, the excitation source and the detection system light paths are at 90° with respect to one another, and the sample window is positioned at about 30° with respect to the excitation source light path. A quartz tungsten halogen lamp serves as the excitation source. Radiation from this lamp is filtered with a 0.2 m monochromator to provide broadband excitation (typically 20 nm FWHM and 40 nm base width, for 6 mm slits). The entrance slit of the spectrograph is opened at 30 μm for absorption measurements and 1 mm for emission measurements. The spectral resolution is 0.1 nm for the absorption spectra presented here, and about 1 nm for the emission spectra. The band positions given in this study are averaged over several experiments and the errors correspond to one sigma.

III. RESULTS

The absorption spectrum of the perylene cation isolated in a Ne matrix is shown as a solid line in Fig. 1. This spectrum compares well (allowing for the matrix-induced shift) to the absorption spectrum of the perylene cation isolated in an Ar/CCl$_4$ matrix.[5] Transitions are assigned following Ref. 6. The strongest absorption band falls at 525.1 ±0.1 nm and is associated with the $D_0(^2A_u) \rightarrow D_5(^2B_{3g})$ transition. The low energy $D_0(^2A_u) \rightarrow D_1(^2B_{3g})$ transition is weak. The bands associated with this transition show a multicomponent splitting which is not observed in Ar matrices. For example, the origin of the transition consists of at least five components at 791.7, 792.7, 793.6, 794.3, and 794.8 ±0.1 nm. This splitting can arise from the presence of different sites within
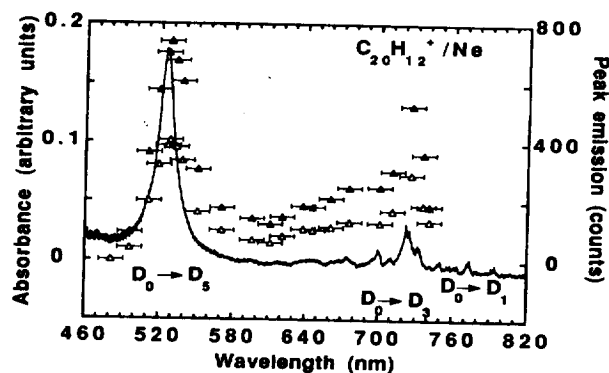

FIG. 1. The visible absorption spectrum of the perylene cation $(C_{20}H_{12}^{+})$ isolated in a Ne matrix (solid line). The triangles represent fluorescence excitation spectra. The peak intensities of the strongest emission bands (Fig. 2) at 794.1 (plain triangles) and 817.3 nm (empty triangles) are plotted vs the central wavelength of the excitation band. The 20 nm wide excitation bandwidth is indicated by the horizontal bars.
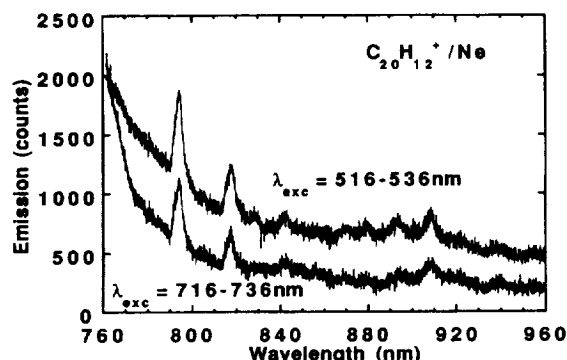
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FIG. 2. The $D_0(^2A_u)\leftarrow D_1(^2B_{3g})$ fluorescence spectrum of the perylene cation ($C_{20}H_{12}^+$) isolated in a Ne matrix at 4.2 K. The same emission spectrum is induced by pumping the two strongest absorption bands of the cation (525 and near 723 nm) with a 20 nm FWHM band. The spectra have not been corrected for the instrumental response of the system.

the solid matrix and/or from transitions involving low vibrational frequencies of the perylene cation. In particular, low frequencies at 13 and 48 cm^{-1} have been deduced from jet measurements of the S_1 state of neutral perylene[7] and identified as the low frequency modes of the molecule.[8] These spectral details will be discussed in a forthcoming paper.[9]

A set of emission bands are observed to the red of the first absorption system when exciting in the region of the strong 525.1 nm absorption band (Fig. 2, upper trace). A similar emission spectrum is obtained when exciting in the region encompassing the $D_0(^2A_u)\rightarrow D_3(^2B_{2g})$ transition, centered near 723 nm (Fig. 2, lower trace).

The first (highest energy) emission band falls at 794.1 ±0.1 nm with a shoulder at 792.3±0.1 nm. To check that the perylene cation is indeed responsible for this emission, we have measured the excitation spectrum. The upper spectra

(plain and empty triangles) in Fig. 1 represent the peak intensities of the two strongest emission bands at 794.1 and 817.3 nm as a function of the central wavelength of the excitation band. The excitation band is about 20 nm wide at half-maximum in each case as indicated by the horizontal bars in Fig. 1. To remove any contribution from the second order of the neutral precursor strong fluorescence, which falls between 420 and 520 nm, a red filter (Model BG 715) has been installed between the sample and the collection optics. The agreement shown in Fig. 1 between the absorption and the fluorescence excitation spectra indicates that the perylene cation is the carrier of the strongest emission features displayed in Fig. 2. The weaker emission features to the red seem to be related to the strongest features.

The 794.1 nm emission band is very close to the first electronic transition of the perylene cation and, in particular, to the 794.3 nm absorption component. Thus, we assign the 794.1 nm emission band to the fluorescent emission associated with the 0–0 transition from the $D_1(^2B_{3g})$ to the $D_0(^2A_u)$ state. The other emission bands seen at lower energies probably arise from transitions between the lowest level of the D_1 state to various excited vibrational levels of the ground state D_0 (see Table I). Shoulders observed on the blue side of the emission bands are likely due to fluorescence from a different matrix site, as the shoulder observed at 792.3 nm is very close to the 792.7 nm absorption component.

The emission spectrum of the perylene cation isolated in an Ar matrix at 4.2 K has also been measured and is compared in Fig. 3 to the Ne matrix spectrum. The origin of the emission band at 792.2±0.1 nm in an Ar matrix is slightly red-shifted compared to the origin of the $D_0\rightarrow D_1$ transition measured at 791.2±0.1 nm in absorption.[5,9] Excitation spectroscopy confirms that each (strong) band is related to the perylene cation.

TABLE I. Fluorescence band positions and vibrational spacings of the perylene cation isolated in Ne and Ar matrices at 4.2 K. The band intensities are characterized as strong (s), medium (m), weak (w), and very weak (vw). Blue shoulders (sh) are observed in Ne matrices, which are attributed to the presence of a different site in the solid matrix. The spacings associated with this site are indicated by an asterisk (*). All symmetrical (a_g) frequencies calculated for the D_0 state (Ref. 6) are reported for comparison.

| Ne matrix		Ar matrix		Calculations
λ (nm)	Δν (cm^{-1})	λ (nm)	Δν (cm^{-1})	Δν (cm^{-1})
792.3±0.1 (sh)	0* (−28±2)			
794.1±0.1 (s)	0	792.2±0.1 (s)	0	
815.4±0.1 (sh)	356±1*			
817.3±0.2 (s)	356±2	815.3±0.1 (s)	358±3	363
		820.0±0.1 (w)	428±2	486
828.8±0.2 (vw)	526±2	828.2±0.2 (vw)	549±4	572
842.3±0.1 (w)	720±1 (356×2)			834
869.7±0.3 (vw)	1094±5			1043, 1120
878.4±0.8 (vw)	1207±10			1188
		883.4±0.1 (s)	1303±2	1308
891.3±0.1 (sh)	1400±1*			
893.5±0.1 (w)	1400±2	890.8±0.1 (s)	1397±2	1362, 1418, 1478
906.5±0.2 (sh)	1589±1*			
908.8±0.2 (m)	1589±2	907.3±0.2 (s)	1601±1	1557, 1636
938.5±0.1 (vw)	1937±2 (1589+356)			
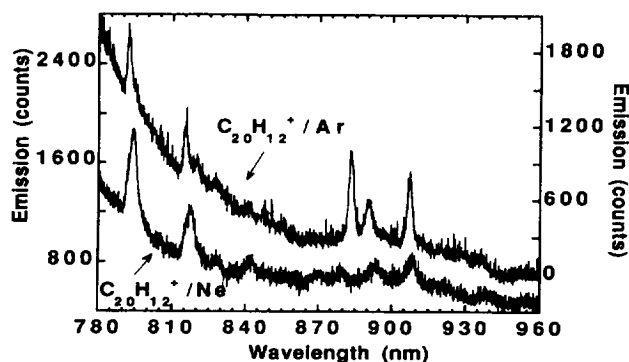
FIG. 3. The $D_0(^2A_u) \leftarrow D_1(^2B_{3g})$ fluorescence spectrum of the perylene cation ($C_{20}H_{12}^+$) isolated in Ar (upper trace) and Ne (lower trace) matrices at 4.2 K. The emission is induced by pumping the strong $D_0(^2A_u) \rightarrow D_5(^2B_{3g})$ absorption band at 525.1 and 534.8 nm in Ne and Ar matrices, respectively, with a 20 nm FWHM band. The emission spectra have not been corrected for the instrumental response of the system.

The positions of the emission bands and the associated vibrational spacings are summarized in Table I. The spacing values of 358, 549, 1397, and 1601 cm^{-1} measured in Ar matrices are in good agreement with the values of 356, 526, 1400, and 1589 cm^{-1} measured in Ne matrices, and compare well with theoretical calculations, supporting their assignment as fundamental frequencies of the D_0 state of the perylene cation. Figure 3 shows that the relative intensities of the emission bands observed in the 880–910 nm range, compared to the bands observed in the 790–830 nm range, are much stronger in Ar than in Ne matrices. Also, the strong 883.4 nm band in the Ar matrix, which corresponds to a spacing of 1303 cm^{-1} from the 0–0 band, is not observed in Ne. These differences observed between the two matrix environments will be discussed in detail in Ref. 9.

IV. CONCLUSION

We report the fluorescence spectra of the perylene cation isolated in neon and argon matrices. Evidence is found for medium-induced perturbations as well as site selectivity. This will be discussed in detail in a forthcoming paper.[9] Due to its fluorescence properties, the perylene cation seems to be an attractive candidate for studies of the electronic properties of an isolated PAH ion in molecular beams. From an astrophysical point of view, these studies show that PAH ions can also be considered as potential carriers of DIBs seen in emission. However, as with all DIB assignments, measurements on species in the gas phase are needed.

ACKNOWLEDGMENTS

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