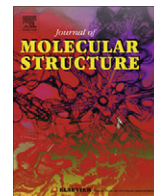




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Fluorescence of protonated pyrene and coronene in neon matrices

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ABSTRACT

Fluorescence spectra of protonated pyrene and coronene in solid neon have been observed. Laser excitation of the $S_n \leftarrow S_0$ transitions of the cations results in an extended, vibrationally-resolved $S_1 \rightarrow S_0$ fluorescence with onset at 487.8 and 695.4 nm for protonated pyrene and coronene, respectively. Vibrational assignment of the spectra has been made on the basis of the calculated frequencies of normal modes in the ground electronic state. The astrophysical relevance of the frequencies inferred for these protonated cations is discussed.

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1. Introduction

Studies on protonated polycyclic aromatic hydrocarbons (H-PAHs⁺) have been initiated over 50 years ago by Olah on organic carbocations. These were obtained by dissolving PAHs in strong acidic solutions and were studied by means of IR, electronic and NMR spectroscopy [1–3]. A novel interest on H-PAHs⁺ arose several years ago and was associated with the hypothesis that H-PAHs⁺ can be responsible for the unidentified infrared emission bands (UIR) observed in many astronomical objects, and the diffuse interstellar bands [4–7]. It was also postulated that H-PAHs⁺ play a role of catalysts in the synthesis of H_2 in the interstellar medium (ISM) [8,9].

Several medium size H-PAHs have been studied in the infrared region by means of single photon dissociation of tagged H-PAH⁺ ions as well as their multi-photon dissociation [10–15]. Some of them have been studied in the optical domain in the gas phase and in neon matrices [16–20]. Recently, the electronic spectrum of an astrophysically model molecule – protonated coronene in a neon matrix has been reported [20]. In the present contribution the wavelength-dispersed fluorescence of protonated pyrene and coronene are presented and the inferred ground state vibrational frequencies are discussed in their astrophysical context.

2. Experiment

The experimental set-up used has been described [21]. Protonated pyrene (H-Py⁺) and protonated coronene (H-Cor⁺) were produced in a hot cathode discharge source from ethanol vapor

mixed with an appropriate aromatic hydrocarbon. The reaction involves proton transfer from protonated ethanol to PAH in the ion source [20]. Electrostatic lenses extracted the ions and guided them through a static bender, where they were separated from neutral species, into a quadrupole mass filter. After mass selection, the cations of interest were codeposited with a mixture of neon and chloromethane onto a rhodium-coated sapphire plate held at 6 K. CH_3Cl mixed with neon in the ratio 1:20,000 was used; it suppresses ion neutralization during deposition by capturing free electrons and reduces the space charge of the matrix.

Electronic absorption spectra were recorded in the 220–1100 nm range by passing broadband light of a halogen or a high-pressure xenon lamp through the matrix parallel to the sapphire substrate. The light exiting was transmitted by a bundle of quartz fibers to a spectrograph equipped with a CCD camera.

Wavelength-dispersed fluorescence spectra were obtained from the same matrix by the excitation of the cations with a pulsed, tunable laser of $\sim 3 \text{ cm}^{-1}$ bandwidth and $\sim 2\text{--}30 \text{ mJ}$ energy as described [22]. The emission was collected with a short-focus lens perpendicular to the matrix surface and 45° to the laser beam. The optical signal was transmitted through a bundle of quartz fibers to the spectrograph and recorded with CCD camera. The spectra were measured in 50–65 nm overlapping sections starting $\sim 2 \text{ nm}$ above the excitation wavelength to eliminate saturation of the CCD. In each section the emission was averaged over 1000 laser shots.

3. Results

3.1. Protonated pyrene

The absorption spectrum of protonated pyrene in a neon matrix has been reported recently. Three electronic transitions have been

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detected in the 250–500 nm range and assigned to the 1H-Py⁺ isomer on the basis of the experimental observations and theoretical calculations [20]. The strongest system with origin at 487.5 nm was assigned to the $S_1(^1A') \leftarrow S_0(^1A')$ transition (Fig. 1, black). It is characterized by a strong, sharp origin band and extended vibrational structure; from its analysis several frequencies in the excited $S_1(^1A')$ electronic state have been obtained. Higher energy electronic transitions of 1H-Py⁺ observed are much weaker. Their origins lie at 378.6 and 279.2 nm and correspond to the $S_3(^1A') \leftarrow S_0(^1A')$ and $S_4(^1A') \leftarrow S_0(^1A')$ transitions, respectively.

Laser excitation of any absorption band in the 487.5 nm system of 1H-Py⁺ (top panel of Fig. 1) induces fluorescence which starts at ~488 nm and continues to longer wavelengths. The vibrationally-resolved spectrum obtained after excitation into the 474.3 nm absorption band is shown in Fig. 1 (magenta trace). Weak features seen above 530 nm are reproducible and they extend to 590 nm. The long-wavelength edge of the absorption overlaps with the short-wavelength one of the fluorescence at 487.5 nm and is the zero-phonon line of the origin band of the $S_1(^1A') \leftarrow S_0(^1A')$ transition of 1H-Py⁺.

A weaker emission was observed following the excitation of two other electronic transitions of 1H-Py⁺: $S_3 \leftarrow S_0$ at 378.6 nm and $S_4 \leftarrow S_0$ at 279.2 nm. The spectra are shown, together with the respective absorptions, in the middle and bottom panels of Fig. 1. Structured emission has been detected in each case, though a broad absorption band has been excited (middle trace). The position of the bands and their relative intensities in the fluorescence spectra are identical with the ones recorded upon excitation of the first electronic transition of 1H-Py⁺. The present fluorescence study confirms our earlier assignment that two UV absorption systems with onsets at 378.6 nm and at 279.2 nm belong to the same molecule as the 487.5 nm one, namely 1H-Py⁺.

Because the strongest fluorescence band coincides with the origin band of the first absorption system and no other peak has been detected at the shorter wavelength, the emission seen in Fig. 1 is the transition from the zero vibrational level of the $(1)^1A'$ excited state of 1H-Py⁺ to vibrationally excited levels in the \tilde{X}^1A' ground state. A fast internal conversion of the higher electronic states to the $(1)^1A'$ state and vibrational relaxation takes place prior to the emission, a common behavior of large molecules.

The positions of the most prominent bands along with the vibrational frequencies derived from the fluorescence spectrum of 1H-Py⁺ are collected in Table 1. It should be noted, that the wavenumbers $\tilde{\nu}/\text{cm}^{-1}$, which are given in tables and were used for the vibrational frequencies obtained, are calculated as reciproc-

Table 1

Band maxima (± 0.1 nm) of the $(1)^1A' \rightarrow \tilde{X}^1A'$ fluorescence of protonated pyrene, 1H-Py⁺, in a 6 K neon matrix. Intensity is indicated as strong or medium (all others are weak).

λ_{Ne} (nm)	$\tilde{\nu}$ (cm^{-1}) ^a	$\Delta\tilde{\nu}$ (cm^{-1})	a' (calc.)	Assignment ^b
487.8 s	20,499	0		$0_0^0 (1)^1A' \rightarrow \tilde{X}^1A'$
494.3	20,229	270		
495.7	20,172	327	343	ν_{50}
497.4	20,105	394	400	ν_{49}
498.6 s	20,057	442	448	ν_{48}
499.4 m	20,023	476	486	ν_{47}
502.0 s	19,920	579	586	ν_{44}
504.2	19,833	666	674	ν_{43}
505.3	19,789	710	718	ν_{42}
507.2	19,718	781	787	ν_{41}
507.9 m	19,691	808	813	ν_{40}
509.9 m	19,611	888		$2\nu_{48}$
510.9	19,574	925	937	ν_{39}
513.6 m	19,472	1027		$\nu_{48} + \nu_{44}$
514.6	19,433	1066		$\nu_{47} + \nu$
517.2 m	19,334	1165	1169	ν_{32} or $2\nu_{44}$
519.0 m	19,269	1230	1224	ν_{29}
519.7 m	19,241	1258	1244	ν_{27}
520.8	19,201	1298		
522.8	19,127	1372	1379	ν_{23}
523.7 m	19,095	1404	1409	ν_{21}
525.8	19,019	1480	1490	ν_{17}
526.2	19,005	1494	1507	ν_{16}
528.5	18,920	1579	1578	ν_{14}
529.3	18,893	1606	1593	ν_{13}
529.7 m	18,880	1619	1620	ν_{12}
536.4	18,644	1855		
542.7	18,426	2073		
546.8	18,287	2212		

^a $\tilde{\nu} = 1/\lambda_{\text{Ne}}$.

^b Vibrational assignment is based on a' modes (cm^{-1}) of 1H-Py⁺ in its electronic ground state computed with DFT/B3LYP/cc-pVDZ (scaled by 0.98): 343, 400, 448, 486, 492, 526, 586, 674, 718, 787, 813, 937, 968, 991, 1083, 1119, 1137, 1153, 1169, 1183, 1197, 1224, 1234, 1244, 1317, 1332, 1359, 1379, 1395, 1409, 1421, 1427, 1450, 1490, 1507, 1547, 1578, 1593, 1620, 1642.

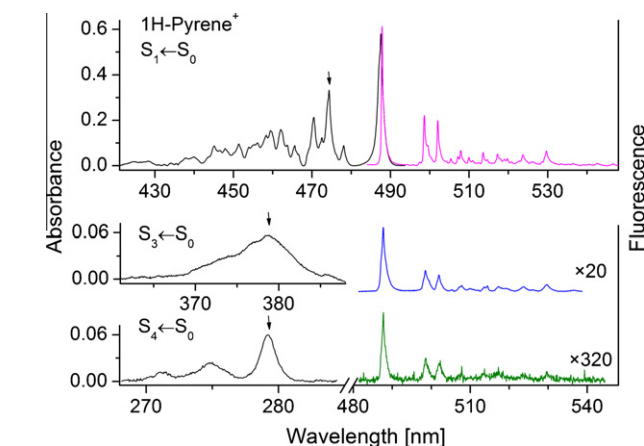


Fig. 1. Electronic absorption (left) and fluorescence (right) spectra of protonated pyrene (1H-pyrene⁺ isomer) in a neon matrix. The fluorescence was observed upon laser excitation at the wavelengths indicated with arrows.

cal of the corresponding wavelengths. In gas-phase spectroscopy corrections for the refractive index of air are required. In order to provide correct wavenumbers (in vacuum) for measurements in neon matrices refractive indexes of both air and neon have to be taken into account. Such corrections, however, are not relevant in rare gas matrices, because the bands are broad and the shifts are less than the position uncertainty.

The strongest fluorescence band is the onset of the electronic transition. Two other peaks spaced from the origin by 442 and 579 cm^{-1} dominate the emission. Their overtones and combinations are also apparent. In order to assign the transitions, calculations of the frequencies of the normal modes of 1H-Py⁺ using density functional theory (DFT) with the B3LYP functional and the cc-pVDZ basis set were carried out. The cation has 50 totally symmetric normal modes (a' symmetry), which can be active in the fluorescence. The calculated frequencies are given in the footnote of Table 1 and are compared, after scaling by 0.98, with the observed ones. The modes of energy above 3000 cm^{-1} are not included, because no fluorescence bands were detected in the corresponding region. The agreement between the calculated and the observed frequencies, particularly for the lowest-energy modes, is good. Somewhat less certain is the assignment of the bands with ground state frequencies >1000 cm^{-1} due to a congestion of normal modes in this region.

Recently, infrared transitions of a number of protonated polycyclic hydrocarbon cations have been studied in the gas-phase by infrared multiphoton dissociation spectroscopy (IRMPD) by observing H-atom or H₂ loss [15,23]. Protonated pyrene was also among them, with four strong broad bands in the 1100–1600 cm^{-1} range and two weaker ones below 1100 cm^{-1} . The ob-

served IR peaks are broad ($\sim 30\text{ cm}^{-1}$) mainly due to the multiphoton character of the IRMPD process. In the neon matrix the resolution of the fluorescence bands of 1H-Py^+ was around 5 cm^{-1} and more than 20 normal modes are identified in the spectrum. This then provides a large set of vibrational frequencies of 1H-Py^+ in its electronic ground state. The neon matrix to gas phase shift should not be larger than 16 cm^{-1} (1% of the transition energy) for the modes below 1600 cm^{-1} [24].

3.2. Protonated coronene

Laser excitation into any absorption band of the $S_1 (^1A') \leftarrow S_0 (^1A')$ electronic system of protonated coronene (H-Cor^+) results in emission in the near infrared. The fluorescence spectrum obtained after excitation at 678.5 nm , where a strong absorption band next to the origin is located, is shown in top panel of Fig. 2 together with the respective absorptions. The spectrum is characterized by well resolved vibrational structure which is a mirror image of the absorption system. The strongest band is the origin and it partially overlaps with the onset of the absorption. Almost equally strong emission was detected once the onsets of the $S_n \leftarrow S_0$ ($n = 2-4$, all of $^1A'$ symm.) transitions have been excited. The resulting fluorescence spectra are shown in bottom panel of Fig. 2. The fluorescence observed upon excitation to the S_n states of H-Cor^+ indicates that the main relaxation channel is internal conversion to S_1 . In the case of 1H-Py^+ the intensity of the fluorescence decreases with the excitation to the higher electronic states (S_3 , S_4) which subsequently decay non-radiatively to S_0 faster than to S_1 .

Several fundamental vibrations have been derived from the fluorescence spectrum of H-Cor^+ and are gathered in Table 2. The assignment of the vibrations given is based on the calculated frequencies of the normal modes using the DFT method with B3LYP functional and cc-pVDZ basis set. The agreement between the observed frequencies and calculated ones after scaling by 0.98 is quite good. The assignment in the $1000\text{--}1250\text{ cm}^{-1}$ range is tentative, because there are many calculated modes in this range with frequencies within $20\text{--}30\text{ cm}^{-1}$ of the observed values.

Protonated coronene has also been studied in the gas phase by the IRMPD method [15]. The obtained spectrum is composed of several broad bands, as was the case with 1H-Py^+ . The inferred frequencies are compared with the neon matrix data given in Table 2. Not all vibrations observed in the gas phase have counterparts in the fluorescence spectrum of H-Cor^+ . For some of the modes the difference between the gas phase and neon matrix is as large as 30 cm^{-1} . The frequencies in the gas phase, due to the broadness

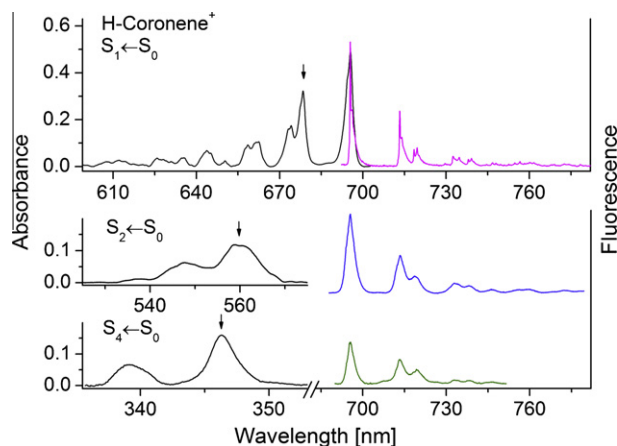


Fig. 2. Electronic absorption (left) and fluorescence (right) spectra of protonated coronene in a neon matrix. The fluorescence was observed upon laser excitation at the wavelengths indicated with arrows.

Table 2

Band maxima ($\pm 0.1\text{ nm}$) and the vibrational assignment of the $(1) ^1A' \rightarrow \bar{X} ^1A'$ fluorescence of protonated coronene, H-Cor^+ , in a 6 K neon matrix.

λ_{Ne} (nm)	$\bar{\nu}$ (cm^{-1}) ^a	$\Delta\bar{\nu}$ (cm^{-1})	a' (calc.)	Assignment ^b
695.4	14,381	0		$0_0^0 (1) ^1A' \rightarrow \bar{X} ^1A'$
713.4	14,018	363	357/360	ν_{70} [or ν_{69}]
718.5	13,918	463	462	ν_{66}
719.5	13,898	483	484/484	ν_{64} [or ν_{63}]
729.6	13,707	674	670/671	ν_{59} [or ν_{58}]
732.4	13,654	727		$2\nu_{70/69}$
734.5	13,615	766	761	ν
737.9	13,552	829		$\nu_{70/69} + \nu_{66}$
738.9	13,533	848		$\nu_{70/69} + \nu_{64/63}$
746.8	13,390	991	977/980	$\nu_{52/51}$
748.1	13,368	1013	1006	ν_{50}
752.6	13,288	1093		$3\nu_{70/69}$
754.4	13,255	1126	1129	ν_{48}
756.3	13,222	1159	1153	ν_{44}
759.7	13,163	1218	1215	ν_{41}
761.3	13,135	1246	1243	ν_{37}
768.0	13,021	1360	1355	$2\nu_{59/58}$ or ν_{32}
772.6	12,943	1438	1441	ν_{25}
774.1	12,919	1462	1464	$4\nu_{70/69}$ or ν_{23}
778.1	12,852	1529	1526	ν_{20}
783.9	12,756	1625	1624/1636	$\nu_{14/13}$

^a $\bar{\nu} = 1/\lambda_{\text{Ne}}$.

^b Vibrational assignment is based on the a' modes in the electronic ground state of protonated coronene obtained with DFT/B3LYP/cc-pVDZ (scaled by 0.98): 357, 360, 371, 377, 462, 473, 484, 484, 546, 620, 658, 670, 671, 751, 761, 788, 807, 911, 977, 980, 1006, 1062, 1129, 1140, 1144, 1148, 1153, 1186, 1200, 1215, 1222, 1226, 1229, 1243, 1306, 1313, 1318, 1355, 1365, 1378, 1388, 1397, 1404, 1418, 1425, 1441, 1459, 1464, 1484, 1518, 1526, 1543, 1561, 1593, 1610, 1618, 1624, 1636 cm^{-1} .

of the peaks in the spectrum, were determined with a large error. On the other hand the neon matrix fluorescence data show a random shift in comparison to the gas-phase values.

4. Astrophysical implications

Coronene is a reasonably sized molecule which is often considered as a model of PAHs in the discussions of their role in the ISM. According to one hypothesis, protonated PAHs can be the carriers of the UIR bands observed in emission from variety of astronomical objects [4]. Another hypothesis states that above a certain size the protonated PAHs “lose identity” and their IR spectra are similar and closely resemble UIRs [15,23]. Therefore experimental data on the vibrations of protonated pyrene and coronene are desirable.

The wavelength-dispersed fluorescence spectra of protonated pyrene and coronene isolated in 6 K neon matrices provide a better set of vibrational frequencies in the ground state than the IRMPD spectra recorded in the gas phase. In order to compare the vibrations of these two cations their fluorescence spectra are plotted on a wavenumber scale with their origins shifted to the same position (Fig. 3). The spectra differ particularly in the low frequency range, where two bands dominate. These originate from an in-plane deformation of the PAH skeleton. Higher frequencies are observed for these vibrations in the case of 1H-Py^+ . They are 442 and 579 cm^{-1} , the latter is the ring-breathing mode. In the case of H-Cor^+ the lowest frequency vibrations lie at 363 and 483 cm^{-1} and the latter is the ring-breathing mode.

Protonated PAHs (1H-Py^+ , H-Cor^+) once electronically excited decay radiatively. UIR bands are assumed to result from the electronic excitation of PAHs⁺ and/or H-PAHs⁺ by UV light of the nearby stars. The cations subsequently decay nonradiatively to high vibrational levels of the electronic ground state, which relax radiatively in the IR and may cause the UIR bands.

The fluorescence spectra of 1H-Py^+ and H-Cor^+ measured experimentally are compared with the positions of UIR bands marked

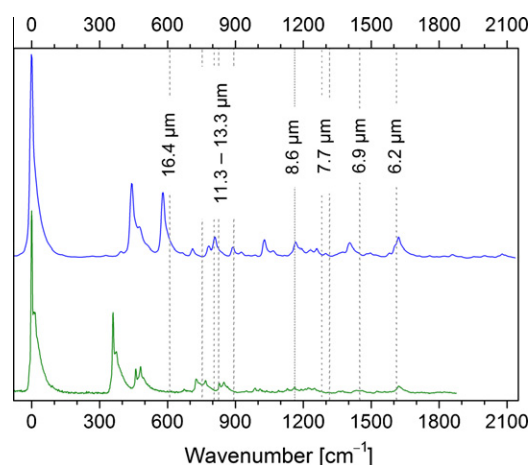


Fig. 3. Comparison of the vibrational frequencies derived from the fluorescence spectra of protonated pyrene (blue) and protonated coronene (green) in neon matrices. The origin bands are shifted to the same position. The spectral positions of several UIR bands are indicated with dashed lines. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

with vertical broken lines in Fig. 3 [25]. The vibration around 1620 cm^{-1} is observed for both cations and it coincides with the $6.2\text{ }\mu\text{m}$ UIR band. Though the fluorescence spectra provide frequencies of many normal modes of the cations, the intensities derived from these spectra can differ from those, measured with IRMPD technique in the middle infrared region. In the former case they reflect the geometry change upon electronic excitation of the cation and depend on the Franck–Condon factors. In the IRMPD spectra these are dependent on the multiphoton and the action character of the method used.

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