

Cavity ring-down spectroscopy of jet-cooled 1-pyrenecarboxyaldehyde ($C_{17}H_{10}O$) and 1-methylpyrene ($C_{17}H_{12}$) cations

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Abstract

To study the correlation between pyrene-like species and the diffuse interstellar bands (DIBs), we have investigated the electronic transitions of 1-pyrenecarboxyaldehyde⁺ and 1-methylpyrene⁺, which were prepared with a pulsed discharge slit nozzle and detected by cavity ring-down spectroscopy. Several vibronic bands were observed near the $\lambda 4428$ DIB is detected. Time-dependent density functional theory calculations were performed to aid the assignment of these bands. It is found that none of the observed bands correlate with the $\lambda 4428$ DIB. The effect of side groups on the vibronic spectrum of pyrene⁺ is discussed.

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1. Introduction

The study of interstellar dust is important to understand the evolution of the interstellar medium. Polycyclic aromatic hydrocarbons (PAHs) are an important component of interstellar dust in galactic and extragalactic environments. PAHs are thought to carry the ubiquitous infrared emission bands (UIBs) and some of the diffuse interstellar bands (DIBs) seen in absorption in the near ultraviolet to near infrared spectra of stars that are obscured by diffuse interstellar clouds [1]. Interstellar PAHs can be neutral or ionized depending on the environmental conditions (density and radiation field). In diffuse interstellar clouds, for instance, PAHs are expected to be present as free, cold, neutral molecules and ions [2]. An extensive laboratory effort has been devoted over the past decade to the study of the spectroscopy of free PAH ions. This effort was essentially based on matrix isolation spectroscopy (MIS) where the PAH molecules and ions were isolated in solid inert gas matrices [3]. Measurements of the electronic spectra of the pyrene cation in inert gas matrices of Ar and Ne sug-

gest this cation or its substituted forms as potential carriers for the strong $\lambda 4428$ DIB [4]. As a result, the absorption spectra of the cold methylpyrene, ethylpyrene and pyrenecarboxyaldehyde cations trapped in solid inert gas matrices of Ar and Ne have been reported and discussed in the context of the diffuse interstellar bands [5–7]. In particular, the 1-methylpyrene cation has been proposed to be the common carrier of the $\lambda 4428$ and $\lambda 7565$ DIBs based on its MIS spectrum in Ne [7].

Although major advances were made possible in laboratory astrophysics by the use of MIS, definitive conclusions could not be reached due to the perturbation induced by the solid matrix on the intrinsic spectral characteristics (band position and profile) of the trapped species. Recently, cavity ring-down spectroscopy in free jets [8–11] and laser mass spectroscopy [12,13] techniques have been successfully applied to this problem leading to new insights into the vibronic spectroscopy and the intramolecular dynamics of free PAH ions. The electronic absorption spectrum of the pyrene cation ($C_{16}H_{10}^+$) in the gas phase has now been measured [10] and *definitely excluded* the pyrene cation as the carrier of the $\lambda 4428$ DIB. In this Letter, we report direct absorption measurements in the gas phase of the vibronic bands of the 1-pyrenecarboxyaldehyde ($C_{17}H_{10}O^+$) and 1-methylpyrene cations ($C_{17}H_{12}^+$). We also

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examine the implications of these new laboratory data for the diffuse interstellar bands.

The experimental and theoretical approaches are briefly described in Section 2. The experimental results are discussed in the following section. The conclusions are discussed in Section 4.

2. Experiment and calculations

The experimental apparatus has been described in detail previously [14,15]. In brief, a pulsed supersonic free jet containing 1-methylpyrene (TCI America, 97.0%) or 1-pyrenecarboxyaldehyde (Sigma–Aldrich, 99.7%) seeded in Ar carrier gas was prepared with a pulsed discharge slit nozzle (PDN) [16]. The PDN consists of a heated copper sample reservoir and a 10 cm long \times 200 μ m wide slit, which is sealed from inside by a Vespel (Dupont, SP-22 Grade) slit poppet driven by three synchronized pulsed solenoid valves (General Valve Series 9). 1-Methylpyrene or 1-pyrenecarboxyaldehyde was placed on the bottom of the sample reservoir and heated to high temperature to ensure adequate evaporation. Two stainless knife-edge electrodes are mounted outside the PDN on each side of the slit. The two electrodes are separated by an even gap of 400 μ m and configured as the cathode of a high voltage pulse generator. The PDN assembly itself is configured as the anode. The 1-methylpyrene or 1-pyrenecarboxyaldehyde cations were produced by DC discharge of the jet beam. Wavelength calibration was achieved by monitoring the Ar* atomic lines generated in the discharge.

The supersonic beam containing 1-methylpyrene⁺ or 1-pyrenecarboxyaldehyde⁺ was probed by cavity ring-down spectroscopy. The spectra were probed using a Nd:YAG (Quanta-Ray Lab 150 from Spectra-Physics) pumped dye laser (Quanta-Ray PDL-2 from Spectra-Physics) with Coumarin 440 dye (Exciton). The ring-down cavity consists of two high-reflectivity (99.99% at 430 nm) concave (6 m curvature radius) mirrors (Los Gatos Research) mounted 55 cm apart. The typical ring-down time of this setup was 10 μ s. The ring-down signal was collected by a photo sensor module (H6780-04 from Hamamatsu) and digitized by a 20 MHz 12 bit acquisition board (Adlink, PCI9812). The data were then processed by a PC program and the cavity losses were extracted.

To assist the assignment of the spectra of 1-pyrenecarboxyaldehyde⁺ and 1-methylpyrene⁺. We have carried out density functional theory (DFT) [17–19] and time-dependent density functional theory (TDDFT) [20,21] calculations of the vertical transition energies of several low-lying singlet states of these two cations. All the DFT and TDDFT calculations were performed with the TURBOMOLE 5.7 code [22]. The vertical transition energies were calculated with the BP86 functional [23,24] and the split valence polarization (SVP) [25] basis set ([3s2p1d]/[2s1p]). To speed up the calculations, we used the resolution of identity (RI) approximation [26,27], which was implemented for BP86/SVP in TURBOMOLE. The RI approximation allows for effi-

Table 1

Excitation energies and oscillator strengths of 1-pyrenecarboxyaldehyde⁺ and 1-methylpyrene⁺

State	Excitation energy (cm ⁻¹)		Oscillator strength ^b
	BP86/SVP ^a	Experimental	
<i>1-Pyrenecarboxyaldehyde⁺</i>			
D ₁	1081.9		4.33E–4
D ₂	8432.1		1.66E–4
D ₃	11947.1		1.18E–2
D ₄	15081.1		3.96E–3
D ₅	15601.7		8.84E–5
D ₆	18053.2		7.78E–4
D ₇	19139.9		1.34E–2
D ₈	22115.3	22426.0	2.50E–1
D ₉	23400.9		1.29E–3
D ₁₀	23462.5		6.94E–3
<i>1-Methylpyrene⁺</i>			
D ₁	9035.6		3.49E–4
D ₂	13380.8		1.33E–2
D ₃	15656.4		7.05E–3
D ₄	19707.0		1.88E–2
D ₅	22747.6	22652.0	2.33E–1
D ₆	23955.4		1.77E–5
D ₇	24836.2		9.77E–7

^a Vertical transition energies calculated at the BP86/SVP level of theory.

^b Values are calculated at the BP86/SVP level of theory.

cient computation of the electronic Coulomb interaction and leads to more than a tenfold speedup compared to the conventional method. The geometry optimizations were performed in the C₁ point group although the optimized geometries of the two cations are shown to have a plane symmetry (C_s point group) within the calculation error. The calculated vertical transition energies of the two cations are reported in Table 1.

3. Results and discussion

3.1. 1-Pyrenecarboxyaldehyde⁺ (C₁₇H₁₀O⁺)

Fig. 1 presents a cavity ring-down spectrum of 1-pyrenecarboxyaldehyde⁺ in the 22 370–22 600 cm⁻¹ (447.0–442.5 nm) spectral range. The spectrum was recorded 2 mm downstream of the slit nozzle with the PDN assembly maintained at a stable temperature of 140 °C. The backing pressure of Ar was 1.0×10^5 Pa, and the background pressure was 10.5 Pa. A high voltage of 700 V was applied to the electrodes to generate a discharge. Three weak (<10 ppm) vibronic bands, labeled A–C, were observed above the noise level (\sim 2 ppm) in this spectral region. At the experimental S/N ratio, we could not determine if other weaker features (e.g., the two shoulders of B and C in the blue) are real spectral features. We fitted the observed bands to Lorentzian profiles. The fitted positions and Lorentzian widths are listed in Table 2. We could not observe these bands when the PDN assembly was kept at room temperature or the discharge was turned off. The observed strongest band A was found to be blue shifted by \sim 5.9 nm from the strongest band of 1-pyrenecarboxyal-

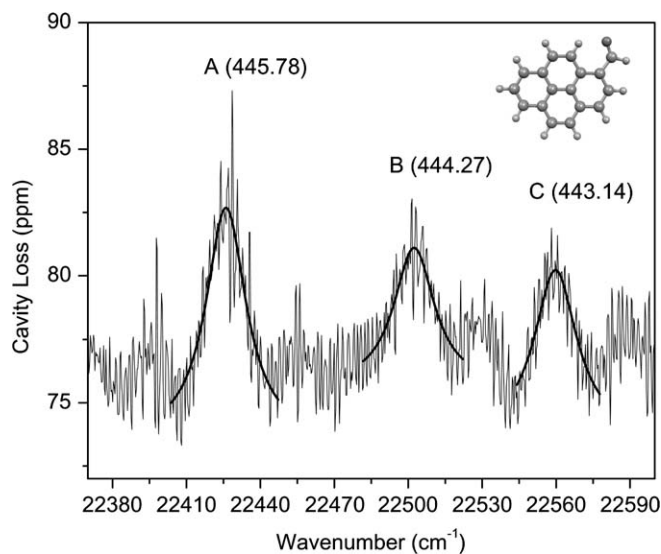


Fig. 1. Cavity ring-down spectrum of 1-pyrenecarboxyaldehyde⁺. The smooth solid lines represent Lorentzian fits of the bands. The values in the parentheses are fitted Lorentzian band positions in the air in units of nm.

Table 2

Band positions and Lorentzian widths for bands in the cavity ring-down spectra of 1-pyrenecarboxyaldehyde⁺ and 1-methylpyrene⁺

Band	Position ^a	Width ^a
<i>1-Pyrenecarboxyaldehyde</i> ⁺		
A	22426.0(3)	19.9(20)
B	22502.3(4)	20.4(33)
C	22559.5(4)	21.3(30)
<i>1-Methylpyrene</i> ⁺		
A	22652.0(12)	31.2(53)
B	22672.7(8)	15.7(29)

^a The values are in units of cm⁻¹.

dehyde⁺ isolated in an Ar matrix [6]. This spectral shift is close to the 7.3 nm shift of the 436.2 nm D₅ ← D₀ transition of the pyrene cation isolated in an Ar matrix [4]. Based on these observations, we assign the strongest spectral feature A to a vibronic transition associated with 1-pyrenecarboxyaldehyde⁺. By comparing with the calculated electronic transition wavenumbers listed in Table 1, we assign the spectral feature A to a vibronic feature of the D₈ ← D₀ electronic transition that has an oscillator strength factor of 0.25. Due to possible fragmentation of the molecular precursor as observed in the similar pyrene⁺ experiment [10], we could not determine if bands B and C belong to the 1-pyrene cation or its fragments, although bands A, B, and C have similar Lorentzian widths of 20 cm⁻¹, which correspond to a similar lifetime of ~120 fs. The spacings between A and B, and between A and C are 76.3 and 133.5 cm⁻¹, respectively. We have performed a Frank–Condon (FC) calculation using the normal coordinates obtained from our DFT and TDDFT calculations. The calculated FC spectrum failed to reproduce features B and C, indicative of either the existence

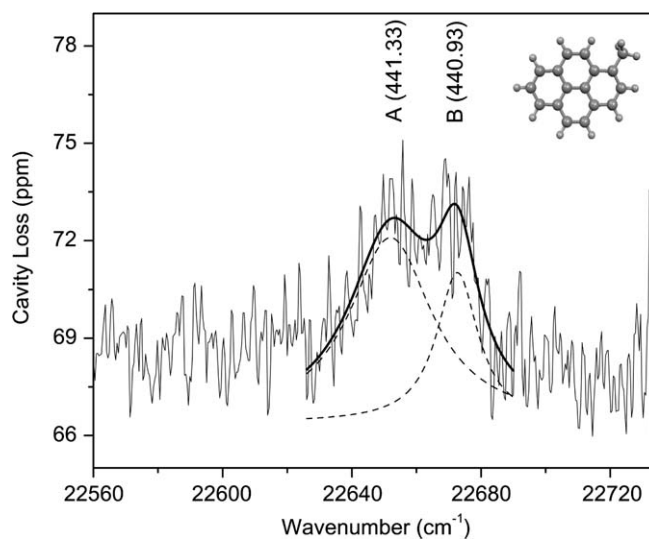


Fig. 2. Cavity ring-down spectrum of 1-methylpyrene⁺. The two smooth broken lines and the smooth solid line represent respectively the two-peak Lorentzian fits of the bands A and B and the sum of these two Lorentzian peaks. The values in the parentheses are fitted Lorentzian band positions in the air in units of nm.

of strong vibronic interaction that defeats the FC approximation or that features B and C do not belong to the same family as feature A.

3.2. 1-Methylpyrene⁺ (C₁₇H₁₂⁺)

Searching for and detecting the signal of 1-methylpyrene⁺ in the gas phase was proved to be a very challenging task. 1-Methylpyrene begins to decompose at temperatures higher than 80 °C. This limitation to the heating temperature highly limited the concentration of 1-methylpyrene that we could bring into the gas phase. We kept the PDN assembly at a stable temperature of 72 °C and retained all other experimental conditions as those used in the 1-pyrenecarboxyaldehyde⁺ experiments. We could barely discern a spectral feature at ~22660 cm⁻¹, which appears in 3 scans out of 30 scans with similar widths and positions. Fig. 2 presents a combination of these 3 scans in the 22560–22735 cm⁻¹ (443.3–439.9 nm) spectral range. This feature falls about ~2.9 nm to the blue of the strongest band of the 1-methylpyrene⁺ spectrum isolated in a Ne matrix in this spectral range⁷. This spectral shift is very close to the 3.3 nm shift of the 436.2 nm D₅ ← D₀ transition of the pyrene⁺ cation isolated in a Ne matrix [4]. We could not observe these bands when the PDN assembly was kept at room temperature or the discharge was turned off. We therefore tentatively assign this spectral feature to vibronic transitions associated with 1-methylpyrene⁺. A close look at this feature reveals two closely spaced bands, labeled as A and B in Fig. 2. We fitted the two bands with a two-peak Lorentzian function. The fitted positions and widths of the two bands are listed in Table 2. The fitted Lorentzian widths of bands A and B are 31.2 and 15.7 cm⁻¹, respectively, which correspond to lifetimes of

87 and 172 fs, respectively. By comparing with the calculated electronic transition wavenumbers listed in Table 1, we assign the spectral features to the $D_5 \leftarrow D_0$ electronic transition of 1-methylpyrene⁺ with an oscillator strength factor of 0.23. The spacing between bands A and B is 20.7 cm^{-1} , a value which is too small to be attributed to pure vibrational excitation in the upper electronic state but rather to possible vibronic interactions between the vibronic levels of D_5 and those of nearby electronic states.

4. Conclusions

We report for the first time the vibronic spectra of the free, cold 1-pyrenecarboxaldehyde and 1-methylpyrene cations in the gas phase. DFT and TDDFT calculations were performed to aid the assignment of the observed spectral features. A close comparison with astronomical surveys of the DIBs in the blue (440–446 nm range [28,29]) shows that no DIBs are detected at these wavelength positions and none of the absorptions measured in the laboratory is correlated with the strong $\lambda 4428$ DIB. This rules out the 1-methylpyrene and 1-pyrenecarboxaldehyde cations as carriers of the $\lambda 4428$ DIB. This is also confirmed by the difference of the bandwidths between the $\lambda 4428$ DIB and the observed spectral features of 1-methylpyrene⁺ and 1-pyrenecarboxaldehyde⁺. The $\lambda 4428$ DIB has a bandwidth of $\sim 89 \text{ cm}^{-1}$ [30], while the observed features have bandwidths ranging from 15 to 30 cm^{-1} . This indicates the carrier of the $\lambda 4428$ DIB band has shorter lived excited state than the corresponding states of 1-methylpyrene⁺ and 1-pyrenecarboxaldehyde⁺. We note that the relaxation timescales measured for the 1-methylpyrene and 1-pyrenecarboxaldehyde cations are of the same order of magnitude as the relaxation time scales previously reported for the naphthalene and acenaphthene cations [9]. This tends to confirm that internal relaxation in PAH cations is ultra fast occurring on timescales of the order of 100 femtoseconds.

It is very interesting to study the effect of the side groups on the vibronic spectroscopy of the pyrene cation. We noticed that both the methyl and carbonyl groups red shift the spectral feature of the pyrene cation at 436.2 nm by 4.8 nm and 9.6 nm, respectively. They also significantly affect the lifetime of the excited pyrene cation and reduce the bandwidth of the pyrene⁺ 436.2 nm band from 145 to $15\text{--}30 \text{ cm}^{-1}$. In both cases, the substitution with a side group change the pyrene⁺ 436.2 nm band in a way that makes it look more like the $\lambda 4428$ DIB. Although the 1-methylpyrene and 1-pyrenecarboxaldehyde cations can be discarded as the carriers of the $\lambda 4428$ DIB, substituted pyrene cations still represent a viable class of candidates for the $\lambda 4428$ DIB in particular and for the class of broad DIBs in general.

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