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Identification of the fragment of the 1-methylpyrene cation by mid-IR spectroscopy

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Abstract

The fragment of the 1-methylpyrene cation, $C_{17}H_{11}^+$, can exist in two isomeric forms, 1-pyrenemethylium $PyrCH_2^+$ and the tropylium containing species $PyrC_7^+$. We measured the infrared (IR) action spectrum of cold $C_{17}H_{11}^+$ tagged with Ne using a cryogenic ion trap instrument coupled to the FELIX laser. Comparison of the experimental data with density functional theory calculations allows us to identify $PyrCH_2^+$ as the main isomer in our experiments. The IR Multi-Photon Dissociation spectrum was also recorded by following the C_2H_2 loss channel. However the latter spectrum was found to miss the most intense band, likely due to anharmonic effects.

Keywords: PAHs, 22 pole cryogenic ion trap, FEL, Ne tagging spectroscopy
2010 MSC: 00-01, 99-00

1. Introduction

The photoproduct of the 1-methylpyrene cation, $C_{17}H_{11}^+$, has been pointed out in matrix-isolation studies as a candidate of interest to account for some of the diffuse interstellar bands including the strongest one at 4428 Å [1]. This has motivated experimental studies using the ion trap setup PIRENEA in which $CH_3-C_{16}H_9^+$ ions were trapped, irradiated by UV-VIS photons and its photofragment, $C_{17}H_{11}^+$, could be isolated. First multi-photon dissociation (MPD) spectra were obtained in order to reveal the structure of these ions [2]. Rapacioli et al. performed extensive calculations on the possible isomers and isomerisation pathways. These studies have shown that both the 1-pyrenemethylium isomer, $PyrCH_2^+$, and the isomer containing a tropylium cycle, $PyrC_7^+$ (see Fig. 1), could

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be present under the experimental conditions used in [2]. In fact, theoretical calculations showed several isomerisation pathways with barrier heights in the range 3.5 – 4.0 eV [3]. This, together with the fact, that both isomers coexist at formation, could explain why the recorded band in MPD measurements were so broad.

Infrared (IR) spectroscopy is an obvious technique to assign absorption bands to the PyrCH_2^+ and PyrC_7^+ species and thus disentangle the nature of the 1-methylpyrene cation photoproduct. Similarly to the case of the electronic transitions described above, absorption of multiple photons at IR wavelengths can be used to probe IR transitions of stored ions in an ion trap. This technique is well-known as IRMPD spectroscopy and has been successfully applied to different types of molecules and molecular complexes including polycyclic aromatic hydrocarbons (PAHs), which are of interest for this study [4, 5]. A drawback of the technique is that it implies the heating of the trapped ions by successive IR photon absorption. As a result, anharmonic effects, which lead to modifications of the IR spectrum with internal temperature, can therefore induce strong deviations of the recorded spectra compared to linear IR absorption spectra [6]. In a case like the PyrCH_2^+ and PyrC_7^+ species, an additional complication can arise from isomerisation processes induced by the heating.

The recent development of a cryogenic trap instrument [7] at the FELIX (Free Electron Lasers for Infrared eXperiments) Laboratory [8] opens new perspectives for this study. Indeed, it allows to use a rare gas tagging often referred to as messenger technique which provides information on the IR spectrum of the cold ion-rare gas complex upon the absorption of a single photon. This type of spectra was earlier reported in molecular beam experiments, in particular on jet-cooled complexes of cationic naphthalene-Ar, phenanthrene-Ar and phenanthrene-Ne [9, 10]. The possibility to build and store such complexes in a cryogenic ion trap opens new perspectives [11, 12], in particular to isolate and study fragments of the parent species.

In this article, we present the first IR spectrum of the Ne tagged $\text{C}_{17}\text{H}_{11}^+$ species together with the IRMPD spectrum of the bare cation. Comparison with harmonic IR spectra computed within the Density Functional Theory (DFT) scheme allows us to discuss the structure of this ion.

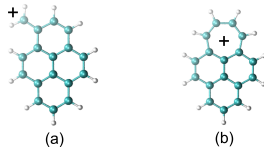


Figure 1: Topological formulas of the two isomers of $\text{C}_{17}\text{H}_{11}^+$: PyrCH_2^+ (a) and PyrC_7^+ (b).

2. Experimental

The experimental spectrum has been recorded on the FELion beamline at the FELIX¹ Laboratory at the Radboud University in The Netherlands. The FELion instrument at the beam line [7] consists of a cryogenic 22-pole rf ion trap equipped with two quadrupole mass filters allowing to mass select and analyse the ions to be studied, as well as products created in the trap. The ions of interest were created in a storage ion source [13] via electron bombardment of the 1-methylpyrene neutral gas, evaporated directly into the UHV chamber from a solid 1-methylpyrene sample (Sigma-Aldrich). The sample was heated to a temperature of 40° C in order to achieve sufficient vapour pressure. Several thousand ions of mass-selected C₁₇H₁₁⁺ cations ($m/z = 215$) were stored in the trap for each experimental cycle, while one of the following two spectroscopic techniques was applied:

IR Pre-Dissociation (IR-PD) of the weakly bound complex with Ne. The trap was operated at a nominal temperature of 8 – 9 K. Upon ion injection high quantities of a Ne:He 1:2 gas mixture were introduced in order to promote ternary attachment of Ne atoms to C₁₇H₁₁⁺ cation with a yield of only $\lesssim 1\%$. The depletion (single photon process) of the C₁₇H₁₁⁺ · Ne complex was then recorded as a function of wavelength.

IR Multi-Photon Dissociation (IRMPD) of the primary ion C₁₇H₁₁⁺. These experiments were performed at a trap temperature of about 200 K. He gas was introduced only to aid ion thermalisation and was removed prior to irradiation. The FELIX laser beam was focussed into the trap region to facilitate multi-photon absorption processes. The threshold for fragmentation is estimated to be of the order of tens of consecutive IR photons. The major fragment corresponds to the loss of acetylene, C₂H₂, as also shown in [2]. The number of produced fragment ions at $m/z = 189$ is therefore recorded as a function of wavelength.

The FELIX free electron laser used for the experiment delivers up to 30 mJ into the 22 pole trap in a single macropulse (about 5 μ s long), at 10 Hz repetition rate. The macropulse is composed of micropulses with energy in the 10 μ J range and with typical length in the picosecond range. A spectral bandwidth of approximately 0.5% was used.

3. Results and Discussion

Figure 2 shows the two experimental spectra that were recorded, the IR-PD spectrum in the top panel and the IRMPD spectrum in the bottom panel. The two experimental spectra are rather different. The IR-PD spectrum exhibits several weak bands whereas the IRMPD spectrum exhibits 3 strong bands,

¹Free Electron Lasers for Infrared eXperiments, www.ru.nl/felix, [8]

which match with some of the bands in the IR-PD spectrum. Further insight on the band assignment comes from comparison with the computed DFT harmonic IR absorption spectra of the two isomers PyrCH_2^+ and PyrC_7^+ which are reported in the middle panel. In a recent computational study of the isomerisation reactions of C_7H_7^+ isomers, Kharnaier et al. [14] have concluded that the B3LYP exchange-correlation functional [15] provides good results for molecules of similar size and structure. We therefore optimised the geometries of the two isomers of $\text{C}_{17}\text{H}_{11}^+$ using the B3LYP hybrid functional in conjunction with a 6-31G(d,p) basis set [16]. The calculations were achieved with the Gaussian09 suite of programs [17]. Both isomers were found to have an $^1\text{A}'$ ground-state. The harmonic spectra were obtained by full diagonalization of the weighted Hessian matrix. All band positions were multiplied by a unique scaling factor of 0.975 obtained by adjusting the position of the most intense band in the calculated spectrum of PyrCH_2^+ at 1656 cm^{-1} to the band located at 1615 cm^{-1} in the IR-PD spectrum. This factor is in accordance with those used previously for similar systems [18]. All modes involve C-C stretching and in-plane C-H bending modes (a' symmetry). The spectra of the two isomers are different, with overall more intense bands for PyrCH_2^+ .

Although the IR-PD spectrum is rather noisy due to the difficulty of efficiently tagging the $\text{C}_{17}\text{H}_{11}^+$ cation with Ne (He has been tried as well, with yields even lower than those for Ne), the comparison with the DFT spectra allows us to identify PyrCH_2^+ as the dominant isomer in these experiments. This assignment is based on at least 5 bands as listed in Tab. 1. Instead, the analysis of the IRMPD spectrum is more difficult. Knowing the IR-PD spectrum, we can conclude, that the bands are likely due to PyrCH_2^+ , although only three bands are observed. Surprisingly the band measured at 1615 cm^{-1} in the PD experiments, which according to theory is the strongest in the spectrum of PyrCH_2^+ , has no counterpart in the IRMPD spectrum. A possible explanation is that this band is strongly anharmonic, which indeed has been predicted by Rapacioli et al. in their finite temperature molecular dynamics simulations (cf. [3] and the respective anharmonicity values, χ , listed in Tab. 1). One has to recall that the IRMPD signal reflects the efficiency of absorbing multiple photons within the laser bandwidth, which depends on the evolution of the band position and width, while the internal temperature is increased. A similar effect can be invoked for the other missing band at about 1530 cm^{-1} .

Finally, none of the predicted bands of PyrC_7^+ are observed in our experiments, neither in the IR-PD nor in the IRMPD spectrum. In particular, the strong absorption calculated at 1496 cm^{-1} is absent, which shows that PyrCH_2^+ is indeed the main isomer formed in our experiments. Zins et al. [18] compared the IRMPD spectrum of the tert-butyl derivative of C_7H_7^+ with B3LYP calculations using the same scaling factor of 0.975 as in our work. They concluded that the absence of a characteristic band at 1506 cm^{-1} excludes a significant contribution of the tropylium isomer, which is fully consistent with our studies on the isomers of $\text{C}_{17}\text{H}_{11}^+$. Still, one has to remind that these ions were prepared by electron impact ionization in our study. In order to verify that PyrCH_2^+ would also be the main product in photodissociation experiments, it

would be desirable to combine structural determination with the excitation in the UV-VIS range, i.e. to first produce the photoproduct of the 1-methylpyrene cation and subsequently determine its structure by the IR action spectroscopy described in this work.

In summary, this work demonstrates the benefits of the combination of a widely tunable IR laser source (FELIX) with cold ions prepared in a 22-pole ion trap. A clear relation between the one photon absorption bands of the IR-PD experiment and DFT predictions unravel the structure of the $C_{17}H_{11}^+$ isomer. This method opens perspectives for experiments aiming to probe the role of isomerisation in the photophysics of PAHs.

Table 1: Experimental mid-IR bands recorded for $C_{17}H_{11}^+$ and theoretical mid-IR spectra of $PyrCH_2^+$ (see Fig. 2) obtained in the present work. Anharmonicity factors χ are expressed in $10^{-2} \text{ cm}^{-1} \cdot \text{K}^{-1}$. All wavenumbers ν are in cm^{-1} , numbers in parentheses represent the approximate experimental linewidth (FWHM) of the strongest line component.

Band	Experiment		Calculations	
	ν IR-PD	ν IRMPD	ν DFT-B3LYP	χ from [3]
1.	1240(25)	1223(21)	1236	1.42
2.	1376(9)	1362(23)	1376	–
3.	1529(12)	–	1535	–
4.	1570(21)	1568(26)	1574	–
5.	1615(16)	–	1615	6.75

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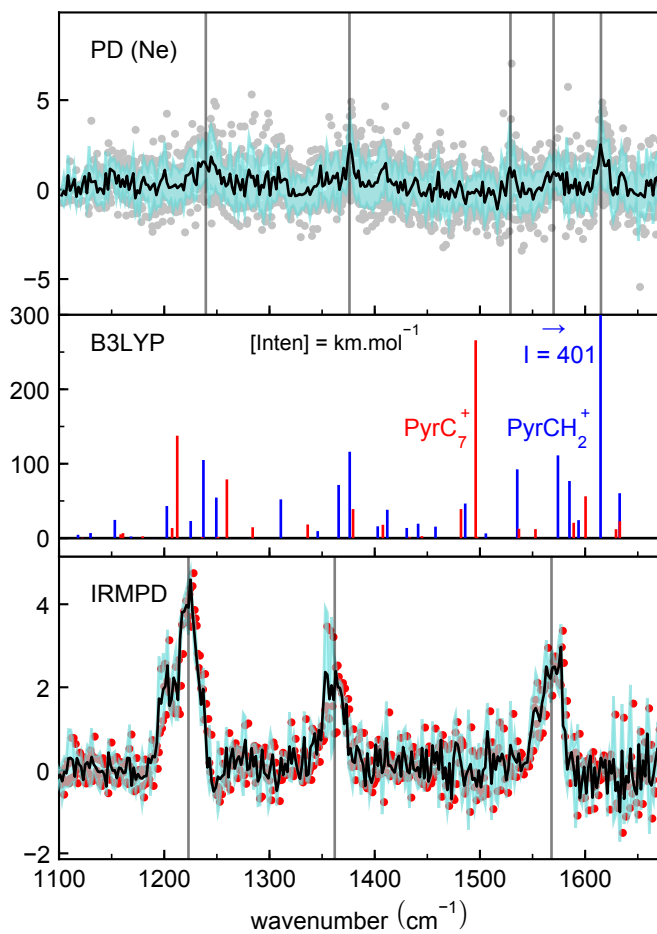


Figure 2: IR spectrum of $C_{17}H_{11}^+$ ($m/z = 215$). Top panel – IR pre-dissociation spectrum of the molecular ion tagged with Ne. Middle panel – stick spectrum corresponding to the scaled DFT harmonic spectra for the two isomers $PyrCH_2^+$ (blue) and $PyrC_7^+$ (red) with intensities in $km.mol^{-1}$. Bottom panel – IR multi-photon dissociation spectrum obtained by recording the fragment at $m/z = 189$ (loss of C_2H_2). For experimental spectra, intensities are in arbitrary units and vertical lines correspond to the identified bands (cf. Tab. 1).