LABORATORY SPECTROSCOPY OF PROTONATED PAH MOLECULES RELEVANT FOR INTERSTELLAR CHEMISTRY

O. Dopfer[1]

Abstract. In this contribution, we summarize the recent progress made in recording laboratory infrared (IR) spectra of protonated polycyclic aromatic hydrocarbon molecules (H^+PAH) in the gas phase. The IR spectra of a large variety of H^+PAH species ranging from benzene to coronene have been obtained by various variants of photodissociation spectroscopy. The employed techniques include single-photon IR photodissociation (IRPD) of tagged H^+PAH ions and IR multiple-photon dissociation (IRMPD) of bare H^+PAH ions. The comparison of the laboratory IR spectra with astronomical spectra supports the hypothesis that H^+PAH ions are possible carriers of the unidentified IR emission (UIR) bands. Moreover, the spectra provide detailed information about the geometric and electronic structure as well as the chemical reactivity and stability of these fundamental hydrocarbon ions.

1 Introduction

The unidentified infrared (UIR) emission bands are observed in a great variety of galactic and extragalactic sources. They are currently attributed to IR fluorescence of UV-excited polycyclic aromatic hydrocarbon (PAH) molecules and their more complex derivatives, such as ionic PAH, (de-)hydrogenated and methyl-substituted PAH, PAH clusters, nitrogen- and silicon-containing PAH, and PAH-metal ion adducts (Léger & Puget 1984; Allamandola *et al.* 1985; Tielens 2008). Recently, also protonated PAH molecules, H^+PAH, have been suggested because laboratory experiments demonstrated that they can readily be formed through efficient protonation of neutral PAH or attachment of H-atoms to PAH^+ radical cations (Snow *et al.* 1998). In addition, their calculated IR spectra identify H^+PAH as promising candidates for UIR band carriers (Hudgins *et al.* 2001).

In order to test the H^+PAH hypothesis, laboratory IR spectra of H^+PAH are required for comparison with astronomical UIR spectra. Such spectra have,

[1] Institut für Optik und Atomare Physik, Technische Universität Berlin, Hardenbergstrasse 36, 10623 Berlin, Germany; e-mail: dopfer@physik.tu-berlin.de

however, been lacking until recently (Lorenz *et al.* 2007), largely due to experimental challenges involved in the generation of high abundances sufficient for spectroscopic interrogation. Recent progress in the development of efficient ion sources and sensitive IR spectroscopic techniques have allowed to obtain the first IR spectra of size-selected protonated aromatic molecules and their weakly-bound clusters in the gas phase by coupling tandem mass spectrometry with resonant vibrational photodissociation spectroscopy (Solca & Dopfer 2001; Solca & Dopfer 2003a). The application of these techniques to protonated aromatic molecules has been reviewed previously (Dopfer 2006). In this contribution, we summarize the results obtained in the past decade for a large variety of H^+PAH ions, ranging from protonated benzene to protonated coronene.

2   Experimental techniques

Several experimental approaches have been used to generate isolated and microsolvated H^+PAH cations in the gas phase for spectroscopic interrogation. Ion and cluster ion generation has been accomplished in an electron-impact or discharge-driven supersonic plasma expansion. This approach was used to produce protonated benzene and naphthalene, $C_6H_7^+$ and $C_{10}H_9^+$, and their weakly-bound clusters with ligands L = Ar, N_2, CH_4, and H_2O (Solca & Dopfer 2002; Solca & Dopfer 2003b; Douberly *et al.* 2008; Ricks *et al.* 2009). Alternatively, isolated H^+PAH can be generated by chemical ionization of PAH in an ion cyclotron resonance (ICR) mass spectrometer using protonating agents, such as CH_5^+ or $C_2H_5^+$, as successfully demonstrated for $C_6H_7^+$ and $C_{10}H_9^+$ (Jones *et al.* 2003; Dopfer *et al.* 2005; Lorenz *et al.* 2007). Larger PAH molecules have low vapour pressure and a feasible option to generate sufficient abundances of their protonated species is electrospray ionization. This technique has been applied to characterize larger H^+PAH ions (Knorke *et al.* 2009), ranging from protonated anthracene, $C_{14}H_{11}^+$, to protonated coronene, $C_{24}H_{13}^+$.

Two major spectroscopic strategies have successfully been employed to obtain IR spectra of isolated and microsolvated H^+PAH ions. The first technique couples modern low-intensity optical parametric oscillator (OPO) laser systems, typically operating in the $1000–4000\,cm^{-1}$ range, with tandem mass spectrometers to record single-photon IRPD spectra of cold $H^+PAH\text{-}L_m$ cluster ions by monitoring the loss of weakly-bound ligands L (Solca & Dopfer 2002; Solca & Dopfer 2003b; Douberly *et al.* 2008; Ricks *et al.* 2009). The low intensities of OPO lasers are usually insufficient to drive multiple-photon processes. The influence of the ligands on the IR spectrum of the central H^+PAH ion can usually be neglected for weakly-bound ligands (*e.g.*, Ar), *i.e.* the IRPD spectra of the tagged species correspond to a very good approximation (to within a few cm^{-1}) to the IR spectra of the bare ion. Moreover, the clusters are cold as they are produced in molecular beams. As a result of the low internal temperature (typically well below 50 K) and the single-photon dissociation process, IRPD spectra display high resolution and sharp transitions with widths of the order of 5 cm^{-1}. Moreover, they display high sensitivity, *i.e.* even transitions with low IR activity can readily be detected.

The IRPD approach has been applied to obtain the first IR spectrum of $C_6H_7^+$ in the gas phase (Solca & Dopfer 2002).

The second spectroscopic strategy couples high-intensity free electron laser (FEL) sources (FELIX and CLIO), operating in the complementary 50–2500 cm^{-1} range, with ion cyclotron resonance (ICR) mass spectrometry to drive IRMPD of isolated, strongly-bound H^+PAH by monitoring either H-atom or H_2 loss (Jones *et al.* 2003; Dopfer *et al.* 2005; Lorenz *et al.* 2007; Zhao *et al.* 2009; Knorke *et al.* 2009). In general, the spectral resolution observed in the IRMPD spectra (circa 30 cm^{-1}) is lower than in IRPD spectra due to the finite bandwidth of the FEL, the broader rotational contour (as the ions probed in the ICR cell are at room temperature), spectral congestion due to overlapping transitions, and spectral broadening arising from the multiple-photon character of the IRMPD process. Typically, several tens of IR photons are required to drive the IRMPD process due to the large dissociation energies for H or H_2 elimination from H^+PAH. As a further consequence of the IRMPD mechanism, weakly IR active transitions with cross sections below a certain threshold are not observed. The IRMPD approach has been utilized to obtain the first IR spectrum of an isolated H^+PAH, namely $C_{10}H_9^+$ (Lorenz *et al.* 2007). Figure 1 compares the IRMPD spectra of a variety of H^+PAH obtained so far, including protonated benzene, naphthalene, anthracene, tetracene, pentacene, azulene, perylene, pyrene, coronene, acenaphthene, and acenaphthylene. While this contribution focuses on the general appearance of the IR spectra and the comparsion with an UIR spectrum representative of a highly-ionized region of the interstellar medium (Tielens 2008; Fig. 1), a full account of the potential energy surfaces with structural and vibrational analyses is given elsewhere (Zhao *et al.* 2009; Zhao 2010). Significantly, apart from benzene H^+, the IRMPD spectra in Figure 1 correspond to the first spectroscopic data of these H^+PAH in the gas phase, providing very valuable information about the geometric and electronic structures as well as the chemical reactivity and stability of these fundamental ions. For an illustration of the information content of these spectra, the reader is referred to a recent analysis of the azuleneH^+ spectrum using quantum chemical calculations (Zhao *et al.* 2009). A similar analysis was performed for all H^+PAH spectra in Figure 1 (Zhao 2010) and will be published elsewhere.

3 Results and discussion

Initial IRPD spectra obtained for $C_6H_7^+$ in the CH stretch range using the tagging technique (Solca & Dopfer 2002; Solca & Dopfer 2003b) demonstrated for the first time spectroscopically that the proton is attached to a C-atom (σ-complex) rather than the π electron system of the aromatic ring (π-complex), a conclusion that also holds for larger H^+PAH. In addition, these spectra do not show coincidences with prominent UIR bands. Subsequent IRMPD spectra reported for isolated $C_6H_7^+$ in the fingerprint range (Fig. 1) using CLIO and monitoring H_2 loss (Jones *et al.* 2003; Dopfer *et al.* 2005) and higher-resolution IRPD spectra of Ar-tagged $C_6H_7^+$ ions (Douberly *et al.* 2008) confirm these initial conclusions.
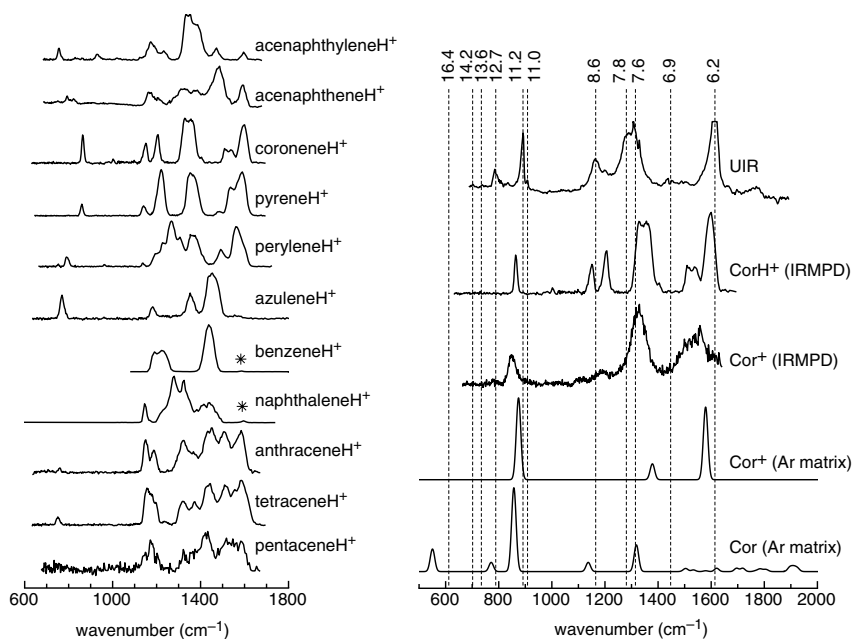
Fig. 1. *Left*: IRMPD spectra of a variety of H$^+$PAH ions (Dopfer 2005; Lorenz *et al.* 2007; Dopfer 2008; Knorke *et al.* 2009; Zhao *et al.* 2009); the spectra of benzene H$^+$ and naphthalene H$^+$ were recorded using CLIO, whereas all other spectra were obtained using FELIX; bands marked by asterisks are largely suppressed due to reduced laser power. *Right*: IR spectra of coronene, coronene $^+$ and coronene H$^+$ compared to an UIR spectrum (Knorke *et al.* 2009). The dashed lines indicate positions of UIR bands in μm.

Next, IRMPD spectra were recorded for $C_{10}H_9^+$, the smallest H$^+$PAH, using CLIO and the major conclusions can be summarized as follows (Lorenz *et al.* 2007). First, the IRMPD spectra of $C_6H_7^+$ and $C_{10}H_9^+$ are very different (Fig. 1), implying a strong dependence of the IR spectra of H$^+$PAH on the number of aromatic rings, at least for small PAH. Second, the IRMPD spectrum of $C_{10}H_9^+$ demonstrates striking coincidences with the UIR spectrum. Both, the positions and IR intensities of the $C_{10}H_9^+$ bands match the astronomical spectrum much better than the IR spectra of neutral and ionized naphthalene. These important conclusions were later confirmed by IRPD spectra of $C_{10}H_9^+$-Ar (Ricks *et al.* 2009).

The close match of the $C_{10}H_9^+$ and UIR spectra called for laboratory IR spectra of larger H$^+$PAH, in order to follow their evolution as a function of PAH size. This was also of importance in the light of astrochemical models, which suggest PAH molecules consisting of 20–80 C-atoms to be photochemically most stable in interstellar clouds (Tielens 2008). To this end, IRMPD spectra of a variety of larger H$^+$PAH species (Fig. 1) have been recorded using FELIX (Dopfer 2008).

Figure 1 compares the IRMPD spectra of linear catacondensed H^+PAH featuring n aromatic rings with $n = 1–5$ (Knorke *et al.* 2009). The $n = 1$ and $n = 2$ spectra are significantly different in appearance, and both differ from those for $n = 3–5$. However, the IRMPD spectra for $n = 3–5$ are rather similar, suggesting convergence of the spectral evolution at around $n = 3$. Comparison of the $n = 3–5$ spectra with an UIR spectrum representative of a highly-ionized region of the interstellar medium (Tielens 2008; Fig. 1) reveals good correspondence for transitions assigned to in-plane CH bend and CC stretch modes. In addition, the highest-frequency CC stretch mode at around 1600 cm^{-1} approaches the 6.2 μm UIR feature with increasing n. The intense, lower-frequency CC stretch modes at 1450 cm^{-1} are characteristic of all linear catacondensed H^+PAH and correlate with the 6.9 μm UIR feature, which is however only weakly observed in the astronomical spectrum. Similar conclusions apply to the 1500 cm^{-1} transition.

Not only are linear catacondensed H^+PAH with $n = 1–5$ probably too small to be photostable, they are also less stable than pericondensed two-dimensional H^+PAH. To this end, we recorded also the IRMPD spectrum of protonated coronene ($C_{24}H_{13}^+$), a pericondensed PAH, which is often considered as the prototypical and representative PAH molecule present in the interstellar medium. Figure 1 compares the available experimental IR spectra for different degrees of ionization and protonation of coronene with the UIR spectrum (Knorke *et al.* 2009). Comparison of the spectra of coronene and coronene$^+$ recorded in an Ar matrix demonstrates the significant impact of ionization on the IR intensities. The coronene$^+$ spectrum recorded in the cold Ar matrix and via IRMPD in the gas phase are similar but illustrate the typical redshift and broadening of bands induced by the IRMPD process. The IRMPD spectrum of coronene$^+$ and coroneneH$^+$ are again similar. The redshifts and broadening effects due to IRMPD are, however, less pronounced for the protonated species due to its lower dissociation energy. Moreover, the bands in the 1100–1200 cm^{-1} range display higher IR activity. Significantly, the intense CC stretch band at 1600 cm^{-1} (6.25 μm) occurs at a higher frequency than for the radical cation and closely approaches the 6.2 μm band observed in the UIR spectrum.

As the UIR bands are caused by IR fluorescence of vibrationally hot species, the vibrational transitions observed are shifted in frequency from the frequencies of fundamental transitions due to vibrational anharmonicities. Similarly, the multiple-photon nature of the IRMPD process also shifts the frequencies to lower values in comparison to fundamental transitions, again via the effect of anharmonicities. Thus, it is indeed meaningful to compare IRMPD spectra with the UIR bands, as both processes and the resulting IR spectra are affected by the same type of vibrational anharmonicity (Oomens *et al.* 2003). In view of this argument, the good agreement between the IRMPD spectrum of coroneneH$^+$ and the UIR spectrum in Figure 1 provides for the first time compelling experimental evidence for the hypothesis that H^+PAH indeed contribute to the UIR spectrum. Future efforts include recording IR spectra of even larger H^+PAH ions in order to follow the spectral evolution as a function of PAH size. In addition, electronic spectra of H^+PAH will be recorded, as they are promising candidates for carriers

of the diffuse interstellar bands (Pathak & Sarre 2008; see also Hammonds *et al.*, elsewhere in this volume). First encouraging results have been obtained for $C_{10}H_9^+$ (Alata *et al.* 2010), which strongly absorbs in the visible range, supporting the hypothesis that larger H^+PAH ions may indeed be carriers of some of the diffuse interstellar bands.

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