Polycyclic Arenes

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Infrared Spectra of Isolated Protonated Polycyclic Aromatic Hydrocarbons: Protonated Naphthalene**

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The five distinct infrared (IR) emission features at 3.29, 6.2, 7.7, 8.6, and 11.3 μm—the so-called unidentified infrared emission bands (UIRs), which recur in similar intensity ratios in different environments of the interstellar medium (ISM)—are widely believed to arise from IR fluorescence of ultraviolet(UV)-excited polycyclic aromatic hydrocarbons (PAHs).[1,2] The quest for the carriers of the UIRs has now mainly turned from neutral[3] to ionized PAHs, whose formation in the ISM is likely and whose IR spectra show a better correspondence with the astronomical data.[4,5] As the attachment of H atoms to ionized PAHs was measured to be fast, the formation of protonated PAHs in the ISM was hypothesized.[6] Their calculated IR spectra[7] verify them as promising candidates;[8] however, no spectroscopic study has been undertaken to date. In addition to their astronomical relevance, protonated PAHs were identified in combustion experiments[9] and studied in superacidic solutions as fundamental intermediates of electrophilic aromatic substitution reactions.[10] Significantly, the IR multiple-photon dissociation (IRMPD)[4] spectrum of protonated naphthalene (naphthaleneH^+) in the informative fingerprint range reported here represents the first spectrum of an isolated protonated PAH.

The IRMPD spectrum was obtained by coupling an ion cyclotron resonance mass spectrometer (ICR) to the Free Electron Laser (FEL) at the Center Laser Infrarouge Orsay.[11,12] NaphthaleneH^+ was generated in the ICR cell by chemical ionization of naphthalene with CH_4 and subsequently irradiated for 3 s.[13] With the laser tuned to a vibrational transition, the ion absorbs several photons (≈ 20) in a stepwise process until the dissociation threshold is reached.[4,5] By monitoring the intensities of parent (I_{parent}) and resulting fragment ions (I_{fragment}) as a function of the laser wavenumber, the IRMPD spectrum is obtained as $R = -\ln(I_{\text{parent}}/[I_{\text{parent}}+\Sigma I_{\text{fragment}}])$. Despite its multiple photonic nature, the IRMPD spectrum predominantly reflects the absorption of the first IR photon (see Ref. [4] for a recent review of the IRMPD mechanism). This observation justifies a comparison of the experimental IRMPD spectrum with a linear (i.e., one-photon) IR absorption spectrum (intensity I). The latter is obtained here by quantum chemical calculations performed at the B3LYP/6-311G(2df,2pd) level.[14] Reported energies are corrected for (unscaled) zero-point vibrational energies. Harmonic frequencies are scaled with a factor of 0.98, which is derived from the recommended procedure[7] in a least squares fit of calculated and experimental frequencies of naphthalene[15] and naphthalene$^+$.[16]

In agreement with previous calculations,[17] the potential energy surface (PES) of naphthaleneH^+ (Figure 1) exhibits three minima with relative energies $\mathbf{1} < \mathbf{2} < \mathbf{3}$.[18] Accordingly, NMR spectroscopic investigations have identified **1** as the thermodynamically stable isomer in superacid solution at −78 °C, and 1,2 H shifts of the excess proton between C1 and C2 could be inferred at −50 °C.[10] As demonstrated in previous experimental and theoretical studies, loss of an H atom is the energetically most favorable fragmentation pathway, with the loss of H_2 (both with a barrierless reverse reaction) requiring additional 25/31 kJ mol^{-1} for the formation of the 1-/2-naphthyl cation.[19,20] The excess energies for protonation with CH_5^+ and $C_2H_5^+$, the major protonating agents in this experiment formed by electron impact of methane,[13] suggest that the generation of any of the isomers **1**–**3** is thermodynamically feasible.

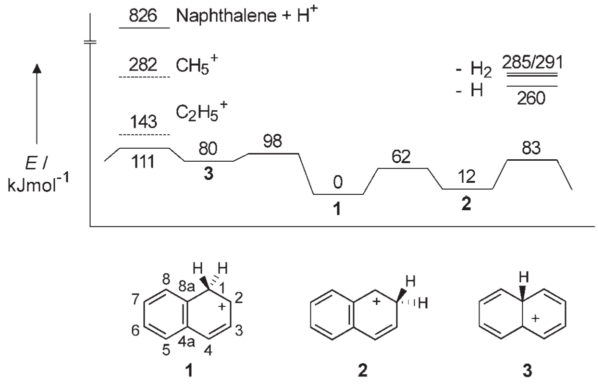

Figure 1. Potential energy surface of naphthaleneH^+ with minima and connecting transition states, including excess energies for protonation with CH_5^+ and $C_2H_5^+$ and energies for loss of H and H_2 (details are available in the Supporting Information[18]).

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However, the long irradiation time of 3 s, necessitated by the low fragmentation efficiency of naphthaleneH$^+$, suggests that collisions with the background of neutral naphthalene should convert any initially formed **2** and **3** into **1**, which is more stable by 12 and 80 kJ mol^{-1}, respectively. Such an equilibration of the reaction mixture has been observed in previous IRMPD studies under similar conditions.[21]

Upon resonant excitation, naphthaleneH$^+$ eliminates H and H$_2$, with a ratio of 36:1 integrated over all features. The IRMPD spectrum (Figure 2) displays a peak at 1164 cm^{-1} with a width of 14 cm^{-1} (A), broad absorption between 1185 and 1528 cm^{-1} composed of several overlapping features (B–F), and a weak transition at 1599 cm^{-1} with a width of 15 cm^{-1} (G).

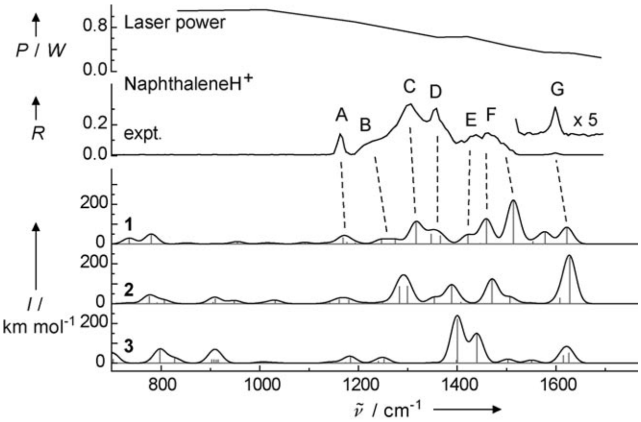

Figure 2. IRMPD spectrum of naphthaleneH$^+$, along with the laser power and calculated linear IR spectra of isomers **1**–**3** (convolution width of 30 cm^{-1}),[26] where *R* and *I* correspond to the measured IRMPD efficiency and the calculated IR intensity, respectively. Experimental and theoretical line positions are provided in the Supporting Information.[18]

This IR signature can apparently not be explained by the calculated linear IR spectrum of **3** (Figure 2), which does not possess a sufficient number of intense lines. In addition, it fails to account for the features C and D and displays its strongest transition at 1400 cm^{-1}, which is also inconsistent with the IRMPD spectrum. Similarly, the calculated spectra of neither **1** nor **2** provide a fully satisfactory match above 1450 cm^{-1}. However, the bands A–F are convincingly explained by the spectrum of **1** (assignment indicated with dashed lines in Figure 2), whereas **2** shows marked discrepancies. This isomer clearly fails to account for the shoulder B and the positions and spacing of the peaks C and D.

Inspection of Figure 2 reveals that difficulties in the assignment of the IRMPD spectrum to the calculated spectrum of **1** arise mainly from the low intensities or absence of the calculated bands above 1500 cm^{-1} in the IRMPD spectrum, whereas the band positions show acceptable agreement. In previous studies with the same experimental setup, vibrations with calculated intensities below 50 km mol^{-1} could frequently not be detected.[11,21,22] Whereas this observation may explain the absence of several transitions below 1100 cm^{-1}, it certainly does not apply to the bands of **1** at 1514, 1578, and 1622 cm^{-1} with predicted IR intensities between 60 and 220 km mol^{-1}. It is also considered unlikely that the moderate decrease in laser power between 1300 and 1600 cm^{-1} (Figure 2) could fully account for these discrepancies.

In order to shed further light on this phenomenon, Figure 3 compares the IRMPD and calculated linear IR spectra of naphthaleneH$^+$ (**1**) with those of benzeneH$^+$,[22,23] where a similar inconsistency is observed. The highest frequency ring mode predicted at 1607 cm^{-1} with an intensity of 76 km mol^{-1} is hardly discernible in the IRMPD spectrum of benzeneH$^+$ (1581 cm^{-1}). Since both species are chemically related and all vibrations in question are almost pure ring modes in the same spectral range, the observations for benzeneH$^+$ and naphthaleneH$^+$ appear to be related. However, it is not clear whether the observed discrepancies should be attributed to artifacts of the calculations, for which there is presently no hint, or to the multiple photonic nature of the IRMPD process, which would point to low intramolecular vibrational energy redistribution (IVR) rates and/or to large cross anharmonicities of these ring modes, both leading to inefficient IRMPD.

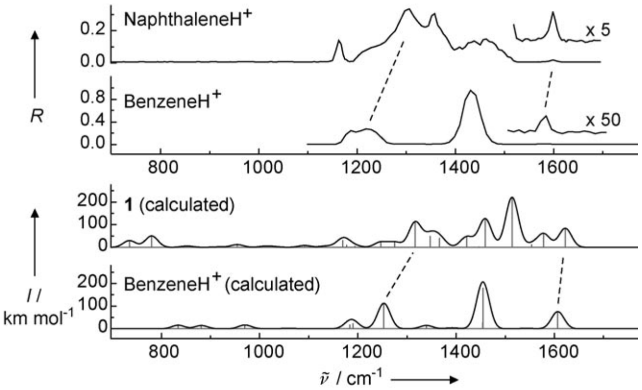

Figure 3. IRMPD spectra and calculated linear IR spectra of naphthaleneH$^+$ (**1**) and benzeneH$^+$ (convolution width of 30 cm^{-1}).[26]

Assuming that the comparison of intensities in the IRMPD and calculated linear IR spectra of naphthaleneH$^+$ is unreliable in the range of the aromatic ring modes, the experimental spectrum is readily assigned to **1**, as expected in case of equilibration of the reaction mixture in the ICR cell.[21] Minor contributions from **2** and **3**, however, cannot be completely ruled out.

The IRMPD spectrum of naphthaleneH$^+$ is much more complex than that of benzeneH$^+$ (Figure 3). The scissoring mode of the aliphatic CH$_2$ group (C), the reactive center in electrophilic aromatic substitution, experiences a blue shift of 83 cm^{-1} (1302 vs. 1219 cm^{-1}), in line with an opening of the HCH bond angle (102.0° vs. 99.8°), whereas the highest frequency ring mode (G), assumed to acount for the 6.2-μm band in the UIR spectra, shifts to higher frequency by 18 cm^{-1} (1599 vs. 1581 cm^{-1}).

In conclusion, the IRMPD spectrum of naphtaleneH$^+$, generated by chemical ionization of naphthalene in an ICR cell, has been recorded and assigned to the most stable isomer

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(**1**). Similar to the case of benzeneH$^+$, the intensities of several ring modes above 1450 cm^{-1} were found to be lower in intensity than predicted by calculations. The IRMPD spectrum of naphthaleneH$^+$ displays much greater spectral complexity than the IRMPD spectrum of benzeneH$^+$, demonstrating the large impact of additional aromatic rings on the IR fingerprint of protonated PAHs. In contrast to benzeneH$^+$, the IRMPD features of naphthaleneH$^+$ closely resemble the astronomical UIR bands, supporting the hypothesis of protonated PAHs in the ISM. For example, the position of band A (1164 cm^{-1}, 8.59 μm) matches closely the 8.6-μm UIR feature, while the bands C and D (1302 and 1355 cm^{-1}, 7.68 and 7.38 μm) can be associated with the 7.7-μm UIR band. Whereas bands E and F do not have pronounced astronomical counterparts, band G (6.25 μm) may be attributed to the 6.2-μm UIR band. Implications for the quest for the carriers of the UIRs will be discussed in detail elsewhere. It is desirable to extend future studies to larger protonated PAHs that are believed to be more stable than naphthaleneH$^+$ under the conditions of the ISM. Furthermore, it is planned to detect the IR spectra in a one-photon process through argon tagging (messenger technique) in order to avoid complications arising from the multiple photonic nature of the IRMPD process.[24,25]

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