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Abstract

The electronic absorption spectra of isolated protonated polycyclic aromatic hydrocarbon molecules, $(PAH)H^+$, are unknown. Recent interest in the absorption spectra of these stable closed-shell molecules arises from the hypothesis that they may be carriers of the long-known but unidentified *Diffuse Interstellar Bands* (DIBs) occurring in the visible to infrared spectral range (400-1300 nm). We report here the first experimental detection of the electronic spectrum of protonated naphthalene, the simplest $(PAH)H^+$, in the 500 nm region, providing compelling spectroscopic support for the hypothesis that $(PAH)H^+$ might indeed be carriers of the DIBs. The large protonation-induced shift in the transition energy (> 40%) from the transition of isoelectronic neutral naphthalene (312 nm) is rationalized by a charge transfer state, which is only accessible in the protonated species.

One sentence summary

Despite its closed shell electronic structure, protonated naphthalene absorbs light in the visible range, providing for the first time compelling spectroscopic evidence for the hypothesis that protonated PAH molecules can be responsible for the *Diffuse Interstellar Bands* (DIBs).

Spectroscopy is the only source of information about the chemical composition of the interstellar medium, which is vital for models rationalising the formation of chemical and biological structures in space. The presence of polycyclic aromatic hydrocarbons (PAHs) in the interstellar medium (ISM) is inferred from the comparison of their laboratory IR spectra with the so-called *Unidentified Infrared Emission bands* (UIRs) (*1, 2*), which recur in similar intensity ratios in different environments of the ISM. In addition to neutral PAHs, ionized and more recently also protonated PAH molecules, PAH^+ and $(PAH)H^+$, have also been considered, as both ionization and protonation are likely to occur in the ISM (*3-8*). Indeed, their laboratory IR spectra are compatible with the astronomical UIR bands (*3, 4, 9*). The so-called *Diffuse Interstellar Bands* (DIBs) provide a further spectroscopic source of information about astrochemical molecules occurring in the ISM (*10-12*). More than 200 bands have been observed in the visible to near infrared spectral range (400-1300 nm), however, none of them could be assigned to molecular carriers so far. In particular, no coincidences have unambiguously been identified between DIBs and the electronic spectra of neutral and ionized PAH molecules (*13-17*). As attachment of highly abundant H atoms to PAH^+ was measured to be fast, the efficient formation of $(PAH)H^+$ in the ISM was hypothesized (*5*). So far, no comparison of the DIBs with electronic spectra of $(PAH)H^+$ could be made, as the required laboratory spectra have been lacking. However, by comparison with the isoelectronic, closed-shell neutral PAH molecules, small $(PAH)H^+$ molecules were not expected to have low-lying electronic states giving rise to absorption in the visible range (*5*). Significantly, the photodissociation spectrum of naphthaleneH^+ reported here represents the first electronic spectrum of an isolated $(PAH)H^+$. The observed transition occurs indeed in the visible region (~500 nm), demonstrating that small and also larger $(PAH)H^+$ molecules are indeed potential DIB carriers. The large shift of the electronic transition upon protonation is rationalized by a charge transfer state, which is only available for the protonated species but should be a general phenomenon for all $(PAH)H^+$. Support for this hypothesis is provided by quantum chemical calculations. In addition to their astronomical relevance, $(PAH)H^+$ constitute a fundamental class of molecules, which were identified in combustion experiments (*18*) and studied in superacidic solutions as fundamental intermediates of electrophilic aromatic substitution reactions (*19*). Moreover, similar to fullerenes and carbon nanotubes, PAH are an interesting

class of material for optical devices, whose optical properties are of fundamental interest.

Early spectroscopic work on (PAH)H$^+$ was conducted in the condensed phase and mainly motivated by their importance as short-lived intermediates in chemical reaction mechanisms (in particular electrophilic aromatic substitution) (*19*). George Olah was awarded the Nobel Prize for Chemistry in 1994 for his important contribution in characterizing a plethora of these carbocations in the condensed phase via NMR, IR, and electronic spectroscopy (*20*). In this period, optical spectra of a variety of (PAH)H$^+$ ions have been reported in super acid media (*21-23*). However, the optical spectra of (PAH)H$^+$ ions in the condensed phase can largely be influenced and perturbed by solvation and counter ions as it is the case for protonated benzene (*24, 25*). We have recently confirmed this conclusion for benzeneH$^+$: while benzeneH$^+$ absorbs in the $\lambda<350$ nm region (*26*), benzene$_2$H$^+$ absorbs in the violet spectral region $\lambda<450$nm (*27*), illustrating the dramatic impact of microsolvation, in this case the addition of only a single molecule, on the optical properties.

In order to unravel the intrinsic structural and electronic properties of these fundamental carbocations and to directly compare to the astronomical UIR and DIB spectra, laboratory IR and electronic spectra of isolated (PAH)H$^+$ ions are required. However, until recently, no spectroscopic information was available on even simple (PAH)H$^+$ ions isolated in the gas phase. Recent technological progress in the development of efficient ion sources and sensitive spectroscopic techniques have enabled to obtain for the first structured spectra of benzeneH$^+$ and naphthaleneH$^+$ in the IR region (*9, 28*), confirming that both ions are σ complexes in their ground electronic states. Since protonated systems are isoelectronic to their neutral counterparts, at first glance a drastic change in the electronic absorption spectrum upon protonation is not expected. Only small spectral shifts have indeed been observed for tyrosineH$^+$ (*29, 30*), adenineH$^+$ (*31*) and a variety of substituted benzene derivatives (*26*) and were thus expected also for isolated naphthaleneH$^+$, the simplest (PAH)H$^+$.

We briefly review the present knowledge on naphthaleneH$^+$. Previous calculations on the potential energy surface of the ground electronic state demonstrate that the C_1 protonated isomer is slightly more stable than the C_2 protonated species (*9, 32*), in line with both the NMR spectra in solution (*19*) and IR spectra in the gas phase (*9*). The absorption spectrum of naphthaleneH$^+$ has been observed in HF solution at 400 nm, which is blue-shifted compared to the one of benzeneH$^+$ recorded under similar conditions (*22*). As the absorptions of larger (PAH)H$^+$ are, however, expected to shift to the red, this experimental finding addresses again the nature of the absorbing species and the perturbing role of the solvent (*22*).

Figure 1 shows the electronic absorption spectrum of naphthaleneH$^+$ obtained via photodissociation of mass-selected ions. The experimental setup has been described previously (*27*). NaphthaleneH$^+$ ions are produced by a discharge ignited in a pulsed supersonic expansion and accelerated into a reflectron time-of-flight mass spectrometer. The mass-selected ions are resonantly excited with photons generated by an optical parametric oscillator laser. Resulting fast neutral fragments are detected by a multichannel plate detector, whereas all ions are repelled by an electrostatic field. The spectrum in figure 1 is obtained by recording the neutral fragment signal as a function of the laser wavelength. The absorption of naphthaleneH$^+$ in the visible region starts at 503.5 nm (2.46 eV), which is strongly red shifted from that of the neutral molecule at 312 nm (3.97 eV) (*33*), corresponding to a spectral shift of 40%. The presence of well-resolved vibrational structure shows that the excited state geometry is not drastically different from the one of the ground state and that the excited state lifetime is not ultra short. This observation seems to be in contrast to theoretical and experimental results obtained for benzeneH$^+$ (*26, 34*). The width of the origin transition of 12 cm^{-1} in Fig. 1, obtained from a Gaussian line shape analysis, implies that the excited state lifetime is longer than 0.5 ps.
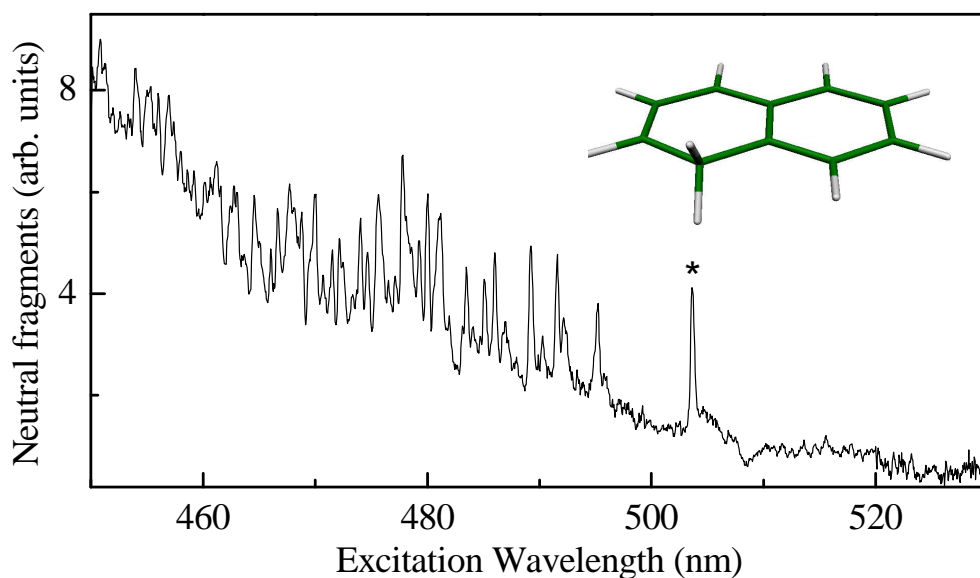
Figure 1. *Part of the photodissociation spectrum of mass-selected naphthaleneH$^+$ in the vicinity of the S$_1$ origin transition at 503.5 nm (origin band, indicated by an asterisk).*

The ground state structures of the three possible isomers of naphthaleneH$^+$ have been calculated at the ri-MP2/cc-pVDZ level using the Turbomole package (*35*). In agreement with previous work (*9, 32*), the most stable one is the C$_1$ isomer shown in Fig. 1. The excited state calculation at the ri-CC2/cc-pVDZ level yields vertical excitation energies of 2.95 eV and the adiabatic one to 2.56 eV, the latter of which is in very good agreement with the experimental transition (2.46 eV). The observed state is thus assigned to the S$_1$ state, corresponding to the HOMO-LUMO excitation. These orbitals are visualized in Fig. 2 (left panel). The HOMO is localised on the benzene ring without proton, while the LUMO is mainly localised on the protonated part of the molecule, indication the charge-transfer character of the excited state. This scenario is analogous to benzene$_2$H$^+$, which also absorbs in the visible region (*27*) and has a similar orbital scheme (Fig. 2, right). The second excited state of naphthaleneH$^+$ corresponds to the (HOMO-1)-LUMO transition and does not have this charge transfer character. It is similar to the transition of the neutral molecule, with a calculated vertical energy of 3.48 eV.
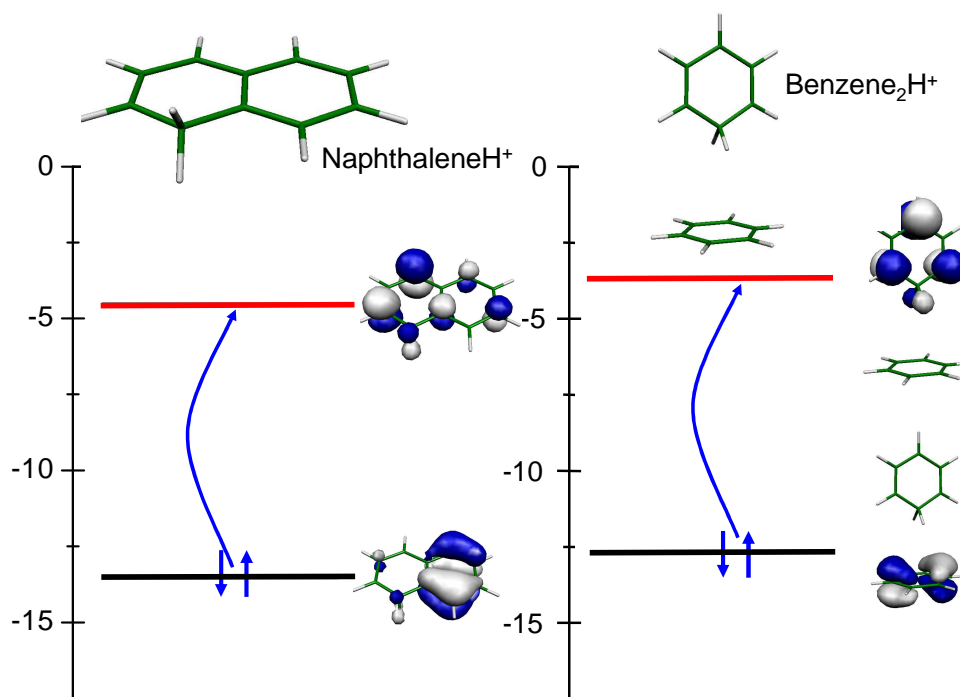
Figure 2. *Comparison of energy and shape of selected molecular orbitals of (benzene)$_2$H$^+$ (right) and of naphthaleneH$^+$ (left). Similar to (benzene)$_2$H$^+$, the HOMO (black line) of naphthaleneH$^+$ is localized on the unprotonated ring, whereas the LUMO (red line) is more localised on the ring containing the excess proton. The resulting HOMO-LUMO excitation, giving rise to the charge-transfer transition observed in the optical range, is indicated by a blue arrow.*

In the benzene$_2$H$^+$ case, a very simple model helps to rationalize why the electronic absorption of this species is considerably lower in energy than its neutral isoelectronic counterpart (*27*). Figure 3 visualizes the HOMO and LUMO orbitals of benzene$_2$H$^+$ and its fragments benzeneH$^+$ and benzene. In first approximation, the HOMO-LUMO gaps are similar for benzeneH$^+$ and benzene. However, the HOMO of benzeneH$^+$ is significantly lower in energy, because the positive charge increases the ionisation energy due to larger Coulomb attraction. Thus, in benzene$_2$H$^+$ the HOMO is localized on the benzene part, whereas the LUMO is localized on the benzeneH$^+$ moiety. Consequently, the HOMO-LUMO electronic transition corresponds to a charge transfer state, which is lower in energy as compared to the transitions

localized on each of its constituents. The charge-transfer state of benzene$_2$H$^+$ leads to an intense absorption observed in the visible region, in agreement with theory (*27*).
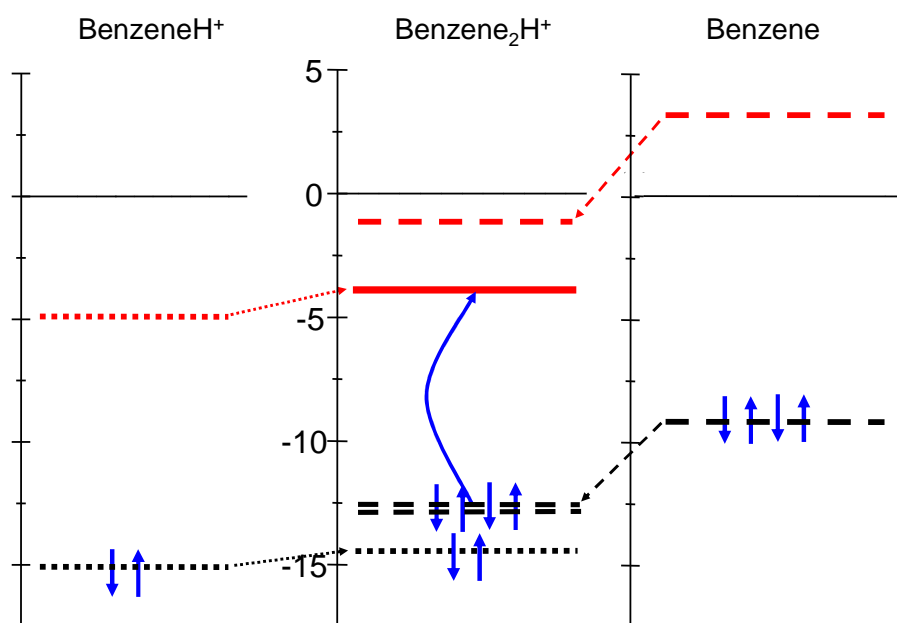

Figure 3. *Molecular orbitals of (benzene)$_2$H$^+$ (middle) compared to those of benzeneH$^+$ (left, dotted lines) and benzene (right, dashed lines). The color code is the same as in Figure 2. The energies of the benzeneH$^+$ orbitals are shifted to lower energy as compared to benzene because the ionisation potential of the charged species is higher due to the additional Coulomb interaction between the outgoing electron and the positive charge.*

Comparison of the benzene$_2$H$^+$ orbitals with those of naphthaleneH$^+$ reveals certain similarities. In naphthaleneH$^+$, the HOMO is also confined to the ring without proton, while the LUMO is localized more on the protonated ring. Thus, the additional proton decouples the two aromatic rings of naphthalene, with the consequence of generating the low-energy S$_1$ charge-transfer state. For larger (PAH)H$^+$, the HOMO-LUMO gap of the unprotonated moiety is expected to decrease as a function of the number of rings, due to extended electron delocalization. When this gap will become smaller than the HOMO-LUMO gap of the protonated ring, then the S$_1$ state will loose its charge transfer character and turn into a regular π-π^* transition. Its transition

energy will then be lower than the charge transfer state and thus lower than the S_1 transition of naphthaleneH$^+$. Consequently, according to this simple molecular orbital consideration, the lowest electronic absorption bands of all (PAH)H$^+$ ions are predicted to occur in the visible range, in agreement with the predictions of recent ab initio calculations (*6, 7*).

There is increasing strength in the hypothesis that (PAH)H$^+$ are potential candidates for DIB carriers (*5-7, 9*). Following photochemical stability arguments, smaller (PAH)H$^+$ molecules are usually considered to be less favourable candidates, and indeed there is no coincidence between the naphthaleneH$^+$ spectrum in Fig. 1 (in particular the origin band) and strong DIBs (*12*). In this context, it is however worth mentioning that coincidences of naphthalene$^+$ and the DIBs have been suggested recently (*8*). The key result of the present work is to demonstrate that free (PAH)H$^+$ ions indeed absorb strongly in the visible region and the spectrum in Fig. 1 presents the first direct unambiguous experimental evidence for this conclusion. Thus, for the first time there is compelling spectroscopic support for the (PAH)H$^+$ hypothesis. Obviously, optical spectra of larger (PAH)H$^+$ ions are needed for testing the DIBs hypothesis and corresponding experiments are currently underway.

Acknowledgments

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