Infrared spectroscopy of mass-selected aromatic and diamondoid molecular ions: a laboratory quest for the organic inventory in space

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Citation for published version (APA):
Chapter 4

Aryl\(^+\) Systems II. Aromatic Carbon Architecture and the Triplet-Singlet Energy Gap\(^*\)

The ubiquity of polyaromatic hydrocarbons (PAHs) in space has important implications to extra-terrestrial chemistry. Contrary to terrestrial conditions, their transient molecular forms are crucial in the low-density astrophysical environments. The loss of an H atom from a PAH cation is a plausible conjecture since strong UV photon fluxes and shock-induced collisions are conditions common to many space environments, and can induce C–H bond rupture. This event leads to the creation of a transient PAH form known as an aryl cation. Additionally, photo-induced chemistry (which is common on grain mantles subject to energetic starlight) is known to proceed via aryl\(^+\) intermediates. After giving laboratory evidence for the formation of triplet aryl cations with focus on the naphthyl\(^+\) system, I follow up in extending the study on aryl\(^+\) systems in terms of their molecular electronic structures, photochemistry, and rationalise possible roles in astrophysical settings. Similar to naphthyl\(^+\), the laboratory spectra in the 6–18 \(\mu\)m range of two other aryl\(^+\) species, indicate that they have a triplet electronic configuration. Electronic calculations on systems as large as the mono-dehydrogenated circumcoronene cation (C\(_{54}\)H\(_{17}\)) provide further evidence for the higher stability of a triplet state as compared to the singlet. The IR signatures reveal that an isolated PAH cation before and after H-atom loss are qualitatively similar, particularly in the 6–9 \(\mu\)m region involving the skeletal CC stretching modes, so that triplet aryl cations are also compliant with the general match between PAH mid-IR features and the interstellar UIR bands. The establishment of a triplet electronic ground state suggests that interstellar scenarios should consider the possible influence of triplet aromatic chemistry as well as of the aryl\(^+\) optical properties.

4 Aryl\textsuperscript{+} Systems II

4.1 Introduction

The universally observed mid-infrared emissions (the unidentified infrared, UIR, emissions), typical of a wide diversity of UV-energized astrophysical environments, provide key evidence for the ubiquitous presence of PAH structures in space. Numerous theoretical and laboratory investigations on the IR activity of PAHs and some of their derivatives (Hudgins & Allamandola 1995, Hudgins et al. 2005, Langhoff 1996, Langhoff et al. 1998, Mattioda et al. 2003, Oomens et al. 2006b, Pauzat et al. 1992, Ricca et al. 2011, Ricks et al. 2009, Szczepanski & Vala 1993) convincingly show that the major interstellar features—consistently observed around 3.3, 6.2, 7.7, 8.6 and 11.3 \( \mu \text{m} \)—coincide with IR absorptions due to the CC stretching- and CH bending- vibrations of PAH molecules (Allamandola et al. 1985, Léger & Puget 1984). Moreover, PAHs with partially filled \( \pi \)-orbitals have been suggested to be the carriers of some of the diffuse interstellar bands (DIBs), optical absorption bands in the spectra of stars (Duley 2006b, Snow & Destree 2011).

Although mono-dehydrogenated PAH\textsuperscript{+} species have been studied to some extent using theoretical methods (Duley 2006a, Jolibois et al. 2005, Malloci et al. 2008, Pauzat et al. 1997), experimental characterization is challenging because of their transient nature, owing to the highly reactive carboxocation center. Studies in solution or even in rare-gas matrices may therefore be only of partial astrophysical relevance and experiments in complete isolation are necessary. Mass spectrometry provides an ideal platform for studies on the isolated ions. Bierbaum’s group (Le Page et al. 1999a,b) studied reactions of mono-dehydrogenated PAH ions (e.g., naphthyl\textsuperscript{+} and pyrenyl\textsuperscript{+}) with atomic and molecular species of interstellar interest and revealed that their reactivity depends on their overall spin. Also, Ascenzi et al. (2004) studied ion–molecule reactions of naphthyl\textsuperscript{+} with \( \text{H}_2 \) and \( \text{D}_2 \), showing again that understanding the reactivity requires knowledge of the electronic spin character of the mono-dehydrogenated PAH ion.

Mono-dehydrogenated PAH (i.e., aryl) cations possess two possible ground electronic configurations: (1) \( \pi^\rho \sigma^0 \) for a closed-shell singlet structure or (2) \( \pi^{\rho-1} \sigma^1 \) for an open-shell triplet structure, where \( \rho \) is the number of \( \pi \)-electrons in the neutral non-dehydrogenated PAH form. In (1), the \( \pi \)-bonding orbitals are fully occupied and the positive charge is largely localized on the vacant nonbonding \( \sigma \)-orbital of the dehydrogenated carbon atom, the carboxocation center (C\textsuperscript{+}). The C\textsuperscript{+}-atom then tends to become sp hybridized, inducing a flattening of the CC\textsuperscript{+}C-ring angle. In the alternative configuration (2), one \( \pi \)-electron is missing and the nonbonding \( \sigma \)-orbital is occupied by an unpaired electron. This electron largely restores its normal sp\textsuperscript{2} hybridization, recovering the hexagonal geometry of the ring. For this configuration, the charge is no longer concentrated on the C\textsuperscript{+} atom, but rather delocalized over the \( \pi \)-system. For the phenyl cation, C\textsubscript{6}H\textsubscript{5}\textsuperscript{+}, the prototypical aryl\textsuperscript{+} system, the relative stability of triplet and singlet states in terms of the geometric and electronic effects described above has been extensively discussed (Nicolaides et al. 1997). Here, the energy cost is smaller for structural ring strain than for having a hole in the \( \pi \)-system, and thus, the singlet is situated ca. 1 eV below the triplet (Hrusak et al. 1997). Establishing the ground electronic state for aryl\textsuperscript{+} systems is a central issue in organic chemistry and may have important consequences for PAHs in astrophysical settings as well.
In this chapter, a study of the electronic structures and spectral properties of the naphthyl$^+$ ($\text{C}_{10}\text{H}_7^+$), phenanthryl$^+$ ($\text{C}_{14}\text{H}_9^+$), and pyrenyl$^+$ ($\text{C}_{16}\text{H}_9^+$) aryl cations is presented using IR multiple-photon dissociation (IRMPD) spectroscopy and quantum-chemical calculations. Singlet and triplet states of aryl$^+$ systems differ substantially in the carbon-bonding geometry and this is reflected in their IR spectra. The experimental and quantum-chemical methods are described in Section 4.2. The results and discussion on the UV- and IRMPD-fragmentation, electronic calculation, and IR characterization and harmonic frequency analysis are presented in Section 4.3. Section 4.4 discusses the behavior of the singlet–triplet (S–T) energy gap for systems larger than those studied here experimentally. Section 4.5 establishes the effects of mono-dehydrogenation on the PAH IR spectra, and discusses the implications for interstellar UIR emissions. The final section briefly discusses the relevance of mono-dehydrogenated PAH ions in space in terms of their chemical role and altered optical properties in the context of the DIBs.

4.2 Laboratory Methods

4.2.1 Experiments

The formation of the three aryl cations in a Paul ion trap was achieved by UV photolysis of their corresponding bromo-PAH molecular precursors as described in the previous chapter (see Sec. 3.2.1).

4.2.2 DFT Computations

Electronic structure calculations were performed using density functional theory (DFT) in the form of the hybrid electron-exchange-correlation functional B3LYP (Becke 1993) and the Gaussian-type triple-$\zeta$ 6–311+G($d,p$) basis set. Polarization functions $p$ and $d$ are added to H and C atoms, respectively, allowing molecular orbitals to spatially expand asymmetrically around the atomic nuclei. A priori, diffuse functions are not necessary, however, we add them to C atoms as an exercise to explore their effect as a function of basis set size and spatial flexibility. Their influence was found to be minimal and results are presented with them. For each mono-dehydrogenated PAH$^+$ species, there are several structural isomers depending on which of the carbon atoms is dehydrogenated. Two optimizations are performed for each structural isomer assuming a singlet and a triplet electronic ground state. Ground-state energies with zero-point energy correction of optimized structures are given in electron volts (eV).

Harmonic frequency analysis is performed on each optimized structure at the same level of theory. Scaling of the computed harmonic frequencies by 0.97 is applied to compensate empirically for the anharmonicity of the vibrational potential wells. Theoretical spectra are then generated by convoluting the mode frequencies with a Lorentzian line-shape function with an FWHM of 30 cm$^{-1}$. This FWHM value corresponds to the typical bandwidths observed in the experimental IRMPD spectra.

For the lowest-energy aryl$^+$ isomers, additional computations were run using the Handy–Cohen O3LYP approach (Cohen & Handy 2001), which employs a modified ex-
change functional that provides more flexibility than B3LYP by abandoning Dirac’s uniform electron gas condition. It has been suggested that this functional yields improved molecular parameters (Baker & Pulay 2002), in particular also vibrational frequencies for (transition-metal containing) open-shell systems (Baker & Pulay 2003).

Supplementary electronic calculations were carried out for five additional aryl+ structures that allowed us to extrapolate the behavior of the singlet–triplet (S–T) energy gap. These are the mono-dehydrogenated PAH forms of coronene (C_{24}H_{11}^+, 7 rings), ovalene (C_{32}H_{13}^+, 10 rings), and circumcoronene (C_{54}H_{17}^+, 19 rings), as well as the five-membered ring species fluoranethene (C_{16}H_{5}^+, 4 rings) and corannulene (C_{20}H_{9}^+, 6 rings). The same level of theory was used although diffuse functions were omitted to reduce the computational cost. Also, molecular orbitals were expanded in a Gaussian-type double-ζ 6–31G(d,p) set of basis functions (for C_{32}H_{13}^+ and C_{54}H_{17}^+). These small changes do not influence the conclusions reached in Sec. 4.4. We note that all optimized structures correspond to true minima as their respective vibrational coordinates form a complete set of positive frequencies. All computations were performed using Gaussian 03 and 09 at the SARA computing center in Amsterdam.

4.3 Results and Discussion

4.3.1 Photochemistry

UV irradiation at 193 nm induces ionization and rapid C–Br bond cleavage in the singly halogenated aromatic precursors, yielding the corresponding mono-dehydrogenated PAH aryl-cation. Figure 4.1 shows the mass analysis of photoproducts during a complete experimental sequence for naphthyl+ (Fig. 4.1a), phenanthryl+ (Fig. 4.1b), and pyrenyl+ (Fig. 4.1c) ions. Two mass spectra are superimposed: one (blue) recorded just after UV photolysis and isolation of the aryl cation, and the second (red) recorded after resonant IR irradiation, averaged over the 6-18 µm range. A residual population of the halogenated precursor is observed with ion intensities of 17% ± 1%, 45% ± 1%, and 23% ± 1% for the naphthyl+ (m/z 127), phenanthryl+ (m/z 177), and pyrenyl+ (m/z 201) ions. Further adjustments to minimize the precursor ion results in severe deterioration of the target aryl-cation signal. The double mass peak observed in the precursor signals is due to the two stable isotopes of the bromine atom, 79Br and 81Br, at nearly equal natural abundances.

The fragmentation chemistry of ionized PAHs has been extensively studied (e.g., Cui et al. 2000, Ekern et al. 1998, Gotkis et al. 1993b). Prior to dissociation, high vibrational excitation causes ring opening and further rearrangements (e.g., isomerization) eventually leading to the ejection—fairly independent of the precise PAH species—of the same neutral units (Pachuta et al. 1988). For example, C_{2}H_{2}-loss from azulene** and naphthalene** (two C_{10}H_{8}** isomers) both lead to the formation of benzocyclobutadiene** at m/z 102 (Cui et al. 2000). In addition, aryl+ ions may exist in different isomeric forms, which may have different unimolecular dissociation rates, although interconversion between them via 1,2-hydride shifts is a relatively facile rearrangement for aryl cations (see 3.3.2). Finally, each of the structural isomers has two possible potential energy surfaces (singlet or triplet) for
4.3 Results and Discussion

Figure 4.1 – Mass spectra of (a) naphthyl$^+$ ($m/z$ 127, $C_{10}H_7^+$), (b) phenanthryl$^+$ ($m/z$ 177, $C_{14}H_9^+$), and (c) pyrenyl$^+$ ($m/z$ 201, $C_{16}H_9^+$) as produced by UV photoionization (in blue) from their bromo-substituted PAH precursors and after subsequent FEL-induced IR photodissocia-
tion (in red).
which the fragmentation pattern may be different. The mass spectra show products involving the loss of multiple carbon atoms. These occur through C\textsubscript{2n}H\textsubscript{x} neutral losses, where \( n = 1, 2, ..., 5 \), and \( x \) is the number of hydrogen atoms. Channels involving H- and H\textsubscript{2}-loss are also observed (see for instance, the low-mass flank of the naphthyl\textsuperscript{+} mass peak in Fig. 4.1a), though not fully resolved from the strong mass peak of the parent aryl cation. For the three species studied here, a higher dissociation efficiency of H-loss compared to H\textsubscript{2} loss is observed (see, e.g., for naphthyl\textsuperscript{+} in Fig. 4.1a, in red). For intact PAH cations fragmented by UV irradiation, H\textsubscript{2} loss was observed to be more efficient than H loss (Ekern et al. 1998, Gotkis et al. 1993b).

Naphthyl\textsuperscript{+} appears highly susceptible to decomposition after the non-resonant 193 nm irradiation of bromonaphthalene. The excess energy stored after its formation relaxes through dissociation channels involving four- and six- carbon atom losses. In case of its parent radical ion, naphthalene\textsuperscript{•+}, direct UV/vis broadband irradiation leads to its total decomposition (Ekern et al. 1998). For phenanthryl\textsuperscript{+}, UV-induced photodissociation only produces C\textsubscript{2}H\textsubscript{12}-loss ions, similar to what was observed for direct UV irradiation of the phenanthrene\textsuperscript{•+} radical ion (Ekern et al. 1998). UV photolysis of bromopyrene clearly produces the C\textsubscript{2}H\textsubscript{2}-loss fragment ion of pyrenyl\textsuperscript{+} at \( m/z \) 175 as well as the \( m/z \) 149 ion. The latter is successfully ejected after the low-mass rf-cutoff isolation. Small amounts of residual C\textsubscript{2}H\textsubscript{2}-loss fragment ions remain observable after mass-isolation of pyrenyl\textsuperscript{+} and naphthyl\textsuperscript{+} (Fig. 4.1, in blue).

On-resonance IR irradiation induces several product ions (see mass spectra in red in Fig. 4.1) as well as a small (<10%) depletion of the parent aryl cation. Apart from H and H\textsubscript{2} losses, IRMPD fragments for naphthyl\textsuperscript{+} are C\textsubscript{2}H\textsubscript{10}, C\textsubscript{4}H\textsubscript{8}, and C\textsubscript{6}H\textsubscript{6} losses (similar to UV photolysis; Ekern et al. 1998), where the primary ion products are \( m/z \) 101 (C\textsubscript{2}H\textsubscript{4}-loss) and \( m/z \) 76 (overall C\textsubscript{4}H\textsubscript{4}-loss). For phenanthryl\textsuperscript{+}, the only IRMPD product ion apart from H and H\textsubscript{2} loss is due to C\textsubscript{2}H\textsubscript{4} loss, although further decay channels may be unobservable as a result of the relatively poor signal-to-noise ratio for this ion. The main IRMPD product C\textsubscript{12}H\textsubscript{7}\textsuperscript{+} (\( m/z \) 151) resulting from C\textsubscript{2}H\textsubscript{2}-loss amounts to about 7% ± 1% of the initial phenanthryl\textsuperscript{+}. An extra fragment mass peak at \( m/z \) 152 also indicates loss of a C\textsubscript{2}H unit. The nearly equal spectral responses in \( m/z \) 151 and \( m/z \) 152 corroborate the common parent phenanthryl\textsuperscript{+}. As suggested for C\textsubscript{2}H\textsubscript{2}-loss from the phenanthrene\textsuperscript{•+} radical cation (Ling & Lifshitz 1998), the identity of \( m/z \) 152 likely corresponds to biphenylene\textsuperscript{•+} or acenaphthylene\textsuperscript{•+}. For pyrenyl\textsuperscript{+}, IRMPD produces ions down to \( m/z \) 71 (see Fig. 4.1c, in red), which is rather intriguing considering the assumed stability of its pericondensed carbon frame (Ekern et al. 1998, Ling et al. 1995). The \( m/z \) 71 ion may result from direct C\textsubscript{10}H\textsubscript{12}-loss or alternatively from a sequential decay processes. The main IRMPD product is the C\textsubscript{2}H\textsubscript{2}-loss product ion at \( m/z \) 175.

One last pertinent question regarding the aryl\textsuperscript{+} photochemistry is the mass-product branching ratios along FEL-wavelength. For example, in naphthyl\textsuperscript{+}, is the \( m/z \) 101: \( m/z \) 76 ratio equal for all the IRMPD bands? On the one hand, it is expected that \( m/z \) 76 is the doublet state molecular ion of ortho-benzyne, which could form in a spin-allowed fashion from either the singlet or triplet naphthyl\textsuperscript{+} ions. On the other hand, the extent to which C\textsubscript{2}H\textsubscript{2} is expelled to give \( m/z \) 101 might differ between singlet and triplet ions. An alternative scenario is envisioned if instead of direct C\textsubscript{4}H\textsubscript{4} loss, \( m/z \) 76 occurs via
sequential decomposition, i.e. $m/z$ 127 → $m/z$ 101 → $m/z$ 76. Here, the branching ratio is constant but still, assuming a presence of singlet naphthyl+, the fate of $C_2H_2$ ejection depends again on the total spin of naphthyl+.

### 4.3.2 Electronic and Geometric Structures and Energetics

The highest occupied molecular orbital (HOMO) of a neutral PAH molecule corresponds to one of the $\pi$-orbitals delocalized over the entire PAH (Dewar & Worley 1969). Thus, ionization of a PAH results in only marginal structural changes; the symmetry point group remains the same in both neutral and cationic forms (unless the PAH is of high symmetry and undergoes Jahn–Teller distortion in the radical cation form). While removal of an H-atom from a large PAH$^+$ system appears to constitute only a marginal modification as well, it has a number of important consequences: (1) different structural isomers can be formed, (2) the molecular symmetry is lowered considerably, and (3) the electronic configuration changes, which may induce stabilization of higher spin states that results in noticeable geometrical changes.

![Figure 4.2](image)

**Figure 4.2** – Carbon structures of the naphthalene radical cation and its two mono-dehydrogenated naphthyl$^+$ isomers. Relative energies (eV) with respect to the lowest-energy triplet isomer and structural parameters calculated at the B3LYP/6–311+G(p,d) level of theory are indicated. The S–T gaps are calculated as (b) 0.005 eV and (c) 0.004 eV. The $E_a$ value reported for the radical cation corresponds to the adiabatic binding energy of the H atom plus the hydrogen ionization energy (13.6 eV).
For each mono-dehydrogenated PAH$^+$ isomer studied here, DFT optimizations were carried out assuming both a singlet and a triplet ground electronic state, corresponding to configurations where the nonbonding \( \sigma \)-orbital on the dehydrogenated C$^+$ atom is empty (\( \pi^0 \sigma^0 \)) or singly occupied (\( \pi^{\sigma-1} \sigma^1 \)), respectively. Note that we do not consider open-shell singlets, as they are known to lie substantially higher in energy (Laali et al. 2002).

The electronic structure of the naphthyl$^+$ ion (C$_{10}$H$_7^+$) has been theoretically studied in some detail, although there are notable discrepancies among the different levels of theory (Ascenzi et al. 2004, Du et al. 1993, Fujiwara et al. 1996, Laali et al. 2002). Depending on the approach, the triplet state is placed either below or above the singlet state. Experimentally, ion–molecule reactions (Ascenzi et al. 2004, Le Page et al. 1999b, Slegt et al. 2007a) have addressed the possible stability of the triplet relative to that of the singlet, though no direct determination of the ground electronic state was possible. Based on IR ion spectroscopy, we showed in Chapter 3 that triplet naphthyl$^+$ dominates the gas-phase ion population in our experiment, although a small contribution of singlet naphthyl$^+$ could not be ruled out. In addition to the choice of electronic states, two isomeric mono-dehydrogenated naphthyl$^+$ structures exist, 1-naphthyl$^+$ and 2-naphthyl$^+$ (Figure 4.2), since the neutral naphthalene molecule (C$_{10}$H$_8$) has two nonequivalent H atoms. The triplet 1-naphthyl$^+$ ion is lowest in energy at the B3LYP/6–311++G** level of theory, though by an insignificantly small margin compared to singlet 1-naphthyl$^+$. We also pointed out that the 2-napthyl$^+$ ion, which is computed to be 5 kJ mol$^{-1}$ (0.05 eV) higher in energy for either electronic state, likely undergoes a 1,2-hydride shift forming the more stable 1-naphthyl$^+$ ion under our experimental conditions. Similar structural rearrangements may occur in other mono-dehydrogenated PAH$^+$ species. Typically, the lowest energy isomer corresponds to one where the carbocation center resides on a carbon surrounded by a region of high electron density, stabilizing the positive charge, and thus lowering the overall energy of the structure.

Determining the ground-state energy for the phenanthryl$^+$ ion (C$_{14}$H$_9^+$) requires the optimization of five isomeric mono-dehydrogenated PAH$^+$ structures (Fig. 4.3) in two electronic states, as the C$_{2v}$ geometry of the parent phenanthrene (C$_{14}$H$_{10}$) possesses five nonequivalent hydrogen atoms. The singlet-triplet (S–T) energy gap is 0.15 eV on average, always in favor of the triplet state. All triplet structures have a planar C$_s$ symmetry. For the singlet, structural isomers 1 and 9 conserve planarity, but the remaining isomers (2, 3, and 4) exhibit an out of plane distortion along the CC$^+$C rim. This deformation may act to stabilize the carbocation through the influence of adjacent \( \sigma \)-orbitals. The triplet structure with the carbocation located in position 4 is calculated to be lowest in energy; this indicates an increased electron density in the bay area of the molecule where the (formally) positively charged carbon atom is stabilized. As shown in Chapter 6 or in Piest et al. (2001), IR spectra suggest that open-shell radical cations with a phenanthrene carbon skeleton (i.e., ionized forms of phenanthrene and nitrogen-substituted phenanthrene) possess an intricate vibronic structure (owing to a low-lying electronic state), which hampers a reliable localization of the true doublet ground electronic surface (Bally & Borden 1998). As described in the next section, the triplet-state monodehydrogenated phenanthrene cation, phenanthryl$^+$, may retain this phenomenon making the IR characterization using a standard DFT harmonic frequency analysis less definite.
4.3 Results and Discussion

Figure 4.3 – Carbon structures of the phenanthrene radical cation and its five mono-dehydrogenated phenanthryl + isomers. Relative energies (eV) with respect to the lowest energy triplet isomer and structural parameters calculated at the B3LYP/6–311+G(p,d) level of theory are indicated. The S–T gaps are (b) 0.121 eV, (c) 0.154 eV, (d) 0.140 eV, (e) 0.212 eV, and (f) 0.114 eV. The $E_a$ value reported for the radical cation corresponds to the adiabatic binding energy of the H atom plus the hydrogen ionization energy (13.6 eV).

For pyrenyl + ($C_{16}H_9^+$), removal of an H-atom from the $D_{2h}$ symmetry pyrene radical cation results in three mono-dehydrogenated PAH + structural isomers (see Fig. 4.4). The average S–T gap is about 0.42 eV in favor of the triplet, which is nearly three times as high as the S–T gap for phenanthryl +. As the number of $\pi$-electrons increases, the triplet state becomes increasingly stabilized over the singlet. This is explained by the electron-donating effect of the additional aromatic rings, which diffuses the positive charge over the entire structure and thus increases the gas-phase stability (Laali et al. 2002), analogous to the well-known decreasing ionization potentials with increasing PAH size. Of the three pyrenyl + isomers, the hydrogen atom is removed from the carbon in position 1 for the lowest energy structure. In the next section, we show that the IR spectra corroborate the increased stability of the triplet state.

4.3.3 Vibrational Spectra in the 6–18 $\mu$m Wavelength Range

Figures 4.5–4.7 compare the DFT spectra under the harmonic approximation for the various mono-dehydrogenated PAH + isomers with the experimental IRMPD spectra. This
Figure 4.4 – Carbon structures of the pyrene radical cation and its three monodehydrogenatedpyrenyl$^+$ isomers. Relative energies (eV) with respect to the lowest-energy triplet isomer and structural parameters calculated at the B3LYP/6–311+G(p,d) level of theory are given. The S–T gaps are (b) 0.565 eV, (c) 0.239 eV, and (d) 0.473 eV. The $E_a$ value reported for the radical cation corresponds to the adiabatic binding energy of the H atom plus the hydrogen ionization energy (13.6 eV).

permit us to evaluate the isomer formed in the ion trap as well as its ground-state electronic configuration. The naphthyl$^+$ IRMPD spectrum was discussed previously in Chapter 3 and is described here briefly for completeness. The spectrum is obtained from integrating the yields of $m/z$ 101 and $m/z$ 76 ions, and it exhibits six resolved bands (listed in Table 4.1) plus several additional minor features. Both 1- and 2-bromonaphthalene precursors give the same spectral response that is best reproduced by the spectrum predicted for triplet 1-naphthyl$^+$. In our previous analysis we noticed the anomalously high relative intensities of the 9.89 and 17.2 $\mu$m (1011 and 580 cm$^{-1}$) features that could indicate the presence of a minor fraction of singlet naphthyl$^+$ ions, although relative intensities
4.3 Results and Discussion

![Figure 4.5](image-url) - Gas-phase IR spectrum of the naphthyl cation (gray) superimposed onto the theoretical IR spectra (B3LYP/6–311+G(p,d), frequencies scaled by 0.97) of the two mono-dehydrogenated structural isomers in their singlet (left) and triplet (right) states.

in an IRMPD spectrum may be misleading indicators of relative populations. Nevertheless, from the overall good agreement between theoretical and experimental spectra, we conclude that the triplet 1-naphthyl$^+$ ion is the dominant species in the ion trap.

The phenanthryl$^+$ IRMPD spectrum (Fig. 4.6) is obtained by integrating the fragment ion yields at $m/z$ 152 and $m/z$ 151, and reveals ten absorption bands as listed in Table 4.1. Assigning the IR bands of phenanthryl$^+$ is less straightforward than for naphthyl$^+$ due to the possible contributions of many isomers, with two different spin states (see Fig. 4.3). In addition, IR spectroscopic evidence shows that open-shell phenanthrene derivatives exhibit notable differences between calculated (via standard DFT) and experimental spectra (see sec. 4.3.2). For example, B3LYP calculated vibrational frequencies for the phenanthrene radical cation (Piest et al. 2001) and for one of its singly nitrogen-substituted variants, the phenanthridine radical cation (see Chapter 6) strongly deviate from their experimental spectra in the 9–12 $\mu$m IR region, where in-plane symmetry modes—typically with CH bending character—are located. In contrast, for protonated phenanthridine, with a closed-shell electronic configuration, a calculation at the same level of theory accurately reproduces the experimental spectrum (see Chapter 6). This suggests that difficulties calculating spectra are inherent to phenanthrene$^+$ systems with partially filled orbitals (i.e., open shells), which therefore include the triplet phenanthryl$^+$ system. Note that a low-lying electronic state may perturb the ground state via vibronic interactions or may cause
Table 4.1 – Gas-phase IR absorption bands for naphthyl\(^+\), phenanthryl\(^+\), and pyrenyl\(^+\) recorded via IRMPD spectroscopy.

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<tr>
<th>Naphthyl(^+)</th>
<th>Phenanthryl(^+)</th>
<th>Pyrenyl(^+)</th>
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<tr>
<td>(\mu m)</td>
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<td>6.73</td>
<td>1485</td>
<td>s, r</td>
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<tr>
<td>7.25</td>
<td>1380</td>
<td>m, r</td>
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<tr>
<td>8.36</td>
<td>1196</td>
<td>s, r</td>
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<tr>
<td>9.89</td>
<td>1011</td>
<td>m, r</td>
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<tr>
<td>13.6</td>
<td>735</td>
<td>s, r</td>
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<tr>
<td>17.2</td>
<td>580</td>
<td>m, r</td>
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Notes. [a] Intensity: strong (s), medium (m), weak (w), very weak (vw); Spectral resolution: resolved (r), semi-resolved (sr), shoulder (sh).

Despite possible shortcomings in the theoretical approach, Fig. 4.6 clearly shows that regardless of the structural isomer, the ion population contains predominantly triplet phenanthryl\(^+\). All B3LYP theoretical spectra for the—well behaved—singlet phenanthryl\(^+\) isomers fail to match the experimental phenanthryl\(^+\) spectrum. The computed S–T energy gaps of around 0.15 eV suggest that the triplet state is indeed substantially more stable than the singlet state for phenanthryl\(^+\).

In general, distinction between singlet and triplet states can be clearly made (vide supra), however, it is less obvious which of the triplet phenanthryl\(^+\) isomers is present. In the experiment, the Br-atom is initially cleaved off at position 9, but the calculated spectrum for triplet 9-phenanthryl\(^+\) provides a poor match to the experimental spectrum, especially for the bands observed near 8.03 and 13.7 \(\mu m\). Accordingly, triplet 9-phenanthryl\(^+\) lies +0.05 eV higher in energy than the most stable isomer, triplet 4-phenanthryl\(^+\). It is moreover expected that under our experimental conditions, 9-phenanthryl\(^+\) can isomerize via 1,2-hydride shifts (see 3.3.2). Three major features are observed between 11 and 16 \(\mu m\), which are roughly reproduced by all calculated spectra except for those of 1- and 9-phenanthryl\(^+\). In Fig. 4.6, the computations for the remaining triplet spectra have trouble reproducing the intense band observed at 8.03 \(\mu m\) as well as the relative intensities of some of the bands. While contributions from 3-phenanthryl\(^+\) cannot be excluded on the basis of the present calculations, the best qualitatively overall match with the spectrum is found for triplet 2- and 4-phenanthryl\(^+\) isomers.

At this point, we should note that an IRMPD spectrum relies on the absorption of multiple (~50–100) IR photons. Particularly in congested regions of the spectrum, this excitation process can induce small shifts in the frequencies, broadening of the bands, and
4.3 Results and Discussion

Figure 4.6 – Gas-phase IR spectrum of the phenanthryl cation (gray) superimposed onto the theoretical IR spectra (B3LYP/6–311+G(p,d), frequencies scaled by 0.97) of the five mono-dehydrogenated structural isomers in their singlet (left) and triplet (right) states.
Figure 4.7 – Gas-phase IR spectrum of the pyrenyl cation (gray) superimposed onto the theoretical IR spectra (B3LYP/6-311+G(p,d), frequencies scaled by 0.97) of the three mono-dehydrogenated structural isomers in their singlet (left) and triplet (right) states.

deviations in the relative band intensities as compared to a linear absorption spectrum. While such effects have been extensively described qualitatively (Boyarkin et al. 2002, Grant et al. 1978, Marinica et al. 2006, Oomens et al. 2006b), they can often not be evaluated quantitatively because they require knowledge of the vibrational level structure up to high excitation energies, involving for instance anharmonic coupling parameters that are generally not known. Comparing IRMPD spectra with linear computed spectra has therefore become common practice. Second, we note that while the B3LYP functional has been widely applied to predict (spectral) properties of PAH species, its performance for triplet PAH systems such as studied here has not been explicitly verified. While it is
not the purpose of this study to perform an exhaustive computational analysis of the aryl cations, the spectra of the lowest-energy triplet isomers were also computed using the O3LYP functional (Cohen & Handy 2001). Results of these calculations are shown as the green trace in Figure 4.6. For the triplet 4-phenanthryl$^+$ isomer, the relative intensities of the bands in the congested 6–9 µm region appear to match the experiment more closely. As a final note, we remark that the assignment of the experimental spectrum to a specific structural isomer is not of particular interest to the astrophysical implications of this study (vide infra); the discussion below is mainly motivated by the experimental establishment of a triplet electronic state, as clearly suggested by the comparisons in Figs. 4.5–4.7.

The pyrenyl$^+$ IRMPD spectrum was recorded from fragment channels $m/z$ 176 and $m/z$ 150, revealing five major, relatively broad absorption bands (Table 4.1, Fig. 4.7). The DFT computations predict the triplet 1-pyrenyl$^+$ to be the most stable isomer (see sec. 4.3.2). Comparing the IRMPD spectrum with the computed spectra in Fig. 4.7, we find that the match with triplet 1-pyrenyl$^+$ is indeed better than with any of the other calculated spectra. Despite the broadening of the bands in the 6–9 µm region, the three main components are reasonably well reproduced by the calculation. A contribution of singlet 1-pyrenyl$^+$ can be excluded since the predicted band structure in the 13–18 µm region is not in agreement with the experimental spectrum. Singlet contributions from 2-pyrenyl$^+$ and 3-pyrenyl$^+$ isomers are discarded as well since the predicted bands near 13 µm and 10 µm, respectively, are not observed. Despite the clear match with triplet 1-pyrenyl$^+$, triplet contributions from 2-pyrenyl$^+$ and 3-pyrenyl$^+$ cannot be ruled out completely because their theoretical spectra resemble that of 1-pyrenyl$^+$ particularly in terms of band positions. However, the staircase-like shape of the relative intensities of the three bands in the 6–9 µm region is better reproduced by the spectrum of the triplet 1-pyrenyl$^+$ ion than by the two other triplet isomers. Therefore, we conclude that the triplet 1-pyrenyl$^+$ isomer dominates the ion population in our trap.

## 4.4 Singlet–Triplet Energy Gap

There is a notable tendency of the S–T energy gap to increase with π-system size (see sec. 4.3.2). Using computational methods, the behavior of the S–T gap is further explored for larger systems as well as for systems containing a five-membered carbon ring, as listed in sec. 4.2.2. Figure 4.8 shows a plot of the calculated S–T gap as a function of the number of aromatic rings in the molecule. The S–T gap curve is obtained by fitting a third-order polynomial to the energy gaps of the six-membered aryl$^+$ systems (except for the energy gap value of the single-ring phenyl cation and the two five-membered species).

A fairly linear rise is observed up to about eight aromatic rings and a leveling off of the curve sets in around the 10-ring species $C_{32}H_{13}^+$, evolving asymptotically toward the mono-dehydrogenated PAH$^+$ form of circumcoronene, $C_{54}H_{17}^+$. This behavior can be understood by considering the structural benefits that a large π-system provides to the ring bearing the carbocation center. First, for the triplet state species, the CC°C angles are 127° and 126°.8 for the largest systems $C_{32}H_{13}^+$ and $C_{54}H_{17}^+$, respectively, which is comparable to the angles found in the smaller systems (see Figs. 4.5–4.7). In the singlet state
Figure 4.8 – Singlet-triplet energy gap in eV as a function of PAH size (expressed as the number of carbon rings). The mono-dehydrogenated PAH cations are represented by solid squares: $\text{C}_{10}\text{H}_7^+$ (2 rings), $\text{C}_{14}\text{H}_9^+$ (3 rings), $\text{C}_{16}\text{H}_9^+$ (4 rings), $\text{C}_{24}\text{H}_{11}^+$ (7 rings), $\text{C}_{32}\text{H}_{13}^+$ (10 rings), and $\text{C}_{54}\text{H}_{17}^+$ (19 rings). The S–T curve is obtained from a third order polynomial fit to the S–T energy gaps of these aryl$^+$ systems ($-0.37x + 0.23x - 0.015x^2 + 4.3 \times 10^{-4}x^{-3}$). PAH cations containing a five-membered ring are represented by open circles: $\text{C}_{16}\text{H}_9^+$ (four rings) and $\text{C}_{20}\text{H}_9^+$ (six rings).

species, the CC$^+$C angle is 131° for $\text{C}_{54}\text{H}_{17}^+$, whereas in a system as small as $\text{C}_{24}\text{H}_{11}^+$ it is 140°. Hence, the sixfold symmetry of the carbocation-bearing ring in the singlet species gradually recovers as the number of aromatic rings increases. Electronic stabilization due to the large number of π-electrons slowly becomes as effective as one electron occupying the empty non-bonding σ-orbital, hence directly stabilizing the carbocation. This transition occurs for monodehydrogenated PAH$^+$ species containing around 30–35 carbon atoms, which sets an upper limit to the S–T gap of about 0.85 eV.

A turning point in the S–T gap curve is expected when the mono-dehydrogenated PAH$^+$ is sufficiently large so that singlet and triplet configurations have equal stabilization effects on the carbocation-bearing ring. This occurs when the CC$^+$C angle (a value between 120° and 127°) is equal for both spin configurations. For even larger systems, monodehydrogenation is expected to have no further structural consequences and the carbocation-bearing ring sustains a nearly perfect six-fold symmetry.
Interestingly, in a singlet mono-dehydrogenated PAH system as large as C_{54}H_{17}^+, one of the CH groups neighboring the carbocation is noticeably out of the plane, and the overall structure is slightly curved. Smaller singlet mono-dehydrogenated PAH^+ structures exhibit a similar behavior, which suggests that the hexagonal carbon architecture of the carbocation-bearing ring is prioritized over the planar symmetry. It is counterintuitive that some small singlet mono-dehydrogenated PAH^+ isomers retain the planar C_4 symmetry (see Sec. 4.3.2), while for the larger singlet systems the C_4 structure is not a true stationary minimum (or does not converge employing a common basis set). Whether or not these observations are merely computational artifacts or have a true physical meaning requires further investigation.

Figure 4.8 shows as well that the two five-membered mono-dehydrogenated PAH^+ species (open circles) do not follow the S–T gap trend for the six-membered ring species, even if their sizes fall within the linear regime. The S–T gap of mono-dehydrogenated fluoranthene (C_{16}H_{9}^+) containing three six-membered and one five-membered ring is about 0.11 eV, which is considerably lower than the isomerically averaged S–T gap for the four-ring counterpart species pyrenyl^+ (Fig. 4.4). More dramatic is the case for mono-dehydrogenated coronulene (C_{20}H_{9}^+, one five-membered ring surrounded by five six-membered rings in a bowl-shaped geometry), in which the S–T gap is reversed in favor of the singlet state. The non-planar carbon architecture of coronulene gives rise to specific charge mobility effects (Kato & Yamabe 2006) that are absent in planar PAH structures, as manifested in the IR vibrational activity of the coronulene cation (see Chapter 7). The curved geometry of this structure readily stabilizes the carbocation in its singlet state.

### 4.5 Aryl^+ Spectra and the Interstellar UIR Bands

An essential concept in the assignment of PAH species as carriers of the UIR emissions is the effect of ionization on the IR spectra. Although it was already realized early on that aromatic species may easily ionize under interstellar conditions (Allamandola et al. 1989), the remarkable effects of ionization on the IR spectra were first revealed by Pauzat et al. (1992) and experimentally verified by Szczepanski & Vala (1993). Apart from the CH stretching modes in the 3 µm region, the IR intensities in PAH spectra increase substantially upon ionization, where the CC stretching modes and CH in-plane bending modes are significantly more enhanced than the CH out-of-plane bending modes (Allamandola et al. 1999, Pauzat et al. 1992). Although it has not been the purpose of this study to provide a detailed comparison between aryl^+ spectral features and interstellar emission spectra, it is of interest to compare the IR spectra of the mono-dehydrogenated PAH cations to those of the corresponding radical cation PAHs (i.e., non-dehydrogenated); for the mono-dehydrogenated species to be similarly astrophysically relevant, their IR spectra should resemble those of radical cation PAHs. The effects of dehydrogenation on the IR spectra of PAH cations can be understood from the electronic structure of the mono-dehydrogenated PAH ions.

The occupancy of aromatic π-orbitals in the doublet radical cation and in the triplet-mono-dehydrogenated PAH is the same, both species having a π frontier orbital with an
unpaired electron. This implies that the overall carbon bonding character in the two ions is comparable. In contrast, in singlet-state mono-dehydrogenated PAH ions, the aromatic-$\pi$-orbitals are fully occupied. Figure 4.9 displays frontier orbitals (i.e., the HOMOs) for the radical cation PAH (doublet, $\pi^{\rho-1}\sigma^0$), the closed-shell mono-dehydrogenated cation (singlet, $\pi^\rho\sigma^0$), and the open-shell mono-dehydrogenated cation (triplet, $\pi^{\rho-1}\sigma^1$). Notably, the $\alpha$-electron spin orbitals of the doublet radical cation and the triplet-mono-dehydrogenated cation have electron density distributions that are qualitatively indistinguishable. This is expected as both systems have a half-filled $\pi$-orbital as the HOMO, and the other half-filled orbital associated with the nonbonding $\sigma$-orbital in the triplet (not shown in the figure) has marginal influence on the $\pi$-bonding network. Consequently, the doublet and triplet PAH structures share a common carbon-bonding architecture and the IR activity of CC modes is expected to be similar.

Figure 4.10 compares the gas-phase IR spectra of naphthalene, phenanthrene, and pyrene in their triplet-mono-dehydrogenated cationic and doublet-radical cationic forms (Oomens et al. 2000). The absorption band patterns in the 6–9 $\mu$m range show that the
4.5 Aryl$^+$ Spectra and the Interstellar UIR Bands

**Figure 4.10** – Gas-phase IR spectra of the PAH radical cations naphthalene, phenanthrene, and pyrene (blue) compared with those of their mono-dehydrogenated derivatives (red), recorded by IRMPD spectroscopy. Similar absorption features are observed for both PAH forms as a result of their similar open-shell $\pi$-configuration. The total spin $S$ is equal to 1 for a triplet state and equal to 1/2 for a doublet state.

In-plane symmetry modes (with typical CC stretching character) of both forms are indeed comparable. The broader bandwidths observed in the triplet-mono-dehydrogenated PAH$^+$ spectra are likely the result of the lower symmetry as compared with that of the radical cation and the possible contribution of more than one isomer. The lower signal-to-noise ratio is a result of larger shot-to-shot fluctuations in the precursor ion intensity, probably induced by an inherent competition between the aryl cation and the bromo-PAH ion. In the 11–16 µm range of the spectrum, where mainly the out-of-plane CH bending modes are located, a typical redshift of absorption bands is observed for the triplet mono-dehydrogenated PAH ions. Evidently, one CH bending oscillator is missing compared with the radical cation, and this reduces the CH class character of the mono-dehydrogenated ring (Allamandola et al. 1989), which then shifts the CH out-of-plane bending modes to lower frequencies.
4.6 Astrophysical Implications

The chemical role of mono-dehydrogenated PAH ions in space. The experiments reported here clearly show that under isolated conditions mono-dehydrogenated PAH$^+$ species feature a triplet ground electronic state, suggesting that interstellar PAH chemistry may entice more than singlet (PAH neutrals, closed-shell ions) and doublet (radical cation PAHs) species. When modeling interstellar PAH chemistry, one should therefore not only consider thermodynamics but also spin aspects (Schwarz 2004). Recent experiments on the reactivity of carbon chains ($C_n^-$ and $HC_n^-$) and carbanions with H, N, and O atoms revealed interesting examples of the influence of spin conservation and interconversion in interstellar chemistry (Eichelberger et al. 2007, Yang et al. 2010). For instance, reaction rate constants for singlet carbanions were found to be larger when reacting with triplet O atoms than with quartet N atoms, since for the former the reaction proceeds via spin-allowed barrierless pathways, while in the latter, it is spin forbidden (Yang et al. 2010). Dedicated experiments have already addressed the gas-phase reactivity of various mono-dehydrogenated PAH ions (Ascenzi et al. 2004, Keheyan 2001, Le Page et al. 1999a,b). These experiments provide information on the absolute reaction rates, which are of fundamental importance in numerical models of the interstellar chemistry. However, characterization of the spin state of the ion populations was based on the reaction products observed in the mass spectrum and DFT calculations. Complementary methods probing the electronic nature of the mono-dehydrogenated PAH$^+$ reactants more directly such as the present study could elucidate the reaction mechanisms more unambiguously.

The reaction of $C_{10}H_7^+$ with H$_2$ was studied by two different methods illustrating the difficulties in understanding the reaction dynamics when a proper characterization of the electronic state is not available. First, Le Page et al. used a selected ion flow tube (SIFT) to observe the formation of the intermediate $C_{10}H_9^+$, which is stabilized by a three-body collision (Le Page et al. 1999b). Later, employing an ion beam tandem mass spectrometer, Ascenzi et al. observed an associative reaction leading to the same $C_{10}H_9^+$ product, but because of the lower pressures, it subsequently stabilizes by hydrogen atom evaporation yielding the $C_{10}H_8^{++}$ radical cation (Ascenzi et al. 2004). Although both studies conclude that $C_{10}H_7^+$ is prominently reactive with H$_2$, Le Page et al. concluded that singlet-state $C_{10}H_7^+$ is responsible for the observed reaction (supported by the observed non-reactivity with H, O, and N atoms). On the other hand, based on a theoretical coupled cluster calculation, Ascenzi et al. conjectured that singlet- and triplet-state $C_{10}H_7^+$ ions equally contribute to the observed reaction pattern. While our experiments do not rule out a small singlet-state contribution (see Chapter 3), they show that triplet-state $C_{10}H_7^+$ dominates the ion population. The possible influence of different experimental conditions on the formation of either state, such as the energy imparted and the background pressure, requires more careful study especially for the naphthyl cation, where the two electronic states lie so close in energy.

The reactivity patterns of $C_{16}H_9^+$ were likewise characterized using SIFT mass spectrometry (Le Page et al. 1999a). These experiments revealed that, in contrast to the $C_{10}H_7^+$ ion, $C_{16}H_9^+$ undergoes associative reactions with H, O, and N atoms. Based mainly on quantum-chemical computations and orbital symmetry considerations, these reactivity
patterns were understood as the C\textsubscript{16}H\textsubscript{9}+ ion having a triplet state (Le Page et al. 1999a), which is in this case corroborated by our results.

As suggested by the SIFT and IRMPD studies of naphthyl\textsuperscript{+}, the formation process of a mono-dehydrogenated PAH ion may determine its final spin. In space, these species could form by statistical dissociative ionization (Léger et al. 1989), so that homolytic CH bond cleavage following photoionization would produce a singly occupied non-bonding $\sigma$-orbital, i.e., a triplet state cation. However, which of the possible electronic states is produced directly may not be important, as conical intersections have been suggested to rapidly interconvert the two spin states to whichever is lower in energy (Aschi & Harvey 1999, Nicolaides et al. 1997).

**Optical properties and the DIBs.** Although the carriers of the DIBs (Jenniskens & Desert 1994, Sarre 2006, Snow 2001) remain mysterious and subject of lively debate (Foing & Ehrenfreund 1994, Herbig 2000, Motylewski et al. 2000, Sorokin & Glownia 1995), PAH species have been mentioned more than once as viable candidates (Bréchignac & Pino 1999, Ehrenfreund et al. 1995, Iglesias-Groth et al. 2008, Parisel et al. 1992, Salama et al. 1999). The stability of triplet-state mono-dehydrogenated PAH ions as established here experimentally in combination with the similarity of their IR spectra to those of radical cation PAHs—and thus to the interstellar UIR emission bands—sheds new light on this issue. Owing to the electronic configuration of the triplet state, electronic transitions in the triplet mono-dehydrogenated PAH ion can promote an electron to either of the empty $\beta$ spaces of the two corresponding singly occupied molecular orbitals (SOMOs). This introduces optical properties different from its corresponding PAH radical cation, which possesses only one partially occupied SOMO. The electronic transitions involving such singly occupied $\pi$-orbitals were previously shown to fall in the visible region and have in fact been suggested to carry some of the DIBs (Duley 2006a). Specifically, using the semi-empirical INDO method for triplet 1-naphthyl\textsuperscript{+}, relevant electronic transitions were predicted at 621 nm and 456 nm, and at 617 nm and 460 nm for the less stable isomer triplet 2-naphthyl\textsuperscript{+} (Du et al. 1993). Here, a standard time-dependent DFT (TD-DFT) calculation using the B3LYP functional on the optimized electronic structure of triplet 1-pyrenyl\textsuperscript{+} revealed two transitions involving one of the anti-bonding SOMOs with particularly high oscillator strengths at 667 nm and 409 nm ($f = 0.0266$ and 0.2283, respectively). It should be noted that while such quantum-chemical calculations are useful to investigate electronic structures and to provide an estimate for the wavelengths of electronic transitions, it is clear that they are currently by no means sufficiently accurate to reliably assign DIB transitions (as also recognized by others, see, e.g., Du et al. 1993). However, in combination with our experiments, these computations suggest that triplet-state aryl cations are interesting candidates to be investigated by emerging experimental methods in gas-phase UV/vis ion spectroscopy (Citir et al. 2006, Dzhonson et al. 2007, Stearns et al. 2007), which can establish vibronic band positions to about 1 cm\textsuperscript{-1} accuracy.
4 Aryl\(^+\) Systems II

4.7 Conclusions

Using a Paul-type ion trap coupled to the beamline of an infrared FEL, three mono-dehydrogenated PAH ions (naphthyl\(^+\), C\(_{10}\)H\(_7^+\); phenanthryl\(^+\), C\(_{14}\)H\(_{9}^+\); pyrenyl\(^+\), C\(_{16}\)H\(_{9}^+\)) were spectroscopically investigated via resonant IRMPD spectroscopy to probe their electronic structures in the gas phase. IR characterization shows that the isolated mono-dehydrogenated PAH ions possess a triplet ground electronic state (\(\pi^0\sigma_1\)). The singlet state (\(\pi^0\sigma^0\)), having fully occupied \(\pi\)-orbitals, is computed to be less stable, which is confirmed by the observed IR spectra. Electronic structure calculations on systems up to the size of mono-dehydrogenated circumcoronene (C\(_{54}\)H\(_{17}^+\)) reveal that the magnitude of the S–T gap levels off to a value around 0.8 eV. The IR spectra of the triplet mono-dehydrogenated PAH ions resemble those of the corresponding (doublet) radical cation PAHs closely, owing to the similar occupancy of \(\pi\)-orbitals. This also implies that these mono-dehydrogenated species may contribute to the UIR emission bands from UV-dominated regions, as has been suggested for radical cation PAHs. The establishment of triplet PAH ions produced by H-atom abstraction from radical cation PAHs further suggests that new avenues may be explored in the modeling of interstellar ion–molecule chemistry involving PAH species. Moreover, these triplet state species may be considered in the search for carriers of the DIBs, as the optical properties of triplet PAH species are altered compared to their singlet or doublet state counterparts.