Infrared spectroscopy of mass-selected aromatic and diamondoid molecular ions: a laboratory quest for the organic inventory in space
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The attribution of the astronomical UIR emissions to polyaromatic hydrocarbon (PAH) molecules is a key argument in favor of the abundant occurrence of organic matter in space. For interstellar regions predominantly energized by far-UV photons (e.g., diffuse clouds), PAH molecules may lose one or more hydrogen atoms since the C–H bond energy typically lie in the 4–6 eV range ($< h\nu_{\text{FUV}}$); in either neutral or cationic state, and roughly independent of size. In this chapter, the aryl carbocation form is introduced which is characteristic of a singly dehydrogenated PAH positive ion. The ion-trapping experimental technique for the production of aryl$^+$ molecular systems is exposed and evidence of aryl$^+$ formation is giving for the two-ring system, naphthyl$^+$. The IR spectroscopic characterization shows that the ground state of the mass-selected naphthyl$^+$ population exhibit a triplet spin electronic configuration. Evidence is shown as well for electronic stabilization of the dehydrogenated carbon (carbocation center) via 1,2-hydride shift isomerization.

3 Aryl$^+$ Systems I

3.1 Introduction

The formation of polycyclic aromatic hydrocarbon (PAH) molecules in space constitutes an essential phase in the interstellar carbon cycle (Henning & Salama 1998). In astrophysical environments, PAHs are subject to numerous physical and chemical processes (Tielens 2005) that can modify their chemical form and hence their physico-chemical properties. Depending on the local interstellar conditions, a PAH population may include ionized, (partially) dehydrogenated, or heteroatom substituted PAHs as well as PAHs in spin states other than singlet (or doublet for radical cations). Although it is now widely accepted that an important fraction of the interstellar gas-phase PAHs is ionized (Allamandola et al. 1999, Sloan et al. 1999), compelling identification of individual PAH ions—e.g., through their optical or microwave spectra—is thus far lacking (Klemperer 2011). It is not unconceivable that interstellar PAH chemistry yields (transient) molecular forms with properties that are yet to be identified.

The UV photon flux is an important physical parameter transforming the interstellar PAH population through photoionization and photodissociation (Allain et al. 1996a,b, Allamandola et al. 1989, Ekern et al. 1998, Le Page et al. 2003, Léger et al. 1989, Omont 1986). In interstellar clouds of moderate to high UV-photon flux densities, hot gas-phase PAHs and their ions—transiently heated by the absorption of UV photons—generally relax by IR fluorescence (vibrational de-excitation with typical rate constants around $10^2 \text{ s}^{-1}$) (Allamandola et al. 1989, Léger et al. 1989). However, relaxation through unimolecular dissociation becomes important when its rate is comparable to the IR emission rate (Allamandola et al. 1989, Jochims et al. 1994, Léger et al. 1989). The lowest energy dissociation channel is typically H-atom loss (Holm et al. 2011, Jolibois et al. 2005), but at higher internal energies and/or for small species, H$_2$ and C$_2$H$_x$ losses are also common (Allamandola et al. 1989, Jochims et al. 1994, Léger et al. 1989, Omont 1986).

In order to survive typical UV dominated environments on a cosmic timescale, it is estimated that an isolated PAH should contain at least around 30–40 carbon atoms (Allain et al. 1996a, Jochims et al. 1994, Le Page et al. 2003). Although the aromatic carbon frame is tightly bonded, UV irradiation effectively induces loss of peripheral H atoms in space (Léger et al. 1989). The high propensity for UV-induced H loss was experimentally observed for smaller systems (Ekern et al. 1998, Gotkis et al. 1993b, Jochims et al. 1994). Since the C–H bond dissociation energy is roughly independent of PAH size (Fujiwara et al. 1996, Holm et al. 2011), it is conceivable that a broad size range of PAH cationic species exists in a partially dehydrogenated state. Thus, it is of interest to investigate the physical properties of these partially dehydrogenated PAH ions and their influence on interstellar chemistry. Here we focus on singly dehydrogenated PAH cations. Possible astrophysical implications are explored in Part II of this study (Chapter 4).

The loss of a H atom from a PAH cation leaves behind a positive dehydrogenated carbon—the carbocation center, C$^+$. The outcome is a mono-dehydrogenated PAH (aryl) cation which is highly reactive, and thus, short lived. This poses a challenge for laboratory determination of their physical and chemical properties (Schleyer & Maerker 1995).

In general, aryl cations are an important class of carbocations. The character of the ground electronic state of the archetypal aryl$^+$, the phenyl cation (C$_6$H$_5^+$), has long been
3.1 Introduction

Figure 3.1 – Illustration of phenyl\textsuperscript{+} (top, C\textsubscript{6}H\textsubscript{5}\textsuperscript{+}) and 1-naphthyl\textsuperscript{+} (bottom, C\textsubscript{10}H\textsubscript{7}\textsuperscript{+}) systems in singlet- and triplet-spin electronic configurations. The orbitals $\pi$ and $\sigma$ are bonding and non-bonding types, respectively.

subject of debate (Taft 1961, Dill et al. 1976, Nicolaides et al. 1997, Hrusak et al. 1997, Winkler & Sander 2006). As a singlet state, there is an empty $\sigma$ orbital on the C\textsuperscript{+} atom (Dill et al. 1976) that induces re-hybridization ($sp^2 \rightarrow sp$) causing a substantial deformation of the hexagonal frame. A thought experiment consisting in transferring an electron from the $\pi$ system to the vacant $\sigma$ orbital, has the consequence of restoring the $sp^2$ hybridization at the cost of forming a triplet electronic state ($^3B_1$) and sacrificing the aromaticity of the system (Taft 1961). By now, a singlet ground state ($^1A_1$) about 77 kJ mol\textsuperscript{-1} lower in energy than the triplet has been firmly established (Hrusak et al. 1997).

Figure 3.1 illustrates the above ideas which are applied as well to the naphthyl cation. For the fully hydrogenated neutral molecules, benzene and naphthalene, six and ten 2$p$ valence electrons, respectively, form $\pi$ molecular orbitals above and below the molecular ring(s) plane. Pauli exclusion principle states that no two electrons can occupy the same quantum state, and therefore, there are three and five pairs of spin up (↑) and spin down (↓) electrons arranged into three (benzene) and five (naphthalene) $\pi$ orbitals.

Contrary to C–C and C–H $\sigma$ orbitals, aromatic C–C $\pi$ orbitals are not part of the local binding between nuclei, but delocalized over the molecule. This lowers down the overall energy and provides structural stability. Removal of an electron from the highest energy $\pi$-orbital leads to the formation of a radical cation and an unpaired $\pi$ electron. If then, an H atom detaches, the original orbital energy-level configuration is disrupted and the energy ordering changes, since one carbon no longer sustains a perfect $sp^2$ atomic-orbital hybridization. While in the singlet configuration (Figure 3.1, middle) the original energy level degeneracy is yet conserved, in the triplet configuration (Figure 3.1, right) which involves the occupancy of a nonbonding electron in the vacant $\sigma$ orbital induces
a new degeneracy. The outcome is a distorted closed shell ion (singlet) or an open shell undistorted ion (triplet).

Electron-donating substituents as well as an increased π system reduce the energy required to remove a π-electron, decreasing the energy gap between triplet and singlet states (Laali et al. 2002, Winter & Falvey 2010, Lazzaroni et al. 2008). For the naphthyl cation both states are close in energy at the density functional theory (DFT) level (Laali et al. 2002, Ascenzi et al. 2004, Slegt et al. 2007a) although other methods place the triplet either notably lower (Fujiwara et al. 1996, Du et al. 1993) or higher (Ascenzi et al. 2004, Klippenstein 1997). The observed reactivity of naphthyl+ in solution was interpreted as resulting from a singlet-state cation (Slegt et al. 2007a). Electron donation of solvent molecules into the vacant σ-orbital stabilizes the singlet relative to the triplet, which is indeed borne out by DFT calculations (Slegt et al. 2007a). Gas-phase studies are thus required to evaluate the intrinsic stability of both spin states and while various mass-spectrometric studies on C10H7+ have been reported (Ascenzi et al. 2004, Gotkis et al. 1993a, Ho et al. 1995) they do not probe its (electronic) structure. Spectroscopy of the gas-phase ion could directly reveal its structure. A gas-phase IR spectrum was recently reported for the phenyl cation (Patzer et al. 2010) by Ar-tagging photodissociation spectroscopy (Bieske & Dopfer 2000, Douberly et al. 2007). Although rare-gas tagging is considered to induce negligible perturbations to the system under study, this is not the case for aryl carbocations, where the in-plane binding of the Ar atom to the C+ center results in substantial electron density donation into the vacant σ-orbital (Patzer et al. 2010). In order to determine the ground state of the isolated naphthyl cation, such a strategy might thus artificially enhance the stability of the singlet state. Instead, we employ here IR multiple photon dissociation (IRMPD) spectroscopy of bare naphthyl+ isolated in a quadrupole ion trap.

In this chapter the gas-phase formation of aryl+ molecular systems in an ion trap is presented by UV photolysis of bromo (Br) aromatic precursors. The outcome of the IRMPD spectroscopic characterization of naphthyl+ is discussed in connection with its electronic ground state and molecular structure. In Part II (Chapter 4) the discussion is extended to larger aryl+ molecules (phenanthryl+ and pyrenyl+).

3.2 Methods

3.2.1 Laboratory Formation of Aryl Cations

The aryl cations are generated by ArF laser (193 nm) photolysis of the corresponding bromo-PAH species. The precursor molecules 1- and 2-bromonaphthalene, 9-bromophenanthrene, and 1-bromopyrene were purchased from Sigma-Aldrich (Zwijndrecht, The Netherlands) and used without further purification. The instrumental setup consists of a Paul-type quadrupole ion trap (Paul 1990), which is employed for storage and mass selection of the molecular ions. The trap is coupled to a linear time-of-flight (TOF) mass spectrometer for mass analysis.
Figure 3.2 – Left to right sequence of the experimental technique employed to produce an aryl cation in a Paul-type quadrupole ion trap, including characterization of its electronic molecular structure with IRMPD spectroscopy.

Once the vapor of a halogenated PAH precursor (e.g., bromonaphthalene, C\textsubscript{10}H\textsubscript{7}Br) is admitted to the vacuum chamber, a 193 nm UV excimer laser is focused into the center of the ion trap, ionizing the neutral precursor. Depending on the size of the delocalized $\pi$-electron network, the ionization energy of aromatic molecules (including their halogenated derivatives) falls within the 6–9 eV range (Dewar & Worley 1969, Gotkis et al. 1993b), so that the absorption of two 193 nm photons provides sufficient energy (12.8 eV) to remove an electron from the highest $\pi$ orbital represented by $\textcircled{1}$ in Fig. 3.2. The appearance energy to form the naphthyl cation C\textsubscript{10}H\textsubscript{7}$^+$ from neutral C\textsubscript{10}H\textsubscript{7}Br is about 12 eV (Gotkis et al. 1993a). Homolytic C–Br bond cleavage in the C\textsubscript{10}H\textsubscript{7}Br$^{•+}$ ion proceeds through a loose transition state (Gotkis et al. 1993b) so that the formation of the naphthyl cation is a statistically efficient process. The complete UV dissociative ionization process yielding the C\textsubscript{10}H\textsubscript{7}$^+$ ion is summarized by the reaction

$$
C_{10}H_7Br (S = 0) + h\nu \rightarrow [C_{10}H_7Br^{•+}]^* \left( S = \frac{1}{2} \right) + e^- \left( S = \frac{1}{2} \right)
$$

$$
\rightarrow C_{10}H_7^+ (S = b) + Br^{•} \left( S = \frac{1}{2} \right) + e^- \left( S = \frac{1}{2} \right)
$$

where $S$ is the total spin (multiplicity $= 2S + 1$) of the system and $b$ can be singlet ($b = 0$) or triplet ($b = 1$), since the pathways toward either state are spin allowed. The generation
3 Aryl$^+$ Systems I

of the C$_{14}$H$_9^+$ and C$_{16}$H$_9^+$ ions from their halogenated bromo precursors occurs through analogous reaction mechanisms. In this chapter an analysis is presented for the naphthyl cation, while the next chapter (Part II) presents the analysis for the phenanthryl and pyrenyl cations.

Photofragmentation of the halogenated precursors (as well as of the mono-dehydrogenated PAH ions) is observed after UV laser irradiation. Therefore, UV-induced products smaller than the target species are axially ejected from the trap prior to IR irradiation by briefly raising the low-mass cutoff of the trap via a temporary increase of the RF amplitude. Optimization of the ratio of formation of the desired aryl cation over the radical cation halogen precursor is achieved by fine tuning of the RF amplitude and precursor’s vapor pressure. We note that the fragmentation behavior of different halogenated precursors may change the intramolecular processes preceding the C–X bond cleavage inducing different unimolecular fragmentation yields (Zhang et al. 2008), although such effects have not been further investigated here.

3.2.2 DFT Computations

Electronic structure calculations of naphthyl$^+$ in its two electronic spin states and two isomorphic configurations are done employing density functional theory (DFT) in the form of the B3LYP functional. The molecular orbitals are constructed using a Gaussian-type basis set 6-311G++(p,d) that includes polarization and diffuse functions for both H and C atoms. Computation of harmonic vibrational frequencies is done on the optimized structures and no imaginary frequencies were found. Stick spectra are convoluted with a 20 cm$^{-1}$ full width at half maximum (fwhm) Lorentzian function. The Gaussian 03 suite of programs was employed and applied at the SARA computing facility in Amsterdam.

3.3 Results and Discussion

3.3.1 Triplet Ground State

Figure 3.3 shows the equilibrium geometries for the singlet and triplet minima of the 1- and 2-naphthyl$^+$ isomers, which are of C$_s$-symmetry except for singlet 2-naphthyl$^+$, which optimizes to a non-planar C$_1$ geometry (Slegt et al. 2007a, Klippenstein 1997). The singlet ($^1$A$'$) and triplet ($^3$A$''$) structures for each of the isomers are found to be virtually iso-energetic. Independent of the electronic state, the 2-naphthyl cation is about 5.4 kJmol$^{-1}$ higher in energy than the 1-isomer.

The carbon frame of the singlet structures is significantly distorted from the naphthalene D$_{2h}$ geometry. The CC$^+$C angle amounts to 149°, reflecting the tendency to form a linear CC$^+$C bond typical for an $sp$-hybridized carbon atom (Winter & Falvey 2010). In the triplet state, the angle becomes 127°, close to the hexagonal 120° angle, as a consequence of the restored $sp^2$ hybridization due to the $\pi$-electron transferred to the empty $\sigma$-orbital. As compared to C$_6$H$_5^+$, the larger $\pi$-system in C$_{10}$H$_7^+$ makes removal of a $\pi$-electron more facile so that the energetic penalties for geometry distortion (singlet) and formation of a bi-radical (triplet) become competitive.
3.3 Results and Discussion

Figure 3.3 – Gas phase IR spectrum of the C_{10}H_{7}^+ aryl cation (top) compared to theoretical spectra of triplet 1-naphthyl^+ (a), singlet 1-naphthyl^+ (b), triplet 2- naphthyl^+ (c), and singlet 2-naphthyl^+ (d).
Table 3.1 – Comparison of observed and computed IR absorption bands.

<table>
<thead>
<tr>
<th>Expt freq[^{[a]}]</th>
<th>Theory freq[^{[a,b]}]</th>
<th>Int[^{[c,d]}]</th>
<th>C[^{c}]</th>
<th>description[^{[c]}]</th>
</tr>
</thead>
<tbody>
<tr>
<td>580</td>
<td>586</td>
<td>10</td>
<td>A’’</td>
<td>ring oop deformation</td>
</tr>
<tr>
<td>735</td>
<td>750</td>
<td>98</td>
<td>A’’</td>
<td>CH oop bend</td>
</tr>
<tr>
<td>1011</td>
<td>1010</td>
<td>14</td>
<td>A’’</td>
<td>CH ip bend/ring breathing</td>
</tr>
<tr>
<td>1196</td>
<td>1110</td>
<td>29</td>
<td>A’’</td>
<td>CH ip bend/ring deform</td>
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<tr>
<td>1143</td>
<td>1143</td>
<td>52</td>
<td>A’’</td>
<td>CH ip bend</td>
</tr>
<tr>
<td>1207</td>
<td>1207</td>
<td>118</td>
<td>A’’</td>
<td>CH ip bend/CC stretch</td>
</tr>
<tr>
<td>1241</td>
<td>1241</td>
<td>35</td>
<td>A’’</td>
<td>CH ip bend/CC stretch</td>
</tr>
<tr>
<td>1380</td>
<td>1347</td>
<td>25</td>
<td>A’’</td>
<td>CH ip bend/ring deform</td>
</tr>
<tr>
<td>1369</td>
<td>1369</td>
<td>46</td>
<td>A’’</td>
<td>CC stretch/CH ip bend</td>
</tr>
<tr>
<td>1408</td>
<td>1408</td>
<td>18</td>
<td>A’’</td>
<td>CH ip bend</td>
</tr>
<tr>
<td>1485</td>
<td>1497</td>
<td>88</td>
<td>A’’</td>
<td>CC stretch/CH ip bend</td>
</tr>
</tbody>
</table>

[a] In cm\(^{-1}\), [b] For triplet 1-naphthyl\(^{+}\), [c] In km mol\(^{-1}\), [d] Only bands with intensities > 12 km mol\(^{-1}\) included (except 585 cm\(^{-1}\) band), [e] mode description: ip = in plane; oop = out of plane.

The strongest IRMPD feature near 1196 cm\(^{-1}\) consists of four convoluted bands calculated at 1110, 1143, 1207 and 1241 cm\(^{-1}\) for triplet 1-naphthyl\(^{+}\), characterized mainly by CH in-plane bending vibrations involving some CC-stretching character as well. The relative intensities of the bands observed at 1011 and 580 cm\(^{-1}\) appear larger than what is predicted for triplet 1-naphthyl\(^{+}\), perhaps reflecting a small contribution of singlet 1-naphthyl\(^{+}\), which exhibits absorptions predicted around 1000 cm\(^{-1}\) and at 584 cm\(^{-1}\). It is important to note, however, that relative intensities may not be accurately reproduced by our spectroscopic method, which is based on the absorption of multiple photons (Oomens et al. 2006b), and that calculated absorption cross-sections may be less reliable. Nonetheless, the overall comparison between measured and calculated spectra clearly suggests that triplet naphthyl\(^{+}\) dominates the ion population.

### 3.3.2 1,2–Hydride Shift

The IRMPD spectrum of C\(_{10}\)H\(_7^+\) obtained with 1- and 2-bromonaphthalene isomers as precursor are identical (see Fig. 3.4) and the experimental spectrum shown in the top panel of Fig. 3.3 represents an average of several runs. This lends experimental evidence of isomerization to the more stable 1-naphthyl\(^{+}\), occurring when 2-bromonaphthalene is used. Isomerization by a 1,2-hydride shift is indeed expected to be efficient as the 3-center-2-electron transition state in carbocations is aromatic (Douberly et al. 2007) and was in fact suggested to explain the observed reactivity in solution (Slegt et al. 2007a).

Computed spectra for singlet and triplet states of both naphthyl\(^{+}\) isomers are also shown in Fig. 3.3. Clearly, the 1-naphthyl\(^{+}\) triplet spectrum matches the experimental data better than any of the other computed spectra, although the spectra of both triplet state isomers are sufficiently similar to not rule out the presence of any triplet
3.3 Results and Discussion

![Figure 3.4](image)

**Figure 3.4** – Comparison of naphthyl$^+$ IRMPD spectra recorded from 1-bromonaphthalene (top) and 2-bromonaphthalene (bottom) precursors.

2-naphthyl$^+$. Nonetheless, regardless of the isomer, triplet naphthyl$^+$ clearly dominates over singlet naphthyl$^+$. Table 3.1 lists experimental and calculated band positions for the $^3A''$-1-naphthyl$^+$ ion confirming the good agreement.

3.3.3 Thermodynamic Stability or Kinetic Stability?

The observation of a triplet state may reflect its lower energy relative to the singlet state, but propensities in the formation of the naphthyl cation should also be considered. Firstly, the relative energies of the two states as predicted by DFT may not be accurate. Values for the singlet-triplet energy gap obtained using other computational methods indeed show significant scatter, favoring the triplet state — PM3 (Fujiwara et al. 1996) CISD, ROHF (Du et al. 1993) HF (Klippenstein 1997) — or the singlet state — MP2, (Klippenstein 1997) CCSD(T)(Ascenzi et al. 2004)) by substantial amounts —. This result suggests that a multireference approach as has been applied to the phenyl (Hrusak et al. 1997) and vinyl (Winter & Falvey 2010) cations may be required in this case as well. On the other hand, the study on substituted vinyl cations found good agreement between DFT and CASPT2 values for the singlet-triplet gap (Winter & Falvey 2010), encouraging the use of low-cost DFT methods.

It may be wondered whether there are propensities that preferentially form one of the two electronic states during C–Br bond cleavage. For instance, formation of the phenyl cation from the neutral $C_6H_5^+$ radical by photoionization favors the higher-energy triplet state due to better Franck-Condon overlap (Hrusak et al. 1997). Analogously, homolytic
C–Br bond cleavage in the C\textsubscript{10}H\textsubscript{7}Br\textsuperscript{++} radical cation would lead to the triplet naphthyl cation. However, most gas-phase reactivity studies involving the naphthyl cation have largely ignored possible implications of the different spin states (Gotkis et al. 1993a, Ho et al. 1995) or simply assumed both states to occur (Ascenzi et al. 2004). Moreover, H-atom abstraction (HAA) from the benzene cation was first assumed to produce the (higher-energy) triplet phenyl cation (Klippenstein 1997), but later studies suggested that an intersystem crossing occurs on the dissociation pathway, rapidly converting the system to the (lower-energy) singlet state (Nicolaides et al. 1997). Spin isomerization between singlet and triplet states has also been suggested to occur rapidly for a series of para-substituted phenyl cations, p-X-C\textsubscript{6}H\textsubscript{4}\textsuperscript{+}, such that the lower-energy state is always found independent of how the species was formed (Aschi & Harvey 1999). This rapid spin conversion is induced by the low minimum energy crossing point (MECP) connecting the two electronic surfaces and the non-negligible spin-orbit coupling (SOC) constants (Aschi & Harvey 1999). Assuming that the additional ring in the naphthyl cation behaves as an electron-donating substituent (Laali et al. 2002, Slegt et al. 2007a), rapid spin relaxation is expected to occur here as well. The unambiguous assignment of the IR spectrum in Fig. 3.3 then suggests a triplet electronic ground state for the naphthyl cation.

3.4 Conclusions

The production of a gas-phase aryl\textsuperscript{+} molecule (naphthyl\textsuperscript{+}) in an ion trap was demonstrated. Moreover, the IR spectrum of the mass-selected naphthyl cation (C\textsubscript{10}H\textsubscript{7}\textsuperscript{+}) was recorded by IRMPD spectroscopy, providing the first experimental spectrum of an isolated, bare aryl cation. Comparison of the experimental spectrum with spectra calculated for singlet and triplet naphthyl\textsuperscript{+} shows that a triplet-state ion is predominantly formed. In general, this study shows that changes in the electronic structure induce geometric distortions that can be clearly distinguished in the IR spectra recorded with the IRMPD spectroscopic technique. Furthermore, it is suggested that 1,2-hydride shifts occur under our experimental conditions. In the next chapter, electronic stabilization and spectral properties are studied for phenanthryl\textsuperscript{+} and pyrenyl\textsuperscript{+} aryl cations.