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):
Alvaro Galue, H. (2012). Infrared spectroscopy of mass-selected aromatic and diamondoid molecular ions: a laboratory quest for the organic inventory in space
Perhaps one of most profound revelations in the history of science is that all chemical elements\(^1\) that make up everything around us were once fabricated in the interior of stars. On Earth, PAH molecules are easily formed as by-products during combustion of hydrocarbon fuels, and are some of the most stable large hydrocarbons known. The interstellar UIR bands show that PAHs occur as well in space. The ubiquity and resistance of PAHs is a consequence of their electronic properties since the sea of $\pi$ electrons flowing above and below the molecular plane, provide PAH structures with high thermodynamical stability. On the other hand, this network of $\pi$-electron bonds gives rise to novel electronic properties that are exploited to create innovative functional materials. This chapter presents the case of picene and pentacene, which are two PAHs made up of the same number of carbon and hydrogen atoms, but owing to their different geometry, picene can be used to make superconducting materials, while for pentacene this is not possible. Here, the electronic structures of the isolated picene and pentacene cations are studied by infrared multiple-photon dissociation spectroscopy and quantum-chemical calculations. The experimental spectra reveal subtle differences that are traced back to the effective charge distributions in both systems, where picene\(^+\) exhibits significant intramolecular $\pi$-charge dynamics as compared to pentacene\(^+\). A link between charge mobility along CC in-plane symmetry modes and degree of dynamic electron correlation was found. This result implies that, contrary to pentacene\(^+\), correlated electron dynamics is important in picene\(^+\), and is an underlying intramolecular difference between both five-ring PAH systems.

\(^*\)Based on: H. Alvaro Galué, and J. Oomens, 2012 (To be submitted).

\(^1\)With the exception of the light elements hydrogen, helium, and lithium which were formed in the Big Bang nucleosynthesis.
8 Five-ring containing PAHs

8.1 Introduction

The discovery of superconductivity in alkali-metal doped picene (A\textsubscript{x}picene) at a critical temperature (T\textsubscript{c}) as high as 18 K (Mitsuhashi et al. 2010) defines a new class of high-T\textsubscript{c} carbon-based superconductors (Kubozono et al. 2011), and offers new avenues towards understanding the electron-pairing mechanism. Interestingly, materials based on the structural isomer pentacene fail to exhibit superconductivity beyond the metallic behavior. The molecular hydrocarbon structures of picene and pentacene are portrayed in Fig. 8.1.

Prior to the discovery of superconductivity in A\textsubscript{x}picene, alkali-metal fullerides, A\textsubscript{x}C\textsubscript{60} (Durand et al. 2003), were the only \textit{sp\textsuperscript{2}}-carbon molecular-based superconductors. Evidence indicates that A\textsubscript{x}C\textsubscript{60} materials are conventional Bardeen-Cooper-Schrieffer (BCS) superconductors (Gunnarsson 1997) in which the pairing mechanism is largely mediated by electron-phonon interactions (Schluter et al. 1992, Hebard 1992). However, by looking at the magnetic behavior of the entire fulleride family of superconductors in proximity of the metal–Mott-insulator transition (Durand et al. 2003) — characterized by strong electron-electron repulsive interactions — it has been recognized that an electronic mechanism is at the origin of the electron pairing here as well (Capone et al. 2009). Electronic band studies have suggested that K\textsubscript{3}-doped picene is also a Mott insulator and thus a highly electron-correlated system (Kim et al. 2011, Giovannetti & Capone 2011).

Although superconductivity entices the electronic properties of the solid, an important link towards the understanding of the superconductivity in C\textsubscript{60}- and picene-based materials is the nature of their conduction bands as determined by the electron-accepting molecular orbitals of the single molecules. Most studies have focused on the solid picene, but studying the single molecule in complete isolation could shed light on the electronic properties and thus on the mechanisms of superconductivity.

Picene and pentacene, two isomers of C\textsubscript{22}H\textsubscript{14}, belong to the family of polycyclic aromatic hydrocarbons (PAHs), in which all carbon atoms are \textit{sp\textsuperscript{2}}-hybridized forming planar, hexagonal ring structures, and hydrogen atoms are \textit{σ}-bonded to the peripheral vertex carbons. In pentacene, the five hexagonal carbon rings are linearly fused (i.e., acene-like edges), while in picene the five carbon hexagons are arranged in a zigzag fashion (i.e., phenanthrene-like edges). Intuitively, one may expect that their geometric structures lead to differences in the electronic properties, which is indeed observed in the computed molecular orbital configurations (vide infra). The inherent \textit{π}-conjugation permits electrons in atomic \textit{p}_z-orbitals to circulate throughout the molecule (electron delocalization), resulting in highly stable structures with exceptional magnetic and electrical attributes.

In their neutral forms, picene is more stable than pentacene by ca. 0.678 eV, which is explained by the orbital phases analogous to the prototypical systems phenanthrene and anthracene (Fukui 1982). This is for instance reflected in the HOMO-LUMO gap of 4.22 eV for picene as compared to 2.2 eV for pentacene. However, upon removal of a \textit{π} electron, the stability is reversed in favor of pentacene\textsuperscript{+} and the energy difference is 0.2041 eV. This is an additional indication of a HOMO (which becomes SOMO upon ionization) that is distributed over a larger number of CC bonds in picene and therefore possesses increased bonding character. In contrast, the HOMO of pentacene is localized on fewer
bonds and upon ionization the weaker bonding character of those bonds does not com-
promise the overall stabilization as much as in picene. It is furthermore of interest to note
that before ionization, the energy distance between the HOMO and the next lower MO
(HOMO-1) is 0.27 eV for picene and 1.29 eV for pentacene. The small energy difference
between the HOMO and HOMO-1 in picene is essential to its geometry and is retained
in the radical cation. As a consequence, the geometry of picene\(^+\) is also determined by
the HOMO-1, while for pentacene\(^+\) it is essentially determined by the singly occupied
HOMO, i.e. the SOMO of the radical cation (Kato et al. 2002).

Certain properties of A\(_3\)C\(_{60}\) materials are similar to those of A\(_4\)picene materials. For
instance, in both materials there is a degeneracy of the electron-accepting molecular or-
bitals. Due to the high symmetry of C\(_{60}\), the conduction band of the crystal derives from
the threefold-degenerate t\(_{1u}\) LUMO. This yields a high density of electronic states at the
Fermi level of solid C\(_{60}\). Although picene possesses a lower symmetry, its a\(_2\) LUMO and
b\(_1\) LUMO+1 are (accidentally) very close in energy and this induces a pseudo-degeneracy
(Rosseinsky & Kosmas 2010). In contrast, such an accidental degeneracy between the b\(_{3u}\)
LUMO and b\(_{1g}\) LUMO+1 does not occur in pentacene and this may be an essential dif-
ference between picene and pentacene isomers, and a possible general explanation for the
origin of superconductivity in \(\pi\)-conjugated hydrocarbon materials.

In this work, the electronic properties of the single molecules, picene and pentacene,
in a hole-doped charge-state, i.e. as a radical cation, are studied by probing their molecu-
lar structures via infrared multiple photon dissociation spectroscopy. Certainly, the picene
molecular unit of the corresponding superconducting materials does not have a radical
cationic form, yet it exhibits an open-shell configuration as in the case of A\(_3\)picene su-
perconductors. Thus, it is of interest to learn about these electronic spin configurations in
picene and pentacene molecular systems. Additionally, various quantum-chemical meth-
ods that differ in the level of electron exchange-correlation dynamics were applied to both
cations. The vibrational mode analysis in connection with the effective charge distribu-
tions is used to interpret the electron dynamics, and understand the underlying nature of
the electronic structures and corresponding molecular orbital open-shell configurations.

8.2 Laboratory Methods

The infrared vibrational spectra of doublet ground-state picene and pentacene cations are
recorded via IR multiple-photon dissociation (IRMPD) spectroscopy. The vapor of one
of the C\(_{22}\)H\(_{14}\) species is brought into the inner volume of a Paul-type quadrupole ion trap,
where a focused 193 nm UV-laser photo-ionizes the neutral molecules. One of the delo-
calized \(\pi\)-electrons is removed (hole-doping) from the b\(_1\) picene or b\(_{2g}\) pentacene highest-
occupied molecular orbitals (HOMOs). Their Koopmans’ ionization energies correspond
to the spin-restricted Hartree-Fock orbital energies of b\(_1\) (−7.5 eV) and b\(_{2g}\) (−6.25 eV)
HOMOs. These energies are in good agreement with the experimental values of 7.48 eV
(NIST Chemistry webook) and 6.61 eV (Stahl & Maquin 1984), which suggest that in
both species the orbital relaxation effects (as a consequence of reducing by one the total
number of electrons) cancel out those effects due to electron correlation dynamics.
The parent ions are mass selected by briefly increasing the RF electric field amplitude of the ion trap setting the low-mass cut-off of the ion trap to just below the mass of \( C_{22}H_{14} \), thus ejecting all species with lower mass-to-charge ratio (e.g. UV induced fragment ions). Subsequently, the ions are irradiated with a high-fluence IR laser beam generated by a free electron laser (FEL, Oepts et al. 1995). A FEL macropulse of ca. 60 mJ contains about 5000 micropulses and the transform-limited bandwidth is fixed at ca. 1\% of the central wavelength. During a macropulse many photons are absorbed—as mediated by intramolecular vibrational energy redistribution (IVR) (Lehmann et al. 1994)—if the laser wavelength is in resonance with a vibrational transition of picene\(^+\) (or pentacene\(^+\)). This leads to a population of very hot ions that relaxes by statistical unimolecular dissociation (Bragrashvili et al. 1985) producing ionic fragments. The parent \( S_P \) and fragment \( S_{m_f} \) ion signals are detected with a time-of-flight (TOF) mass spectrometer coupled to the trap. The absorption cross section is approximated as the integrated dissociation yield \( D \) computed from the \( m \)-th fragment as \( \sum_m S_{m_f}^m / (\sum_m S_{m_f}^m + S_P) \). The multiphoton absorption process may introduce relative band intensities deviating from those found in a one-photon absorption spectrum as a result of anharmonic couplings at high internal energies, making observed absolute intensities generally less reliable. Nevertheless, in most cases relative intensities compare reasonably well with theoretical predictions and can therefore provide useful information.

The equilibrium geometries and vibrational modes are calculated employing ab initio Hartree-Fock (HF) theory in the spin-restricted open-shell ROHF formalism (Binkley et al. 1974), and the local spin-density approximation (LSDA) plus a variety of exchange-correlation gradient-corrected formalisms. These are the LSDA gradient-corrected exchange-only Becke 1988 functional (B, Becke 1988), the B form plus gradient-corrected correlation LYP functional (BLYP) (Becke 1988), and the hybrid B3LYP functional that includes generalized exchange-correlation gradient corrections and some degree of exact HF exchange energy (Becke 1993). The basis function set used to build the molecular orbitals is a triple-\( \zeta \) Gaussian-type 6-311G plus polarization functions (d, p) on C and H atoms. The ROHF approach ignores spin polarization which permits us to assess the degree of spin contamination. The advantage of ROHF is that it provides a good wavefunction since spin-orbitals are not artificially mixed (i.e. zero spin contamination), which ought to result in a value of the total spin \( S^2 \) of 0.75 for the doublet radical cations under study. The results of the most comprehensive electron-exchange-correlation theoretical level employed, B3LYP/6-311G(d,p), are referred to throughout the paper unless stated otherwise.
Table 8.1 – Infrared absorption bands of picene* and pentacene* as observed via IR-MPD spectroscopy and their assignments as based on comparison with computed spectra.

<table>
<thead>
<tr>
<th></th>
<th>Picene*</th>
<th>Pentacene*</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>experimental</td>
<td>theory[b]</td>
</tr>
<tr>
<td></td>
<td>µm</td>
<td>cm⁻¹</td>
</tr>
<tr>
<td>6.38</td>
<td>1567</td>
<td>m,sr,sh</td>
</tr>
<tr>
<td>6.62</td>
<td>1511</td>
<td>s,r</td>
</tr>
<tr>
<td>6.95</td>
<td>1438</td>
<td>w, sr,sh</td>
</tr>
<tr>
<td>7.45</td>
<td>1342</td>
<td>m,sr,sh</td>
</tr>
<tr>
<td>7.87</td>
<td>1271</td>
<td>s,r</td>
</tr>
<tr>
<td>8.28</td>
<td>1208</td>
<td>m,sr,sh</td>
</tr>
<tr>
<td>8.82</td>
<td>1134</td>
<td>m,sr</td>
</tr>
<tr>
<td>10.06</td>
<td>994</td>
<td>w,sr</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>12.14</td>
<td>824</td>
<td>w,r</td>
</tr>
<tr>
<td>13.56</td>
<td>737</td>
<td>w,r</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>18.81</td>
<td>532</td>
<td>vw,†</td>
</tr>
<tr>
<td>21.87</td>
<td>457</td>
<td>vw,†</td>
</tr>
</tbody>
</table>

[a] Intensity, classified as strong (s), medium (m), weak (w), or very weak (vw); feature: resolved (r), semi-resolved (sr), shoulder (sh); proposed (†).
[b] B3LYP/6–311G(p,d) level of theory; irrep (symmetry species), frequency (cm⁻¹), IR intensity (km/mol).
[c] Approximate assignment based on normal mode with highest IR activity.
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Table 8.2 – All-in contributions (in %) of IR-active modes (per symmetry species) to the total IR activity of picene$^+$ ($C_{2v}$) and pentacene$^+$ ($D_{2h}$) according to ROHF, B, BLYP and B3LYP formalisms and gas-phase IR spectra (EXP).

<table>
<thead>
<tr>
<th></th>
<th>$C_{2v}$ / $D_{2h}$</th>
<th>ROHF</th>
<th>B</th>
<th>BLYP</th>
<th>B3LYP</th>
<th>EXP</th>
<th>Modes</th>
</tr>
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<tbody>
<tr>
<td>picene$^+$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>35A$_1$</td>
<td>1.53</td>
<td>6.06</td>
<td>5.73</td>
<td>3.42</td>
<td>–</td>
<td>ν1, ν2, ..., ν35</td>
<td></td>
</tr>
<tr>
<td>16B$_1$</td>
<td>0.98</td>
<td>6.54</td>
<td>7.51</td>
<td>4.22</td>
<td>8</td>
<td>ν36, ν37, ..., ν68</td>
<td></td>
</tr>
<tr>
<td>34B$_2$</td>
<td>97.49</td>
<td>87.39</td>
<td>86.76</td>
<td>92.36</td>
<td>92</td>
<td>ν69, ν70, ..., ν102</td>
<td></td>
</tr>
<tr>
<td>pentacene$^+$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>17B$_{1u}$</td>
<td>4.86</td>
<td>7.29</td>
<td>6.33</td>
<td>3.61</td>
<td>7</td>
<td>ν60, ν61, ..., ν76</td>
<td></td>
</tr>
<tr>
<td>17B$_{2u}$</td>
<td>92.53</td>
<td>81.83</td>
<td>80.97</td>
<td>88.16</td>
<td>65</td>
<td>ν77, ν78, ..., ν93</td>
<td></td>
</tr>
<tr>
<td>9B$_{3u}$</td>
<td>2.61</td>
<td>10.88</td>
<td>12.70</td>
<td>8.23</td>
<td>28</td>
<td>ν94, ν95, ..., ν102</td>
<td></td>
</tr>
</tbody>
</table>

8.3 Results

Figure 8.1 shows the optimized picene$^+$ (top) and pentacene$^+$ (bottom) geometries and their gas-phase IRMPD spectra in the range of 5.5 to about 25 $\mu$m (1818 to 400 cm$^{-1}$). Going from the neutral to the cation in both molecules, the 26 CC bonds increase (decrease) in length whenever the HOMO has a bonding (anti-bonding) character for the given bond. The larger number of bonds lengthening in picene$^+$ indicates the increased $\pi$-bonding character of the, therefore more delocalized, HOMO as contrasted to pentacene$^+$. Within the FEL tuning range both cations possess 76 of the total $3N-6=102$ vibrational modes. Table 8.1 lists the IR features identified in the two spectra with the characteristic central frequencies. Since ions reach high internal energies in the photo-excitation process before dissociation, observed frequencies typically suffer from an anharmonic redshift that amounts to around 1–3% as compared to harmonic calculations (Oomens et al. 2003b). Harmonic frequencies are therefore empirically scaled by a factor of 0.97.

Both spectra show a strongly IR-active high-frequency region (i.e., 6–9 $\mu$m range) as compared to the longer wavelength part (>9 $\mu$m), with an overall similar intensity pattern and individual IR bands that notably correlate. Nevertheless, subtle differences reveal both picene$^+$ and pentacene$^+$ effective molecular-charge distributions through their effects on the derivatives of the dipole moment, $\mu = \sum_a q_ar_a$ (summing over all $a$ atoms), with respect to each of the normal-coordinates $Q_i$ (see eq. 2.28). The observable IR-band intensity $I_{IR}$ for the $i$-mode and $\mu$ are related as $I_{IR} = const \times (\partial\mu/\partial Q_i)^2$, where a meaningful transformation of $Q_i$ into internal coordinates of the molecule is assumed (in Chapter 2 the notation $A_i$ is used instead of $I_{IR}$). The change of $\mu$ along the $i$-th normal coordinate expands as $\partial\mu/\partial Q_i = q \partial r/\partial Q_i + r \partial q/\partial Q_i$ (summation over all atoms is assumed). The first term is the contribution due to the equilibrium partial charges $q_o$ on the atoms (e.g., Mullikean charges), while the second term is a measure of charge redistribution as a consequence of vibrational motion, also referred to as first-order fluxes (Decius & Mast 1978). This intramolecular charge dynamics may reflect strong electron-electron/electron-hole Coulombic interactions depending on the normal coordinate.
8.3 Results

Figure 8.1 – Gas-phase IR vibrational spectra of picene$^+$ (top) and pentacene$^+$ (bottom). The relative intensity is the normalized integrated dissociation yield. Absorptions bands (µm) are listed in Table 8.1 with their corresponding positions in cm$^{-1}$ and theoretical assignations. The optimized geometries illustrate the increase (+) or decrease (−) in CC-bond length upon ionization. The spectra in the insets zoom in on weak bands observed in the long-wavelength sections of the spectra.

On account of its overall C$_{2v}$ symmetry, the vibrational modes of picene$^+$ are distributed over four symmetry representations as 35A$_1$ + 17A$_2$ + 16B$_1$ + 34B$_2$. For the higher-symmetry D$_{2h}$ pentacene$^+$, the modes expand as 18A$_g$ + 7B$_{1g}$ + 9B$_{2g}$ + 17B$_{3g}$ + 8A$_u$ + 17B$_{1u}$ + 17B$_{2u}$ + 9B$_{3u}$. The assignments of the experimental spectra as based on the B3LYP computed spectra are listed in Table 8.1. In order to assess charge correlation effects on individual modes, Figs. 8.3 and 8.4 show a comparison between experimental and computed spectra at the four levels of theory, which incorporate different degrees of electron correlation. The total IR activity is spread over 85 IR-active modes in picene$^+$ and 43 IR-active modes in pentacene$^+$. For each cation, these modes are grouped according to the symmetry and the contributions (in %) of each group to the total IR activity are listed in Table 8.2. For instance, the 34 in-plane symmetry B$_2$ modes of picene$^+$ contribute 92.36 % to its total IR activity at the B3LYP level, while for pentacene$^+$ the 17 in-plane B$_{2u}$ modes contribute 88.16%.
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8.4 Discussion

As observed in Fig. 8.1, theory properly predicts that in-plane symmetry CC-stretching modes located in the 6–9 µm range (B₂ and B₂ᵤ for picene+ and pentacene+, respectively) carry most of the IR activity (see assignments in Table 8.1 and contributions per symmetry in Table 8.2). In fact, the experimental estimate of the contribution of picene+ B₂ modes is 92%, which is very close to the contribution predicted at the B3LYP level. Precisely, the IR activity of picene+ is concentrated in the 6.62 µm (1511 cm⁻¹) and 7.87 µm (1271 cm⁻¹) absorption bands, which are attributed to the ν₇₈ and ν₈₄ B₂ modes, and which make up for 51% of the total computed B₂ IR activity. The relatively weak bands observed at 12.14 µm (824 cm⁻¹) and 13.56 µm (737 cm⁻¹) are assigned to the B₁-symmetry out-of-plane CH-bending modes ν₅₈ and ν₅₉, and practically make up for the remaining 8% (4.22% computed) of the total IR activity of picene+. The totally symmetric A₁ modes are predicted to account for 3.4% of the total IR activity and are therefore so weak that they remain unobserved in the measured spectrum.

For the B₂ᵤ modes of pentacene+, there is a sizable discrepancy between experimental and B3LYP estimated contributions to the overall spectral intensity. Contrary to picene+ that has only two modes carrying most IR activity, in pentacene+ there are several in-plane symmetry modes with comparable medium intensities, and therefore, this introduces a larger statistical error in the rough estimation of their contributions to the total IR activity. On the other hand, of the IR activity due to B₃ᵤ out-of-plane modes, we estimate that only ν₉₅ (10.9 µm/914 cm⁻¹) and ν₉₇ (13.6 µm/736 cm⁻¹) already contribute 60%, in close agreement with the 68% predicted (the remaining 32% is distributed over ν₉₄, ν₉₆, ν₉₈–ν₁₀₂).

Theory shows that despite the notable difference in relative intensities between picene+ (ν₅₈ and ν₅₉) and pentacene+ (ν₉₅ and ν₉₇) out-of-plane bands—being due to CH-bending vibrations asymmetric with respect to the molecular plane—the two pairs are equivalent (i.e., ν₅₈ ↔ ν₉₅ and ν₅₉ ↔ ν₉₇) in terms of intrinsic IR activity (see similar km/mol values in Table 8.1). Extensive work on out-of-plane CH deformations in a variety of hydrocarbon molecules has evidenced the correlation between vibrational intensities and the magnitude of the effective charges on the H-atoms (Gussoni 1990). Accordingly, we conclude here that no significant variations exist between equilibrium H-atom charges of picene+ and pentacene+, whereas a small charge flux component between H atoms and sp²-hybridized C atoms is fairly equivalent in both systems (Gussoni et al. 1984). This is indeed seen in our calculations where variations of the Mulliken charges q⁺₉ in both molecular ions fall within 0.11e < q⁺₉ < 0.13e.

The frequency difference, Δω, between pentacene+ ν₉₇ and picene+ ν₅₉ modes observed in the experimental spectra is ca. 0.1%, in close agreement to the predicted 0.4%. Conversely, the pentacene+ ν₉₅ band presents a frequency blue-shift of 10% (or 12% prediction) as compared to the picene+ ν₅₈ band. According to the computed k₉₅ and k₅₈ force constants, the 12% increase in ω corresponds to a 50% increase in k. This considerable variation in force cannot be attributed to different internal coordinate changes, Δϕᵢ (CH bending angles with respect to the molecular plane) and ΔRᵢ (CH bond lengths), as both ions show no sizeable differences in nuclei displacements along these two modes.
8.4 Discussion

Based on the understanding that static charge contributions to the respective observables \( (\partial \mu / \partial Q_{95})^2 \) and \( (\partial \mu / \partial Q_{58})^2 \) are roughly identical, the increment in net electric restoring force (or \( k \) which is proportional to the net charge) in pentacene\(^{+}\), is necessarily attributed to an induced charge-flux component. Owing to the direction of this component\(^2\), this does not sum up to the term \( (\partial \mu / \partial Q_{95})^2 \), however, it stills adds an extra scalar contribution to the restoring force (hence its frequency).

The estimate of the intensity ratio (using the ordinate-axis values in Fig. 8.1) of most IR-active in-plane–to–out-of-plane symmetry bands for picene\(^{+}\) is \[ \frac{I_{IR}(\nu_{58}) + I_{IR}(\nu_{59})}{[I_{IR}(\nu_{58}) + I_{IR}(\nu_{59})]} = 4, \] while for pentacene\(^{+}\) is \[ \frac{I_{IR}(\nu_{95}) + I_{IR}(\nu_{97})}{I_{IR}(\nu_{95}) + I_{IR}(\nu_{97})} \approx 1.6 \] (see mode assignments in Table 8.1). Since \( I_{IR}(\nu_{58}) + I_{IR}(\nu_{59}) \approx I_{IR}(\nu_{95}) + I_{IR}(\nu_{97}) \) in terms of absolute IR intensities, picene\(^{+}\) \( (\partial \mu / \partial Q_{78})^2 \) and \( (\partial \mu / \partial Q_{85})^2 \) observables are intrinsically larger than pentacene\(^{+}\) \( (\partial \mu / \partial Q_{85})^2 \) and \( (\partial \mu / \partial Q_{87})^2 \) observables. For instance, the picene\(^{+}\) \( \nu_{84} \) mode \( (7.87-\mu \text{m band}) \) is predicted to be about twice as intense as the pentacene\(^{+}\) \( \nu_{85} \) mode \( (7.61-\mu \text{m band}) \). In view of the identical isomeric nature and high symmetry of both molecular ions, it is reasonable to conclude that the considerable extra contribution to the picene\(^{+}\) dipole derivatives does not arise solely from the displacement of static C-atom charges, but from substantial charge fluxes generated along \( \pi \)-bonds in picene\(^{+}\). The larger charge flux activity in picene is inherently connected to its global structural arrangement.

In pentacene\(^{+}\), long-range charge-flux contributions to its strongest IR-active modes, e.g. \( \nu_{85} \), are influenced by orbital mixings with the unoccupied \( \beta_{73} \)-HOMO (Torii 2000). For instance, our computations show that the in-plane vibrational pattern along the \( y \) direction during the strongest \( \nu_{85} \) mode correlates with the orbital phase of the HOMO, hence, inducing a strong polarization across the two outer aromatic rings. That is, while the bonding and anti-bonding character of the CC bonds of a ring are strengthened, the ring reflected on the \( xz \) plane is subject to the opposite effects. Similarly, in order to explain the substantially larger dipole derivatives in picene\(^{+}\), a stronger mixing with the unoccupied \( \beta_{73} \)-HOMO is necessarily accompanied by larger charge mobility. This is again evidenced by the vibrational pattern, for instance, of the \( \nu_{84} \) mode that clearly correlates with the HOMO phase and has the same 180\( ^{\circ} \) out-of-phase vibrations between the two outer rings. The vibrational patterns of pentacene\(^{+}\) \( \nu_{85} \) and picene\(^{+}\) \( \nu_{84} \) modes can be seen in Fig. 8.2.

Notably, CC modes in picene\(^{+}\) exhibit larger charge fluctuations as compared to CC modes in pentacene\(^{+}\). Although this is an important conclusion, it does not establish a direct link that could explain the difference in electronic properties in their solid forms, and which could give rise to phenomena such as superconductivity in the case of picene. Nevertheless, the consequences of charge mobility can be further explored.

A simplification in the ROHF formalism involves the averaged electron-interaction (mean-field) approximation. Effects of this approximation are tested and compared here\(^2\).
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Figure 8.2 – The in-plane symmetry vibrational modes $\nu_{85}$ and $\nu_{84}$ of pentacene$^+$ and picene$^+$. Note the alternation (out-of-phase) between stretches of CC bonds with respect the xz plane. This type of vibrational patterns in $\pi$-conjugated aromatic systems yield significant y-direction charge-fluxes across the structures, and explains the large intensities (km/mol) of $\nu_{85}$ and $\nu_{84}$ modes. The level of theory used to calculate these modes is B3LYP/6-311G(p,d).

for pentacene$^+$ and picene$^+$, where differences are then attributed to the degree of dynamical electron-correlation exhibited by each of the cations. In addition, density functional theory (DFT) is applied to both cations with different levels of exchange-correlation sophistication as described in the theoretical section.

Results of the computations are shown first for pentacene$^+$ (Fig. 8.3) where it is seen that the mean-field approximation gives a reasonable prediction of the experimental IR spectrum. Although the intensities are wrongly assigned among individual modes, the overall intensity pattern predicted by ROHF is similar to what is measured (Fig. 8.3a). Moreover, the spectral pattern predicted by ROHF generally agrees with the patterns computed by the three DFT methods. The DFT methods sensitively correct the frequencies by displacing the intensity pattern to higher frequencies as the sophistication of exchange-correlation treatment is improved (going from B to BLYP, and to B3LYP). The ROHF absolute intensities of $\nu_{95}$ and $\nu_{97}$ B$_{3u}$ modes are 61 and 110 km/mol, in agreement with the B3LYP approach. This suggests that the inclusion of electron correlation has little influence on the static charges of the H-atoms in pentacene$^+$.

In sharp contrast to pentacene$^+$, the ROHF approach yields a spectrum that significantly deviates from the experimental IR spectrum of picene$^+$ (see Fig 3b). The primary source of the large discrepancy is naturally the lack of spin polarization. This asserts that the interactions of the unpaired $\alpha$ electron with the bonding $\alpha$ and $\beta$ electrons of neighboring spinorbitals are not incorporated in the picene$^+$ ROHF wavefunction. Con-
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Figure 8.3 – Vibrational IR activity of pentacene$^+$. The gas phase IR spectrum (EXP, a), the ab initio mean-field approximation spectra (ROHF, b), and DFT spectra (B, c; BLYP, d; B3LYP, e). The black vertical lines indicate experimentally determined band positions in panel a. Line heights represent the empirical intensity classification of Table 8.1.

subsequently, a poor performance of the mean-field approximation is inherent to the ROHF approach, which is attributed to the intricate electronic nature of picene$^+$ (as compared to pentacene$^+$). Although a full understanding of the exact correlation dynamics involving the unpaired $\alpha$ electron requires further scrutiny, it is clear that the ROHF method is inadequate to describe the correlated motion of electrons, which is then reflected in the predicted IR intensities of some of the vibrational normal modes. For instance, the in-plane B$_2$-symmetry modes $\nu_{92}$ and $\nu_{93}$ have incorrectly been assigned 26% of the total B$_2$ IR activity (see Fig. 8.4b). On the other hand, the three DFT methods employed here correct these anomalous band intensities. Moreover, the inclusion of functional gradient-correction to the correlation energy (LYP, Figs. 8.4d, 8.4e) further improves the intensity pattern of the CC-stretching modes observed in the experimental IR spectrum (Fig 8.4a).

Hence, as suggested by both experimental and theoretical spectra, the in-plane sym-
Figure 8.4 – Vibrational IR activity of picene\(^+\). The gas phase IR spectrum (EXP, a), the ab initio mean-field approximation spectra (ROHF, b), and DFT spectra (B in panel c; BLYP in panel d; B3LYP in panel e). The black vertical lines indicate experimentally determined band positions in panel a. Line heights represent the empirical intensity classification of Table 8.1.

Symmetry modes possess much larger intensities for picene\(^+\) as compared to pentacene\(^+\). Therefore, a link is observed between in-plane charge mobility in CC bonds and dynamic correlation in C\(_{22}\)H\(_{14}\) conjugated \(\pi\)-electron systems; in particular, for picene\(^+\), in contrast to pentancene\(^+\), substantial charge mobility is accompanied by an increase in dynamical electron correlation.

A pertinent question is if other observables within the available information can provide further evidence for this conclusion. The IR activity of CC modes is believed to be due to an orbital coupling mechanism (Torii et al. 1999, Torii 2000) in which the HOMO mixes with lower energy orbitals of the right phase. Close examination of the spinorbitals of b\(_1\) (picene\(^+\)) and b\(_{2g}\) HOMOs (pentacene\(^+\)) in Figure 8.5 shows that the \(\phi_7^{19}\) (HOMO) spinorbital for picene\(^+\) differs between ROHF and B3LYP levels, while for pentacene\(^+\) they are qualitatively indistinguishable.
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Figure 8.5 – Electron density distributions of key frontier spin-orbitals for picene$^+$ (a) and pentacene$^+$ (b). Note the large discrepancies for $\varphi_{73}$ calculated at the ROHF and B3LYP levels for picene$^+$, whereas these orbitals are qualitatively similar for pentacene$^+$. Top to bottom: the energies and orbital symmetries for (a) are $-9.75 \text{ eV (A}_2\text{)}, -9.56 \text{ eV (A}_2\text{)}, -9.5 \text{ eV (B}_1\text{)}$, and $-5.6 \text{ eV (B}_1\text{)}$. For (b) are $-9.75 \text{ eV (A}_u\text{)}, -9.37 \text{ eV (A}_u\text{)}, -8.67 \text{ eV (B}_2\text{g)}, and$ $-4.9 \text{ eV (B}_2\text{g)}$.

Finally, the gap between the two frontier spinorbitals (the $\varphi_{73}^\alpha$ spinorbital (HOMO) and its corresponding unoccupied $\varphi_{73}^\beta$ spinorbital) in the vicinity of the Fermi level is 1.19 eV for picene$^+$ and 1.27 eV for pentacene$^+$ (see Fig. 8.6). While these two gaps have similar values, the subsequent occupied spinorbitals are tightly spaced in picene$^+$ as compared to pentacene$^+$, in which they appear rather scattered. In picene$^+$, the gaps between HOMO ($\varphi_{73}$) and HOMO-1 ($\varphi_{72}$) spinorbitals are 0.256 eV ($\alpha$’s) and 0.066 eV ($\beta$’s). This gives a sort of pseudo-degeneracy. In pentacene$^+$ the gaps between HOMO ($\varphi_{73}$) and HOMO-1 ($\varphi_{72}$) are 1.096 eV ($\alpha$’s) and 0.711 eV ($\beta$’s). These sizeable energy gaps suggest that the (one-electron) spinorbitals would not strongly mix along vibrational modes (of right phase) as contrasted in picene$^+$, where the same spinorbitals are in close proximity. Thus,
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Figure 8.6 – Molecular-Orbital (MO) energy levels of pentacene\(^+\) (left) and picene\(^+\) (right). The level of theory used is B3LYP/6-311G(p,d). In both cations, the MO no.73 is the SOMO (HOMO in the neutral forms), and thus, 73A (\(\phi_73^\alpha\)) is occupied and 73B (\(\phi_73^\beta\)) is unoccupied.

as expected, the distributions of \(\alpha\) and \(\beta\) spaces of the HOMO-1 in pentacene\(^+\) are B3LYP-\(\phi_72^\alpha = B3LYP-\phi_72^\beta\), while for picene\(^+\) the \(\alpha\) and \(\beta\) spaces of HOMO-1 are B3LYP-\(\phi_72^\alpha \neq B3LYP-\phi_72^\beta\).

8.5 Conclusions

The experimental spectra of isolated hole-doped picene and pentacene are recorded via infrared multiple-photon dissociation spectroscopy. The general resemblance between both recorded spectra attests their isomeric nature. However, subtle differences are observed particularly in the in-plane symmetry modes, for which the total IR activity of \(\pi\)-electron bonds is probed. It is shown that in-plane-symmetry CC modes are strongly IR-active in picene\(^+\) as a result of charge-deformation contributions to the dipole derivatives, i.e., the observable IR intensities. This reflects the higher degree of electron delocalization in picene\(^+\) as compared to pentacene\(^+\), and is an indication of picene\(^+\) intramolecular charge
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dynamics. By applying an electron mean-field approximation (in the form of ROHF) to picene$^+$ and pentacene$^+$, a link between correlated electron dynamics and in-plane CC mode charge polarizability is found. This result suggests that compared to pentacene$^+$, picene$^+$ is a highly dynamically correlated system.

The difference in electron dynamics between pentacene$^+$ and picene$^+$ is thus manifested in their IR spectra and their calculated orbital wavefunctions. It is believed that these differences also lie at the origin of the diversity in functionality of materials based on both molecules (Kubozono et al. 2011). Single-molecule results may thus provide further insight into the emergence of bulk properties such as in particular superconductivity in picene-based materials.