The hidden life of cosmic carbon
Infrared fingerprint spectroscopy and fragmentation chemistry of gas-phase polycyclic aromatic hydrocarbons
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Chapter 7

The infrared spectrum of dibenzo[a,l]pyrene

In this Chapter, we present the experimental Infrared Multiple Photon Dissociation spectrum of cationic dibenzo[a,l]pyrene (C_{24}H_{14}^+) in the 6–40 µm / 250–1650 cm\(^{-1}\) range and compare it to the Density Functional Theory calculated spectrum. We aim to understand how irregularity affects the infrared spectrum and fragmentation chemistry of PAHs. Dibenzo[a,l]pyrene is ideal for this purpose, because it is an asymmetric, non-planar molecule, for which all vibrational modes are in principle IR-active. This is reflected in the richness of both the observed and calculated absorption spectra, which show a reasonably good match. Comparison between experiment and theory enables us to come to a detailed assignment of the observed bands. The periphery of the molecule contains almost all possible types of edge geometry, posing complications for the conventionally used designations of out-of-plane C–H bending modes in the 11–14 µm region, which serve to determine the average PAH edge structure in astronomical objects. The fragmentation mass spectra reveal facile 2H-loss and no [2C, 2H]-loss, even though irregular PAHs with structural protrusions are generally thought to be easily photofragmented. We speculate that these protrusions lead to both the ease in 2H-abstraction, and the stability to resist [2C, 2H]-loss.
Chapter 7. The infrared spectrum of dibenzo[a,l]pyrene

7.1 Introduction

Polycyclic aromatic hydrocarbons (PAHs) are by now commonly accepted as the carriers of the Aromatic Infrared Bands (AIBs), the strongest set of interstellar infrared (IR) emission bands between 3 and 20 µm [47]. These bands are detected throughout many objects in the interstellar medium (ISM) [32, 61, 271, 299]. Interstellar PAHs occur in various shapes and sizes, which are often deduced from the intensity ratios of bands in the 11–14 µm range, the spectral region characteristic for the out-of-plane bending modes of aromatic C–H bonds (CH_{oop} modes) [47, 50, 140, 272, 300–305].

The number of neighboring H atoms per ring is the main factor in determining the peak position in this 11–14 µm range, and has led to their designation as being solo, duo, trio or quartet hydrogen atoms [47]. The left panel in Fig. 7.1 shows these arrangements, and all other periphery types for the molecule studied in this Chapter. All four types of CH_{oop} modes are reported to have their own distinctive wavelength ranges, based on the spectra of smaller, highly symmetric PAHs [301]. However, the coupling between solo and duo CH_{oop} modes, and between duo and trio CH_{oop} modes, interferes with such distinctions in asymmetric, irregular PAHs [302, 303].

For all considered CH_{oop} bands, the peak positions for cationic PAHs move to shorter wavelengths with respect to their neutral counterparts [50, 301–303]. There is now a rather strong consensus that the strong, astronomically observed 11.2 µm band is caused by solo CH_{oop} vibrations of neutral PAHs, whereas its small 11.0 µm side-band is caused by solo CH_{oop} vibrations of cationic PAHs [50, 300, 301, 303, 304, 306]. The origin of the strong 12.7 µm-band is less clear. This band is suggested to be of both mixed duo/trio and cationic/neutral character [300–302, 305], although it was proposed that out-of-plane C–C–C (CCC_{oop}) vibrations of armchair-edged, neutral PAHs could also contribute significantly [272]. PAHs with pendant rings present relatively strong quartet CH_{oop} modes around 13.5 µm [275, 300, 301, 303, 306].

Figure 7.1: The molecular structure of dibenzo[a,l]pyrene, with labeling for the C–H and edge peripheries (left), and the labeling for the individual hydrogen atoms, and the pendant [a,l] rings and corresponding vibration propagation axes, based on IUPAC rules (right).
In spite of the pervasive idea that PAHs with pendant rings are less stable [245, 307, 308], these quartets could be significant contributors to this 13.5 µm band [300]. The postulation that compact, coronene-like PAHs are more stable than irregular ones is mostly based on dissociation studies on small, unrepresentative PAHs and turned out to be invalid [15]. Zigzag edges in room-temperature graphene self-repair to form armchair edges, and armchair edges in PAHs have been proposed to be more resistant to C₂H₂-losses than other edge structures [137, 152, 272, 309, 310]. This edge structure also has implications for the hydrogen chemistry inside an astronomical object. Hydrogen atoms in cove and bay regions experience sterically hindered which increases the likelihood of 1,2-hydrogen shifts, and thus forming aliphatic C–H₂ groups, promoting H and H₂ abstraction [88, 92, 210].

Dibenzo[a,l]pyrene is the ideal testing ground to answer how irregularity influences the infrared absorption and emission spectrum and how these irregular species fragment. It consists of a cove and a bay region, and one solo, one duo, one trio, and two quartet C–H sites, plus an armchair edge and two zigzag edges. In this Chapter, we report on a study of the spectral signatures and fragmentation of this highly-irregular, non-planar PAH. We present its gas-phase, infrared multiple photon dissociation (IRMPD) spectrum in the range of 250–1650 cm⁻¹. We also present the accompanying harmonic DFT spectrum to interpret and compare with the experimental data. The IRMPD fragmentation is also outlined, as well as the astrochemical context of our findings.

### 7.2 Methods

#### 7.2.1 Experimental

The IR spectrum was measured using the Fourier Transform Ion Cyclotron Resonance Mass Spectrometer (FT-ICR MS) beamline of the intra-cavity free-electron laser FELICE [132]. A detailed description of this apparatus is presented in Chapter 3 of this thesis.

Dibenzo[a,l]pyrene (C₂₄H₁₄, \( m/z = 302 \), LGC standards) was brought into the gas-phase from an effusive sublimation source heated to 130°C. The gaseous molecules were ionized in an electron impact ionization source, with 20 eV electrons. The resulting ions were directed into a quadrupole mass selector, used in radio-frequency (rf) guiding mode only. They were subsequently led into a quadrupole ion trap with rectilinear rods [180], which is segmented into three parts for optimal pulse compression. There, the ions were collisionally cooled with room-temperature argon gas at a pressure of 10⁻² mbar. The thermalized ion cloud was extracted into a large, electrostatic quadrupole bender, which aligns the ion cloud with both the FT-ICR and the laser. Through a large, 2 cm radius, 1 m long, rf-guiding quadrupole, the ions were led towards the final cell of the four ICR trapping cells, positioned along the central axis of the FT-ICR magnet and the intra-cavity laser. The center of cell 1 is located in the focus of the laser cavity, while cells 2, 3, and 4 are each positioned 100 mm away from the previous cell. Measurements have been performed in the storage cell with the lowest possible photon densities, cell 4, to avoid unnecessary spectral broadening and too stringent alignment constraints. During storage
in the ICR cell, masses other than the desired \( m/z = 302 \) were ejected by means of a Stored Waveform Inverse Fourier Transform (SWIFT) pulse [135]. The ion cloud was then exposed to a single FELICE macropulse, after which the mass spectrum was recorded. The ion intensity of each fragment mass is recorded as a function of the FELICE frequency. In the 650–1700 cm\(^{-1}\) range, the detuning of the undulator was increased from 3\( \lambda \) to 6\( \lambda \), and the macropulse length was decreased from 10 \( \mu \)s to 5 \( \mu \)s in an effort to reduce saturation.

The IRMPD spectrum was calculated as the ratio of the total fragment ion intensity and the total ion intensity, \( i.e. \) the sum of both fragment and parent masses. This gives the IRMPD yield \( Y(\nu) \) at frequency \( \nu \) as:

\[
Y(\nu) = \frac{1}{P(\nu)} \ln \left( \frac{N_{\text{par}}(\nu)}{N_{\text{par}}(\nu) + N_{\text{frag}}(\nu)} \right),
\]

for which \( N_{\text{frag}} \) and \( N_{\text{par}} \) are the total fragment and parent mass counts, respectively, and \( P(\nu) \) is the macropulse energy. To this end, a small fraction of the light was coupled out through a 0.5 mm hole in the middle of the cavity end mirror. This light was directed onto a Coherent EPM1000 power meter, and used to measure the laser pulse energy before and after each measurement. The resulting power-corrected \( Y(\nu) \) is then normalized to its maximum. Wavelength calibration was performed concurrently with the measurements, by directing the outcoupled beam onto a grating spectrometer (Princeton Instruments SpectraPro). The spectral bandwidth is near transform-limited and \( \sim 0.6\% \) of the full-width at half maximum (FWHM).

### 7.2.2 Computational

Density functional theory (DFT) calculations were performed using the Gaussian16 package [155]. For the harmonic calculations, the B3LYP functional was used [159, 160], which has previously been shown to accurately predict the infrared spectra of PAHs [199]. A 6-311++G(2d,p) basis set was used to optimize the molecular structure and compute the harmonic vibrational spectrum. A scaling factor of 0.975 was applied to the calculated frequencies to line them up the observed gas-phase spectrum. For comparison with the experimental spectrum, the calculated stick spectrum has been convolved with a 30 cm\(^{-1}\) Gaussian line shape.

### 7.3 Results and Discussion

Figure 7.2 shows the IRMPD mass spectrum of cationic dibenzo[a,l]pyrene \((m/z = 302)\), recorded at 1200 cm\(^{-1}\). Next to the nearly-depleted parent ion, three ion fragments are observed, at \( m/z = 301, 300, \) and 298, corresponding to loss of H, 2H and 4H. At weaker resonances, small amounts of \( m/z = 299 (\sim 3H) \) ion signal are observed as well. The loss of 2H/H\(_2\) is dominant, and no C-loss fragments are observed, in agreement with UV photodissociation results on the same molecule [92, 138].
Sterically hindered groups in the bay and cove regions of PAHs could play a role in the catalysis of H to H\(_2\) in the ISM [88, 92, 152, 290, 291]. This hypothesis has been supported through the modeling of interstellar PAHs in photodissociation regions (PDRs) [80, 81]. Furthermore, armchair edges could induce additional structural stability, since the presence of PAHs with armchair edges has been deduced from the high intensity of the 12.7 µm armchair deformation band near strong UV sources [272]. This stabilizing effect is, however, not fully understood, as there is currently no explanation for the large [2C, 2H]-loss that was observed from cationic isoviolanthrene (C\(_{24}H_{18}\)\(^+\)) using IRMPD conditions similar to this study [129]. Isoviolanthrene is an asymmetric molecule with two long armchair edges, but loses much more [2C, 2H] than the perylene, peropyrene, or ovalene molecules that were studied in the same publication. The cove region and presence of a trio in dibenzo[a,l]pyrene is what sets it apart from isoviolanthrene, and we suggest that future photodissociation studies focus on these differences to find what leads to the stability or fragility of these irregular PAHs.

Figure 7.3a displays the IRMPD spectrum of cationic dibenzo[a,l]pyrene. A plethora of bands is observed, consistent with the non-planar, asymmetric character of the ion, allowing all vibrational modes to have non-zero intensities. This is especially visible in the 1100–1650 cm\(^{-1}\) region, where a multitude of transitions gives rise to a broad structure. The MIR bands are saturated due to the high power of FELICE and strong absorptions of the molecule in this region. This saturation leads to an apparent underestimation of the normalized intensity in this range as the yield is maximized but still divided by the (too) high laser fluence. The positions the broad experimental bands were determined by...
Figure 7.3: The experimental IRMPD spectrum (a) and the scaled harmonic DFT spectrum (b) of
dibenzo[a,l]pyrene (C_{24}H_{14}^+). The experimental spectrum has been constructed from two measurement sets, overlapping around 650 cm$^{-1}$. Both (a) and (b) include a magnified inset, displaying the lower-intensity modes in more detail.
7.3. Results and Discussion

TABLE 7.1: Observed band wavelengths (in µm), frequencies (in cm\(^{-1}\)), band widths (in cm\(^{-1}\)), and normalized yield \(Y\), in comparison with calculated frequencies (in cm\(^{-1}\)) and IR intensities (in km\(\cdot\)mol\(^{-1}\)), with descriptions of the observed modes. Harmonic frequencies are scaled by a factor 0.975. *oop: out-of-plane; *ip: in-plane; *E/C: elongation/compression; *deform.: deformation; *antisym.: antisymmetric*

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Harmonic calculations</th>
<th>Mode description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wavel. (µm)</td>
<td>Freq. (cm(^{-1}))</td>
<td>Norm. (Y) (arb. u.)</td>
</tr>
<tr>
<td>21.4</td>
<td>468</td>
<td>0.12</td>
</tr>
<tr>
<td>19.2</td>
<td>520</td>
<td>0.13</td>
</tr>
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<td>16.9</td>
<td>590</td>
<td>0.18</td>
</tr>
<tr>
<td>15.6</td>
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<td>0.16</td>
</tr>
<tr>
<td>13.4</td>
<td>749</td>
<td>0.38</td>
</tr>
<tr>
<td>12</td>
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<td>897</td>
<td>0.05</td>
</tr>
<tr>
<td>8.5</td>
<td>1177</td>
<td>0.36</td>
</tr>
<tr>
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</tr>
<tr>
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</tr>
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<td>6.4</td>
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</tr>
</tbody>
</table>
deconvolution using Gaussian curves with a FWHM of 30 cm$^{-1}$. These and three narrow bands at 468, 520, and 749 cm$^{-1}$ are given in the Figure and in Table 7.1. Two very weak, but significant features were also observed at 831 and 896 cm$^{-1}$, and are shown more clearly in the magnified inset. Over the entire range from 250–1650 cm$^{-1}$, at least fourteen bands can be identified, as listed in the Figure as well as in Table 7.1. The spectrum shows typical ionic character with active regions largely located between 6–9 µm (1100–1600 cm$^{-1}$) and above 12 µm (450–800 cm$^{-1}$) with the strongest bands on the blue side. Between 250–450 cm$^{-1}$ and 800–1100 cm$^{-1}$, little to no activity is observed. However, there are two very weak features, at 831 and 897 cm$^{-1}$, which are noisy but significant.

The harmonic DFT spectrum is displayed in panel (b), and shows a good match with the IRMPD spectrum. The theoretical peak positions given in the Figure correspond to the convolved features. The underlying individual modes are listed in Table 7.1. The dense, rich structure in the 1100–1600 cm$^{-1}$ region agrees well in terms of shape. The significant differences in intensity ratios in this region can be attributed to both the saturation and the coupling between the densely packed modes that is not accounted for in this harmonic calculation. The derived band frequencies in the 250–1100 cm$^{-1}$ range match well, with no deviations larger than 18 cm$^{-1}$. This agreement is less good when comparing band intensities and shapes. The experimental bands in this region are more narrow and symmetric than predicted by theory. Convolving the theoretical spectrum with a more narrow FWHM of 20 cm$^{-1}$ does not resolve this discrepancy, but instead worsens the match in both shape and peak position, as split features appear which are not observed in the experiment. Theory predicts many more bands of similar intensity, resulting in broader and less symmetric spectral features. More importantly, where theory distributes the intensity over many bands, lowering the average intensity, experiment reveals fewer bands that appear much stronger. This is particularly interesting in view of the search for fingerprints.

Table 7.1 also lists the descriptions of the assigned vibrational modes. Assignment of the experimental bands was determined by matching the highest-intensity theoretical modes coinciding with the corresponding observed band. The listed descriptions give the dominant vibrational character of the assigned theoretical modes. To aid in the description of the (primary) modes, the different hydrogen positions on the molecule have been unambiguously labeled following IUPAC rules [311]. We identify two principal ‘axes’ consisting of rows of three fused rings, labeled A and L after the [a] and [l] positions on the central pyrene. This labeled structure is shown in the right panel of Fig. 7.1, further detailing the different structures that can be identified in the molecule.

Also listed in Table 7.1 are the band positions in µm as to best compare the assigned modes of the irregular dibenzo[a,l]pyrene to the those reported in literature for the more symmetric species. When we compare experiment to our DFT calculations, and then to the conventional wavelength ranges in which the same vibrations are found, we observe several discrepancies which are caused by the strong coupling between the different modes in this cation. Spectral differences relative to symmetric species are mostly expected in the CH$_{oop}$ mode range (700–950 cm$^{-1}$) due to the irregular periphery. The highest-intensity
7.3. Results and Discussion

The observed 749 cm\(^{-1}\) band, which falls into the conventional 734–761 cm\(^{-1}\) range for quartet CH\(_{\text{oop}}\) modes [301]. The broad theoretical feature at 763 cm\(^{-1}\) contains several different modes, but the dominant one shows quartet character. This shows that even for a highly irregular PAH such as dibenzo[a,l]pyrene, the CH\(_{\text{oop}}\) bands remain a suitable diagnostic tool. The observed 590 cm\(^{-1}\) / 16.9 \(\mu\)m band is assigned to a mode that mixes a typical CCC\(_{\text{oop}}\) motion at the armchair edge [272] and a CH\(_{\text{oop}}\) mode of most H atoms. In rylene, this CCC\(_{\text{oop}}\) appears at 12.7 \(\mu\)m (787 cm\(^{-1}\)). The long wavelength at which this mode is observed here, shows that armchair edge modes are not likely to manifest at the same wavelength for different classes of PAHs. The experimental 639 cm\(^{-1}\) band is best described as an antisymmetric elongation/compression (E/C) of the two pendant rings. E/C modes are more commonly associated with the far-infrared (< 600 cm\(^{-1}\) / > 16 \(\mu\)m) [140, 280], but the relatively short wavelength at which it is observed here can both be due to the ion’s relatively small size and to the coupling of the pendant rings with the central pyrene [275].

As is common for most PAHs [47], the activity between 1100 and 1650 cm\(^{-1}\) can be largely attributed to C–C stretching and in-plane C–H bending. Ring deformations tend to follow either the A or the L vibration propagation axis (see Fig. 7.1) and modes often couple along one of the planes along those axes. However, a few strong CC\(_{\text{ip}}\) stretching modes involving both peripheral rings are also present in the theoretical prediction. The wealth of predicted lines shown in Fig. 7.3b, and the difficulty to match them to the observed bands in Fig. 7.3a underscores the necessity for an anharmonic calculation, which could drastically change the intensity ratios and band shapes across the whole spectrum. We calculated the Quartic Force Field anharmonic spectrum using B3LYP/N07D — which has been successfully used for PAH cations in the past [143], but this resulted in modes with unrealistic relative intensities and large positive corrections (see Chapter 5 and Appendix A). Anharmonic calculations for large molecules are still problematic and dedicated benchmark effort is needed [312].

IR spectra of similarly low-symmetry PAHs are scarce [115, 129, 303, 318]. To our knowledge there is only one such spectrum in the mid-infrared, namely of isoviolanthrene, which has a C\(_2\) symmetry and two long armchair edges [129]. In Fig. 7.4, the dibenzo[a,l]pyrene spectrum (dark green) is compared to the previously reported isoviolanthrene spectrum (violet) in the 6–10 \(\mu\)m range, exhibiting a very similar shape. Two distinct features between 6.1–7.0 \(\mu\)m are observed, as well as a broader range with less structure between 7.0–8.9 \(\mu\)m, ending with little to no activity in the 8.9–10 \(\mu\)m range. In the same publication, the isoviolanthrene spectrum was compared to the spectrum of a D-class astronomical object [299, 319]. Here, it was argued that as the D-class spectrum does not line up with the spectra of more regular PAHs, irregular PAHs might be contributors to D-class spectra in addition to regular PAHs. The same D-class spectrum is shown in Fig. 7.4 (blue) in addition to an A-class spectrum (purple) [299] and an IRMPD spectrum of a regular PAH (light green, pyrene, Chapter 6). The vertical dotted lines are placed to guide the eye to the peak positions of the D-class spectrum. When we first compare the D-class spectrum to the isoviolanthrene and dibenzo[a,l]pyrene spectra, it is clear
Chapter 7. The infrared spectrum of dibenzo[a,l]pyrene

Figure 7.4: IRMPD spectra of cationic pyrene (pyr; light green), cationic dibenzo[a,l]pyrene (dbALp; dark green) and cationic isoviolanthrene (iso; violet) [129], and the astronomical IR spectra of an A-class (IRAS 23133+6050; violet) [313–315] and a D-class (IRAS 05110–6616; blue) astronomical object [316, 317].
that none of the features provide a good match. Both irregular PAHs show too much activity in the 6.1–7.0 µm range, and the distinct astronomical features at 6.9 and 7.3 µm are not reproduced by the experiment. However, compared to the distinct bands shown in the spectrum of a regular PAH like pyrene, the broad range between 7.0–8.9 µm is more similar to the long, reddening tail from 7.6 µm to 9.0 µm. Both irregular PAHs show a more pronounced mismatch with the class-A spectrum than with the class-D spectrum. Further study on mid-infrared spectra of irregular PAHs is needed to investigate whether they could be significant contributors to class-D astronomical spectra.

Dibenzo[a,l]pyrene’s fragmentation mass spectrum has revealed facile 2H/H₂-loss, and no [2C, 2H]-loss, underlining the catalytic potential of PAHs with sterically hindered C–H groups. However, the previously mentioned isoviolanthrene molecule easily fragments through the loss of [2C, 2H] under similar IRMPD conditions. Considering that both of these molecules have the armchair edges, we conclude that the presence of armchair edges alone is not sufficient to predict structural stability.

We also presented the IRMPD spectrum of cationic dibenzo[a,l]pyrene, and compared it to scaled, harmonic DFT calculations. This has led to the conclusion that the spectrum shows a rich C–C stretching and CH$_{\text{ip}}$ bending structure in the 1100–1650 cm$^{-1}$ region, a CH$_{\text{oop}}$ bending region (700–950 cm$^{-1}$) which is dominated by a typical quartet mode at 749 cm$^{-1}$, and a FIR-range with modes that are strongly shifted in band position compared to regular, symmetric species. Overall, a good match between theory and experiment is found in terms of peak position, but less so in terms of band shape and relative intensity.

The irregularity and amount of IR-active modes in dibenzo[a,l]pyrene demands for a comparison with anharmonic calculations. However, both anharmonic calculations did not yield successful results. Dedicated theoretical studies are needed to determine the best approach, which falls outside of the scope of this work.

Comparison to a previously reported spectrum of an asymmetric PAH, isoviolanthrene, has revealed a close resemblance. Comparison to a class-D astronomical spectrum yielded a possible explanation for the long reddening tail starting at 7.6 µm, but also showed large mismatches in other parts of the spectrum. Further studies of how spectra of irregular PAHs manifest themselves in astronomical observations are thus highly of interest. Such studies are presently underway.