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Chapter 5

Near edge X-ray absorption mass spectrometry on coronene

We have investigated the photoionization and photodissociation of free coronene cations C_{24}H_{12}^{+} upon soft X-ray photoabsorption in the carbon K-edge region by means of a time-of-flight mass spectrometry approach. Core excitation into an unoccupied molecular orbital (below threshold) and core ionization into the continuum both leave a C 1s vacancy, that is subsequently filled in an Auger-type process. The resulting coronene dications and trications are internally excited and cool down predominantly by means of hydrogen emission. Density functional theory was employed to determine the dissociation energies for subsequent neutral hydrogen loss. A statistical cascade model incorporating these dissociation energies agrees well with the experimentally observed dehydrogenation. For double ionization, i.e. formation of intermediate C_{24}H_{12}^{3+} trications, the experimental data hint at loss of H^{+} ions. This asymmetric fission channel is associated with hot intermediates, whereas colder intermediates predominantly decay via neutral H loss.

5.1 Introduction

The formation and stability of polycyclic aromatic hydrocarbons (PAHs) is of key relevance for many research fields ranging from astrochemistry [1] to combustion research [2]. In particular gas-phase PAH interactions with energetic photons have been the subject of intense study, because of the direct relevance of such processes in astrophysical environments [3] and because of the opportunities of PAH photoionization as a tool for analytical chemistry [4].

In a series of pioneering experiments, using synchrotron radiation, Leach and coworkers have investigated VUV photoionization of a variety of gas-phase neutral PAHs by means of photoelectron-photoion coincidence spectroscopy [5, 6] or by photoionization mass spectrometry [7]. Upon moderate excitation, PAH cations dissociate predominantly by neutral H or H$_2$ loss or acetylene loss, with appearance photon energies increasing with PAH size. For instance, the appearance energy for H loss is 13.81 eV for benzene and 18.7 eV for coronene [8]. Note, that direct loss of C atoms from the PAH backbone have so far only been observed in atomic collision experiments [9, 10], where the energy transfer to the C atom needs to exceed 25.5 eV [11]. For small systems such as benzene and naphthalene, appearance energies for H and H$_2$ are similar, whereas e.g. for coronene, H$_2$ loss requires about 1.4 eV more internal energy and acetylene loss is not observed at all [8]. Calculated absolute photoabsorption cross sections [12] for neutral PAHs and for their respective cations are in very good agreement with experimental data. For all PAH species studied, the VUV absorption spectrum is dominated by a broad continuum between 10 eV and 30 eV that peaks between 15 eV and 20 eV and that is quantitatively similar for ions and neutrals.

Upon UV or VUV photoionization, large astrophysically relevant PAHs such as coronene are subject to H or H$_2$ loss. However, these channels are outcompeted by non-dissociative ionization, by far. Inner-shell photoexcitation or photoionization involves larger excitation energies and accordingly opens up more fragmentation channels, e.g. successive H loss. However, beyond the VUV range, experimental data on PAH photoionization is scarce. At the C K-edge, Hübner et al. [13] have performed a high resolution near edge X-ray absorption spectroscopy (NEXAFS) study on naphthalene, and found evidence for a strong coupling between electronic transitions and vibronic excitations. Very recently, in a combined experimental and theoretical NEXAFS investigation of anthracene, Klues et al. [14] showed that final state relaxation effects due to excitations from localized hole states have to be taken into account for an accurate interpretation of the experimental data. The molecular response upon K-edge photoabsorption, i.e. PAH fragmentation has not been investigated, yet.

The investigation of neutral PAH molecules upon photoionization is experimentally straightforward, because effusive targets can be produced by mere evaporation. It is notoriously difficult to study photoionization of ions, because the traditional crossed beam or merged beam experiments require high intensity ion beams. To our knowledge, no such studies have been performed for PAHs, yet. A complementary approach towards photoionization of PAH cations is the use of ra-
diofrequency (RF) ion traps for collection of a sufficiently dense cationic target. In pioneering experiments, a commercial [15] or a home-built tandem mass spectrometer [16] was interfaced with synchrotron beamlines to investigate photoionization and photofragmentation of large cationic biomolecules.

In a recent study, K-edge photoexcitation at a fixed energy of 285 eV was used to study the relaxation of highly excited superhydrogenated PAHs [17]. Here, we report on the first near edge X-ray absorption mass spectrometry (NEXAMS) study on a PAH cation, scanning the full K-edge absorption energy range (283-305 eV). The data were obtained by interfacing our apparatus with a soft X-ray beamline at the BESSY II synchrotron. By comparison of experimental data with quantum chemical calculations, it will be shown that the degree of dehydrogenation can be used to estimate the internal energy of the intermediate multiply ionized molecule. A statistical cascade model is used to correlate the dehydrogenation with branching ratios as a function of internal energy. Finally, evidence for the transition from neutral H loss to H+ loss in coronene trications will be presented.

5.2 Experimental method

The experiments were performed on the soft X-ray beamline U49/2-PGM1 at the BESSY II synchrotron facility (Helmholtz Zentrum Berlin, Germany) using our tandem mass spectrometer setup [16]. Briefly, a beam of coronene cations was produced by an electrospray ionization (ESI) source, phase space compressed in a radio frequency (RF) ion funnel and further guided by a linear (RF) ion guide. The molecular cations were mass selected by a quadrupole mass analyzer and then trapped in an RF ion trap. The setup was operated in a pulsed mode and in order to reach sufficiently high target densities, each cycle started with an ion accumulation period of 400 ms. The ions were collisionally cooled within a spherical volume with a diameter of about 400 µm in the center of the trap by using a helium buffer gas. Following accumulation, the buffer gas was pumped away during 200 ms after which the ions were exposed to the soft X-ray photons. The photon beam was pulsed by an optical shutter and monitored by a SXUV-type silicon p-n junction photodiode. The photon exposure time varied between 700 and 1800 ms, depending on the ionization/fragmentation cross section for a specific photon energy. After each photon exposure period, a second helium buffer gas pulse was applied to collisionally cool energetic fragments. The trap content was extracted to a linear time-of-flight (TOF) mass spectrometer and detected on a micro-channel-plate (MCP) detector. The detector signal was processed by a 1 GHz digitizer.

To accurately quantify the net effect of the photon beam on the target molecules, two additional data cycles were performed for each spectrum. To obtain the contribution from the photoionization of the residual gas, a mass spectrum was recorded for an empty trap (ESI-off). The initial trap content was determined by extraction of the trap content into the TOF spectrometer, without prior photon exposure (photons-off). The helium buffer gas was applied in all three cycles. The net effect of the photons on the target was then obtained by subtracting the ESI-off spectrum
and the photons-off spectrum from the main spectrum.

The coronene molecules were purchased from Sigma Aldrich (Germany) and were of $\geq 99$ % purity. Coronene cations were produced by adding 50 $\mu$l of 10 mM AgNO$_3$ to 1 ml saturated solution of coronene in ethanol, which leads to the following reaction: $\text{C}_{24}\text{H}_{12} + \text{Ag}^+ \rightarrow \text{Ag(s)} + \text{C}_{24}\text{H}_{12}^+$. The solution was then pumped through the ESI needle at a 0.2 ml/h flow rate. For the natural $^{13}$C isotope abundance of 1.1 %, the abundance of singly isotopic coronene at $m/\bar{q}=301$ is 20 % and the abundance of doubly isotopic coronene at $m/\bar{q}=302$ is 3 %.

The TOF mass spectrum was calibrated by fixing the $\text{C}_{24}\text{H}_{12}^+$ parent peak at $m/\bar{q} = 300$ and the two stable silver isotopes at $m/\bar{q} = 106.9$ and 108.9. The ion yield was normalized to the exposure time, the photon flux and the intensity of the parent peak. The quantum efficiency of the photodiode was assumed to be constant over the limited range of photon energies (283-305 eV).

A NEXAMS spectrum is the normalized photoionization/photodissociation product yield as a function of the photon energy. We extracted NEXAMS spectra from mass spectra recorded over the photon energy range from 283 to 305 eV. The step-size was adjusted to the anticipated spectral features, varying from 0.25 eV up to a few eV at an energy resolution of 150 meV.

5.3 Results and discussion

5.3.1 General features of the mass spectra

The initial electronic processes that occur upon coronene near C K-edge photoabsorption are summarized in figure 5.1. Generally speaking, two sequences can be distinguished above and below ionization threshold. For photon energies above the ionization threshold, ionization of the $\text{C}_{24}\text{H}_{12}^+$ parent ion leads to formation of $\text{C}_{24}\text{H}_{12}^{2+}$. Subsequently, the K-hole gets filled by an Auger decay and the emission of an Auger electron leaves $\text{C}_{24}\text{H}_{12}^{3+}$ trications. Below the ionization threshold, instead of an ionization, initially the 1s electron gets excited to an unoccupied electronic orbital. The consecutive Auger decay here increases the charge state by one, leading to the formation of $\text{C}_{24}\text{H}_{12}^{2+}$ dications. Note that in the following the terms dication and trication will be used to address all doubly and triply charged ions, independent of the number of lost H atoms.

In figure 5.2 six mass spectra are displayed which were taken after absorption of photons with energies 285, 288, 290.5, 293.5, 295, and 300 eV. The main spectral features shift from dications, $m/\bar{q} = 146 - 150$ (blue lines) to trications, $m/\bar{q} = 98 - 100$ (red lines), when crossing the ionization threshold. Both the dications and the trications show a distribution of peaks due to the loss of hydrogen. This dehydrogenation strongly depends on the amount of energy which is deposited into the molecule.

The mass spectrum has some further features at $m/\bar{q} = 85, 86, 87, 109, 110, 111, 120, 121, 122, 123, 124, 132, 133, 134, 135,$ and 136 which can be assigned to $\text{C}_n\text{H}_m^+$ type fragments. The intensity of these fragments increases with increasing photon
energy.

5.3.2 NEXAMS spectra

Figure 5.3 displays the NEXAMS spectra for dications and trications. These spectra can be compared with previously published NEXAFS data on coronene [18] and smaller PAHs [14, 19, 20]. In contrast to NEXAFS data, where the total photoabsorption yield is directly recorded without any distinction between subsequent molecular response channels, NEXAMS is an action spectroscopy technique in which ion yields are the observables for photoabsorption. In general, a PAH absorption spectrum is affected by three main parameters: (i) the density of unoccupied states, (ii) energetic shifts of the C 1s energy, due to differences in chemical environment (∼0.5 eV), and (iii) the core-hole effect (several eV’s). The dication spectrum has a strong resonance around 285 eV which originates from a 1s → π* transition. This peak has an internal substructure, due to contributions at 285 and 285.5 eV, which originates from the two different types of C atoms in coronene: the inner C-atoms bound to three other C atoms (285.5 eV) and outer C atoms bound to one H atom and two C atoms (285 eV) [18].

The dication spectrum has broader features at 288.5, 290.5, and 293.5 eV. On basis of the NEXAFS studies [20, 19, 14] on smaller PAHs we assign the features at 288.5 and 290.5 to a mix of higher lying π* orbitals, σ* orbitals, and Rydberg states. In earlier studies on coronene [18] and anthracene [14], the broad feature at 293.5 eV has been assigned to transitions to σ* orbitals.

The red spectrum in figure 5.3 shows NEXAMS data for the trications. The
Figure 5.2: Normalized mass spectra induced by photons with energies 285, 288, 290.5, 293.5, 295, and 300 eV interacting with coronene cations. The spectra are all normalized to the irradiation time, photon flux and coronene target intensity. The solid lines indicate the boundaries for the areas leading to the NEXAMS spectra in figure 5.3. The dashed lines correspond to the NEXAMS spectra in figure 5.7.

Highest yields occur for photon energies exceeding the core ionization threshold. Below 294 eV, the trication spectrum is very similar to the dication spectrum i.e. the $\pi^*$, $\sigma^*$, and Rydberg transitions are clearly observed. Below threshold the ratio between dications and trications is 4:1.

The presence of a significant sub-threshold double ionization channel is not expected from the scheme in figure 5.1. There are two possible routes towards this channel: two electron Auger decay and knock-out processes. Two electron Auger decay can occur either simultaneous by Auger Double Ionization (ADI) or sequential by Double Auger Ionization (DAI). In both cases the K shell vacancy is filled by emission of two electrons from valence orbitals, in this case leaving a tricationic parent:

$$M^+ + h\nu \rightarrow M^{+*} \xrightarrow{ADI/DAI} M^{3+*} + 2e^-.$$  \hspace{1cm} (5.1)

Similar double Auger decays have been observed, for instance for krypton [21], argon [22], and carbonmonoxide [23].
An alternative explanation based on regular Auger decay is the knock-out of a weakly bound valence electron by the Auger electron:

\[
M^+ + h\nu \rightarrow M^{+\ast} \xrightarrow{\text{Auger}} M^{2+\ast} + e^- \xrightarrow{\text{e.i.}} M^{3+\ast} + 2e^-.
\] (5.2)

To a certain degree this process type is comparable to photon double ionization processes which were recently studied [24] for PAHs. This study revealed double to single ionization ratios of 20-30 % for absorption of 270 eV photons, although, only 5 % is attributed to a knock-out mechanism ([24],Figure 14). The excess energy of the emitted electrons from the valence shell in that particular case, is in the same range as the energy of the Auger electrons in our experiments, e.g. approximately 220-250 eV.

### 5.3.3 Dehydrogenation and fragmentation dynamics

For a quantitative investigation of dication de-excitation by hydrogen loss, the respective mass spectral features were disentangled by fitting Gaussian line profiles to the spectral features. Highest yields were found for \( m_2 = 147, 148, 149, \) and 150, associated with 6H, 4H, and 2H emission and intact dications, respectively. The
Figure 5.4: NEXAMS spectra for $\text{C}_{24}\text{H}_{12}^2+$ (a), $\text{C}_{24}\text{H}_{10}^2+$ (b), $\text{C}_{24}\text{H}_8^2+$ (c), and $\text{C}_{24}\text{H}_6^2+$ (d), illustrating the strong dependence of the dehydrogenation on the photon energy.

NEXAMS spectra for these processes are displayed in figure 5.4. Figure 5.4a shows that formation of intact dications is mainly triggered by C 1s $\rightarrow \pi^*$ transitions around 285 eV. Figure 5.4b shows the NEXAMS spectrum associated with 2H loss. This channel is also triggered by the C 1s $\rightarrow \pi^*$ transition, but occurs also at higher photon energies. The NEXAMS spectrum associated with 4H emission is plotted in figure 5.4c. This channel is triggered by a C 1s $\rightarrow \pi^*$ transition around 285 eV and by C 1s $\rightarrow \sigma^*$ and Rydberg transitions around 293.5 eV. The loss of 6H (figure 5.4d) is strongest at energies around 293.5 eV. Similar NEXAMS spectra for the trications are presented in figure 5.5. Figure 5.5a-c show a sharp intensity increase at a photon energy of 294 eV, i.e. the threshold energy for direct core ionization and efficient trication production. Below the threshold, a contribution from the C 1s $\rightarrow \pi^*$ transitions around 285 eV does appear in the trication yields (fig. 5.5). The NEXAMS spectrum associated with 6H emission (figure 5.5d) is very similar to the NEXAMS spectrum of 6H emission from $\text{C}_{24}\text{H}_{12}^2+$ (figure 5.4d).

Remarkably, the data reveals that the dication yields for $\text{C}_{24}\text{H}_{10,8,6}^2+$ are non-zero above ionization threshold. Clearly, C 1s ionization followed by an Auger process (fig. 5.1a) leaves the molecule at least triply charged. The production of dications
is either caused by a charge separation process, i.e. the loss of H\(^+\) instead of neutral H or by excitation to shape resonances [25].

For tricationic coronene, the charge separation process has the form:

\[ M^{3+} \rightarrow [M - H]^{2+} + H^+. \]

The occurrence of this reaction is further supported by the fact that no above-threshold formation of C\(_{24}H_{12}^{3+}\) is observed (figure 5.4a). Note that reaction 5.3 is conceptually very similar to the superasymmetric fission occurring in multiply charged fullerenes. For C\(_{60}\) charge states exceeding 3\(^+\) [26, 27], C\(^+\) loss becomes dominating over neutral C\(_2\) evaporation. Holm et al. [28] have calculated the adiabatic dissociation energies for neutral H loss and for H\(^+\) loss from coronene to be 5.2 eV and 11.4 eV for the monocation and 4.7 eV and 8.0 eV for the dication, respectively.

Clearly, H\(^+\) loss is thus ruled out for these charge states. For the coronene trication, however, the adiabatic dissociation energy for H\(^+\) loss becomes lower than the competing neutral H loss channel [28]. Paris et al.[29] have recently investigated hydrogen loss from coronene as a function of charge state, while explicitly including associated energy barriers and considering different spin multiplicities.

Figure 5.5: NEXAMS spectra for C\(_{24}H_{12}^{3+}\) (a), C\(_{24}H_{10}^{3+}\) (b), C\(_{24}H_{8}^{3+}\) (c), and C\(_{24}H_{6}^{3+}\) (d).
Their results are qualitatively similar, regarding the transition from neutral H loss to asymmetric fission: Starting with the coronene trication, loss of ionic species is predicted to be dominant.

Experimentally, we find the above-threshold ratio between coronene dications and trications, to be 1:3, indicating that charge separation is possible but not yet dominating for triply charged coronene. It has to be noted here, that analog to sub-threshold double ionization, there should be a comparable branching ratio for above-threshold triple ionization, leading to formation of intermediate C_{24}H_{12}^{3+}. However, this charge state contributes to the trication channel as for the tetracation, the first hydrogen loss is expected to be solely an asymmetric fission process leading to H^+ loss.

In the context of dehydrogenation and asymmetric fission, it is interesting to look into the average H loss as a function of photon energy, as this quantity reflects the molecular internal energy prior to the breakup process. Figure 5.6 displays the respective data for dications (a) and trications (b). Above threshold, both for dications and for trications the average dehydrogenation remains constant. This independence on the photon energy is in line with the simple scheme in figure 5.1 for above threshold photoabsorption, as the increase in photon energy is entirely transferred to the ejected C 1s electron via direct ionization. The average dehydrogenation above threshold is \( \approx 4.0 \) for dications and only \( \approx 2.0 \) for trications. For trications, H^+ loss leading to dications appears to be more likely for internally hot trications, whereas neutral H loss is related to internally colder ones. This underlines the notion that the tricationic charge state of coronene marks the opening of the charge separation channel. Neutral H loss, however, still dominates, in particular for modest internal energies.

Below the ionization threshold, for dications (figure 5.6) a roughly linear increase of average H loss with the photon energy is observed. The increase is a straightforward consequence from the scheme in figure 5.1: with increasing photon energy, higher lying unoccupied bound orbitals become resonant and consequently, the molecular ion is left in a higher excited state. For trications, a similar trend is observed, albeit at slightly higher dehydrogenation states. The abovementioned below-threshold double ionization processes (see equations 5.1 and 5.2) are likely to leave the formed trications with higher excitation energy.

The second possible explanation of dication formation above core ionization threshold is the aforementioned excitation to shape resonances. Such resonances, above ionization threshold, have been observed previously for neutral coronene [18] and benzene [25]. The excitation energy associated with these resonances is higher and consequently should involve stronger dehydrogenation (and even multifragmentation) which is not observed experimentally. We therefore conclude that the influence of shape resonances is probably weak for the channels under study.

Clearly, dehydrogenation and deprotonation are the prime fragmentation channels, however, at high energy depositions PAH skeleton fragmentation becomes relevant. Figure 5.7 displays NEXAMS spectra of nine PAH fragments which are all formed after breaking the carbon skeleton of coronene. The line color corresponds to the dashed lines in figure 5.2. The NEXAMS spectra for smaller fragment cations
show strong peaks at 293.5 and 300 eV. Therefore, it is clear that these fragmentation channels are mainly linked to the photoexcitation into the $\sigma^*$ orbitals. There are two explanations why higher energetic $\sigma^*$ orbitals are the gateway to these fragments: statistical fragmentation and local bond weakening.

In statistical fragmentation the fragmentation depends on the amount of energy which is deposited in the molecule. For core excitation processes this quantity depends on the binding energy of the associated unoccupied orbital. The energy deposition via the 293.5 eV $\sigma^*$ orbital is 8.5 eV more than the energy deposition via the 285 eV $\pi^*$ orbital. The energy deposition which is induced by the subsequent Auger decay remains constant for both excitations. The deposition of higher amounts of energy explains the stronger fragmentation pattern, just below core ionization threshold.

The dominance of $\sigma^*$ resonances in the fragment NEXAMS spectra can also be explained by a pump-probe type of process. In the first step, a $\sigma^*$ bond is weakened by the absorption of a soft X-ray. This bond weakening is rapidly followed by a large energy deposition into the molecule induced by an Auger decay. If the electronic excitation in this particular bond is not yet dissipated to vibrational degrees of freedom when the Auger decay occurs, this type of process can play a role.

Figure 5.6: The average hydrogen loss for dications (a) and trications (b).
5.3.4 Evaporation model

Under the assumption that in vibrationally hot PAHs, consecutive H loss competes with infrared (IR) photon emission, one may use a basic cascade model to describe the relaxation of the coronene molecules or PAH molecules in general. The main ingredients for such a model are the infrared photon emission rate, the hydrogen binding energy, and the internal energy. In this scenario, the dissociation probability for dissociation step $i$ can be written as,

$$ P_{i}^{diss} = \frac{k_i e^{-E_i/kT_i}}{n_{max} + 1} + k_i e^{-E_i/kT_i} $$

(5.4)
with pre-exponential factor \( k_i = \frac{kT_{\text{eff}}^i}{h} \exp(1 + \frac{\Delta S_{i,0}}{R}) \) and average PAH temperature \( T_{\text{av}}^i = \sqrt{T_{\text{eff}}^i \times T_{\text{eff}}^{i,0}} \). \( T_{\text{eff}}^{i,0} \) and \( T_{\text{eff}}^{i,n_{\text{max}}} \) correspond to the effective temperatures when 0 or \( n_{\text{max}} \) infrared photons have been emitted, respectively ([30]). The effective temperature at step \( i \) is defined as,

\[
T_{\text{eff}}^i = 2000 \left( \frac{T_{E,i}}{N_C} \right)^{0.4} \left( 1 - 0.2 \frac{E_i}{T_{E,i}} \right) \quad (5.5)
\]

in which \( E_i \) is the dissociation energy and \( T_{E,i} \) is the total vibrational energy at step \( i \) [30]. We further set the maximum number of emitted photons \( n_{\text{max}} = 6 \) [30] and the entropy change \( \Delta S = 2.5 \text{ cal/mol} \) [31]. For coronene the number of \( C \) atoms is \( N_C = 24 \). Typical IR emission rates are between 1 and 1000 s\(^{-1}\) [8]. We adopted \( k_{IR} = 10 \text{ s}^{-1} \) from reference [32]. \( R, h, \) and \( k \) are the gas constant, Planck’s constant and the Boltzmann constant, respectively. We used DFT to determine \( E_i \) for atomic and molecular hydrogen loss and the transition states for molecular hydrogen loss. The calculations were performed by using the B3LYP [33, 34] functional and a 6-31G(d) basis set as implemented in the GAUSSIAN09 package [35]. The molecular structures were optimized to a minimum (all real frequencies) or to a transition state (one imaginary frequency) after which the frequencies were calculated. The energies were obtained by subtracting the zero-point energy (corrected by the empirical scaling factor 0.9806 [36]) from the total energy. Table 5.1 lists all calculated dissociation energies and transition states.

The mass spectra (figure 5.2) reveal strong preference for even numbers of H losses over odd numbers of H losses. This suggest that coronene loses hydrogen either by emission of \( H_2 \) or by emission of hydrogen pairs. To investigate the

<table>
<thead>
<tr>
<th>( C_{24}H_{12}^{q+} \rightarrow C_{24}H_{12-1}^{q+} + H )</th>
<th>( i )</th>
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<tr>
<td>( i = 1 )</td>
<td>4.7</td>
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<tr>
<td>( i = 2 )</td>
<td>4.2</td>
<td>3.8</td>
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<td>( i = 3 )</td>
<td>4.7</td>
<td>5.1</td>
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<td>( i = 4 )</td>
<td>4.0</td>
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<td>( i = 5 )</td>
<td>4.9</td>
<td>5.2</td>
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<tr>
<td>( i = 6 )</td>
<td>4.0</td>
<td>3.9</td>
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<td>( i = 7 )</td>
<td>4.8</td>
<td>5.1</td>
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\( C_{24}H_{12}^{q+} \rightarrow C_{24}H_{10}^{q+} + H_2 \) | 5.2 | - |
competition between H loss and H$_2$ loss, we extended equation 5.4 as follows:

$$P^{\text{diss}}_{a} = \frac{k_a e^{-E_a/kT_a}}{k_{IR} + k_a e^{-E_a/kT_a} + k_b e^{-E_b/kT_b}}$$

$$P^{\text{diss}}_{b} = \frac{k_b e^{-E_b/kT_b}}{k_{IR} + k_a e^{-E_a/kT_a} + k_b e^{-E_b/kT_b}}$$

$$P^{\text{intact}} = \frac{k_{IR} e^{-E_a/kT_a} e^{-E_b/kT_b}}{k_{IR} + k_a e^{-E_a/kT_a} + k_b e^{-E_b/kT_b}}$$

(5.6)

The labels a and b represent the two competing channels of H loss and H$_2$ loss, respectively. For C$_{24}$H$_{10}^{2+}$, the respective dissociation energies are $E_a = 4.7$ eV and $E_b = 5.2$ eV. Figure 5.8 shows the dissociation probabilities as a function of excitation energy $T_E$ for coronene dications. It is clear that, in the relevant energy regime, H loss strongly dominates over H$_2$ loss. Therefore, here H$_2$ loss is not included in the full cascade model. Only sequential H loss is considered.

The dehydrogenation state probability for the $i^{th}$ hydrogen loss is defined as follows:

$$D_i(T_E) = (1 - P^{\text{diss}}_{i+1}(T_E)) \prod_{k=0}^{i} P^{\text{diss}}_k(T_E)$$

(5.7)
Figure 5.9 displays $D_i(T_E)$ for $i=0-5$ as a function of the excitation energy $T_E$. The loss for even numbers of hydrogen clearly dominates over the odd ones, entirely in line with the experimental data (see figure 5.2). In order to simulate the mass spectra, an excitation energy distribution has to be implemented in the model. The branching ratios for the loss channel corresponding to the $i^{th}$ hydrogen loss $A_i$ can then be determined using

$$A_i = \int D_i(T_E)P(T_E)dT_E.$$  \hspace{1cm} (5.8)

$P(T_E)$ is the normalized vibrational energy distribution of the system. Under the assumption that the intramolecular vibrational energy redistribution quickly transforms electronic excitation into vibrational energy, it is appropriate to extract an approximation of $P(T_E)$ from an Auger electron spectrum. Because the electronic orbital structure is similar for aromatic hydrocarbons, we use the well-investigated Auger electron spectrum of benzene ([37],fig 7).

To obtain the excitation energy distribution for the formation of dications by 285 eV photons, 3.7 eV was added to account for the additional excitation energy which is deposited by populating the $\pi^*$ orbital in the $C(1s) \rightarrow \pi^*$ transition (fig. 5.1). To simulate the mass spectra for other photon energies, the excitation energy distribution was shifted correspondingly. For instance, for 293.5 eV the excitation energy distribution was up shifted by 8.5 eV, with respect to the 285 eV photon case.

For comparison with the experimental data synthetic spectra were generated by using Gaussian based functions:

$$G(x) = \Sigma(A_i + 0.25A_{i-1})e^{-\frac{(x-\mu_i)^2}{2\sigma^2}}$$  \hspace{1cm} (5.9)

with for $\mu_i$ the molecular mass-over-charge ratio and for $\sigma$ the standard deviation deduced from the experimental peak widths. The term $0.25A_{i-1}$ contains the 20 \% abundance of one mass unit heavier coronene isotopes present in the target.

Figure 5.10 compares the experimental dication mass spectra at 285, 288, 290.5, and 293.5 eV photon energies. The simulations show similar trends as the experimental data: a strong preference for even H loss channels and a gentle shift towards higher dehydrogenation with increasing photon energy. However, the loss of 4 and 6 H is slightly overestimated in the simulations. Note that the competition of other channels than H loss increases with higher degrees of dehydrogenation. These competing processes are not included in the model, possibly leading to an overestimation of higher dehydrogenation states.

5.4 Conclusion

We have investigated the response of gas-phase coronene cations $C_{24}H_{12}^+$ upon soft X-ray photoabsorption around the carbon K-edge. Inner shell excitation or ionization leave a carbon 1s vacancy, which is subsequently filled in an Auger type
process, leading to the formation of intermediate $C_{24}H^{2+}_{12-i}$ and $C_{24}H^{3+}_{12}$ cations. The Auger mechanism and (below threshold) the excitation into unoccupied molecular orbitals leaves these intermediates internally hot, leading to swift deexcitation, predominantly by means of hydrogen loss. Density functional theory was employed to determine the dissociation energies for the successive neutral H loss steps. A statistical cascade model based on these dissociation energies was found to reproduce the experimentally obtained dehydrogenation states well. The model is however limited to neutral H or $H_2$ loss from coronene dications and does not explicitly include charge separation processes, predicted to occur for higher charge states. The experimental data strongly indicates, that the intermediate $C_{24}H^{3+}_{12}$ trication is subject to a competition of neutral H loss and asymmetric fission leading to $H^+$ loss, with the neutral channel dominating and the fission channel being strongest for internally hot parent ions.

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Figure 5.10: Zoom-in on the experimental mass spectra (dark blue lines) around the dication feature for photon energies 285, 288, 290.5, and 293.5 eV, compared with simulated mass spectra (light blue).

5.5 References


