Infrared spectroscopy of mass-selected aromatic and diamondoid molecular ions: a laboratory quest for the organic inventory in space
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Two infrared (IR) broad emissions at 3.43 and 3.53 µm from the dusty cocoons of the infant stars HD 97048 and Elias 1 show a remarkable agreement with calculated CH- and CH₂-group vibrational absorption features of large, neutral molecular (nano)diamondoids with tetrahedral symmetry (T₄). In this chapter, two of the smallest species of the diamondoid molecular family, diamantane and triamantane, are studied by IR multiple-photon dissociation (IRMPD) spectroscopy using the free electron laser FELIX. Chemical ionization of the neutral parent diamondoid molecule in a Paul-type RF ion trap is accompanied by H-atom loss, forming a stable closed-shell carbocation in both cases (diamantyl⁺ and triamantyl⁺). Comparing the IRMPD spectra with harmonic DFT calculations permits to determine the structures of the species isolated in our ion trap. For instance, the comparisons suggest that H-atom abstraction occurs on a tertiary carbon (CH group) rather than on a secondary carbon (CH₂ group), as also indicated by the calculated relative energies of the various isomers. Using available experimental data and further DFT calculations, we extend our spectroscopic study to include the neutral forms of adamantane, diamantane and triamantane. Substantial differences are observed between the IR spectra of neutral and ionic species. In the ions, the 3 µm CH stretching modes become much weaker, while the other mid-IR modes strongly gain in intensity. An intense band centered at 1200 cm⁻¹ due to a CH/CH₂ bending mode appears to be characteristic of the dehydrogenated cationic species. Finally, the intensities of the low frequency modes (≤ 900 cm⁻¹) associated with carbon cage deformations appear to be most sensitive to the ionization and dehydrogenation state of the diamondoids.

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5.1 Introduction

Diamondoid molecules are closed structures made of $sp^3$-hybridized tetrahedral carbon atoms, and hydrogen atoms terminating the peripheral dangling bonds (see Fig. 2.3). The carbon frame of these molecules resembles the face-centered cubic diamond lattice (the diamond carbon cage), and therefore, these species exhibit diamond-like properties such as rigidity, strength, and thermodynamic stability (Dahl et al. 2003). The simplest diamondoid, consisting of a single diamond carbon cage, adamantane ($C_{10}H_{16}$), has been first synthesized by Prelog & Seiwerth (1941), but a much more efficient synthesis was discovered by Schleyer in 1957. Diamantane ($C_{14}H_{20}$) and triamantane ($C_{18}H_{24}$) consist of 2 and 3 face-fused diamond cages, respectively. Like adamantane, they can be synthesized in solution by carbocation-mediated thermodynamically controlled equilibration reactions (Farooq et al. 1988). Higher diamondoids cannot be synthesized by these methods (Fărcașiu et al. 1977, Osawa et al. 1980). Recently, Dahl et al. (2003) succeeded in isolating pure samples of higher diamondoid molecules from crude oil (Lin & Wilk 1995). The samples isolated range from adamantane to undecamantane and permit the study of the spectra and structures of this family of molecules.

Due to their remarkably high stability, the presence of diamond-like species in different regions of space has been hypothesized for several decades (see e.g. Saslaw & Gaustad 1969). In 1987, Lewis et al. reported the first extraction of nanometer-sized diamonds from meteorites supporting the suggested presence of these molecules in the interstellar medium (ISM). Furthermore, two broad emission features centered at 3.43 $\mu$m and 3.53 $\mu$m (about 2830 and 2915 cm$^{-1}$) observed towards two Herbig stars, HD 97048 and Elias 1, have been attributed to large gas-phase diamondoid molecules or nanoparticles (Guillois et al. 1999). In addition, a broad absorption feature observed towards several sources at 3.47 $\mu$m (2880 cm$^{-1}$) has been suggested to indicate the presence of these molecules in ices present in dense clouds (Brooke et al. 1996). However, other assignments for this feature have also been proposed (Dartois & d’Hendecourt 2001) and these are now considered to be more likely.

While it was originally considered that only diamondoid nanocrystals larger than about 50 nm could be the carriers of the two emission features at 3.43 $\mu$m and 3.53 $\mu$m (Chen et al. 2002, 2003, Jones et al. 2004), the IR spectra of molecular diamondoid species revealed that these much smaller higher diamondoids could also be responsible for the two emission features (Pirali et al. 2007).

Here, we consider the experimental infrared spectra of cationic diamondoid molecules. Based on computed optical properties, Bauschlicher and coworkers concluded that cationic species could also contribute to the observed emission signal (Bauschlicher et al. 2007). These calculations indicate, however, that the band positions in the 3 $\mu$m spectral range are similar for neutral and cationic species. This makes it difficult to distinguish between neutral and ionic diamondoids in interstellar emission spectra. Indeed, to date only two bands at 3.43 $\mu$m and 3.53 $\mu$m have been suggested to be due to diamondoid species. For both the cations and the neutrals, these modes involve symmetric and antisymmetric hydrogen stretching motions of the $CH_2$ and $CH$ groups on the edges and surfaces of the diamondoid molecules. All other IR active modes are about ten times weaker than
the CH stretching modes in neutral diamondoids, but this is not the case for their cations (Bauschlicher et al. 2007).

In addition, the photo-physical processes underlying the interstellar emission remain poorly understood. Similar to diamond crystals and unlike PAH molecules, diamondoids show very weak absorption bands in the UV spectral range (Bauschlicher et al. 2007), which are moreover close to their ionization potentials. Emission features arising from these molecular species are therefore expected to be observable only when the UV radiation field is intense, which suggests in turn that cationic species might be abundant in those regions. We note further that the ionic forms of diamondoids, and especially their carbocation forms as studied in this work, are also well known as the intermediates in the synthesis of the lower diamondoids (Olah et al. 1985, Farooq et al. 1988). Moreover, they were shown to be important intermediates in the site-specific functionalization of diamondoid molecules (Fokin et al. 2005).

Several spectroscopic studies of diamondoid species have been reported to determine their structures, see e.g., Filik et al. (2006), who studied the Raman spectra of diamondoids as large as heptamantane. IR spectra have been obtained using attenuated total reflection (ATR) spectroscopy and compared with density functional theory (DFT) calculations at different levels of theory (Oomens et al. 2006a). Gas-phase emission spectra of adamantane, diamantane and triamantane have been recorded in the 3 µm region using an experimental set-up described in Pirali & Vervloet (2006). Chiral properties of helical diamondoids have been evidenced by circular dichroism spectroscopy in the optical and infrared (Schreiner et al. 2009). Recently, accurate ionization potentials of the first five diamondoid molecules (adamantane, diamantane, triamantane, tetramantane and pentamantane) in the gas phase have been obtained using VUV radiation from the Bessy synchrotron (Lenzke et al. 2007). Several x-ray studies provided information on the HOMO-LUMO gap of diamondoid species (Willey et al. 2006), which is of interest for semiconductor research. Finally, various computational studies have investigated the properties of diamondoid molecules, see e.g. Yan et al. (2003), Filik et al. (2006), Bauschlicher et al. (2007).

Experimentally very little is known about the gas-phase structure and properties of cationic diamondoids. Polfer et al. (2004) reported the IR spectrum of the gas-phase adamantyl cation (C$_{10}$H$_{15}$), i.e. the dehydrogenated adamantane cation, constituting the first experimental IR spectrum of a gas-phase cationic diamondoid species, which allowed to determine the structure of the most stable isomer. The hydrogen atom can be detached from two distinct C atoms, giving rise to two isomeric structures for the adamantyl cation (Yan et al. 2003). The IR spectrum showed good agreement with the calculated spectrum of the lowest energy isomer. Relative energies of the cationic species in solution have been studied because of their relevance in the synthesis of diamondoid molecules and their derivatives (Fokin et al. 2005, 2000).

In this work, we record the InfraRed Multiple Photon Dissociation (IRMPD) spectra of diamantyl and triamantyl cations using the experimental methods of Polfer et al. (2004). We present a spectroscopic comparison of the infrared features of the neutral and carbocationic species.
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5.2 Laboratory Methods

5.2.1 Experiments

The IRMPD spectra of the diamantyl and triamantyl cations were recorded using the free electron laser FELIX (Oepts et al. 1995) in a quadrupole ion trap coupled to a time-of-flight mass spectrometer (R.M. Jordan, California). This instrument has been used previously to record IRMPD spectra of several cationic polycyclic aromatic hydrocarbons (PAHs) (Oomens et al. 2003b) and is described in Chapter 2. The spectra presented here have been obtained applying experimental methods similar to those used to record the infrared spectrum of the adamantyl cation (Polfer et al. 2004). Here we give only a brief description.

Diamondoid molecules possess only very weak electronic absorption bands, which are located at energies close to the ionization potential (IP) (Bauschlicher et al. 2007). The IPs of the five smallest neutral diamondoid molecules have been experimentally determined (Lenzke et al. 2007) and the values for adamantane, diamantane and triamantane are 9.23 eV, 8.80 eV and 8.57 eV, respectively. While two 193 nm (6.4 eV) photons from a ArF excimer laser surpass these energies, ArF photo-ionization of diamondoid species is not attained as these species do not possess low-lying electronic states and consequently, the first ArF photon is never absorbed. In case of PAHs, these species possess strong $\pi-\pi^*$ transitions, and ArF laser irradiation can effectively remove an electron by the sequential absorption of two 6.4 eV photons.

As used previously for adamantane (Polfer et al. 2004), efficient ionization of diamondoids can be achieved via charge transfer (CT) from cationic species with a high ionization potential (IP). Benzoic acid is therefore vaporized together with the diamondoid molecule in the ion trap chamber, which produces abundant cationic UV photofragments (Oomens et al. 2003a, 2004) (in particular the benzoyl cation at $m/z$ 105) with IPs higher than those of the diamondoid molecules under study. Storing the benzoyl cation in the trap for typically 100 ms produces abundant diamondoid ions by charge transfer ionization.

Diamantane and triamantane vapor are produced by placing the solid samples in an oven kept at a temperature of about 44°C and 64°C, respectively. All species lower in mass than the parent diamondoid (benzoic acid, its fragments and diamondoid fragments) are axially ejected from the trap by increasing the RF voltage for few ms. It is known that diamondoid cations may undergo rapid hydrogen atom loss leading to a stable closed-shell molecular species. We therefore expect to have isolated diamantyl and triamantyl cations rather than the diamantane and triamantane radical cations, although the mass resolution of the ion trap/TOF mass spectrometer is not sufficient to confirm this from the mass spectrum. However, analysis of the IRMPD spectra obtained confirms the identity of the ions as the dehydrogenated diamondoid cations, similar to what was observed for adamantane (Polfer et al. 2004).

The mass-selected ion cloud is irradiated with the intense FELIX IR beam, which is sharply focused in the center of the quadrupole trap. When the wavelength of FELIX is in resonance with an IR active mode of the ion, multiple photon absorption occurs, mediated by intramolecular vibrational redistribution (IVR), which is very efficient for
5.2 Laboratory Methods

Figure 5.1 – Comparison of B3LYP computed spectra for the D1 isomer of the diamantyl cation. Increasing the basis set beyond 6-31G(d,p) does not noticeably change the harmonic frequencies. The red trace represents a 20 cm$^{-1}$ FWHM Gaussian convolution of the stick spectra. Note that the harmonic frequencies have not been scaled in this figure.

Such large species. Tens to hundreds of IR photons are thus absorbed by a single molecule, raising its internal energy to above the dissociation threshold. Upon resonance, loss of CH, $\text{C}_2\text{H}_4$, $\text{C}_3\text{H}_6$ and $\text{C}_4\text{H}_8$ is observed using the TOF mass analyzer. Loss of $\text{C}_2\text{H}_4$ is the most abundant dissociation channel and the final IRMPD spectra of the parent molecules are obtained by co-adding the intensities of all photofragments as a function of wavelength of the FEL. The wavelength of the FEL is calibrated against a grating spectrometer and the relative fragmentation intensities are corrected for slowly decreasing FEL power towards short wavelengths. Because the spectra are obtained through multiple photon excitation, the experimental band centers are expected to be slightly red-shifted compared to a linear absorption experiment (Oomens et al. 2003b). The shift depends on the (unknown) anharmonicity of the vibrational modes involved in the excitation process, but is usually on the order of less than 10 cm$^{-1}$.

IR spectra of the carbocations of adamantane, diamantane and triamantane are compared with those of the corresponding neutral molecules in the gas phase. To this end, the gas-phase spectrum of adamantane has been taken from the NIST webbook*. The 600–3100 cm$^{-1}$ spectrum of gas-phase diamantane has been recorded here using an IFS125 Bruker interferometer. The room-temperature vapor of diamantane was leaked into a

*webbook.nist.gov
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150-m absorption pathlength cell (White type arrangement of the multipass optics). The cell has been baked several days before injecting the sample and the interferometer was continuously evacuated during spectrum acquisition to limit the intense absorption of water vapor lines. Because of its low vapor pressure at room temperature, we could not record the gas-phase spectrum of triamantane with the same technique. Therefore, the triamantyl cation spectrum is compared to the solid state spectrum of neutral triamantane recorded using attenuated total reflection (ATR) spectroscopy (Oomens et al. 2006a).

5.2.2 DFT Calculations

The various isomeric structures of the diamantyl and triamantyl cations were optimized using density functional theory (DFT) computations as implemented in Gaussian03. All calculations employed the B3LYP functional and the 6-31G(d,p) basis set to optimize the structures and compute the IR spectra. Similar levels of theory have been successfully applied to similar-sized hydrocarbon species including diamondoids (Fokin et al. 2000, Filik et al. 2006, Oomens et al. 2006a). In addition, B3LYP calculations on the lowest energy isomer of the diamantyl carbocation show that increasing the basis set beyond 6-31G(d,p) does not lead to an appreciable change in the calculated vibrational spectrum (see Fig. 5.1). All carbocation structures are assumed to possess a closed-shell electronic structure. Calculated frequencies are scaled by 0.975 for the mid-IR vibrational modes and by 0.95 for the CH stretching modes to account for the different anharmonicities of these vibrational modes.

Computed spectra of the three isomers of the diamantyl cation are shown in Fig. 5.3. The three isomers (structures D1, D2, and D3) of the diamantyl cation arise from H-atom abstraction at three distinguishable sites. All secondary carbon atoms (i.e. CH groups) are symmetrically equivalent in diamantane and H-abstraction from one of them forms isomer D3. There are two symmetrically distinguishable tertiary carbon atoms (i.e. CH groups) in diamantane: one where the tertiary C atom is connected to three CH2 groups (D2) and one where the tertiary C-atom is connected to two CHs and one CH2 (D1). Calculations were also performed for the triamantyl cation, which possesses 7 isomers: 4 isomers result from H-loss from a tertiary carbon and 3 isomers from H-loss from a secondary carbon. We note here that the relative energies found for the different tertiary carbon dehydrogenated isomers compare well to those reported previously in Fokin et al. (2005). The structures of the isomers are shown in Fig. 5.4.

5.3 Spectra and Structures

5.3.1 Energetics of H-atom Loss

While the mass resolution of our ion trap/TOF mass spectrometer is insufficient to determine whether the parent ion is the diamondoid radical cation or the corresponding closed-shell dehydrogenated cation, the IR spectra (vide infra) strongly suggest that the dehydrogenated cation (carbocation) is formed in the experiment. This is similar to what has been
observed in the experiments on ionized adamantane (Polfer et al. 2004), where the resolution was just sufficient to observe the difference. In that paper, a rationale was given for why the adamantyl cation is observed rather than the adamantane radical cation and we believe that a similar reasoning applies here. Aliphatic hydrocarbons have a narrow energy gap between ionization potential (IP) and appearance energy (AE) of the singly dehydrogenated cation. For instance, according to the NIST Chemistry Webbook, the difference $AE - IP$ amounts to 1.1 eV for ethane and to only 0.6 eV for propane, while the IPs are on the order of 11 eV. For adamantane, the difference $AE - IP$ was estimated to be around 1.4 eV (Polfer et al. 2004). Any excess energy deposited in a non-resonant ionization scheme, such as the chemical ionization used here (but also broadband VUV ionization as may occur in circumstellar environments), will thus likely result in the singly dehydrogenated ion (carbocation).

To further exclude the possibility that the radical cation diamondoid is responsible for the spectra observed instead of the carbocation, we compared the experimental spectra with computed spectra for the diamondoids in their radical cation form (see Fig. 5.2). The adamantane cation spectrum was previously calculated at the $C_{3v}$ structure (Fokin et al. 

\[\text{Figure 5.2} - \text{Comparison of the experimental diamondoid spectra (black) with calculated spectra (blue) for the diamondoids in their radical cation form. The poor match observed for all three species strongly suggests that the radical cations are not produced in our experiment.}\]
Figure 5.3 – IRMPD spectrum of the diamantyl cation (gray trace in all panels) compared with DFT calculated spectra for the three isomers of the diamantyl cation. The stick spectra (black) were convoluted with a 20 cm\(^{-1}\) Gaussian line shape (red trace). The isomeric structures are shown where the H-atom is abstracted from the highlighted C-atom and where all H-atoms have been omitted for clarity.

Although their HOMOs are known to be non-degenerate (Fokin et al. 2000), it was necessary to relax the symmetry of the diamantane and triamantane radical cations to \(C_s\) to mitigate difficulties in the SCF convergence and to remove imaginary frequencies. Figure 5.2 clearly shows that no spectral match is found between the radical cation calculated spectra and the experimental data. In combination with the accurate mass determination for adamantane, the AE versus IP considerations given above, and the spectral match with the closed-shell carbocation structures (\textit{vide infra}), this strongly suggests that the diamondoid ions are observed in their dehydrogenated form. This forms the basis for the discussion that follows.

5.3.2 IRMPD Spectrum and Structure of the Diamantyl Cation

The experimental IRMPD spectrum obtained using the diamantane sample is shown in Fig. 5.3. As was the case for the adamantyl cation (Polfer et al. 2004) and for the reasons given in the previous section, we expect that the spectrum observed is that of the dehydrogenated diamantane cation, i.e. the diamantyl cation \((C_{14}H_{19}^+)\), rather than that
5.3 Spectra and Structures

Table 5.1 – Observed and calculated band centers (in cm$^{-1}$) of the diamantyl cation.

<table>
<thead>
<tr>
<th>DFT frequency</th>
<th>IR int</th>
<th>IRMPD frequency</th>
</tr>
</thead>
<tbody>
<tr>
<td>601</td>
<td>23</td>
<td>594</td>
</tr>
<tr>
<td>650</td>
<td>10</td>
<td>653</td>
</tr>
<tr>
<td>703</td>
<td>8</td>
<td>726</td>
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<tr>
<td>722</td>
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<td>842</td>
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<tr>
<td>1462</td>
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<td>1474</td>
</tr>
<tr>
<td>1489</td>
<td>21</td>
<td>1474</td>
</tr>
</tbody>
</table>

1 Scaled by 0.975.
2 Units of km/mol.

of the diamantane radical cation (C$_{14}$H$_{20}^+$). For the radical cation diamondoids, there is some doubt as to where the charge is localized (Bauschlicher et al. 2007), since there are several distinct CC bonds which can be ionized (note that the charge is not delocalized as in PAHs). In the dehydrogenated diamondoid cations under study here, this is not the case: the charge is localized on the carbon atom where the H-atom is removed, forming a carbocation. However, there are multiple isomers for each of the dehydrogenated diamondoid cations, as there are distinct carbon atoms from which the H-atom can be abstracted. These isomers are classified as C1 or C2 type depending on whether the H-atom is removed from a tertiary (CH) or a secondary (CH$_2$) carbon, respectively.

While for adamantane, all CH moieties as well as all CH$_2$ moieties are equivalent based on symmetry arguments, this is not the case for diamantane. Here, two symmetrically distinct tertiary carbons exist, while all secondary carbon atoms are equivalent, which results in three isomers for the diamantyl cation, two of C1 type and one of C2 type. These isomers are labelled as D1, D2 and D3 and their structures are shown in Fig. 5.3, where all H-atoms have been omitted for clarity and the dehydrogenated C-atom is highlighted.

While the structural differences between the different isomers of the diamantyl cation may appear to be marginal, their calculated spectra present clear differences, which can be used to reliably assign the experimental spectrum. Figure 5.3 compares the experimental
Table 5.2 – Relative electronic energies for the different isomers of the adamantyl, diamantyl and triamantyl cations at the B3LYP/6-31G(d,p) level of theory.

<table>
<thead>
<tr>
<th>#</th>
<th>Sym</th>
<th>C1/C2</th>
<th>ΔE eV</th>
<th>ΔE kJ/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>adamantyl cation (C_{10}H_{15}^+)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A1</td>
<td>C_{3v}</td>
<td>C1</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>A2</td>
<td>C_s</td>
<td>C2</td>
<td>0.492</td>
<td>47.5</td>
</tr>
<tr>
<td>diamantyl cation (C_{14}H_{19}^+)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>D1</td>
<td>C_s</td>
<td>C1</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>D2</td>
<td>C_{3v}</td>
<td>C1</td>
<td>0.133</td>
<td>12.8</td>
</tr>
<tr>
<td>D3</td>
<td>C_1</td>
<td>C2</td>
<td>0.511</td>
<td>49.3</td>
</tr>
<tr>
<td>triamantyl cation (C_{18}H_{21}^+)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>T2</td>
<td>C_s</td>
<td>C1</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>T1</td>
<td>C_1</td>
<td>C1</td>
<td>0.037</td>
<td>3.6</td>
</tr>
<tr>
<td>T4</td>
<td>C_s</td>
<td>C1</td>
<td>0.103</td>
<td>10.0</td>
</tr>
<tr>
<td>T3</td>
<td>C_s</td>
<td>C1</td>
<td>0.138</td>
<td>13.3</td>
</tr>
<tr>
<td>T5</td>
<td>C_1</td>
<td>C2</td>
<td>0.490</td>
<td>47.3</td>
</tr>
<tr>
<td>T7</td>
<td>C_s</td>
<td>C2</td>
<td>0.526</td>
<td>50.8</td>
</tr>
<tr>
<td>T6</td>
<td>C_1</td>
<td>C2</td>
<td>0.576</td>
<td>55.6</td>
</tr>
</tbody>
</table>

1 C1/C2: H-loss from tertiary/secondary C-atom.

IR spectrum with the calculated spectra of each of the three isomers. It is immediately seen that the match with isomer D1 is much better than with any of the other isomers; Table 5.1 compares the experimental band centers with the band centers resulting from a convolution of the D1 computed spectrum with a 20 cm\(^{-1}\) FWHM Gaussian band profile. In the D1 isomer of the diamantyl cation, the H-atom is lost from one of the six equivalent tertiary carbon atoms that form a ‘belt’ fusing the two diamondoid cages.

For structure D2, where the H-atom is lost from one of the two tertiary carbons at the apical positions of the molecule, the mismatch with the experimental spectrum is especially evident in the 1200–1400 and the 700–900 cm\(^{-1}\) regions. The calculated spectrum for D3 exhibits bands roughly at the right frequencies, but with very different relative intensities, so that the match with the experimental spectrum is not nearly as good as for D1.

The calculated relative energies for the three isomers as listed in Table 5.2 support the assignment of the IRMPD spectrum to D1, since isomers D2 and D3 are higher in energy than D1 by 0.1 eV and 0.5 eV, respectively. In addition, from solution-phase reactivity studies, the belt position H-atoms are known to be more labile than the apical position H-atoms (Olah et al. 1985).

The assignment to structure D1 is analogous to that identified for the adamantyl cation previously (Polfer et al. 2004, Yan et al. 2003) using IRMPD spectroscopy and DFT cal-
calculations, respectively. There, it was concluded that H-atom loss to form the closed-shell carbocation occurs preferentially from a tertiary carbon, rather than from a secondary carbon. In general, calculations predict that in the gas phase the tertiary carbocations are more stable than the secondary ones by typically 0.5 eV.

### 5.3.3 IRMPD Spectrum and Structure of the Triamantyl Cation

Given our observations for adamantane (Polfer et al. 2004) and diamantane, it is likely that ionization of triamantane is accompanied by rapid H-atom loss resulting in the closed-shell triamantyl cation (C$_{18}$H$_{23}^+\cdot$). Not unexpectedly, the situation becomes more complicated for the triamantyl ion, as seven distinct isomers of the triamantyl cation exist (see Fig. 5.4). Four isomers are obtained by H-atom loss from a tertiary carbon atom (C1 type isomers) and three by H-atom loss from a secondary carbon atom (C2 type isomers). The four C1 type isomers (labelled T1, T2, T3, T4) have energies within 0.1 eV of each other, while all C2 type isomers (isomers T5, T6, T7) are less stable by around 0.5 eV (see Table 5.2). This energy difference is thus analogous to that found for C1 and C2 type isomers of the adamantyl and diamantyl cations. Of the C1 isomers, T1 and T2 are computed to be substantially more stable than T3 and T4. Although the ions in the trap are not necessarily in thermodynamic equilibrium, a simple Boltzmann distribution at the temperature of the oven would yield a population of T1 around 30% of that in T2, while the population of T3 and T4 would be less than 3%.

The experimental spectrum recorded for the triamantyl cation shown in the lower right panel of Fig. 5.4 displays fairly broad and partly unresolved features. DFT calculated energies for the seven isomers are listed in Table 5.2 and their spectra are shown in the separate panels of Fig. 5.4. The increased molecular complexity and the low symmetry of the systems gives rise to congested spectra, as can be appreciated from the stick spectra. The solid red lines represent 30 cm$^{-1}$ FWHM Gaussian convolutions of the stick spectra. These congested spectra, in combination with a possible mixture of isomers and the higher temperature of the oven are believed to give rise to the fairly unresolved spectrum observed for this species. In the last panel, the experimental IRMPD spectrum is compared with a Boltzmann-weighted sum of the spectra of the C1 type isomers T1 – T4. Despite the low experimental resolution obtained, the features near 1465 and 1195 cm$^{-1}$ appear to be well reproduced by theory. In addition, the shoulder around 1290 cm$^{-1}$ and the broad feature extending from 1000 to 1200 cm$^{-1}$ appear to have a reasonable counterpart in the convoluted theoretical spectra. On the other hand, toward the long wavelength end of the spectrum, the experiment shows more absorption than the convoluted theoretical spectra. Perhaps a higher-than-thermal abundance of isomers T3 and T4 gives rise to this increased absorption. In conclusion, while the present spectrum does not allow to truly identify the contributing isomers, the spectrum shows features that appear to be typical of diamondoid carbocations, as will be discussed further below.
Figure 5.4 – Calculated IR spectra for the 7 isomers of the triamantyl cation represented as stick spectra (black) and 30 cm\(^{-1}\) Gaussian line shape convolutions (red trace). The experimental IRMPD spectrum of the triamantyl cation is shown in the last panel together with the weighted average spectrum of the most stable isomers \(T_1 - T_4\). The structures are also shown, where the H-atom is abstracted from the highlighted C-atom and where all H-atoms have been omitted for clarity.
5.4 Spectral Analysis

The IR spectra of dehydrogenated cationic diamondoids recorded here are compared to their neutral diamondoid counterparts. The three cation spectra are also compared to each other to reveal spectral characteristics for this class of cationic species.

5.4.1 IR Spectra of Adamantane and the Adamantyl Cation

Figure 5.5 compares the gas-phase spectra of neutral adamantane (taken from the NIST Chemistry Webbook) and cationic adamantyl (taken from Polfer et al. 2004) along with their DFT calculated spectra. The calculated spectrum of neutral adamantane reproduces the experimental one reasonably well. Small differences in terms of both frequencies and relative intensities are observed for the 3 µm stretching modes, which may be due to strong anharmonic couplings between these modes not accounted for in the calculations (Pirali et al. 2007). In addition, the frequency of the CH\textsubscript{2} scissor mode ($\nu_{23}$) near 1450 cm\textsuperscript{-1} is substantially overestimated by the DFT calculation; similar shifts for this particular vibration were observed in the IR spectra of a series of higher diamondoids (Oomens et al. 2006a).

Due to its lower symmetry, the adamantyl cation (C\textsubscript{3v}) shows a higher density of IR active transitions than neutral adamantane (T\textsubscript{d}). Nonetheless, the CH\textsubscript{2} scissor mode observed around 1450 cm\textsuperscript{-1} is recognized in both species. Also, the CH\textsubscript{2} rocking modes located near 1100 cm\textsuperscript{-1} and C-C stretching modes near 950–1000 cm\textsuperscript{-1} are found in the same spectral region.

On the other hand, one notices large differences in the intensities of the CH stretching modes relative to the other mid-IR modes in the spectra of the two species. This is best appreciated when comparing the scales on the ordinates of the graphs in Fig. 5.5. Going from the neutral to the cationic system, the calculated intensities of the mid-IR modes
increase by a factor of around 2 - 5, but the CH stretching modes are calculated to become 20 - 50 times weaker. In the calculated spectra, the most prominent peak of the 3 µm region is shifted toward higher frequencies by less than 50 cm$^{-1}$. Another striking difference between the adamantyl and adamantane spectra concerns the band located near 1200 cm$^{-1}$, which is due to CH$_2$ bending vibrations; this band appears as strong as the CH$_2$ scissor modes for the adamantyl cation, but is completely absent in the neutral adamantane spectrum. Similarly in the low frequency region, the cage deformation modes located at frequencies lower than 900 cm$^{-1}$ appear to be especially sensitive to the structure changes between adamantane and the adamantyl cation. For example, the band located near 800 cm$^{-1}$ in the neutral spectrum is blue-shifted by about 50 cm$^{-1}$ for the adamantyl cation. A strong enhancement of intensity is also observed here.

**Figure 5.6** – Comparison of the gas-phase absorption spectrum of neutral diamantane and the IRMPD spectrum of the diamantyl cation. The sharp features in the 1500 - 1600 cm$^{-1}$ range of the spectrum of neutral diamantane are due to residual water vapor in the absorption cell. Calculated spectra for both species are shown along with the experimental spectra.

### 5.4.2 IR Spectra of Diamantane and the Diamantyl Cation

The gas-phase spectra of neutral diamantane and the diamantyl cation are compared in Fig. 5.6. The calculated spectrum of neutral diamantane is in relatively good agreement with the experimental gas-phase spectrum. Some residual water vapor lines due to the $\nu_2$ bending mode are observed in the 1500-1600 cm$^{-1}$ region. As for adamantane, the calculated frequencies of the CH stretching modes around 2900 cm$^{-1}$ match the experimental bands relatively well, while the relative intensities are not well predicted. As for adamantane, strong anharmonic couplings between the closely spaced CH stretching modes of equal symmetry may somewhat compromise the results of the harmonic frequency calculations.

In the mid-IR region, the calculations reproduce the gas-phase spectrum of neutral diamantane reasonably well, both in terms of frequencies and intensities (note that the
Figure 5.7 – Comparison of the experimental and calculated spectra of neutral triamantane (upper panel) and triamantyl cation (lower panel).

rising background <1000 cm\(^{-1}\) is an experimental artefact). This is somewhat in contrast with the ATR spectrum of diamantane published earlier (Oomens et al. 2006a), where the relative intensities of several mid-IR modes showed large differences in comparison with the DFT calculations. Particularly in the 1300–1400 cm\(^{-1}\) spectral range, the CH bending modes showed intensities which were about ten times larger in the ATR spectrum than in the computed spectrum (and in the current in the gas-phase spectrum). Also the lower-frequency bands assigned to deformation modes of the carbon frame and CC stretching modes (at about 650 cm\(^{-1}\), 850 cm\(^{-1}\) and 950 cm\(^{-1}\)) are hardly observable in the gas-phase spectrum, as predicted by DFT, while they were strong bands in the ATR spectrum. We ascribe these discrepancies to unknown matrix effects in the ATR experiments. The main differences between the gas-phase spectra of diamantane and the diamantyl cation are similar to those observed for the adamantane versus adamantyl cation spectra. In the 3 \(\mu\)m region, the vibrational bands of the diamantyl cation are calculated to appear at slightly higher frequencies (shift of about 50 cm\(^{-1}\)) with an intensity that is around ten times lower than that of neutral diamantane.

In the 600–1600 cm\(^{-1}\) spectral range, the intensities of the dehydrogenated cation bands are more intense than for neutral diamantane. The intense 1200 cm\(^{-1}\) band of the diamantyl cation, which is mainly due to a CH/CH\(_2\) bending mode is as intense as the CH\(_2\) scissoring modes between 1400 and 1500 cm\(^{-1}\), while no band is observed here in the neutral diamantane spectrum. As for the adamantane versus adamantyl cation comparison, the low frequency part of the spectrum shows large differences. The 800 cm\(^{-1}\) deformation modes of the neutral are shifted by about 50 cm\(^{-1}\) as compared to the calculated and experimental spectra of the diamantyl cation. An intense mode centered at 600 cm\(^{-1}\) observed in the diamantyl cation spectrum is absent from the neutral diamantane spectrum.
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5.4.3 IR Spectra of Triamantane and the Triamantyl Cation

Due to the low vapor pressure of triamantane, a gas-phase absorption spectrum of the neutral species could not be obtained and hence, Fig. 5.7 shows the neutral triamantane ATR spectrum from Oomens et al. (2006a) together with the calculated DFT spectrum. The relative intensities of several mid-IR modes are observed to be substantially higher than in the DFT calculated spectrum and we assume that this is again an artefact of the condensed-phase nature of the ATR method, as was clearly demonstrated for diamantane. The gas-phase IRMPD spectrum of the triamantyl cation spectrum is reproduced in the lower panel of Fig. 5.7. Because of the rather unresolved appearance of the IRMPD spectrum, a detailed comparison with the neutral triamantane spectrum cannot be performed. Nevertheless, the trends observed in the spectral comparisons of adamantane versus the adamantyl cation and diamantane versus the diamantyl cation appear to be similar here.

Several mid-IR modes have the same frequencies and intensities in the neutral and dehydrogenated cation spectra. The scissoring modes of the triamantyl cation are observed in the 1500 cm\(^{-1}\) spectral region in the broad IRMPD spectrum. The CH bending modes around 1300 cm\(^{-1}\) are also distinguishable in the IRMPD spectrum and fall around the same frequency as in neutral triamantane. The spectral information that can be extracted from the 1000–1300 cm\(^{-1}\) range is limited as a consequence of the unresolved nature of the IRMPD spectrum, but we assume that absorption in the 1000–1100 cm\(^{-1}\) range is due to the C-C stretching modes.

The intense band centered around 1200 cm\(^{-1}\), which appears to be a diagnostic feature for the dehydrogenated cationic diamondoid molecules, is also present in the triamantyl cation spectrum. Again, this band is missing in the spectrum of neutral triamantane.

As for the smaller diamondoids investigated here, the 3 \(\mu\)m bands are calculated to be much weaker in the triamantyl cation spectrum than in the neutral spectrum.

5.4.4 General Features in the Cationic Diamondoid Spectra

Comparison of all three cationic spectra in Fig. 5.8 now provides an opportunity to identify absorption bands characteristic for this class of cationic species, so that they could eventually be searched for in interstellar spectra. The CH stretching modes in the 3 \(\mu\)m spectral range are not good candidates because these bands are weak and, more importantly, overlap severely with the CH stretching bands in the corresponding neutral diamondoids. In general, the band positions in the adamantyl and diamantyl cation spectra between 800 and 1600 cm\(^{-1}\) are very similar forming an interesting fingerprint for this class of cationic hydrocarbons. From the main infrared features of the triamantyl cation near 1195 and 1465 cm\(^{-1}\), its spectrum also appears similar, although clearly the resolution deteriorates as the systems increase in size, which is likely caused by the increasing spectral congestion. The intense band centered at 1200 cm\(^{-1}\) appears to be particularly characteristic in the spectra of the dehydrogenated cationic diamondoids and could be used to distinguish these species from their neutral counterparts. Note, however, that this band located at 8.33 \(\mu\)m falls close to two intense features in the emission spectra of PAHs at 7.8 \(\mu\)m and 8.6 \(\mu\)m. Differences in the spectra of the different cationic diamondoids are
mainly found in the far-IR range below 800 cm\(^{-1}\), where the absorption bands observed are primarily due to cage deformation modes. These modes are generally very delocalized over the molecules and it stands to reason that they would be different for differently sized members of the same class of species. Moreover, comparison with the neutral diamondoid spectra shows that these modes are also sensitive to the change in structure between neutral and carbocationic species.

**5.5 Conclusions**

Experiments employing chemical ionization of neutral diamondoid molecules indicate that ionization is accompanied by facile H-atom loss, leading to more stable closed-shell carbocations. This observation can be rationalized based on the close proximity of the ionization potential and the appearance energy of the singly dehydrogenated ion. One could imagine that this process might also play a role in UV dominated regions of the interstellar medium (ISM), where ionized diamondoid species, if present, occur as closed-shell dehydrogenated species rather than as radical cation species.
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IRMPD spectra were recorded for cationic diamantyl and triamantyl in the 500–1600 cm\(^{-1}\) spectral range. Comparing our IRMPD spectra with DFT calculations permitted to identify the structures of the most favored isomers for the diamantyl and triamantyl cations. As shown for the adamantyl cation (Yan et al. 2003, Polfer et al. 2004), the H-atom abstraction occurs preferentially on a tertiary carbon atom (CH) rather than on a secondary carbon atom (CH\(_2\)), which is also supported by the calculated relative energies of each of the isomers and moreover relates to the behavior in functionalization reactions of diamondoid molecules in solution (Fokin et al. 2005). Of the two isomers of tertiary carbocationic diamantyl, the IR spectrum identifies the lowest energy isomer as being present experimentally. In this isomer, the H-atom is abstracted from one of the 'belt' tertiary carbon atoms rather than from one of the apical carbon atoms, again in line with solution-phase chemistry (Olah et al. 1985, Fokin et al. 2005).

The DFT calculations also provide an assignment for most of the observed vibrational bands of the diamondoidyl cations. While the 3.43 \(\mu\)m and 3.53 \(\mu\)m emission bands are likely dominated by neutral diamondoids, a small contribution to these bands from cationic diamond-like molecules may be present (Bauschlicher et al. 2007). Hence, we compared the IR signatures in the 6–16 \(\mu\)m range of the neutral and carbocationic forms of adamantane, diamantane and triamantane. These are the smaller members of the diamondoid family. Substantial spectral differences were observed in terms of relative intensities of the IR active modes. The calculations suggest that the intensities of the CH stretch modes in the 3 \(\mu\)m region become more than ten times weaker in the dehydrogenated cationic species as compared to the neutrals, similar to what has been reported for radical cation diamondoids —as based on calculated spectra of several higher diamondoid species (Bauschlicher et al. 2007). The bands in the mid-IR range on the other hand, become substantially more intense upon going from the neutral to the cationic species. Overall, this reversal of relative intensities between the 3 \(\mu\)m and mid-IR ranges is similar to what is observed for polycyclic aromatic hydrocarbon (PAH) molecules (Pauzat et al. 1992, Szczepanski & Vala 1993). Finally, in this context, it is also of interest to note that the neutral diamondoid relative band intensities in the mid-IR range as calculated by DFT are well reproduced by the gas-phase diamantane spectrum recorded here, in contrast to previously recorded condensed-phase ATR spectra (Oomens et al. 2006a).