The infrared spectrum of the adamantyl cation

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Abstract

This Letter reports the gas phase infrared spectrum (500–1600 cm⁻¹) of the adamantyl cation (C₁₀H₁₅⁺), the dehydrogenated cation of adamantane. The experimental spectrum is in reasonable agreement with the recently reported theoretical spectrum for the 1-adamantyl isomer [G. Yan, N.R. Brinkmann, H.F. Schaefer, J. Phys. Chem. A 107 (2003) 9479]. An inclusion of vibrational anharmonicities in the linear absorption spectrum to yield a multiple-photon dissociation spectrum improves the theoretical to experimental fitting considerably. The prevalence of the 1-adamantyl isomer, as opposed to the 2-adamantyl isomer, can be rationalized by its lower calculated energy (0.49 eV).

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1. Introduction

Adamantane (C₁₀H₁₆) has a carbon cage structure (tetrahedral symmetry) and is the smallest member of the diamondoid chemical family. In diamondoids, carbon is sp³ hybridised (like in diamond) and the structure is terminated by hydrogens. This family includes diamantane (two cages, C₁₄H₁₈), trimantane (three cages, C₁₆H₂₂), and so on. Adamantane was first synthesized in 1957 by von Ragué Schleyer [1]. Diamondoids can also be isolated from petroleum, which has recently been shown for species up to the size undecamantane (11 cages) [2]. Diamondoids show remarkable rigidity, strength and thermodynamic stability, as well as interesting electronic properties [3], which may be of use in chemical, polymer and pharmaceutical applications.

Moreover, there has been substantial interest in the spectroscopic properties of this class of molecules from an astrophysical view-point. Not only have nanometer-sized ‘diamond-like’ molecules been found in meteorites [4], the occurrence of these compounds in the interstellar medium has also been suggested based on the observation of infrared absorption [5] and emission [6] bands around 3.5 μm (2880 cm⁻¹) in the spectra of protostars. This band has been assigned to the tertiary sp³ carbon (i.e. carbon bound to three carbon atoms) C–H stretching mode, but other explanations have also been put forward [7,8]. Further, evidence for the existence of interstellar diamond could be obtained by comparing the complete vibrational spectra of such diamondoids with astronomical data [9]. Given the presence of strong UV irradiation in the vicinity of stars many of the molecules that have been proposed to exist in interstellar space could also be cationic. In this respect, it may be noted that dehydrogenated closed-shell ions are in general more stable than their radical counterparts [10].

Due to the Coulombic repulsion of ions their gas-phase densities are in general too low to permit direct absorption spectroscopy in the laboratory. In the past decades ‘action’ spectroscopy techniques have been developed to enable a spectroscopic investigation of such compounds [11]. One of these techniques is infrared multiple-photon dissociation (IR-MPD) [12] where resonant absorption of light causes fragmentation of the ion of interest.

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Here, we present the IR-MPD spectrum of the dehydrogenated adamantane cation (C_{10}H_{15}^+), which is also known as the adamantyl cation [13]. The adamantane cation is a radical species and, given its high tetrahedral symmetry, is therefore subject to a non-trivial Jahn–Teller distortion. The adamantyl cation, on the other hand, has a closed-shell ground electronic structure and hence this complication does not arise. Note that if the adamantane cation exists in interstellar space, the adamantyl cation will also be present due to facile hydrogen atom loss from adamantane. The abstraction of a hydrogen atom from the adamantane cation can take place from two distinct sites: either at a carbon that only has one hydrogen bound to it (named 1-adamantyl) [13,14], or at a carbon that has two hydrogens bound to it (named 2-adamantyl) [15]. The density functional theory (DFT)-derived minimum energy structure of the 1-adamantyl cation has C_{3v} symmetry and is calculated to be lower in energy than the 2-adamantyl cation (C_{s} symmetry) by 0.49 eV (B3LYP 6-31G*) [14]. Note that for the 2-adamantyl cation, the higher symmetry C_{2v} structure is slightly higher in energy (0.07 eV) than the C_{s} structure (B3LYP/DZP++) [14], which was also shown by Dutler et al. [16]. Despite the fact that 1-adamantyl is significantly lower in energy than 2-adamantyl, an interconversion of both isomers is not thought to occur due to steric hindrance preventing a 1,2 hydride shift [15].

2. Experimental

The experiments are performed in a ion trap time-of-flight instrument, described in detail elsewhere [17]. As opposed to the polyaromatic species studied previously, adamantane vapor cannot be photoionized using an excimer laser. Two different ionization methods, electron impact (EI) and charge transfer (CT) are therefore employed. For the EI experiments, an electron gun is mounted on the z-axis of the ion trap, opposite to the TOF tube. It is found that the rf amplitude required to trap the ions is relatively high, so that the mass resolution deteriorates substantially, and this method is therefore not further considered here.

CT ionization is effected by addition of benzoic acid vapor, which is photoionized by an excimer laser (ArF, 193 nm). Although the ionization potential (IP) of adamantane (9.2 eV) is slightly higher than that of benzoic acid (9.1 eV) resulting in inefficient CT, the ionization potential (IP) of adamantane (9.2 eV) is slightly higher than that of benzoic acid itself [18]. Thus, the benzoic acid fragment cations (see Fig. 1) drive the CT to background adamantane vapor.

The mass resolution of the ion trap time-of-flight instrument is insufficient to unambiguously establish that only adamantyl (mass 135) and no adamantane (mass 136) cations are present. Nevertheless, it is known that the radical adamantane cation is subject to very facile hydrogen atom loss, giving rise to adamantyl cations; the binding energy of hydrogen is estimated at ≈1.4 eV, based on the IP of adamantane and the appearance energy of C_{10}H_{15} [19]. This has been independently verified by electron impact ionization of adamantane in a Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometer (data not shown), where the adamantane radical cation is observed to lose a hydrogen atom at pressures >1 × 10^{-7} mbar. In the much harsher trapping conditions of a quadrupole ion trap, the adamantane cation would not be expected to be stable. Adamantyl cations are stored in the ion trap for almost 500 ms to allow collisional relaxation of the ions, followed by mass-selective isolation via a temporary (2 ms) increase in the rf voltage amplitude, shifting the low-mass cut-off to just below the adamantyl mass (m/z = 135). The parent adamantyl ions are then irradiated with a pulse (5 μs) from the Free Electron Laser for Infrared eXperiments (FELIX) [20]. FELIX produces high energy (∼60 mJ) macro pulses that are tunable over a very wide range (5–250 μm). Each macro pulse consists of a 1 GHz train of micropulses of about 1 ps duration.

When a vibrational mode of the ion is in resonance with the laser wavelength, multiple photon absorption mediated by intramolecular vibrational redistribution (IVR) can take place [21,12]. When the internal energy of the molecule is sufficiently above the dissociation threshold, relaxation proceeds through fragmentation. The fragment and remaining parent ions are pulse extracted 7 ms after FELIX irradiation into the time-of-flight analyzer tube and are detected on a multichannel plate (MCP) detector. The fragment yield is monitored as a function of wavelength. This yield is then normal

![Fig. 1. Mass spectrum of photoionized (ArF, 193 nm) benzoic acid showing the photodissociation fragments. The ionization potentials (in eV) of the fragments that are thought to ionize adamantane are given in brackets.](image-url)
3. Results and discussion

The infrared multiple-photon dissociation (MPD) of the adamantyl cation shows a rich dissociation chemistry (loss of CH, C₂H₄, C₃H₆, C₄H₈ and C₅H₈) (Fig. 2). The various dissociation channels as a function of wavelength show the same infrared structure (Fig. 3), so that all the channels can be summed to give the total infrared spectrum of the species (shown in Fig. 3). Note that the loss of C₅H₈ has been omitted in this analysis, since it is barely detectable. The loss of C₂H₄ is observed to be the most abundant dissociation channel in these experiments, where the ions are collisionally cooled. For harsher trapping conditions (higher rf amplitude, high pressure >1×10⁻⁵ mbar), the loss of C₃H₆ is the most abundant fragmentation channel (data not shown). The different dissociation channel traces in Fig. 3 also confirm that 967 and 1002, 1060 and 1078, 1170 and 1191 cm⁻¹ are clearly distinct peaks.

The theoretical infrared spectra for 1- and 2-adamantyl calculated by Yan et al. (Fig. 4a and b) shows that the experimental spectrum (Fig. 4c) fits the theoretical spectrum of 1-adamantyl best. It has been our experience that MPD and linear absorption spectra can resemble each other closely [17]. Nevertheless, the MPD process gives rise to a slight redshift and a band broadening due to the vibrational (cross-)anharmonicities, which become important at higher internal energies [22]. A comparison of the linear absorption spectra with the MPD spectra allows important information on the anharmonicity parameters to be obtained [23]. Using a previously reported mathematical model, the experimental spectrum (in Fig. 4c) is fitted and the anharmonicity parameters along with the DFT calculated band positions are summarised in Table 1. Note that the largest source of error in the determination of these parameters is the accuracy of the DFT calculated line positions. Thus, accounting for the effects of MPD, the experimental and theoretical spectra show good agreement, implying that the experimental spectrum can be explained by the presence of the 1-adamantyl isomer only. In the experimental spectrum an almost linear increase of the background level with vibrational frequency is seen, which is probably due to an increasing number of combination modes. This background is not accounted for.
in the model, since no intensity is attributed to combination modes.

The anharmonicity parameter \( a \) describes the shift per vibrational quantum, while parameter \( b \) is a measure of the increase in line width per vibrational quantum [23]. Since all the \( a \) values are negative, a redshift of the bands is observed in the MPD spectrum relative to the linear absorption spectrum, as would indeed be expected. The mode at 1522 cm\(^{-1}\), which is a CH\(_2\) scissoring mode, is significantly redshifted (high negative \( a \) value) in the MPD spectrum. Note that this could either be due to this mode being highly anharmonic, or to an incorrect prediction of the harmonic frequency by the DFT calculation.

The calculated energy difference between 1-adamantyl and 2-adamantyl is 0.49 eV [14], and since both isomers are not expected to interconvert [15], the observed ratio would be determined by the kinetics of the hydrogen detachment under our experimental conditions. The relative energies for adamantane, adamantane cation and the adamantyl cations in the energy diagram (Fig. 5) can be estimated from the known values for

| Experimental frequency (cm\(^{-1}\)) | Calculated frequency (cm\(^{-1}\)) [14] | Anharmonic parameters
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<tr>
<td></td>
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<td>( I \times 10^{17} \text{ cm}^{-1} ) [14]</td>
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<tr>
<td>542</td>
<td>570</td>
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</tr>
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*Note:* only bands with \( I > 2 \times 10^{18} \text{ cm} \) are shown.

\(^{a}\) Anharmonic shift per vibrational quantum.

\(^{b}\) Anharmonic broadening per vibrational quantum.

Fig. 5. Energy diagram of adamantane (\( C_{10}H_{16} \)), adamantane cation (\( C_{10}H_{16}^{+} \)), vibrationally excited adamantane cation (\( C_{10}H_{16}^{+} \)), 1-adamantyl (\( C_{14} \)) and 2-adamantyl (\( C_{14} \)). The rates for hydrogen atom detachment from \( C_{10}H_{16}^{+} \) to yield 1-adamantyl (\( k1 \)) and 2-adamantyl (\( k2 \)) are also shown.
the IP of adamantane, the appearance energy of C_{10}H_{15}^+ [19] and the structural energies derived by Yan et al. [14]. CT ionization of adamantane yields a vibrationally excited adamantane cation (C_{10}H_{16}^+). The internal energy can be estimated from the benzoic acid fragments that are most likely to cause CT ionization of adamantane (see Fig. 1). Thus, the internal energy of C_{10}H_{16}^+ is approximated to be between 2.2 and 3.8 eV above the ground level of C_{10}H_{16}^+. We assume complete energy randomisation over the 72 vibrational modes and an RRK governed unimolecular dissociation [25,26] along barrier-less dissociation coordinates. The ratio of the dissociation rates into the two channels, k_1:k_2, is then calculated to be 10^3:1, which is predominantly determined by the energy difference between both isomers and the large number of vibrational degrees of freedom. Hence, under these conditions the abundance of 2-adamantyl is negligible, which is consistent with the observed spectral profile.

4. Conclusions

In conclusion, we presented the first experimental infrared spectrum of the adamantyl cation, the main ionic dissociation product of adamantane. The spectrum can be well fitted using the MPD spectrum of the 1-adamantyl isomer only. It would be interesting to observe also the spectrum for the adamantane cation, as it might show the effects of the complicated Jahn–Teller interactions. This would require a very gentle ionization and moreover mass isolation and detection with higher resolution, such as available in a FT-ICR mass spectrometer, which has recently been coupled to the beamline of FELIX [24]. These experiments will be pursued in future work.

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References