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Jahn–Teller Distortion of Hydrocarbon Cations Probed by Infrared Photodissociation Spectroscopy

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IR spectroscopy · Jahn–Teller effect · radical cations · structure elucidation · vibronic interactions

Ascertaining the properties of charged molecules in an isolated environment, where perturbations because of interactions with solvent and counterions or matrix effects are minimized, has been a long sought goal in gas-phase ion chemistry and physics. Compared with other approaches, the direct interrogation by spectroscopic means presents the advantage of least perturbing the assayed species. Routine spectroscopic analysis to sample the structure of neutral molecules in the gas phases may be achieved by IR spectroscopy using direct absorption measurements. However, this highly structure-informative spectroscopic tool is not directly practicable for gaseous ions because of the limited, attainable number density. An appropriate approach to the problem was required and the last decade has witnessed an upsurge of studies addressing the structural features of gaseous charged molecules. These reports are largely based on the successful coupling of tunable IR light sources of high fluence, such as free electron lasers or optical parametric oscillator/amplifier (OPO/OPA) table-top lasers, in combination with mass spectrometry for ion manipulation and detection. The ensuing techniques, so called action spectroscopies, do not measure the direct absorption of the incident light beam but the response of the molecule to light absorption.[1–3] Typically, resonant IR (multiple) photon absorption triggers a fragmentation event. By exploiting IR (multiple)photon dissociation (IR(M)PD) spectroscopy several issues have been unambiguously assessed such as the site of proton or metal ion attachment, the covalent bonding network, the presence of noncovalent interactions, the occurrence of conformational equilibria, and the secondary structure of biomolecules.[4–6] In this challenging field a remarkable recent achievement has focused on a prototypical hydrocarbon molecule, namely adamantane, $C_{10}H_{16}$, in its ionized form.[7] Isolated, ionized adamantane, $C_{10}H_{16}^{+\bullet}$, is predicted to present a vibronic interaction (Jahn–Teller effect) imparting it a distorted geometry as now unambiguously demonstrated by IRPD spectroscopy by Dopfer and coworkers.[7]

Adamantane is the highly symmetrical parent molecule of diamondoids, a family of alkanes with diamond-like structure,[8] hypothesized to occur in interstellar media on the basis of indicative vibrational signatures. Neutral adamantane is a spherical-top molecule with tetrahedral symmetry. Because of the interest in the exemplary structure of this molecule, the first rotationally resolved spectrum has been recently obtained by gas-phase Fourier transform IR absorption spectroscopy making use of synchrotron radiation.[9] Out of the 11 IR-active fundamental vibrational modes, three intense bands are in the CH stretching region at 2859.9, 2911.9, and 2937.6 cm^{-1}. Their frequencies are well gauged by B3LYP/cc-pVDZ calculations as shown in Table 1. Figure 1 a shows the stick IR absorption spectrum and the T_d symmetry of adamantane in its $^1A_1$ ground electronic state. For the radical cation the T_d-geometry optimization does not converge to a stable structure. In fact removing an electron from one of the triply degenerate highest occupied molecular orbitals (HOMOs) promotes Jahn–Teller (JT) distortion.[10] JT distortion lifts the degeneracy of the ensuing electronic states yielding a lowest energy structure with lower (C_{3v}) symmetry. As shown in Figure 1 b, the C_{3v} adamantane cation presents three elongated C–C bonds and one substantially long C–H bond on the C_3 symmetry axis.

Table 1: Experimental IRPD absorptions and theoretical IR-active bands in the CH stretching range (in cm^{-1}).

Theory[a] $C_{10}H_{16}$ (T_d, $^1A_1$)	Experiment[9] $C_{10}H_{16}$	Theory[a] $C_{10}H_{16}^{+\bullet}$ (C_{3v}, $^2A_1$)	Experiment[7] $C_{10}H_{16}^{+\bullet}(He)_2$
2931 (276)	2937.6	3007 (19)	2981
2910 (450)	2911.9	2955 (36)	2954
2890 (57)	2858.9		
		2932 (10)	2941
		2873 (9)	2883
		2846 (101)	2868
		2602 (197)	2600

[a] Theoretical values are harmonic frequencies, scaled by 0.96, from B3LYP/cc-pVDZ calculations.[7] Modes are listed with IR intensity (in parentheses) >2 km mol^{-1}.

The highly reactive and elusive nature of $C_{10}H_{16}^{+\bullet}$, combined with the difficulty of attaining an adequate concentration for spectroscopic analysis, are probably responsible for the lack of vibrational spectroscopic data about

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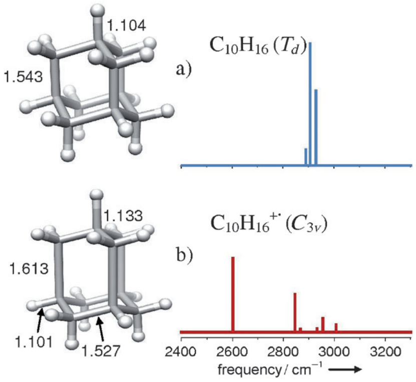

Figure 1. Selected bond distances (in Å) and IR absorption spectrum of a) adamantane and b) the adamantane radical cation calculated at the B3LYP/cc-pVDZ level.[7] The geometric distortion of $C_{10}H_{16}^{+\bullet}$ is exaggerated for illustration.

this and related species. The landmark contribution by Dopfer and co-workers now fills this gap, providing the IR spectrum in the CH stretching range and gaining direct evidence for the operation of JT distortion.[7] The experiment relies on the generation of $C_{10}H_{16}^{+\bullet}$ entrained in a supersonic expansion of He or N_2. Adiabatic expansion considerably cools the ions which form loosely bound adducts with He or N_2. The resonant photon absorption event (heating the charged complex by about 4.5 kJ mol^{-1} at 3000 cm^{-1}) is revealed by the evaporation of the ligand and can be effectively ascribed to energy deposition into the vibrational modes of the nearly unperturbed adamantane radical cation.[2,3] In the resulting experimental IRPD spectrum[7] the distinctive IR feature at 2600 cm^{-1} does not find a counterpart in the IR spectrum of neutral adamantane.[9] B3LYP/cc-pVDZ calculations confirm the experimental finding. In fact, the calculated IR spectrum of $C_{10}H_{16}^{+\bullet}$ shown in Figure 1 b is markedly different from the one of the parent neutral molecule (Figure 1 a). As shown by the data listed in Table 1, the IRPD absorption at 2600 cm^{-1} nicely matches the value predicted at 2602 cm^{-1}. The corresponding local mode is the CH stretching vibration of the elongated bond on the C_{3v} axis. The pronounced red shift (e.g. νCH at 2859 cm^{-1} in neutral adamantane)[9] is a manifestation of the diminished bonding character of this CH group with unique characteristics in the radical cation, as imparted by JT distortion. The experimental spectrum of $C_{10}H_{16}^{+\bullet}$ tagged with two He atoms (Table 1) finds precise correspondence in the calculated spectrum confirming the vibrational and electronic features of $C_{10}H_{16}^{+\bullet}$ and the negligible perturbation by the weakly bound He atoms. Regarding the latter issue, a relevant conclusion comes from the thorough analysis of the IR photodissociation spectra of jet-cooled benzene cations complexed with noble gas atoms.[11] This study has convincingly demonstrated that the spectrum of the Ne complex indeed represents the IR absorption spectrum of the free benzene cation including JT splitting of vibrational modes. A light noble gas tag appears to have no sizeable impact on the JT effect of the bare hydrocarbon cation.

It may be noted that because of four equivalent C_3 symmetry axis in adamantane, the $C_{10}H_{16}^{+\bullet}$ ion will present four equivalent minima of C_{3v} symmetry located around the T_d symmetric geometry. The barrier separating the minima has not been determined. However, at the temperature of the experiment (less than 50 K) the sampled adamantane radical cation conforms to a "static" C_{3v} geometry, testified by the analysis of its IR spectrum.[5] It is conceivable that at higher temperature the increased internal energy will allow the ion to dynamically sample the four C_{3v} symmetric minima in a resultant time-averaged T_d structure.

Besides the benchmark benzene cation,[12] also polycyclic aromatic hydrocarbons (PAH) possessing a three-fold or higher symmetry axis are susceptible to JT distortion upon removal of an electron. The interpretation of their IRMPD spectra has required full JT analysis posing substantial challenges.[1] IR spectra of ionized corannulene, a bowl-shaped PAH of C_{5v} symmetry, have been recently recorded using the FELIX free electron laser.[13] JT distortion from C_{5v} geometry in the corannulene cation has been considered and the computational results evaluated against the IRMPD spectrum have suggested a dynamically distorted system. This may be a consequence of relatively low barriers separating five equivalent C_s minima as well as of the excess energy imparted onto the ion when generated by photoionization of the neutral molecule in the FELIX experiment. The adamantane cation sampled by Dopfer and co-workers is instead a cold ion which may explain the successful IR characterization of a "frozen" JT distorted structure. Fruitful developments may thus be envisioned when this model hydrocarbon cation will be subjected to IR interrogation using different techniques. The appearance of features pertaining to a fluxional system in T_d symmetry and the associated threshold conditions may highlight the structural and dynamical properties of ionized adamantane and related open-shell molecular systems. A valuable complement could be provided by rotationally resolved photoelectron spectroscopy which offers distinct advantages for the study of molecular cations that are subject to JT distortion, although the pattern of spectral lines will be governed by Franck–Condon factors rather than by rigorous selection rules. For example, high-resolution pulsed-field ionization zero-kinetic-energy photoelectron spectroscopy has permitted the investigation of the JT effect in a methane cation.[14] However, the thorough analysis of a larger hydrocarbon system (as large as adamantane) by these means represents a challenge. This underlines once again the remarkable achievement by Dopfer and co-workers who have revealed for the first time the consequence of the JT theorem in the exemplary adamantane cation.

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