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Aromatic Cations

Benzylium versus Tropylium Ion Dichotomy: Vibrational Spectroscopy of Gaseous $C_8H_9^+$ Ions**

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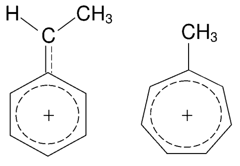
The formation of $C_7H_7^+$ ions as prominent species is recognized as a landmark feature in the mass spectra of alkylbenzenes and related compounds.[1,2] The production of benzylium (**1**) or tropylium (**2**) ions from ionized or protonated toluene, the prototypical alkylbenzene, has been one of the most thoroughly studied processes in gas-phase ion chemistry.[3,4] The formation of **2** from ionized and energetic toluene involves the fast interconversion of toluene and cycloheptatriene radical cations, preceding hydrogen atom loss. The relative yield of **1** and **2** formed under various conditions has been typically determined by ion–molecule reactions, based on the quantitative reactivity of **1** with toluene and alkylbenzenes [Eq. (1)].[5–8]

$$C_7H_7^+ + R{-}C_6H_5 \rightarrow RC_7H_6^+ + C_6H_6 \qquad (1)$$

Reaction (1) proceeds by methylene transfer and is characteristic of the benzylium structure whereas the tropylium ion is unreactive. This reactivity tool has also been used to unveil the structure of the $C_7H_7^+$ ions formed by photofragmentation of $C_7H_9^+$ ions.[4] The latter species were obtained by protonation of either toluene or cycloheptatriene and the structure of the parent ions was elucidated by infrared multiple photon dissociation (IRMPD) spectroscopy.[4,9] To this end, the ion population is generated and stored in the cell of a FT-ICR mass spectrometer where it is allowed to interact with the IR radiation of a free electron laser (FEL) tuned in the mid-IR region. The ensuing IRMPD spectroscopy, performed either at the CLIO (centre laser infra rouge d'Orsay, France) or the FELIX (free electron laser for infrared experiments, in the Netherlands) center, has afforded powerful means for investigating the IR activity of ions obtained by protonation or ionization of aromatic hydrocarbons, which are considered as potential carriers of the unidentified IR emission bands.[10–14] However, this highly informative IR spectroscopy of gaseous ions has so far met with no success with $C_7H_7^+$ ions **1** and **2** and IRMPD spectroscopy of these fundamental species has not yet been reported.

At variance with the tropylium ion,[15] the benzylium ion has not yet become amenable to vibrational spectroscopy in the condensed phase.[16] Only for the cumyl cation (α,α-dimethylbenzyl cation) has a X-ray structure been reported.[17] Very recently, the electronic spectra observed in the visible spectral region of mass-selected benzylium (**1**) and tropylium (**2**) cations embedded in solid neon have been reported.[18] This recent report prompted us to further pursue the IR spectroscopic investigation of benzylium and tropylium ions in the gas phase, where the species are isolated from external influences. To this end, IRMPD spectroscopy has been performed using the CLIO FEL to investigate the methyl-substituted ions **1-Me** and **2-Me**, the next higher homologues of **1** and **2** (Scheme 1).



1-Me **2-Me**

Scheme 1. Benzylium and tropylium isomers of $C_8H_9^+$ ions.

Issues regarding the gas-phase ion chemistry of **1-Me** and **2-Me** including rearrangement pathways have been discussed.[1,19] The two isomeric ions can be selectively formed by distinct routes as shown using Reaction (1). Isomer **1-Me** has been obtained by protonation of styrene, a fairly basic aromatic hydrocarbon endowed with a proton affinity of 840 $kJ\,mol^{-1}$.[20] The proton is delivered on the vinylic β carbon yielding benzylium ion **1-Me**, which gains stabilization from C−H hyperconjugation exerted by the methyl group. The same consideration applies to **2-Me** which is obtained by formal hydride abstraction from 7-methylcycloheptatriene. The two isomeric ions formed through these routes were sampled by IRMPD spectroscopy. The IRMPD spectra obtained by plotting the fragmentation yield R as a function of the photon wavenumber are shown in Figures 1a and 2a for **1-Me** and **2-Me**, respectively. The two spectra are clearly quite different, speaking against any possible interconversion to a common species or isomeric mixture within the time scale of the experiment (few seconds). However, the same fragmentation channels were observed. Indeed, when the IR laser is tuned to an IR-active vibrational mode, for both sampled $C_8H_9^+$ species at m/z 105 the major fragmenta-

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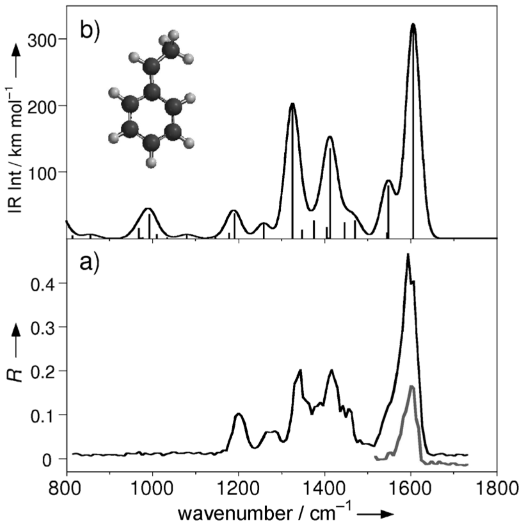

Figure 1. a) IRMPD spectrum and b) calculated IR spectrum of **1-Me**. The spectral region around 1600 cm^{-1} has been recorded also with an attenuated (−3dB) laser beam (gray profile).

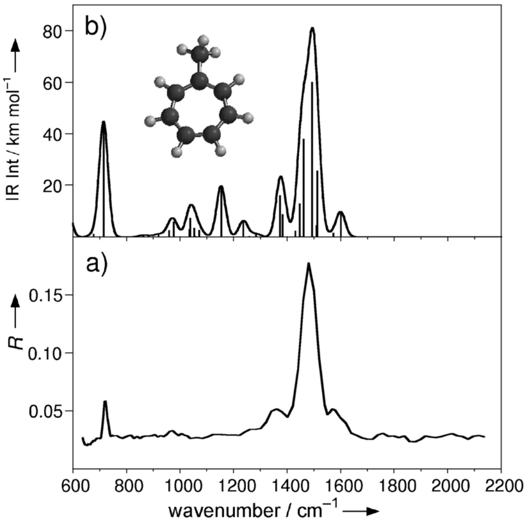

Figure 2. a) IRMPD spectrum and b) calculated IR spectrum of **2-Me**.

tion channel involves loss of [C_2H_2]. The product ion at *m/z* 79 is about twice as abundant as the product ion at *m/z* 103 formed by loss of H_2.

To confirm the structure of the sampled ions and to gain insight into the observed IR features, quantum chemical calculations were carried out at the B3LYP/cc-pVTZ level. The relative energies of the optimized geometries (for Cartesian coordinates and thermodynamic data see Tables S1 and S2 in the Supporting Information) show that at 0 K **1-Me** is 9 kJ mol^{-1} higher in energy relative to **2-Me**, in agreement with reported results of ab initio calculations.[21] The IR spectra calculated for **1-Me** and **2-Me** are displayed in Figures 1 b and 2 b, respectively.

In both Figures 1 and 2, the calculated IR absorption spectra given in panel (b) are represented using stick bars (km mol^{-1}), and a representation of the IR cross section is also given where each IR band is convoluted using a Gaussian function with a width of 20 cm^{-1}, a somewhat smaller bandwidth than typically observed with the experimental platform used.[22] Overall, a good agreement (consistently within ±1.2%) is found between the position of the experimental IRMPD bands and the calculated IR absorption ones, both listed in Table 1. One may notice that on resonance with the strongest band of **1-Me**, for which the predicted IR absorption value is 323 km mol^{-1} (Figure 1, Table 1) the observed value of the IR fragmentation efficiency is on the order of 0.4 (33% of fragmentation). As can be seen in Figure 2 (and also in Table 1), IR absorptions are predicted to be weaker for the **2-Me** isomer, and the IR-induced fragmentation yield is consistently observed to be lower for this isomer. A common trait of the IRMPD spectra of the two isomers is an apparently low activity in the red end of the spectrum when compared with the calculated IR intensities of the expected bands. However, while IRMPD band positions are generally informative, the relative IRMPD intensities have to be taken with caution.[4,23,24] This is due to the fact that nonlinear multiple photon effects may play a role. Furthermore, under our experimental conditions, the laser fluence, which is proportional to $1/\lambda^2$, decreases when the wavelength increases.

Table 1: Observed IRMPD spectral bands and calculated (B3LYP/cc-pVTZ) vibrational frequencies for **1-Me** and **2-Me** ions.

IRMPD[a]	IR[a,b]	Vibrational mode
1-Me		
	786 (29)	out-of-plane CH bend
	993 (36)	in-plane CH bend and CC stretch
1200	1190 (37)	in-plane CH bend
1274	1259 (23)	in-plane CH and CH bend
1340	1325 (199)	asymmetric CH_3 bend
1385	1375 (26)	in-plane CH bend and CC stretch
1414	1413 (135)	symmetric CH_3 and CH bend
1440	1447 (23)	symmetric CH_3 and CH bend
1458	1470 (26)	in-plane CH bend
1554	1548 (79)	ring deformation and CC stretch
1600	1606 (323)	ring deformation
2-Me		
720	716 (45)	out-of-plane CH bend
	1154 (20)	in-plane CH bend and CC stretch
1364	1374 (16)	asymmetric CH_3 and in-plane CH bend
	1386 (9)	symmetric methyl and in-plane CH bend
	1448 (13)	asymmetric CH_3 bend and in-plane CH bend
	1463 (38)	asymmetric CH_3 and in-plane CH bend
1480	1493 (60)	in-plane CH bend
	1513 (25)	ring deformation
1600	1601 (9)	ring deformation

[a] In cm^{-1}. [b] Only major bands (IR intensity greater than 20 km mol^{-1} for **1-Me** and greater than 9 km mol^{-1} for **2-Me**, given in parentheses) are listed.

IRMPD spectroscopy, as exploited in the present contribution, lends us a powerful tool to inquire about the actual presence of either benzylium or tropylium-type ions or of a mixture of the two isomers from various sources and in different gaseous environments, thus solving a long debated question in structural mass spectrometry. At the same time, IR spectroscopy of the gaseous ions provides valuable information on the naked species, unperturbed by matrix, solvent, or counteranion effects. Interestingly, IR spectroscopy using the FELIX FEL in an IR–UV double-resonance scheme has allowed the assignment of vibrational features of neutral benzyl and tropyl radicals in the gas phase.[25] Hopefully, the present results may be extended to the prototypical $C_7H_7^+$ ions soon.[26] Efforts in this direction are underway.

Experimental Section

IRMPD spectroscopy was performed using a mobile FT-ICR mass spectrometer based on a permanent magnet of 1.25 T coupled to the CLIO FEL beamline.[27] $C_8H_9^+$ ions were obtained by chemical ionization of styrene (**1-Me**) or 7-methylcycloheptatriene (**2-Me**) using methane or isobutane, respectively, as reagent gases, admitted by a pulsed valve. The ions were selected, stored in the FT-ICR cell and irradiated for 1–3 s by the IR beam of the FEL which was operated at 35, 40, or 45 MeV, providing photon energies in the 600–2200 cm^{-1} range explored. The photofragmentation yield R ($R = -\log[I_{\text{parent}}/(I_{\text{parent}}+\Sigma I_{\text{fragment}})]$, where I_{parent} and I_{fragment} are the relative abundances of parent and fragment ions, respectively) plotted versus the radiation wavenumber generates the IRMPD spectrum of the sampled ion.

Theoretical calculations were carried out at the B3LYP level using the cc-pVTZ basis set. The structures have been fully optimized and frequency analysis was performed to characterize the stationary points as minima and to obtain IR spectra. Reported energies were corrected for zero-point vibrational energies and harmonic frequencies were scaled by 0.975 in the calculated IR spectra.

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