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IR spectroscopy of protonated toluene: Probing ring hydrogen shifts in gaseous arenium ions

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Dedicated to the memory of Professor Chava Lifshitz.

Abstract

Toluenium ions $[CH_3C_6H_6]^+$, formed by protonation of toluene by $C_2H_5^+$ ions in the cell of a Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometer, have been assayed by IR multiphoton dissociation (IRMPD) spectroscopy. Their IRMPD spectrum compares well with the calculated IR absorption spectra for the *ortho*-, *meta*-, and *para*-toluenium isomers, suggesting a mixture rich in the *ortho*/*para* isomers. When the protonation is effected on perdeuterated toluene, the so-formed ions present IRMPD features characteristic for both CD_2 and CHD groups in the arenium ring. This finding is spectroscopic evidence for the occurrence of ring hydrogen shifts and provides the first example of differentiation of families of isotopomers (bearing either two D-atoms or one D-atom and one H-atom on the tetrahedral ring carbon) by the powerful tool of IRMPD using the tunable IR radiation of a free electron laser.

Keywords: Photodissociation; FT-ICR mass spectrometry; IR spectroscopy; Reactive intermediates; Structure elucidation

1. Introduction

Arenium ions, also named σ complexes or Wheland intermediates, are well established intermediates in electrophilic aromatic substitution reactions [1]. Among the simple, fundamental arenium ions, toluenium ion is the prototypical alkylbenzenium ion, benchmark species in the development of superacid media, theoretical calculations and mass spectrometric approaches for the study of carbocation chemistry both in the gas phase and in solution [2]. A closely related ion, the toluene molecular ion, has also gained remarkable widespread interest. Its primary fragment ion, $C_7H_7^+$, is probably 'the best known of all organic ions ever investigated in the gas phase' [3]. The question of tropylium versus benzylium ion formation from the toluene molecular ion was addressed in landmark studies of Lifshitz who has thoroughly reviewed this long standing issue [4]. In this foreword we remember her insights into the understanding of the unimolecular reactivity of toluene ions, in grateful recognition of her many fundamental contributions to gas phase ion chemistry and physics.

The structure of toluenium ion has been recently characterized in the solid state by X-ray crystallography, proving a *para*-cyclohexadienyl cation character in the solid state environment. This achievement was made possible by the use of novel carborane superacids which produce solid arenium salts when allowed to react with an arene [5]. Similar detailed structural information is unfortunately not readily available for ions in the gas phase, an environment where ionic species are least perturbed by medium effects. However, powerful tools have been developed allowing for the characterization of ion structures by spectroscopic analysis [6]. Conventional IR absorption spectroscopy is not routinely accessible for ions in the gas phase, where problems arise from the low density of the charged species and/or the interference due to the presence of neutral absorbers. Indeed, a growing number of reported IR absorption spectra proceed in parallel with the progress of novel techniques [7].

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In particular, the IR absorption features of gaseous ions can be revealed if the absorption of photon(s) increases the ion internal energy to the point of activating a dissociation process, resulting in a so-called action spectrum. The combination of mass spectrometric techniques for ion generation, storage, and detection with a tunable IR laser source has been exploited to obtain information on the structure of exemplary gaseous arenium ions in two different spectral regions. An access to the 2500–4000 cm^{-1} frequency range was provided by an optical parametric oscillator (OPO) laser. The dissociation of a cluster of the arenium ion with a weakly bound ligand may occur upon absorption of a single photon in resonance with an active mode of the weakly associated arenium species ('messenger' technique) [8]. The IR spectral features in the 'fingerprint' region (600–2200 cm^{-1}) have been determined using a widely tunable free electron laser (FEL) as powerful IR source. In this way IR multiple photon dissociation (IRMPD) spectroscopy of the bare ion is possible and the vibrational features of the arenium ions formed by protonation of benzene, fluorobenzene, and phenylsilane have been reported [9]. This methodology is now applied to protonated toluene ions and also recently extended to the investigation of their dissociation routes [10].

In the present contribution IRMPD spectroscopy is used not just to probe the ions that are formed by gas phase protonation of toluene but also to ascertain their reactivity behavior with respect to ring hydrogen migration processes. These processes, occurring by 1,2-hydrogen-shifts, are well documented in benzenium and alkylbenzenium ions both in solution [1,2a] and in the gas phase [11]. The high rate of the process (ca. 10^7 s^{-1} for the 1,2-shift of a deuterium atom within benzenium ions at 40 °C, as obtained by a radiolytic study at atmospheric pressure [12]) accounts for the complete scrambling of ring hydrogens in metastable benzenium and toluenium ions undergoing elimination of dihydrogen and dihydrogen and methane, respectively [13a], and in benzenium ions formed by photoionization experiments at variable photon energy [13b].

The present experiments are based on the coupling of an IR FEL radiation beam with a Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometer [14], using a compact FT-ICR analyzer [15] at Centre Laser Infrarouge Orsay (CLIO) as previously applied to the study of organometallic species [16], sodiated amino acids [17], protonated dipeptides [18], and the protonated water dimer [19] to name few other studies besides the cited ones on arenium ions [9]. The potential of a similar apparatus employing the free electron laser for infrared experiments (FELIX) [14b] is also described in a growing number of recent studies [20]. This innovative approach was used in the present work to investigate the IRMPD features of toluenium ions from unlabelled and deuterated precursors, thus providing spectroscopic evidence that the sampled species have indeed undergone hydrogen migration processes.

2. Experimental and computational methods

The details of the experimental apparatus coupling the mobile FT-ICR spectrometer [15] with the FEL radiation at CLIO have been thoroughly described [14a]. The ions of interest were formed by protonation of toluene (at 1×10^{-6} mbar) using $C_2H_5^+$ ions obtained from ionization and ion–molecule reactions in a 200 ms long pulse of methane (at 9×10^{-7} mbar). The so-formed protonated toluene ions $[CH_3C_6H_6]^+$ were isolated from other ionic species, allowed to relax in the FT-ICR cell at room temperature for 1 s and then submitted to a 2 s irradiation time. The IR radiation, structured in macropulses (8 μs long, delivered at a repetition rate of 25 Hz, each containing 500 micropulses a few picoseconds long, 16 ns apart), was endowed with a mean power of 600 mW. The FEL was operated at 35 or 40 MeV, thus providing a tunable IR beam in the 600–1600 and 800–2000 cm^{-1} energy range, respectively. Excitation, detection, and quench of the ions in the cell complete the sequence, resulting in a mass spectrum obtained from an ion signal accumulated over four scans. The IRMPD yield R is expressed as a function of the abundances of the parent and fragments ions as $R = -\log[I_{\text{parent}}/(I_{\text{parent}} + I_{\text{fragment}})]$. The R values were not corrected to account for the laser power variations. According to our previous investigations, the IRMPD efficiency (R) scales linearly with the laser power provided that the laser power is higher than a threshold, which in turn strongly depends on the IR cross-section at a given wavelength. Considering that the laser power was fairly constant (600 ± 100 mW) in the course of the present experiments, the R values reported throughout this paper are the raw values.

Molecular structures and relative energies for the isomers of protonated toluene were calculated using hybrid density functional theory (B3LYP) and the 6-311+G(d,p) basis set. Harmonic vibrational frequencies and IR absorption intensities obtained at the same level were used to interpret the IRMPD spectra. Hybrid DFT methods such as B3LYP were found to perform well in describing IR absorption spectra in terms both of relative intensities and of absolute frequencies, provided appropriate scaling factors are used [21]. Harmonic frequencies were scaled by a uniform factor of 0.96 to account for anharmonicity. The same factor was used for zero point vibrational energies.

3. Results and discussion

Toluenium ions were obtained by protonation of toluene by $C_2H_5^+$ ions in a process known to be exothermic by 103.5 kJ/mol [22]. The energy released in the proton transfer process, though partitioned between the two products $[CH_3C_6H_6]^+$ and C_2H_4, may allow the formation of any of the possible ring protonated isomers whose relative energies have been obtained using density functional theory at the B3LYP/6-311+G(d,p) level (Fig. 1 and Table 1). At the same time the protonation exothermicity should not allow skeletal isomerizations, such as a rearrangement to a less stable protonated cycloheptatriene structure because of the high activation energy (180–230 kJ/mol from the *i*-T isomer [10,25a] or ca. 285 kJ/mol from *m*-T [25b]) involved in the process. Indeed, the protonation of toluene effected by either CH_4 or *i*-C_4H_{10} chemical ionization (CI) is observed to yield a uniform $C_7H_9^+$ ion population containing exclusively toluenium ions, irrespective of the CI plasma used,

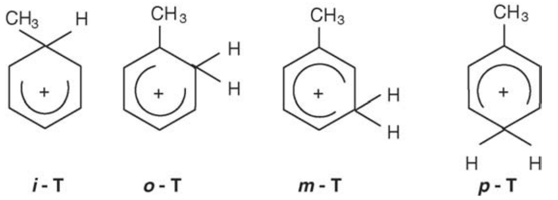


Fig. 1. Isomeric toluenium ions, corresponding to protonation at the *ortho* (*o*-T), *meta* (*m*-T), *para* (*p*-T), and *ipso* (*i*-T) positions of toluene.

according to a recent thorough study of $C_7H_9^+$ ion mixtures probed by the use of ion–molecule reactions [25b]. In the various toluenium isomers the barrier to internal rotation of the methyl substituent is found to be very small [26]. However, in the considered infrared energy range, the vibrational spectra of the various conformers do not differ to any significant extent, as found, for example, for the *o*-T isomer, whose minimum energy conformation has none of the CH bonds of the methyl group in the plane of the ring [26]. The IR spectra of the stable conformer of each toluenium isomer are displayed in Fig. 2, where they may be viewed in comparison with the experimental IRMPD spectrum, reporting the relative yield of fragment ions, *R*, as a function of the photon energy. The maxima of the bands in the IRMPD spectrum occur at 1183, 1252, 1440, and 1593 cm^{-1}. The multiple photon dissociation process proceeds by loss of H_2 (Fig. 3), accompanied by a minor process involving loss of CH_4. The fragmentation of H_2 is endothermic by 102 kJ/mol from *p*-T, the most stable isomer for protonated toluene (Table 1), considering the benzyl cation to be the product species [10,25] and thus requires the absorption of several photons to be activated. One can estimate that at least six photons at 1440 cm^{-1}, the frequency of the most intense band in the IRMPD spectrum, are needed just to surmount the endothermicity of the fragmentation process. Indeed, the process is known to be energy demanding and to involve an activation energy barrier in excess of the reaction endothermicity [10,11a,13a,25,27]. A second minor dissociation pathway is also observed. It corresponds to a loss of methane which only distinctly emerges from background signal when the IR-FEL laser is in resonance with the major vibrational features of the ions, though accounting for less than 10% of the total yield of photofragment ions (Fig. 3). Methane loss was found to occur from metastable toluenium ions in a similarly minor channel with respect to H_2 loss [13a,28].

Table 1
Computed energies of isomeric toluenium ions and fragmentation products

Species	Relative energy[a]
o-T	5.6 (4.6 [23], 7.1 [24])
m-T	21.4 (18.4 [23], 21.3 [24])
p-T	0 (0)
i-T	41.0 (30.9 [23], 37.1 [24])
$C_6H_5CH_2^+ + H_2$	101.8
c-$C_6H_5^+ + CH_4$	248.5

[a] In kJ/mol. Relative energies include zero point energy contributions. All calculations were performed at the B3LYP/6-311+G(d,p) level. Recent literature values obtained at the MP2/6-31G(d)//HF/6-31G(d) [23] and QCISD/6-31+G(d,p) [24] levels of theory are listed in parentheses.

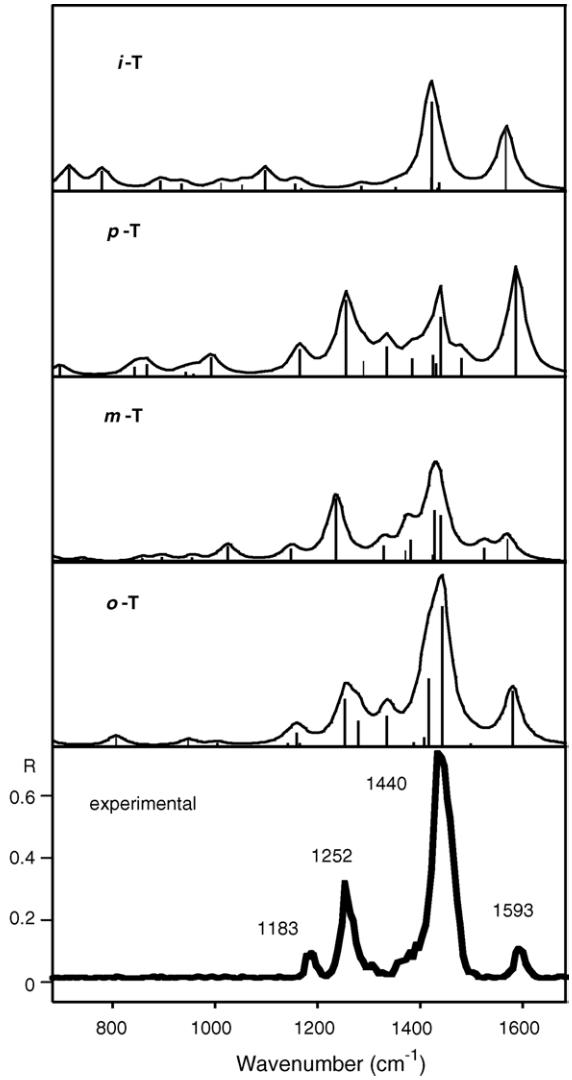


Fig. 2. Experimental IRMPD spectrum of protonated toluene (reporting the IRMPD yield *R*) and computed linear IR absorption spectra of *o*-T, *m*-T, *p*-T, and *i*-T. The relative scales for all calculated spectra are the same.

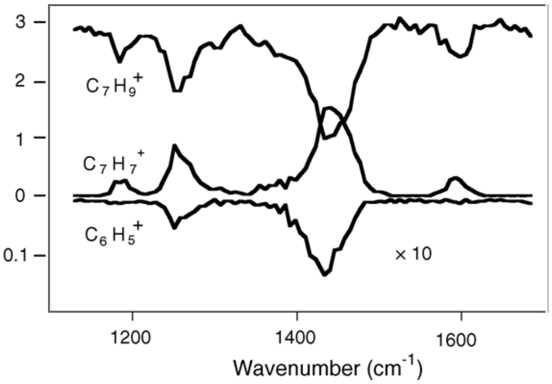


Fig. 3. Profiles of ion abundances for the parent and photofragment ions (in arbitrary units) as a function of IR frequency. The ion abundance profile for the product ion due to loss of CH_4 ($C_6H_5^+$) is magnified by a factor of 10 and is displayed inverted to be distinguished from the one due to H_2 loss.

The loss of methane from the *p*-T isomer of protonated toluene leading to phenylium ion is endothermic by 249 kJ/mol (Table 1). Considering that IRMPD implies slow heating of the ion [29], it is generally assumed that dissociation should occur along the lowest energy pathway. However, the observation of the high energy fragmentation pathway, i.e., the CH_4 loss, may be accounted for by the presence of a substantial activation energy for H_2 elimination, as evident from the remarkable kinetic energy release accompanying this dissociation process [11a,13a,25,27a]. If the translational energy release of 96 kJ/mol [13a,25,27a] is a lower limit of the energy difference between the benzyl cation and dihydrogen as dissociation products and the transition state leading to them [30], then the dissociation process to these products from *p*-T involves an overall barrier of 198 kJ/mol, approaching the endothermicity for the fragmentation to phenylium ion and methane [13a]. Similar competitive fragmentation channels have already been observed using IRMPD under our experimental conditions [9b,c,14a].

Although the thermochemical reasonings outlined in the previous paragraph were based on *p*-T, namely the most stable structure among the isomers of protonated toluene listed in Table 1, the minor predicted energy difference suggests that also *o*-T should contribute to a significant extent to a thermal $[CH_3C_6H_6]^+$ isomer population sampled in the FT-ICR cell. For example, the protonation of gaseous ethyl- and isopropylbenzene is directed to the *ortho*/*para* positions as shown by H/D exchange reactions of arenium ions at atmospheric pressure [31] and *ortho*/*para* protonation of toluene and ethylbenzene is reported by NMR analysis in superacid media [32]. To a general inspection the IRMPD spectrum of protonated toluene may seem in qualitative better agreement with the *o*-T isomer. However, the presence of other isomers, notably *p*-T, is conceivable and should indeed be expected on the basis of their relative energies, though the present IRMPD data cannot be used to extract any quantitative estimate of the relative isomer abundances. The complex sequence of events underlying the IRMPD process includes photon absorption by an active mode, intramolecular vibrational energy redistribution, and the attainment of a transition state geometry leading to dissociation. Any of these events may be affected to a various degree by structural differences, possibly even as fine as those marking the toluenium isomers. A major feature at 1252 cm^{-1} in the IRMPD spectrum is accounted for by the distinct absorptions at 1254, 1235, and 1255 cm^{-1} in the calculated IR spectra of *o*-T, *m*-T, and *p*-T, respectively, associated to the CH_2 'scissor' mode at the tetrahedral ring carbon. This absorption band is obviously not present in the IR spectrum of the *ipso* isomer *i*-T. Also on the basis of its relatively higher energy, the presence of *i*-T appears unlikely. This isomer is in fact considerably less stable than *o*-T, *m*-T, and *p*-T, quite in contrast with the silicon analogue, namely protonated phenylsilane, where the favored *ipso* isomer has been recently identified by IRMPD spectroscopy [9c]. A second comment on the IRMPD spectrum of protonated toluene regards the band at 1593 cm^{-1}. This feature, appearing in correspondence with the bands calculated at 1580, 1570, and 1587 cm^{-1} in the linear IR spectra of *o*-T, *m*-T, and *p*-T, respectively, is associated to a C–C stretching mode of the formal double bonds in the 1,4-cyclohexadienylium representation of the arenium ion. This specific band shows anomalously low intensity in the IRMPD spectrum, at least if a substantial contribution of *p*-T is expected. However, there is precedent for the low activity of this particular mode in the IRMPD spectra of both benzenium and fluorobenzenium ions [9a,b].

When $C_2H_5^+$ ions are allowed to react with toluene-d_8, the initial protonation event at a ring carbon may be followed by 1,2-H/D shifts ending in a mixture of ions differing for the site (*ortho*, *meta*, or *para*) of the methyl substituent relative to the tetrahedral ring carbon and also for the position of the single hydrogen atom within the ion skeleton. Eq. (1) shows an example of the several conceivable pathways that may be accessed following

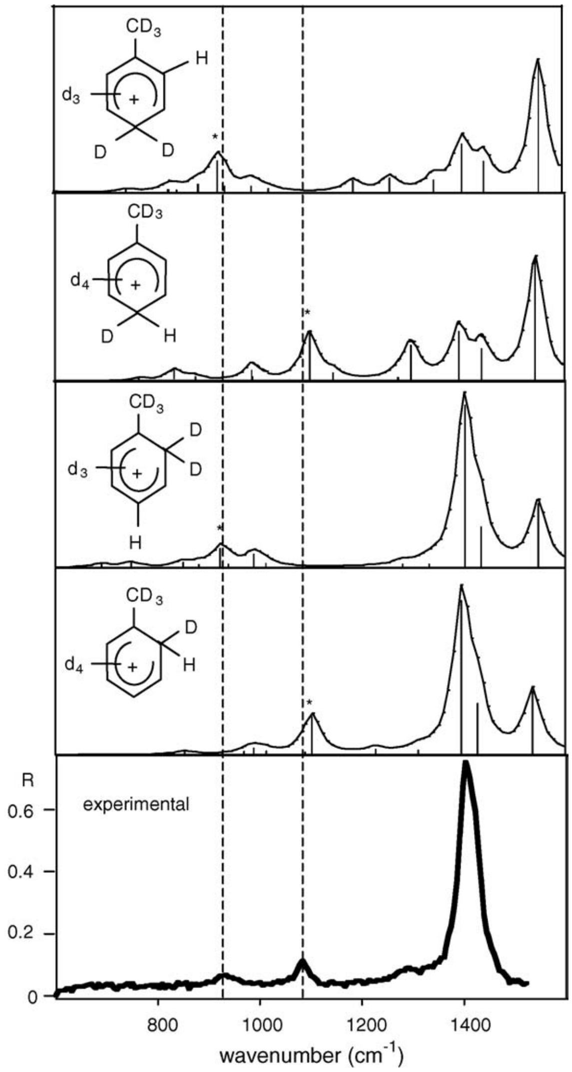
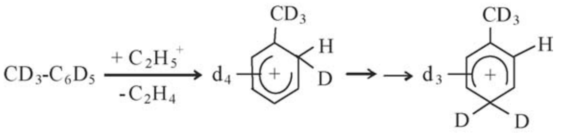


Fig. 4. Experimental IRMPD spectrum of protonated toluene-d_8 (reporting the IRMPD yield *R*), using $C_2H_5^+$ as protonating agent. Computed linear IR absorption spectra are shown for exemplary toluenium ions bearing a ring hydrogen in an otherwise perdeuterated structure. The relative scales for all calculated spectra are the same. The characteristic absorptions associated to the scissoring mode of a CHD or CD_2 group on the ring are marked by asterisks. The vertical dashed lines mark the position of the significant features at 1083 and 928 cm^{-1} in the IRMPD spectrum.

the encounter of $C_2H_5^+$ and toluene-d_8.



(1)

Insight into the so-formed ion mixture can be obtained by viewing the IRMPD spectrum in comparison with the calculated IR spectra of potential candidates. In the variety of conceivable structures two classes of isotopomers can be distinguished for each toluenium ion, namely those bearing the single H atom on the tetrahedral ring carbon and those where the H atom is placed on an sp^2 carbon. The latter ones are formed by at least one D-shift following the initial protonation event. The major feature differentiating the two classes is the presence of either a CHD or a CD_2 group on the ring. The calculated linear IR absorption spectra of exemplary ions are shown in Fig. 4 together with the IRMPD spectrum of protonated perdeuterotoluene. Significant features in the computed spectra are the distinct absorptions due to the 'scissor' mode of a CHD or the CD_2 group on the toluenium ring. The frequencies of these bands fall in the relatively narrow ranges of 1102–1105 and 918–925 cm^{-1}, respectively, for all conceivable isotopomers with an *ortho*/*para* methyl group relative to the tetrahedral carbon, including those shown in Fig. 4. Both features appear clearly in the IRMPD spectrum of protonated toluene-d_8 at 1083 and 928 cm^{-1}, respectively, demonstrating the occurrence of D-shift following the protonation of perdeuterated toluene under the present experimental conditions. The comparatively lower IRMPD signal at 928 cm^{-1} with respect to the band at 1083 cm^{-1} should not be related to a minor abundance of those toluenium isotopomers containing a CD_2 group. In fact, the calculated IR oscillator strength of the CX_2 (X = H, D) 'scissoring' mode decreases in the series $CH_2 > CHD > CD_2$ and the relative intensities of the IRMPD features do not reflect the relative amounts of isotopomeric ions in the mixture.

4. Concluding remarks

The present contribution shows that IRMPD spectroscopy is a useful tool to probe the presence of isotopomeric ions in a gaseous mixture. By this tool, the occurrence of hydrogen shift processes following the protonation of toluene by $C_2H_5^+$ ions is verified in the gas phase by a direct spectroscopic methodology, in agreement with previous evidence on ring hydrogen shifts in toluenium ions formed both in solution and in the gas phase [2a,13a]. It is conceivable that the process may take advantage of the energy imparted by the exothermic protonation reaction by $C_2H_5^+$ ions, allowing the so-formed toluenium ions to pass over the activation energy barrier associated to the hydrogen shift process [1,10,11,25b]. However, the possibility of using IRMPD as a novel probe for testing this type of unimolecular reactivity may open the way to further investigations on the role of factors such as the exothermicity of the protonation event and the consequence of pronounced energy barriers to 1,2-hydrogen shift in appropriately selected arenium ions.

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