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The infrared spectrum of the benzoyl cation

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Abstract

The vibrational spectrum of the gas phase benzoyl cation ($C_6H_5CO^+$) in the 500–2500 cm^{-1} range is presented. Vapor phase benzoic acid is photolyzed/photoionized using an ArF excimer laser and the resulting ionic fragments are stored in a quadrupole ion trap. The benzoyl cation is subsequently isolated and its infrared spectrum is recorded through multiple photon dissociation spectroscopy with a free electron laser. Density functional calculations predict a C_{2v} structure for the benzoyl cation, which is in good agreement with the observed spectrum.

The benzoyl radical, $C_6H_5C^{\bullet}{=}O$, hypothesized already in 1789 by Lavoisier [1], was discovered by Wöhler and von Liebig [2] in 1832 [1] as a derivative of benzaldehyde, a constituent of the oil of bitter almonds, and it was found to be a robust chemical unit.

Removal of the unpaired electron from the benzoyl radical, forms the benzoyl cation with a closed-shell electronic structure. In general, such closed-shell ions form an interesting class of species as they are likely more stable than open-shell ions. For instance, it was recently suggested that closed-shell cationic species may occur in interstellar space [3]. Moreover, this study implicitly shows that the method applied here allows to record infrared spectra and hence obtain structural information on ionic unimolecular reaction products.

Over the past decades, ion storage devices have become standard analytical equipment and despite the relatively low ion densities, various methods have been successfully applied to obtain spectroscopic information on trapped ions [4], both in the UV–Vis [5–7] and infrared [8–10] spectral ranges. Here we apply a widely tunable free electron laser and a quadrupole ion trap [11] to record the infrared multiple photon dissociation (IRMPD) spectrum of the benzoyl cation (as a photo-product of benzoic acid) and discuss the vibrational spectrum of this molecular fragment ion.

The experimental apparatus was described in detail previously [11]. Benzoyl is formed by UV

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[1] At that time, the term radical referred to an inalterable chemical unit, rather than to a 'free radical', i.e., a species having an unpaired electron as in modern terminology.

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photolysis of benzoic acid (C_6H_5COOH) using an ArF excimer laser and subsequent storage of the ionic photo-products in a quadrupole ion trap [12] equipped with a time-of-flight (TOF) mass spectrometer [13]. It was found that under the influence of the focused 193 nm radiation, the benzoic acid parent was completely photodestroyed. The upper trace of Fig. 1, shows the fragmentation pattern induced by the ArF laser, where the main fragment at $m/z = 105$ corresponds to the benzoyl cation, $C_6H_5CO^+$. In addition, many smaller fragments are observed among which the $C_6H_5^+$ cation at $m/z = 77$ and the $C_3H_3^+$ cation at $m/z = 39$. The parent benzoic acid cation visible at $m/z = 122$ is formed by ion-molecule reactions occurring after the UV pulse during the time that the ions are stored in the trap (400 ms). Note that also the protonated benzoic acid cation is formed.

Next, the benzoyl cation is isolated through axial ejection of all ions with $m/z \leqslant 104$ by increasing the rf amplitude [11,14] for 2 ms immediately after the UV pulse. This procedure also removes the benzoic acid cation and its hydrogenated counterpart from the trap suggesting that they are formed from the smaller fragments and not from ionic benzoyl. The result of the rf ejection pulse is a clean isolated sample of cationic benzoyl as seen in the second trace of Fig. 1.

The isolated benzoyl ion cloud is irradiated with the intense narrow-band infrared radiation of the Free Electron Laser for Infrared eXperiments (FELIX [15]), which is focused in the center of the trap. FELIX typically produces 50 mJ macropulses of 5 μs duration, each consisting of around 5000 micropulses of ps-duration. The tuning range of FELIX is 5–250 μm and the range between 4 and 5 μm was scanned separately using the third harmonic of FELIX. In the present experiments, a bandwidth of typically 0.6% FWHM of the central wavelength is used. If the wavelength is in resonance with an infrared transition of the benzoyl cation, multiple photon absorption can occur by virtue of the high laser fluence. It should be noted that *multiple photon* absorption occurs via a sequential (incoherent) process [11,16–18], where the absorption of each photon is followed by redistribution of the energy into the bath of vibrational background states. The ion thus absorbs repeatedly on the $v = 1 \leftarrow v = 0$ transition, thereby partly avoiding the anharmonicity bottleneck that is encountered in a coherent *multiphoton* absorption process, i.e., vibrational ladder climbing.

The effect of IRMPD is illustrated in the lower trace of Fig. 1, where two macropulses of FELIX at $\lambda = 8.7$ μm (1150 cm^{-1}) are applied. Apparently, infrared multiple photon absorption leads almost exclusively to detachment of the C=O group forming the phenyl ion ($C_6H_5^+$) at $m/z = 77$. The dissociation threshold for this channel is estimated to be 3.0 eV (see below), which corresponds to about 25 photons at $\lambda = 10$ μm. A background-free infrared spectrum of the benzoyl cation is obtained by recording the $m/z = 77$ ion yield while scanning the wavelength of FELIX.

Two main pathways for the formation of the benzoyl cation from neutral benzoic acid are conceivable as sketched in Fig. 2. Calculated [19] (B3LYP/D95(d,p)) ionization and dissociation

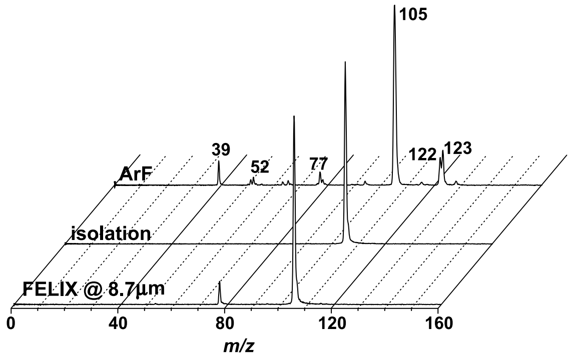

Fig. 1. Mass spectra of 193 nm irradiated benzoic acid. The upper trace shows the ionic products of UV photolysis. The middle trace is obtained after isolation of the benzoyl cation ($m/z = 105$), which upon irradiation with FELIX at $\lambda = 8.7$ μm yields the lower trace.

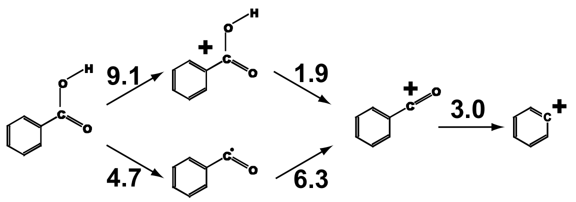

Fig. 2. Possible photodegradation pathways of benzoic acid (energies in eV).

(ΔD_e) energies in eV are indicated and are in good agreement with experimental values [20,21] (where available). When using an ArF laser ($h\nu = 6.4$ eV), these ion energetics suggest fragmentation to occur before ionization as it can proceed through sequential one-photon absorption processes. This is consistent with the absence of the benzoic acid cation as an initial photoproduct.

The infrared spectrum of the benzoyl cation is shown in Fig. 3 and the experimental line positions and relative intensities are given in Table 1. Laser power-dependence measurements were made on different bands yielding a nearly linear behavior. Despite the fact that relative intensities in the IR-MPD spectrum depend in a complex fashion on the (unknown) anharmonicity parameters for each of the vibrational modes, one finds that relative intensities are in general rather close to those in a linear absorption spectrum (represented by the calculated spectrum in Fig. 3). This was already found for various cationic polyaromatic hydrocarbons [11,18], and is probably even more true for the benzoyl ion due to the substantially lower dissociation threshold, which further limits the influence of anharmonicities. Note that some subtle discrepancies in the spectrum of cationic coronene could be accounted for by the effects of vibrational anharmonicity [22]. As the FELIX beam profile in the third harmonic is quite different from that in the fundamental, intensities of the peaks in the 4 μm range relative to those in the rest of the spectrum are only good to within a factor of two.

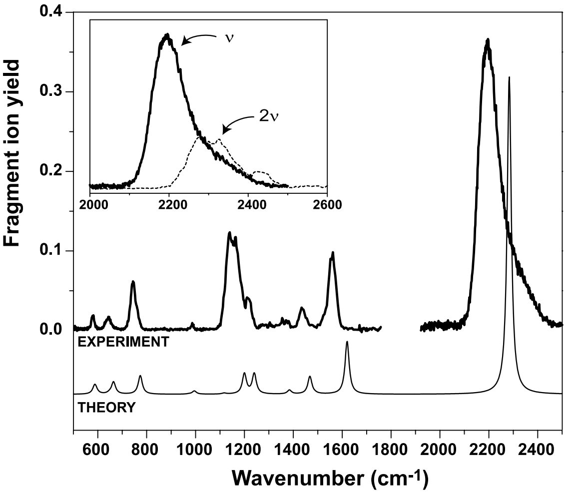

Fig. 3. Experimental and calculated spectra of the benzoyl cation. The inset shows that the blue shoulder on the CO stretch mode is likely due to the overtones of the CH bending modes near 1150 cm^{-1}.

Table 1
Observed and calculated line positions and intensities for the benzoyl cation

B3LYP/D95(d,p)			Experiment		Approximate description^a
C_{2v}	ν^b	$I_{rel}{}^c$	ν	I_{rel}	
b_1	586	0.17 (28)	580	0.16	$\beta'_{CCO}/\beta'_{ring}$
b_1	662	0.23 (37)	641	0.15	β'_{ring}
b_1	772	0.35 (56)	745	0.56	β'_{CH}
a_1	993	0.06 (10)	985	0.08	δ_{ring}
a_1	1198	0.37 (59)	1140	1.00	β_{CH}
a_1	1239	0.39 (62)	1162	0.93	$\beta_{CH}/\sigma_{C\text{–}C}$
			1216	0.35	
b_2	1383	0.07 (12)	1367	0.11	β_{CH}/σ_{CC}
b_2	1467	0.34 (54)	1436	0.26	β_{CH}/σ_{CC}
a_1	1619	1.00 (161)	1558	0.89	σ_{CC}/β_{CH}
a_1	2283	6.00 (966)	2196	>4	σ_{CO}
			≈ 2280	sh	'2 × 1140'
			≈ 2325	sh	'2 × 1162'
b_2	3235	0.06 (10)			σ_{CH}

[a] β ip bend, β' oop bend, σ stretch, δ deformation.
[b] Only bands with intensity $\geqslant 10$ km/mol are listed.
[c] Absolute intensities in km/mol in parentheses.

The FWHM linewidth of the bands varies between 20 and 35 cm^{-1} (100 cm^{-1} for the CO stretch), which is due to a combination of anharmonicity, the spectral width of FELIX and the rotational envelope at room temperature. Simulations performed for the coronene cation [22] show that this width is mainly determined by the anharmonicity parameters of the different vibrational modes. However, for smaller ions and lower dissociation thresholds, the contribution of the rotational envelope to the observed linewidth becomes increasingly more important relative to anharmonic broadening. From the calculated rotational constants we estimate a FWHM rotational envelope on the order of 10–15 cm^{-1} for the benzoyl cation. The FELIX bandwidth of typically 5 cm^{-1} contributes only slightly to the observed linewidth.

The vibrational spectrum of the benzoyl ion in its singlet ground electronic state ($^1A_1$) is calculated using the B3LYP functional and the D95(d,p) basis set as implemented in GAUSSIAN 98 [19]. The optimized geometry for the cation has C_{2v} symmetry, i.e., the C—C=O angle is 180°. Upon ionization of the benzoyl radical, the removal of the unpaired electron from the carbonyl C atom changes the hybridization from sp^2 to sp, which makes the C=O bond substantially stiffer and shifts the calculated C=O stretching vibration from 1881 cm^{-1} in the neutral to 2283 cm^{-1} in the ion.

Calculated and observed vibrational frequencies given in Table 1 are in good agreement if one considers that experimental frequencies are usually slightly red shifted due to the multiple photon absorption process and the inherent influence of anharmonic coupling. Moreover, it is known that the B3LYP functional overestimates frequencies by typically a few percent [23]. With these arguments in mind, an unambiguous assignment of most of the experimental bands can be easily made. However, the relative intensities for the two in-plane CH bending modes around 1150 cm^{-1} appear to be underestimated in the calculation by a factor of three. Moreover, unexplained features are observed at 1216 cm^{-1} and as a blue shoulder on the CO stretching band. An inspection of fundamental frequencies and symmetries in Table 1 shows that the overtones of the two modes around 1150 cm^{-1} should fall just to the blue of the very strong CO stretching mode and that their symmetry allows them to borrow intensity from this mode via a Fermi interaction, thus giving rise to the blue shoulder (see inset of Fig. 3). Similarly, the 1216 cm^{-1} band is possibly due to a combination band involving the 580 cm^{-1} (b_1) and 641 cm^{-1} (b_1) modes, in Fermi interaction with the two bands around 1150 cm^{-1} (both a_1). However, depending on the exact values for the anharmonicity and the Fermi interaction strength, the 1216 cm^{-1} band might also be due to the overtone of the 580 cm^{-1} band.

The increased intensity of the two closely spaced fundamental CH bending modes near 1150 cm^{-1} is possibly due to the nature of the excitation process [22]. Usually, in an ion that is gradually heated by multiple photon absorption, the IR resonance shifts to the red due to anharmonicity and eventually loses spectral overlap with the excitation laser. However, if the spectrum contains two or more closely spaced bands, the blue peak gradually shifts into resonance. As a consequence, the red peak appears stronger than its blue counterpart.

In conclusion, the first infrared spectrum of the benzoyl cation in the 500–2500 cm^{-1} range is presented. The spectrum shows good agreement with DFT calculations over the entire wavelength range investigated. However, it also shows the effects that intramolecular couplings and multiple photon absorption may have on (intensities in) the spectrum. IRMPD using a widely tunable-free electron laser in combination with mass spectrometric techniques for ion storage and isolation is shown to be a useful tool in the study of transient ionic species such as photo-fragmentation products.

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