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Structural characterization of selectively prepared cationic iron complexes bearing monodentate and bidentate ether ligands using infrared photodissociation spectroscopy

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Abstract

The infrared spectroscopy of gaseous ions $Fe(CH_3OCH_3)_2^+$ and $Fe(CH_3OCH_2CH_2OCH_3)_n^+$ (n = 1-2) has been studied in the 800–2000 cm⁻¹ energy range using the coupling of the free electron laser CLIO and an FTICR mass spectrometer, and compared to spectra calculated by ab initio quantum chemistry. The match between experimental and theoretical infrared spectra appears to be very good, the experimental spectra corresponding to the most stable structure predicted by the calculations. Characteristic absorption bands of functional groups have been evidenced, allowing this coupling to be a very powerful tool for structure elucidation in the gas phase.

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1. Introduction

Infrared spectroscopy is a powerful tool to characterize the structure of chemical species. This is particularly true in the gas phase, since the experimental infrared spectra can be directly compared with those calculated by ab initio quantum chemistry. However, in the case of ionic species, the low density available in the gas phase prevents usual absorption measurements. In recent years much effort has been put into the development of experimental methods to study the infrared spectroscopy of gas phase ions, most of them being based on ion photodissociation coupled with mass spectrometric detection. Dissociation induced by light absorption requires either the presence of a low energy dissociation pathway which can be reached upon absorption of one IR photon, or a high irradiation power so that absorption of several photons may occur and induce fragmentation. The former way has been used to get structural information upon complexes presenting weak electrostatic interactions [1]. The scope of this

method can be broadened by using the 'messenger atom' technique [2-5], the complex of interest being bound to a rare gas atom which is ejected upon absorption of one photon in the mid-IR. The latter way, known as infrared multiphoton dissociation (IRMPD), requires a high fluence, initially available only with CO₂ lasers. These lasers provide knowledge of the photofragmentation processes [6-8], but their narrow wavelength range prevents spectroscopic studies. In the recent years, the application of free electron lasers (FEL) which provide high peak power and wide tunability has enabled to record infrared spectra in a large energy range [9-13]. Under these conditions, infrared absorption can be probed by monitoring IRMPD by mass spectrometry. In this respect, Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometers are ideal tools, allowing to selectively prepare ions and to distinguish fragmentation pathways yielding ions of close masses such as H or H₂ loss, because of their high resolution. Coupling of an FT-ICR mass spectrometer with an infrared FEL, recently performed in our group [14-16], opened the way to the direct characterization of selectively prepared ions, including reactive intermediates [17].

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Transition metal complexes bearing bidentate ligands such as dimethoxyethane CH₃OCH₂CH₂OCH₃ (DXE) raise interesting structural questions since the dihapto (η^2) coordination mode does not allow a *trans* geometry which is generally the most stable form of a ML₂⁺ complex. This might induce either ligand activation with C–O bond cleavage, or stabilization of the η^1 form, the low enthalpic loss being counterbalanced by the entropic gain.

In order to directly determine the DXE coordination mode, we present here the infrared spectra of the cationic complexes $Fe(DXE)^+$ and $Fe(DXE)_2^+$, along with the corresponding ab initio calculations. The IR spectrum of the analogous complex $Fe(DME)_2^+$, bearing the monodentate ligand dimethylether CH_3OCH_3 (DME), is also described for comparison. Ion-molecule reactions of DME [18] and DXE [19] with iron cationic complexes have been studied in our group, showing that C–O bond activation occurs in these systems. In the case of the $Fe(DME)^+/DME$ reaction, two pathways are observed, corresponding either to the loss of CH_3° or CH_4 by the $[Fe(DME)_2^+]^*$ intermediate complex. Therefore it is interesting to determine whether soft energy deposition in $Fe(DME)_2^+$ by IRMPD leads to the same products.

2. Experimental and theoretical methods

2.1. FT-ICR mass spectrometer

A compact and easily transportable FT-ICR mass spectrometer has been developed in our laboratory [20]. It is well suited for temporary coupling to a FEL machine. It is based on a structured permanent magnet with a nominal field of 1.25 T. The mass resolution $m/\Delta m$ is better than 70,000 at mass 131. The trap differs from the usual cubic FT-ICR cell by its open structure, allowing wide optical access to the cell center. Primary ions are generated in the cell by electron impact on neutral species admitted through pulsed valves.

2.2. FEL

Tunable infrared radiation is produced by the FEL CLIO [21]. The tuning range is $110-3300 \text{ cm}^{-1}$, although only the region from 800 to 2000 cm⁻¹ is used in the present experiments. Continuous tunability is obtained over a spectral range $\Delta\lambda/\lambda \approx 2.5$. The FEL relative bandwidth is typically 0.3% when the optical cavity is tuned in order to minimize it (at the expense of the peak power). The FEL temporal structure consists of macropulses of 8 µs duration, at a repetition rate of 25 Hz. Each macropulse contains a series of 1–2 ps micropulses at a repetition rate of 62.5 MHz. A macropulse contains up to 40 mJ of energy, with a peak power of 40 MW in each micropulse. The infrared light is focused in the

center of the ICR cell with a 1 m focal length mirror. The beam alignment and mirror position have been set so as to optimize the photofragmentation rates of organometallic species, such as $Fe(CO)_5^+$.

2.3. Experimental sequence

The conditions used for ion preparation are specified below:

- Ions Fe(CO)⁺_n (n = 0-5) are prepared by electron ionization of Fe(CO)₅.
- The Fe(DME)⁺₂ (Fe(DXE)⁺) ions are mass-selected after reaction for 1 s of mass-selected Fe(CO)⁺₂ ions with DME (resp. DXE) pulsed for 100 ms. The Fe(DXE)⁺₂ ions are mass selected after reaction of Fe(CO)⁺_n (n = 0-5) ions with DXE pulsed for 800 ms. The flow of pulsed reactant gases corresponds to 10⁻⁶ Torr static pressure.
- To ensure ion relaxation, a delay of 500–1000 ms is allotted before irradiation.

InfraRed MultiPhoton Dissociation (IRMPD) is evidenced by the appearance of photofragment ions following IR excitation. The fragmentation efficiency, defined as $-\ln(I_{parent})$ where I_{parent} is the relative intensity of the parent ion, is recorded as a function of the wavelength to obtain the infrared spectrum of the parent ion.

2.4. Theoretical calculations

Theoretical calculations are performed with the GAUSSIAN 98 suite of programs [22] using the B3LYP hybrid density functional. For iron, we used the [8s6p4d1f] contraction of the (14s11p6d3f) primitive basis set as recommended by Bauschlicher [23]. A polarized double-zeta basis set was used for the ligands [24]. All the structures calculated were characterized as minima except for (η^1, η^1) Fe(DXE)⁺₂, which presents a small imaginary frequency (i179 cm⁻¹), corresponding to the rotation of the methyl group directly attached to the oxygen atom bound to the metallic center.

The harmonic vibrational frequencies calculated are presented with a scaling factor of 0.98, determined by comparing the calculated and experimental [25] infrared lines of the free dimethylether ligand in the 800–2000 cm⁻¹ range. Each line is convoluted by a lorentzian profile of 50 cm⁻¹ fwhm, in order to facilitate comparison with IRMPD spectra.

3. Results and discussion

The three ions studied lead to several photofragments, resulting from successive and/or parallel fragmentations. The primary processes are the only one reported here. They are identified in different ways, for instance by decreasing the laser power so that the primary photoproducts do not reabsorb light and predominate over the others. Discussion of the sequential fragmentation mechanisms will be published separately.

3.1. $Fe(CH_3OCH_3)_2^+$

The Fe(DME) $_2^+$ ions were irradiated for 1 s with photons of wavelength ranging from 800 to 1600 cm⁻¹. The IRMPD spectrum, obtained with an average laser power of 600–800 mW is shown in Fig. 1, and the corresponding predicted and experimentally observed IR band positions are listed in Table 1.

The most stable calculated structure for this complex is $Fe(DME)_2^+$ in which two intact DME ligands lie in *trans* position around the metallic center (D_{2d} symmetry and quartet spin state, as expected from the calculations on $Fe(H_2O)_2^+$ [26]). There is an excellent agreement between the predictions of theory and the measurements, as reproduced in Fig. 1 and Table 1, both in terms of positions and relative intensities of the infrared transitions. The isomer with the inserted structure



Fig. 1. Experimental (fine line with markers) and theoretical (thick line) infrared spectrum of $Fe(DME)_2^+$. The calculated structure of $Fe(DME)_2^+$ is also given.

 $(DME)Fe(CH_3)(OCH_3)^+$ is predicted to lie 21 kJ mol⁻¹ higher in energy. The strongest band in its calculated infrared spectrum, appearing at 1110 cm⁻¹, is absent from the experimental spectrum, which confirms the Fe(DME)₂⁺ structure predicted by theory.

The remarkable consistency obtained between experimental and predicted spectra was not obviously expected concerning band intensities: while the calculations correspond to one-photon absorption, the IRMPD mechanism represents a much more complex process. The conditions required for this agreement correspond to a relative fragmentation amount comprised between 3% and 20% per macropulse in the absorption peaks. In this range, the fragmentation efficiency was observed to vary almost linearly with the laser power.

The primary photofragments are $Fe(OCH_2)(DME)^+$ (major) and $Fe(OCH_3)(DME)^+$, resulting from loss of CH₄ and CH[•]₃, respectively. The corresponding branching ratio remains comprised between 75% and 95% (generally close to 85%) methane loss, for all wavelengths leading to fragmentation. Interestingly, no DME loss was observed. The constancy of the branching ratio throughout the spectrum, i.e. whatever the nature of the vibration initially excited by IR radiation, is consistent with the hypothesis of fast internal vibrational redistribution (IVR) resulting in energy redistribution over the ion vibration modes prior to the fragmentation process.

3.2. $Fe(CH_3OCH_2CH_2OCH_3)^+$

Mass-selected Fe(DXE)⁺ ions were irradiated for 500 ms with photons of wavelength ranging from 800 to 1800 cm⁻¹. Primary fragmentation consists in a unique process, ethylene loss:

$Fe(CH_3OCH_2CH_2OCH_3)^+ \rightarrow [Fe, C_2, H_6, O_2]^+ + C_2H_4$

The experimental spectrum, recorded for an average laser power of 680 mW, is depicted in Fig. 3, along with the predicted spectra of the lowest energy lying structures.

Table 1

Band positions and relative intensities of the experimental and theoretical spectra of $Fe(DME)_2^+$, along with an approximate description of each mode

Description of the vibrations	Symmetry	Position (cm ⁻¹)		Relative intensity		
		Calculated	Experimental	Calculated	Experimental	
C–O sym. str.	b_2	871	852	1.00	1.00	
C–O asym. str.	e	1017	1015	0.94	0.93	
CH ₃ rock.	e	1137	1155	0.19	0.24	
CH ₃ rock.	b ₂	1248	1258	0.12	0.15	
CH ₃ d-def.	e	1454	1458	0.48	0.31	
CH ₃ d-def. ^a	e	1453				
	b ₂	1473				

^a Type: CH₂ scissoring.



Fig. 2. Calculated structures of the most stable DXE conformer as well as (η^1) - and (η^2) Fe $(DXE)^+$ ions. Distances are given in angströms and angles in degrees.



Fig. 3. Experimental (fine line with markers) and theoretical (thick lines) infrared spectrum of Fe(DXE)⁺. The black/red, grey/blue and dashed/green theoretical spectra correspond to sextet- (η^2) -, quartet- (η^2) - and sextet- (η^1) Fe(DXE)⁺, respectively.

Two non-inserted forms of Fe(DXE)⁺ were considered, the DXE molecule being bound by either one or both oxygen atoms. The corresponding calculated structures are depicted in Fig. 2, as well as the most stable DXE conformer. They are termed as (η^1) Fe(DXE)⁺ and (η^2) Fe(DXE)⁺, where η refers to the actual DXE hapticity in the complex. The (η^2) Fe(DXE)⁺ isomer in a sextet spin state has been found to be lowest energy isomer, but the lowest quartet spin state only lies +8 kJ mol⁻¹. Fe(DXE)⁺ isomers presenting a η^1 coordination are much higher in energy (+94 kJ mol⁻¹), and the lowest spin state is also a sextet, although a quartet spin state isomer has been found only +4.7 kJ mol⁻¹ higher in energy. The Fe⁺-(η^2)DXE binding energy at 0 K is 289 kJ mol⁻¹. This value can be compared to the one calculated for $Cu(DXE)^+$ (297 kJ mol⁻¹) by Koizumi et al. [27] at similar level of theory, also predicting a bidentate coordination. The Fe⁺-(η^1)DXE binding energy at 0 K is calculated to be 195 kJ mol⁻¹. This value is larger but of the same order of magnitude than the value found by Ricca et al. in the case of a water ligand (140 kJ mol⁻¹) [26].

As can be seen in Fig. 2, the experimental spectrum is in very good agreement with the spectrum calculated for (η^2) Fe(DXE)⁺ in both its sextet and quartet spin state. The corresponding predicted and experimentally observed IR band positions are given in Table 2. The strong band appearing at 1019 cm^{-1} corresponds to C-O asymmetric stretching, whereas the weaker band at 1460 cm⁻¹ can be assigned to a combination of bands corresponding to dissymmetric CH₃ deformation and CH₂ scissoring. There is a better agreement between the experimental and the calculated spectrum of the sextet $(\eta^2)Fe(DXE)^+$ isomer, but the predicted difference in the positions of the C-O asymmetric stretching, for example, are too small to conclude. On the other hand, the energetically disfavored (η^1) Fe(DXE)⁺ presents an IR spectrum clearly different from the experimental spectrum. In particular, there is a strong band at 1150 cm⁻¹, which is not observed experimentally.

3.3. $Fe(CH_3OCH_2CH_2OCH_3)^+_2$

Mass-selected $Fe(DXE)_2^+$ ions were irradiated for 500 ms with photons of wavelength ranging from 800 to 2000 cm⁻¹. The experimental spectrum, recorded for an average laser power of 510 mW, is depicted in Fig. 5, along with the calculated spectra of three potential isomers (see below). The corresponding predicted and experimentally observed IR band positions are shown in Table 3.

Three isomers of $Fe(DXE)_2^+$ corresponding to the three $(\eta^1, \eta^1) (\eta^1, \eta^2)$ and (η^2, η^2) combinations of the coordination mode of the two DXE ligands have been

Table 2

Band positions and relative intensities of the experimental and theoretical spectra of Fe(DXE)⁺, along with an approximate description of each mode

Approximate description	Sextet- (η^1) Fe $(DXE)^+$		Sextet-(η^2)Fe(DXE) ⁺		Quartet- (η^2) Fe(DXE) ⁺		Experimental	
	Position (cm ⁻¹)	Relative intensity	Position (cm ⁻¹)	Relative intensity	Position (cm ⁻¹)	Relative intensity	Position (cm ⁻¹)	Relative intensity
C _{ter} –O sym. str.; CH ₂ rock	870	0.86	841	0.26	844	0.19	n.d.	n.d.
Cter-O asym. str.; C-C str.	979	1.00	1024	1.00	1039	1.00	1019	1.00
	1076	0.32	1073	0.19	1074	0.08	1074 ^b	
CH ₂ twist; CH ₃ rock.	1150	0.78		< 0.03		< 0.03		
CH ₃ d-def.; CH ₂ scissoring ^a	1459	0.43	1457	0.28	1456	0.25	1461	0.20

^a Several close absorption bands of the same nature in the calculated spectra, leading to a unique peak after lorentzian convolution. ^b Appears as a shoulder in the main peak.

Table 3 Band positions and relative intensities of the experimental and theoretical spectra of $Fe(DXE)_{2}^{+}$

Approximated description	(η^1, η^1) Fe $(DXE)_2^+$		$(\eta^1,\eta^2)Fe(DXE)_2^+$		(η^2, η^2) Fe $(DXE)_2^+$		Experimental	
	Position (cm ⁻¹)	Relative intensity	Position (cm ⁻¹)	Relative intensity	Position (cm ⁻¹)	Relative intensity	Position (cm ⁻¹)	Relative intensity
C _{ter} –O sym. str.; CH ₂ rock ^a	907	0.88	858 915	0.26	866	0.20	n.d.	n.d.
C _{ter} –O asym. str.; C–C str.	1000 ^a	1.00	1019	0.33	1025	0.06	999 ^b	1.00
C _{ter} –O asym. str.	1088 ^a	0.52	1059 ^a	1.00	1067 1102	1.00 0.14	1056 1093 ^ь	
CH ₃ rock; CH ₂ twist ^a	1147	0.98	1146	0.53	1176	0.06	1188	0.20
CH ₂ twist; CH ₃ rock ^a	1184	0.48	1184	0.21	1233	0.05	1244	0.20
CH ₃ d-def.; CH ₂ scissoring ^a	1461	0.42	1461	0.34	1462	0.22	1473	0.1

^a Several close absorption bands of the same nature in the calculated spectra, leading to a unique peak after lorentzian convolution.

^bAppears as a shoulder in the main peak.

considered, and the optimized structured are given in Fig. 4. In these three isomers, oxygens of two different ligands bind in *trans* from each other and a quartet spin ground state is found. The lowest energy structure corresponds to the $(\eta^2$ -DXE)Fe⁺- $(\eta^2$ -DXE) isomer. The $(\eta^2$ -DXE)Fe⁺- $(\eta^1$ -DXE) and $(\eta^1$ -DXE)Fe⁺- $(\eta^1$ -DXE) isomers lie respectively 47 and 111 kJ mol⁻¹ higher in energy. As expected, the binding energy of the η^1 -DXE in $(\eta^1$ -DXE)Fe⁺- $(\eta^1$ -DXE) (170 kJ mol⁻¹) is of the same order of magnitude as Fe⁺- $(\eta^1$ -DXE). It should be

noted however that the binding energies of η^1 -DXE and η^2 -DXE to (η^2 -DXE)Fe⁺ (144 and 191 kJ mol⁻¹) are significantly smaller than the corresponding binding energies to Fe⁺ (195 and 289 kJ mol⁻¹). Both values are slightly higher than those calculated for the corresponding copper complexes (125 and 168 kJ mol⁻¹, respectively [27]).

The experimental spectrum nicely matches with the IR spectrum calculated for the bis-bidentate (η^2, η^2) Fe(DXE)⁺₂ structure. As for the (η^2) Fe(DXE)⁺, the



Fig. 4. Calculated structures of (η^1, η^1) -, (η^1, η^2) - and (η^2, η^2) Fe(DXE)⁺₂ ions. Distances are given in angströms and angles in degrees.



Fig. 5. Experimental (fine line with markers) and theoretical (thick lines) infrared spectrum of Fe(DXE)₂⁺. The black/red, grey/blue and dashed/green theoretical spectra correspond to (η^2, η^2) -, (η^1, η^2) - and (η^1, η^1) Fe(DXE)₂⁺, respectively. The vertical lines at 915 and 1146 cm⁻¹ help for comparison.

 (η^2, η^2) Fe(DXE)⁺₂ IR spectrum is characterized by two main features. First, a broad band corresponding to deformations of CH₃ and CH₂ scissoring at 1462 cm⁻¹, corresponding to the band at 1473 cm⁻¹ in the experimental spectrum. Second, the most intense band observed in the experimental IRMPD spectrum at 1056 cm⁻¹ could be attributed to the C–O asymmetric stretching modes, the most intense being predicted at 1067 cm⁻¹. The two other (weaker) experimental features at 1188 and 1244 cm⁻¹ could also be assigned from the calculated IR spectrum of (η^2, η^2) Fe(DXE)⁺₂, the former corresponding to CH₃ rock (1176 cm⁻¹) and the latter to CH₂ twist (1233 cm⁻¹).

The (η^1, η^2) Fe(DXE)₂⁺ structure can be excluded since it should lead to photodissociation at 1146 cm⁻¹, where a strong IR absorption band is predicted, whereas this energy corresponds to a minimum in the IRMPD absorption efficiency (see Fig. 5). Similarly, the (η^1, η^1) Fe(DXE)₂⁺ isomer can also be excluded since the IRMPD photofragmentation signal vanishes at 900 cm⁻¹, whereas it is a maximum in the IR absorption spectrum of the (η^1, η^1) Fe(DXE)₂⁺ isomer.

As in the case of $Fe(DME)_2^+$ and $Fe(DXE)^+$, the IRMPD spectrum of $Fe(DXE)_2^+$ is in good agreement with the IR absorption spectrum of the lowest energy isomer predicted by ab initio calculations. It should be noted that a similar (η^2, η^2) structure has been experimentally assigned to $Cu(DXE)_2^+$ based on the comparison of collision-induced dissociation results and ab initio calculations [27].

Primary fragmentation of $Fe(DXE)_2^+$ consists exclusively in ethylene loss, as for $Fe(DXE)^+$:

$$\operatorname{Fe}(\operatorname{DXE})_2^+ \to \operatorname{Fe}(\operatorname{OCH}_3)_2(\operatorname{DXE})^+ + \operatorname{C}_2\operatorname{H}_4$$

For comparison, IRMPD of crown ether complexes of alkali metals or H_3O^+ at 943 cm⁻¹, reported by Peiris et al. [28], follows very different schemes: dissociation of crown ether alkali metal complexes leads to the loss of the ligand at low laser fluences, the dissociation of the crown ether being not observed. Dissociation of crown ether H_3O^+ complexes proceeds via loss of water to generate protonated crown ether, which is fragmented at high fluence through loss of C_2H_4O units. The particular fragmentation behaviour of our DXE complexes may be explained by the possibility for Fe⁺ insertion into the C–O bond.

4. Conclusion

Infrared spectra of three cationic iron complexes bearing ether and diether ligands have been obtained in the gas phase. They appear in very good agreement with the theoretical spectra corresponding to the most stable structure predicted by ab initio calculations. This remains true when the fragmentation observed involves prior isomerization of the complex (as in the case of CH_4 loss from $Fe(DME)_2^+$, implying insertion of the metal in the C-O bond followed by H transfer). The spectrum is characteristic of the structure since an essential condition for photofragmentation is absorption of the first photons by the starting stable ion in its ground state, which occurs exclusively at the absorption wavelengths specific of its structure. Upon further multiphoton absorption, isomerisation may and does occur, allowing fragment formation through the lowest energy pathway.

The three infrared spectra exhibit similarities: a strong band between $1000-1100 \text{ cm}^{-1}$ corresponding to a C–O stretching mode, and a band around 1460 cm⁻¹ corresponding to CH₃ dissymmetric deformation and CH₂ scissoring modes. Comparison with the infrared spectra of the free ligands shows that upon metal coordination the former band is shifted by $\approx 100 \text{ cm}^{-1}$ towards lower energies, as expected from calculations. Such absorption bands appear characteristic of functional groups or structural patterns, similarly to condensed phase infrared spectroscopy. This indicates that even if no calculated spectrum is available, infrared spectroscopy of gas phase ions is a useful tool for structural elucidation.

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