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# Vibrational study of isolated 18-crown-6 ether complexes with alkaline-earth metal cations

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## ABSTRACT

Laser infrared multiple photon dissociation (IRMPD) spectroscopy has been employed to probe the C–O and C–C stretching vibrational modes of 18-crown-6 ether (18c6) complexes with alkaline-earth metals ( $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Sr}^{2+}$  and  $\text{Ba}^{2+}$ ) stored in the cell of a Fourier Transform Ion Cyclotron Resonance mass spectrometer. Computations at the B3LYP/6-311++G(2d,2p) and B3LYP/aug-cc-pVDZ levels of theory agree well with the most salient features of the experimental spectra and allow to characterize the lower energy conformers for each type of complex. A pronounced shift of the C–O stretching band, but not of the C–C band, is found in comparison to the similar IRMPD spectra reported previously for the 18c6 complexes with alkali metals. This is attributed to the tighter coordination and stronger binding of the divalent alkaline-earth cations to the oxygen sites, and to the degree of folding of the crown ether backbone. Nevertheless, the conformational landscape and symmetry constraints of the complexes follow a pattern similar to that found for the alkali metal cations. The most stable conformers evolve from compact  $D_2$  geometries for the smaller cations,  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$ , to more open  $C_2$  configurations for  $\text{Sr}^{2+}$  and to a planar  $D_{3d}$  structure for  $\text{Ba}^{2+}$ .

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## 1. Introduction

Crown ethers constitute one of the most prominent synthetic polymer models in guest–host chemistry, and are the building blocks for a broad range of modern materials [1–3]. Among the most salient properties of crown ethers stands their specific binding of cationic species. Binding selectivity to a large extent is dictated by the size of the cationic guest and the capability of the cyclic ether backbone to build a coordination shell optimizing the interaction of its electron donor oxygen sites with the cation [4,5]. In this sense, crown ethers can be regarded as one of the simplest benchmark substrates resembling the general features of “key-pocket” inclusion complexes.

The ability of crown ethers to form charged complexes has also made them important characters in the development of mass spectrometric (MS) techniques. Early fragmentative MS/MS methods via laser excitation [6] or collisions [7,8], as well as ion mobility methods [9], chose crown ethers as reference systems. In particular, infrared multiple photon dissociation (IRMPD) spectroscopy of crown ether complexes as presented here follows up on some of the important contributions of Eyler and co-workers [6], who

studied crown ether cation complexes about two decades ago and later became one of the pioneers in the use of free-electron laser (FEL) based IRMPD spectroscopy for structural analysis in mass spectrometry [10].

Most studies of crown ethers complexes have been devoted to singly charged guest species, primarily alkali metal cations [4–9,11–24] and small molecular cations, such as oxonium, ammonium and protonated amines [25–27]. The complexation with multiply charged guest species, though less extensively investigated, has also been the subject of considerable attention since the early discovery of crown ethers [28–40]. In the mean time, crown ether moieties have been applied to the development of remarkably specific optical sensors of divalent cations [39–41].

Previous experimental studies of crown ether multivalent cationic complexes have been performed in solution, by means of calorimetry [28,29], conductimetry [29–31], and nuclear magnetic resonance [32] techniques. Those studies have served to establish the relative stabilities of the complexes formed by crown ethers and cations of different sizes. For the alkaline-earth series  $\text{Mg}^{2+}$ – $\text{Ba}^{2+}$ , a general trend of increasing stability with cation size was observed in solvents of different polarity (propylene carbonate, acetonitrile, nitromethane). This trend is exactly opposite to that followed by the corresponding isolated solvent-free complexes, for which crown– $\text{Mg}^{2+}$  is most stable. This remarkable behavior has been rationalized from ab initio calculations by Glendening and Feller,

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in terms of the balance between the crown–cation–solvent non-covalent interactions [37]. The situation is, in fact, qualitatively similar to what is found for the alkali cation series  $\text{Li}^+ - \text{Cs}^+$  [14–16]. In short, the heavier cations lead to complexes with more open crown ring structures for which solvation is facilitated without significant alteration of the coordination network built by the crown ether around the cation. On the other hand, the optimum cage-like arrangement formed by the crown with the lighter cations in the gas-phase, is distorted in solution as the solvent gains access to the charge centre, thereby weakening the crown–metal binding. The results of recent experiments, employing state-of-the-art mass spectrometry and laser spectroscopy techniques to characterize gas-phase complexes, are consistent with such scenario. Those experiments have scoped isolated [4,5,22,24] and hydrated [23] alkali metal cation complexes, as well as one benchmark divalent complex, namely (18-crown-6)– $\text{Mn}^{2+}$  solvated by up to three methanol molecules [34].

In this study, we report on IRMPD laser vibrational spectroscopy of the alkaline-earth ( $\text{Mg}^{2+} - \text{Ba}^{2+}$ ) complexes of 18-crown-6 crown ether (18c6) isolated in an ion cyclotron resonance mass spectrometer. The strategy of the investigation mimics that applied for the alkali cation series in previous works [4,5,21]. The mid-infrared radiation of a free-electron laser is employed to probe the C–O and C–C stretching modes of the complexes. Details of the experimental method are provided in Section 2, together with a description of the computational approach employed to characterize the molecular structures. The results are then discussed and summarized in the subsequent Sections 3 and 4.

## 2. Methodology

### 2.1. IRMPD spectroscopy

Infrared multiple photon dissociation spectra were recorded using a Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometer [42], coupled to the beamline of the free-electron laser FELIX [43,44]. The ionic complexes are produced by electrospray ionization of 1 mM solutions of crown ether and alkaline-earth salt in a water/methanol mixture. Ions are accumulated in a hexapole ion trap and then pulse injected into the ICR cell, where they are mass isolated and irradiated with typically 10 FELIX macro-pulses. Each macro-pulse is approximately 5  $\mu\text{s}$  long, has an energy of about 35 mJ, and consists of trains of micro-pulses with a repetition frequency of 1 GHz. The spectral bandwidth of the radiation amounts to 0.5% of the central wavelength. Further description of typical experimental procedures can be found in Ref. [45].

When the infrared wavelength of the laser is in resonance with a vibrational mode of the complex, sequential multiple photon absorption occurs eventually leading to dissociation of the parent ion. The IRMPD spectrum is constructed by monitoring the total fragment yield, as a function of the wavenumber of the radiation. The intense C–O stretching band was repeatedly probed at several attenuated laser powers in order to avoid potential saturation effects due to depletion of complexes in the laser beam path. The recorded spectra were linearly corrected for the changes in laser pulse energy, in consonance with the non-coherent multiple photon dissociation mechanism driving IRMPD [46].

Table 1 lists the dominant IRMPD fragment ions observed at the maxima of the C–O and C–C stretching bands of each of the alkaline-earth complexes. The relative abundances are obtained from the ratios between the observed intensities for the given fragment and for the parent ion in the mass spectra. Products of three types are observed, namely  $\text{X-M}^{2+}$ ,  $\text{X-M}^+$  and  $\text{X}^+$ , where M denotes the alkaline-earth metal and X an ether fragment. The assignment of 2+

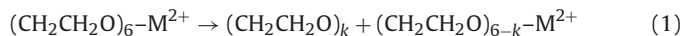
**Table 1**

IRMPD products observed for the 18-crown-6 alkaline-earth complexes scoped in this study. The first line for each cation corresponds to the parent complex. The relative product abundances are obtained from the ratio of the intensity of each fragment to the intensity of the parent complex ion recorded on the maxima of the C–O and C–C stretching bands. Fragment intensities with the laser off resonance were negligible in all cases. For each alkaline-earth cation, the fragments are ordered from top to bottom according to their charge and metal cation content.

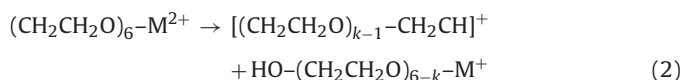
<i>m/z</i>	Assignment	Relative abundances	
		C–O band	C–C band
18c6–Mg <sup>2+</sup>			
144	[(CH <sub>2</sub> CH <sub>2</sub> O) <sub>6</sub> ]–Mg <sup>2+</sup>	1.00	1.00
122	[(CH <sub>2</sub> CH <sub>2</sub> O) <sub>5</sub> ]–Mg <sup>2+</sup>	0.21	0.25
129	[HO–(CH <sub>2</sub> CH <sub>2</sub> O) <sub>2</sub> ]–Mg <sup>+</sup>	0.16	0.11
85	[HO–(CH <sub>2</sub> CH <sub>2</sub> O)]–Mg <sup>+</sup>	0.63	0.14
41	[HO]–Mg <sup>+</sup>	0.12	0.03
71	[(CH <sub>2</sub> CH <sub>2</sub> O)–CH <sub>2</sub> CH] <sup>+</sup>	0.37	0.12
45	[CH <sub>2</sub> CH <sub>2</sub> OH] <sup>+</sup>	0.41	0.09
43	[OCH <sub>2</sub> CH] <sup>+</sup>	0.38	0.10
18c6–Ca <sup>2+</sup>			
152	[(CH <sub>2</sub> CH <sub>2</sub> O) <sub>6</sub> ]–Ca <sup>2+</sup>	1.00	1.00
130	[(CH <sub>2</sub> CH <sub>2</sub> O) <sub>5</sub> ]–Ca <sup>2+</sup>	0.08	0.07
145	[HO–(CH <sub>2</sub> CH <sub>2</sub> O) <sub>2</sub> ]–Ca <sup>+</sup>	0.18	0.10
101	[HO–(CH <sub>2</sub> CH <sub>2</sub> O)]–Ca <sup>+</sup>	0.33	0.07
57	[HO]–Ca <sup>+</sup>	0.27	0.03
71	[(CH <sub>2</sub> CH <sub>2</sub> O)–CH <sub>2</sub> CH] <sup>+</sup>	0.24	0.09
45	[CH <sub>2</sub> CH <sub>2</sub> OH] <sup>+</sup>	0.10	0.02
43	[OCH <sub>2</sub> CH] <sup>+</sup>	0.20	0.05
18c6–Sr <sup>2+</sup>			
176	[(CH <sub>2</sub> CH <sub>2</sub> O) <sub>6</sub> ]–Sr <sup>2+</sup>	1.00	1.00
66	[CH <sub>2</sub> CH <sub>2</sub> O]–Sr <sup>2+</sup>	0.14	0.02
193	[HO–(CH <sub>2</sub> CH <sub>2</sub> O) <sub>2</sub> ]–Sr <sup>+</sup>	0.33	0.18
149	[HO–(CH <sub>2</sub> CH <sub>2</sub> O)]–Sr <sup>+</sup>	0.49	0.11
105	[HO]–Sr <sup>+</sup>	0.54	0.04
71	[(CH <sub>2</sub> CH <sub>2</sub> O)–CH <sub>2</sub> CH] <sup>+</sup>	0.49	0.14
45	[CH <sub>2</sub> CH <sub>2</sub> OH] <sup>+</sup>	0.18	0.04
43	[OCH <sub>2</sub> CH] <sup>+</sup>	0.35	0.09
18c6–Ba <sup>2+</sup>			
201	[(CH <sub>2</sub> CH <sub>2</sub> O) <sub>6</sub> ]–Ba <sup>2+</sup>	1.00	1.00
91	[CH <sub>2</sub> CH <sub>2</sub> O]–Ba <sup>2+</sup>	0.19	0.05
287	[HO–(CH <sub>2</sub> CH <sub>2</sub> O) <sub>3</sub> ]–Ba <sup>+</sup>	0.09	0.10
243	[HO–(CH <sub>2</sub> CH <sub>2</sub> O) <sub>2</sub> ]–Ba <sup>+</sup>	0.31	0.19
199	[HO–(CH <sub>2</sub> CH <sub>2</sub> O)]–Ba <sup>+</sup>	0.31	0.05
155	[HO]–Ba <sup>+</sup>	0.54	0.00
71	[(CH <sub>2</sub> CH <sub>2</sub> O)–CH <sub>2</sub> CH] <sup>+</sup>	0.67	0.17
45	[CH <sub>2</sub> CH <sub>2</sub> OH] <sup>+</sup>	0.14	0.04
43	[OCH <sub>2</sub> CH] <sup>+</sup>	0.33	0.08

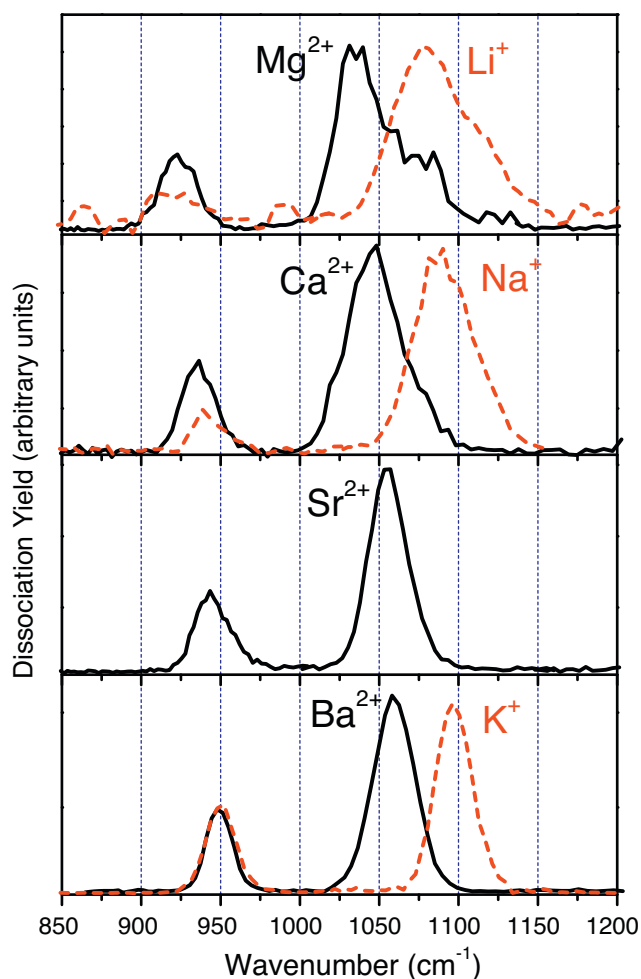
or 1+ charges are consistently supported by the isotopic spacings in the mass spectra.

The  $(\text{CH}_2\text{CH}_2\text{O})_n - \text{M}^{2+}$  IRMPD products are related to the loss of  $\text{CH}_2\text{CH}_2\text{O}$  units through C–O bond cleavages in the crown ring of the parent complex:



On the other hand, the  $\text{X-M}^+$  and  $\text{X}^+$  products must arise from a charge transfer mechanism, involving the reduction of the guest cation to a 1+ charge state. All four alkaline-earth complexes display products of the form  $[\text{HO} - (\text{CH}_2\text{CH}_2\text{O})_{n=2,1,0}] - \text{M}^+$ , and have in common the three ionic ether fragments  $[(\text{CH}_2\text{CH}_2\text{O}) - \text{CH}_2\text{CH}]^+$  ( $m/z = 71$ ),  $[\text{CH}_2\text{CH}_2\text{OH}]^+$  ( $m/z = 45$ ) and  $[\text{OCH}_2\text{CH}]^+$  ( $m/z = 43$ ). The observation of these common products lends support to a common fragmentative route for the four complexes, in which the initial step would be C–O bond cleavage, concerted with reduction of the divalent cation and with the transfer of one H atom from the  $-\text{CH}_2 - \text{CH}_2 -$  moiety to the O-end of the nascent fragment:





**Fig. 1.** Experimental IRMPD spectra of the 18c6 complexes with four alkaline-earth cations included in this study (solid lines). The spectra of the corresponding 18c6 complexes with the alkali cations of similar ionic radius from Ref. [4] are included for comparison (dashed lines). Note the significant red shift of the C–O band (but not of the C–C band) of the alkaline-earth complexes in comparison to their alkali analogs.

According to the relative fragment abundances listed in Table 1, this latter type of dissociation mechanism dominates the IRMPD process.

Fig. 1 shows the IRMPD spectra measured for 18c6–M<sup>2+</sup> (M = Mg, Ca, Sr, Ba). The spectra of the four complexes feature two differentiated bands associated with vibrational modes dominated by C–C (900–1000 cm<sup>−1</sup>) and C–O (1000–1150 cm<sup>−1</sup>) stretching. Weaker bands related to COC angle bending and to CH<sub>2</sub> wagging, torsions and bending, that were visible within 600–1800 cm<sup>−1</sup> in the similar experiments for the alkali cation complexes of 18c6 [4], could not be detected in the present case. The lack of sensitivity to these latter bands is due to the high binding energy of the alkaline-earth complexes, leading to a roughly three-fold greater endothermicity for dissociation in comparison to the alkali metal counterparts [16,37]. Nevertheless, it will be shown that the C–C and C–O bands provide valuable information about the conformational geometry of the complexes, and serve to validate the predictions of the B3LYP computations.

## 2.2. Quantum chemistry calculations

A conformational survey of the 18c6–M<sup>2+</sup> complexes was performed by means of simulated annealing with the Universal

**Table 2**

Free energies (kJ mol<sup>−1</sup>) of the 18c6–M<sup>2+</sup> conformers relevant to the present study. B3LYP/6-311++G(2d,2p) and B3LYP/aug-cc-pVDZ levels of theory are compared. The point symmetry group to which each conformer belongs is indicated. See Fig. 2 and Table 3 for a description of the molecular structure of the most stable conformers. Note that at the room temperature of the present experiments, one *k<sub>B</sub>T* thermal unit equals ~2.5 kJ mol<sup>−1</sup>.

Conformer	Symmetry group	B3LYP 6-311++G(2d,2p)	B3LYP aug-cc-pVDZ
18c6–Mg <sup>2+</sup>			
I	D <sub>2</sub>	0	0
II	C <sub>1</sub>	2.0	1.5
III	C <sub>2</sub>	8.2	7.4
18c6–Ca <sup>2+</sup>			
I	D <sub>2</sub>	0	0
II	C <sub>1</sub>	2.8	2.1
III	C <sub>2</sub>	3.3	1.5
IV	C <sub>2</sub>	8.0	8.2
18c6–Sr <sup>2+</sup>			
I	C <sub>2</sub>	0	0
II	D <sub>3d</sub>	2.1	2.8
III	C <sub>2</sub>	6.2	5.0
18c6–Ba <sup>2+</sup>			
I	D <sub>3d</sub>	0	0
II	C <sub>2</sub>	14.2	12.6

force-field [47]. In addition, the complete set of low energy conformers found for the 18c6 complexes with the alkali cation series in our previous study [4] was considered for reoptimization with the alkaline-earth cations as guests.

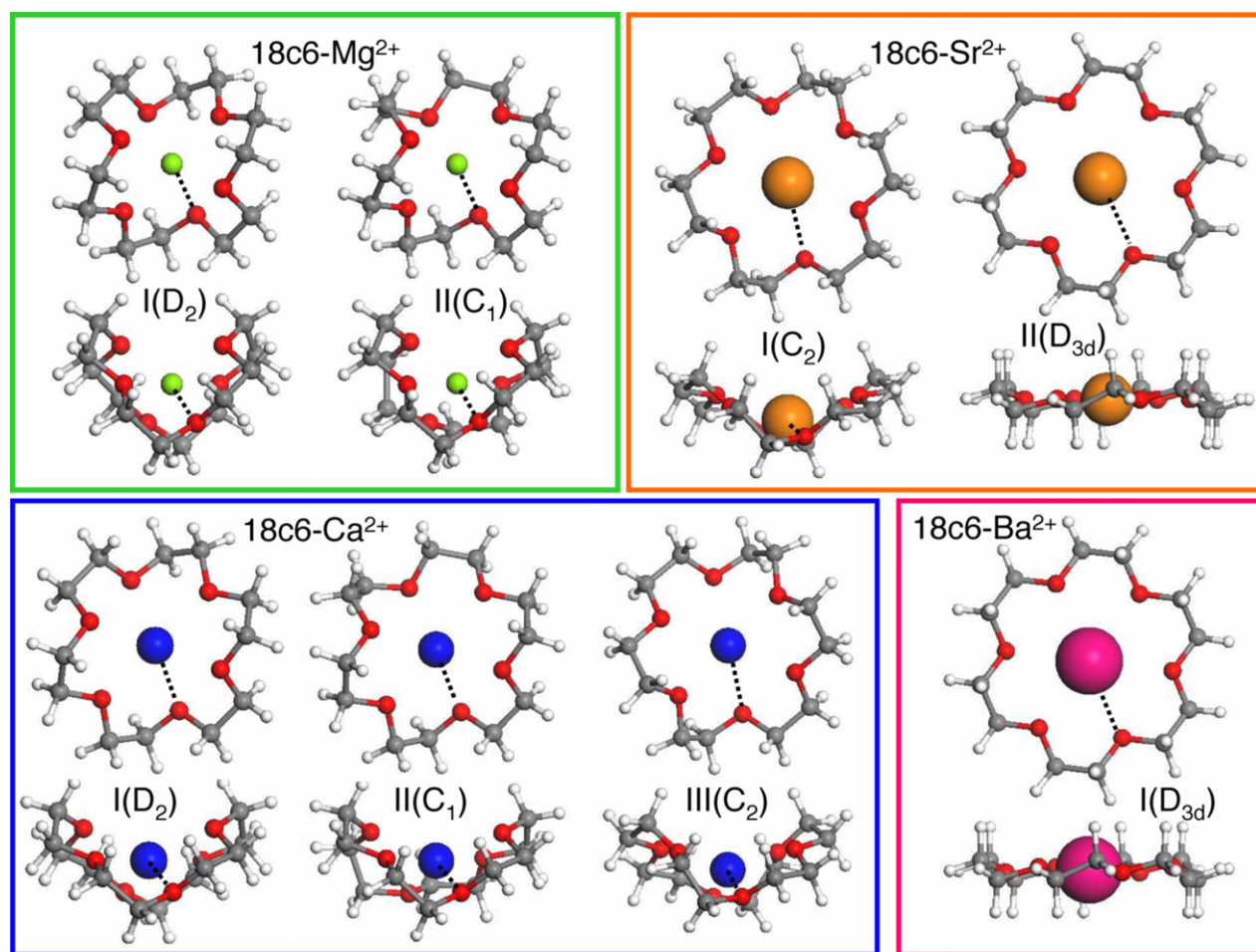
Geometry optimizations of the structures were performed using Density Functional Theory (DFT) with the B3LYP hybrid functional [48]. For the heavier alkaline-earth cations (Sr<sup>2+</sup> and Ba<sup>2+</sup>) the core electrons were treated with the Stuttgart/Dresden effective core potentials [49], whereas Gaussian-type orbitals were used for the valence shells. The C, O, H and lighter alkaline-earth atoms were modelled with the all-electron 6-311++G(2d,2p) or aug-cc-pVDZ basis sets. In order to reduce the basis set superposition error, the counterpoise method [50] was applied. The calculations were carried out with the Gaussian 09 code [51].

All the energies reported are free energies, calculated as the sum of electronic energies plus corrections due to the vibrational zero-point energies and thermal entropy contributions. The B3LYP/6-311++G(2d,2p) harmonic IR spectra shown in the paper were calculated from the convolution of the normal modes of vibration of the optimized structures, with a line broadening of 8 cm<sup>−1</sup>. The computed vibrational frequencies for all the complexes were scaled for comparison with experiment by a factor 0.98, in line with the scaling recommended in previous studies [52].

Table 2 lists the B3LYP free energies of the most stable conformers found in our conformational search for the 18c6–M<sup>2+</sup> complexes. In addition, Fig. 2 and Table 3 describe the molecular geometries of the lowest lying conformers that presumably contribute to the IRMPD signal in the present experiments. Finally, Fig. 3 depicts the harmonic IR spectra predicted by the B3LYP/6-311++G(2d,2p) computation for these latter conformers and compares them with the recorded IRMPD spectra.

## 3. Results and discussion

Fig. 1 compares the IRMPD spectra recorded here for the alkaline-earth complexes with the corresponding spectra of their alkali analogs from Ref. [4]. The ionic radii of the alkaline-earth cations Mg<sup>2+</sup>, Ca<sup>2+</sup>, Sr<sup>2+</sup> and Ba<sup>2+</sup> are 0.72, 1.00, 1.18 and 1.35 Å, respectively. Those of the alkali cations Li<sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup> and Cs<sup>+</sup> are 0.76, 1.02, 1.38 and 1.67 Å. Hence, Mg<sup>2+</sup>, Ca<sup>2+</sup> and Ba<sup>2+</sup> are roughly similar in size to Li<sup>+</sup>, Na<sup>+</sup> and K<sup>+</sup>, respectively, and the IRMPD

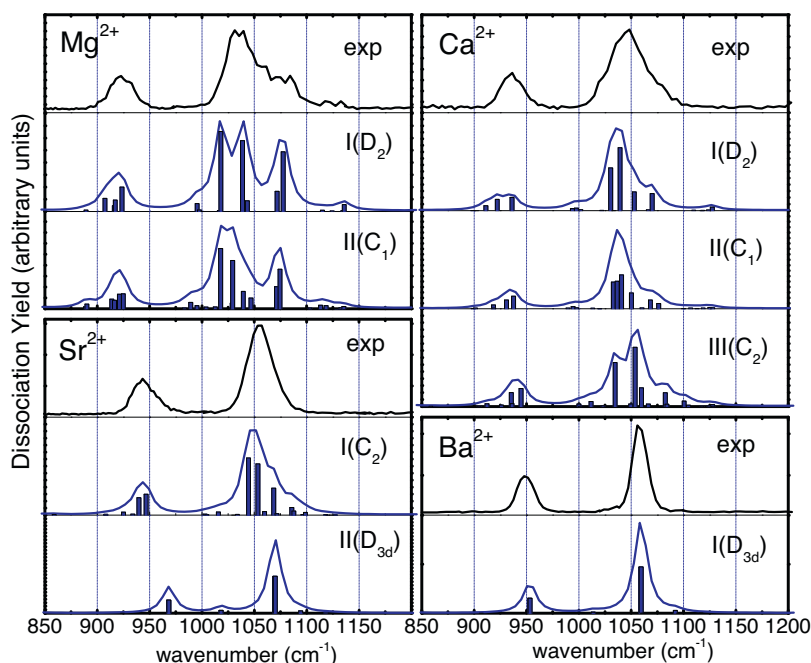


**Fig. 2.** Representation of the most stable B3LYP conformers of the 18c6-M<sup>2+</sup> complexes included in this study. See Table 2 for the relative energies of the conformers. The oxygen atom marked with a dashed binding line to the cation serves as starting point for the (clockwise) sequence of geometrical parameters listed in Table 3 for each conformer.

**Table 3**  
Selected geometrical parameters of the most stable 18c6-M<sup>2+</sup> conformers (M = Mg, Ca, Sr, Ba) predicted by the B3LYP/6-311++G(2d,2p) computations. See Table 2 for the relative energies of the different conformers, and Fig. 2 for a representation of their structure. The set of distances (in Å) and angles (in degrees) starts with the oxygen atom marked with a dashed O–M binding line in Fig. 2, and proceeds clockwise.

Conformer	O–M distances	O–O distances	C–O–C angles	O–C–C–O dihedral angles
18c6–Mg <sup>2+</sup>				
I(D <sub>2</sub> )	2.14, 2.11, 2.14, 2.14, 2.11, 2.14	2.56, 2.56, 2.69, 2.56, 2.56, 2.69	113.8, 117.4, 113.8, 113.8, 117.4, 113.8	38.5, 38.5, 54.2, 38.5, 38.5, 54.2
II(C <sub>1</sub> )	2.15, 2.11, 2.14, 2.14, 2.10, 2.14	2.56, 2.57, 2.74, 2.58, 2.62, 2.67	114.1, 117.5, 117.0, 113.7, 116.9, 113.6	38.4, 38.9, –47.8, –45.8, 47.6, 53.2
18c6–Ca <sup>2+</sup>				
I(D <sub>2</sub> )	2.41, 2.39, 2.41, 2.41, 2.39, 2.41	2.67, 2.67, 2.73, 2.67, 2.67, 2.73	115.6, 116.4, 115.6, 115.6, 116.4, 115.6	44.7, 44.7, 57.6, 44.7, 44.7, 57.6
II(C <sub>1</sub> )	2.42, 2.41, 2.40, 2.42, 2.41, 2.42	2.67, 2.63, 2.71, 2.69, 2.71, 2.72	115.2, 115.9, 119.2, 114.7, 115.0, 114.9	45.0, 43.7, –47.2, –53.5, 51.8, 56.7
III(C <sub>2</sub> )	2.48, 2.41, 2.49, 2.48, 2.41, 2.49	2.66, 2.62, 2.72, 2.66, 2.62, 2.72	113.1, 117.9, 111.9, 113.1, 117.9, 111.9	49.1, –48.3, 54.9, 49.1, –48.3, 54.9
18c6–Sr <sup>2+</sup>				
I(C <sub>2</sub> )	2.62, 2.59, 2.63, 2.62, 2.59, 2.63	2.74, 2.70, 2.75, 2.74, 2.70, 2.75	114.1, 115.1, 111.7, 114.1, 115.1, 111.7	53.7, –52.6, –56.7, 53.7, –52.6, –56.7
II(D <sub>3d</sub> )	2.69, 2.69, 2.69, 2.69, 2.69, 2.69	2.69, 2.69, 2.69, 2.69, 2.69, 2.69	112.4, 112.4, 112.4, 112.4, 112.4, 112.4	–54.2, 54.2, –54.2, 54.2, –54.2, 54.2
18c6–Ba <sup>2+</sup>				
I(D <sub>3d</sub> )	2.77, 2.77, 2.77, 2.77, 2.77, 2.77	2.78, 2.78, 2.78, 2.78, 2.78, 2.78	113.1, 113.1, 113.1, 113.1, 113.1, 113.1	–57.6, 57.6, –57.6, 57.6, –57.6, 57.6





**Fig. 3.** Comparison of the experimental IRMPD spectra with the harmonic IR spectra predicted by the B3LYP/6-311++G(2d,2p) computation for the low lying conformers of the 18c6–M<sup>2+</sup> complexes. See Table 2 for the notation and relative energies between the different conformers. The nominal computed vibrational frequencies (scaled by a factor 0.98) are indicated as histograms. The simulated B3LYP spectra are built via convolution with a gaussian broadening of 8 cm<sup>−1</sup> (full-width-at-half-maximum).

spectra for these cations are compared in Fig. 1. Note that the 18c6–Sr<sup>2+</sup> complex is not included in the comparison, since the size of Sr<sup>2+</sup> lies in between Na<sup>+</sup> and K<sup>+</sup>.

The tighter binding of the divalent alkaline-earth cations leads to a red shift by ca. 40 cm<sup>−1</sup> of the C–O stretching band with respect to the corresponding band of the complex involving the alkali cation of similar size. Noticeably, the C–C bands are not affected by any appreciable shift when the alkaline-earth and alkali cations are interchanged. This observation was not necessarily expected, as the dragging of charge to the oxygen sites induced by the divalent also affects the bond strength of the C–C moieties. As it turns out, the frequency of the C–C stretching modes rather seems to be primarily driven by the degree of folding and dihedral distortion of the ether backbone. The similarity of the position of the C–C stretching bands when increasing the cation charge from 1+ to 2+, while keeping the cation size constant, can then be taken as a hint for similar molecular conformations in the complexes. It can be noted that the C–C band shifts by ca. 40 cm<sup>−1</sup> to the blue in going from the Mg<sup>2+</sup> complex to the Ba<sup>2+</sup> complex, and this behavior can be foreseen to follow from the transition from a folded cage-like conformation for Mg<sup>2+</sup> to a less distorted quasi-planar one for Ba<sup>2+</sup>. Note also that the C–O band shifts less markedly, by ca. 20 cm<sup>−1</sup>, in going from Mg<sup>2+</sup> to Ba<sup>2+</sup>, in this case as a consequence of the decrease in binding interaction with cation size.

The detailed shape of the C–O stretching band in the IRMPD spectra constitutes a key feature in this study which provides further support to the considerations outlined above. The C–O band of the 18c6–Mg<sup>2+</sup> complex is particular broad and structured, suggesting the contribution of several distinct vibrational modes and/or of various conformers. As the size of the cation increases, the C–O band becomes progressively narrower, reaching a full-width-at-half-maximum as small as 18 cm<sup>−1</sup> in the 18c6–Ba<sup>2+</sup> complex. This particularly narrow band plausibly arises from a highly symmetric backbone conformation with identical oxygens, in which the C–O stretching modes are merged into a single degenerate mode. A qualitatively similar overall trend was found in the IRMPD spectra of the alkali cation complexes of 18c6 (see

Fig. 1), which suggests that 18c6–Ba<sup>2+</sup> presumably stabilizes in a D<sub>3d</sub> configuration similar to that of 18c6–K<sup>+</sup> [4]. It will be shown below that the B3LYP computations are in agreement with this expectation.

We incorporate at this point the computational study to the discussion in order to obtain a more involved insight into the experimental results. Table 2 shows that the conformational landscape of the complexes is governed by symmetric molecular arrangements. With decreasing cation size, the geometry of the complex evolves from a planar D<sub>3d</sub> conformation for 18c6–Ba<sup>2+</sup>, to a folded C<sub>2</sub> structure for 18c6–Sr<sup>2+</sup>, and to progressively more folded cage-like D<sub>2</sub> structures for 18c6–Ca<sup>2+</sup> and 18c6–Mg<sup>2+</sup>. The relevance of symmetric conformations in the complexation of 18c6 with metal cations was already a central theme in previous studies [4,35,36]. Remarkably, the D<sub>2</sub> and C<sub>2</sub> geometries are chiral, thereby rendering atropoisomerism as a key feature to the conformational landscape of the system. The term atropoisomerism refers to chirality as an emerging property, arising upon complexation of the crown ether with the cation [53].

The detailed analysis of the IRMPD spectra serves to asset the contribution of the low lying conformers predicted by the B3LYP computations. We begin with the discussion of the 18c6–Ba<sup>2+</sup> complex, for which the planar D<sub>3d</sub> conformer fully accounts for the narrow C–C and C–O bands observed experimentally (see Fig. 3). The computed stretching modes involved in these bands essentially merge into a single degenerate vibrational line, due to the equivalence of the ether groups in this highly symmetric arrangement. According to the present computations, the next excited conformer is a C<sub>2</sub> structure that lies more than 12 kJ mol<sup>−1</sup> higher and is not expected to have a relevant population in the experiments. In comparison to the similar D<sub>3d</sub> conformer for the 18c6–K<sup>+</sup> complex [4], the crown cavity is slightly more stretched toward the cation in 18c6–Ba<sup>2+</sup> (the O–M distance is smaller by 0.05 Å), due to the higher charge of guest cation. As already mentioned, the open configuration of the quasi-planar D<sub>3d</sub> conformer is quite relevant for the behavior of the complex in solution, as it facilitates the solvation of the cation guest. For this reason, in polar solvents 18c6–Ba<sup>2+</sup>

and 18c6-K<sup>+</sup> turn out to be the most stable complexes among the alkaline-earth and alkali cation series, respectively [37].

For the 18c6-Sr<sup>2+</sup> complex, the B3LYP computation leads to a C<sub>2</sub> ground state conformer, whereas the planar D<sub>3d</sub> conformer is predicted to lie within one k<sub>B</sub>T thermal unit higher in energy. The comparison of the B3LYP IR spectra for these two conformers with the IRMPD measurements confirms that the C<sub>2</sub> complex alone reproduces the position and overall envelope of the experimental C–C and C–O stretching bands. In fact, the IRMPD spectrum rules out a relevant contribution from the D<sub>3d</sub> conformer. Only a small contribution (of less than 20% in relative weight) from this latter conformer to the blue flank of the bands would still be compatible with experiment. However, the B3LYP computations predict a free energy within 2–3 kJ mol<sup>−1</sup> for the D<sub>3d</sub> conformer, which corresponds to Boltzmann weights of 30–45%. Hence, it appears that the B3LYP computation overestimates the stability of the D<sub>3d</sub> conformer against the folded configurations; it seems timely to remark this finding since a similar overestimation was found for the 18c6-Na<sup>+</sup> complex in our previous work [4].

The 18c6-Ca<sup>2+</sup> complex is predicted to be most stable in a symmetric folded D<sub>2</sub> conformation, and in two close lying conformers of C<sub>1</sub> and C<sub>2</sub> symmetry. The C<sub>2</sub> conformer III is qualitatively similar to the most stable 18c6-Sr<sup>2+</sup> structure, although it becomes more folded with the reduced size of the Ca<sup>2+</sup> cation. Fig. 3 shows that the experiment is consistent with a joint contribution from these three conformers. Whereas the B3LYP IR spectrum of the D<sub>2</sub> conformer accounts for the main features of the experimental IRMPD spectrum, it however underestimates the signal observed on the blue flank of the C–C and C–O bands, in particular above 950 and 1050 cm<sup>−1</sup>, respectively. The expected contribution of the C<sub>1</sub> conformer does not solve this problem, as the predicted IR spectrum is similar to one of the D<sub>2</sub> conformer. The C<sub>2</sub> conformer does provide the required intensity so that an appreciable contribution from this conformer, not smaller than 50% in relative abundance, is required in order to reproduce the IRMPD spectrum.

Finally, the 18c6-Mg<sup>2+</sup> complex displays the broadest and most structured bands of the series. The B3LYP computations predict folded D<sub>2</sub> and C<sub>1</sub> conformers as most stable. These two conformers resemble those with the same symmetries found for the 18c6-Ca<sup>2+</sup> complex. However, for the 18c6-Mg<sup>2+</sup> system the folding of the crown ring is almost complete, so that the ether chain virtually cages the cation and isolates it from the outer environment. The next higher conformer lies more than 7 kJ mol<sup>−1</sup> above the D<sub>2</sub> conformer and should not contribute to the experiment. The related cage-like conformer of S<sub>6</sub> symmetry investigated by Glendening and Feller for this system [37] lies more than 50 kJ mol<sup>−1</sup> higher in energy. The B3LYP IR spectra of the D<sub>2</sub> and C<sub>1</sub> conformers shown in Fig. 3 readily relate the structure of the C–O band to a marked splitting of the C–O stretching modes into three main components in the folded arrangements. In fact, the experimental IRMPD spectrum correlates well with a 1:1 combination of the spectra of the two conformers.

Overall, the optimum molecular arrangement of the different complexes results from the balance between the oxygen–metal attractions, the oxygen–oxygen repulsions and the flexibility of the crown ring. Taking the lowest energy conformers for each cation as reference, the average O–M<sup>2+</sup> distances in alkaline-earth complexes are of 2.13, 2.40, 2.61 and 2.77 Å for M=Mg, Ca, Sr and Ba, respectively (see Table 3). Such average distances are remarkably close to the optimum O–M<sup>2+</sup> coordination distances of the hydrated alkaline-earth cations, namely lying within 1.94–2.11, 2.30–2.44, 2.46–2.61 and 2.66–2.83 Å for Mg, Ca, Sr and Ba, respectively [37,54,55].

A noticeable difference between the alkaline-earth and alkali cation complexes arises in the stability of the cage-like D<sub>2</sub> conformer. The tighter bonding induced by the divalent guests works

in favour of the D<sub>2</sub> conformation. Indeed, whereas the D<sub>2</sub> conformer constitutes the most stable arrangement for 18c6-Mg<sup>2+</sup>, 18c6-Ca<sup>2+</sup> and 18c6-Li<sup>+</sup>, this is not the case for 18c6-Na<sup>+</sup>. This latter complex displays a C<sub>1</sub> partially folded conformer, followed in stability by the planar D<sub>3d</sub> structure [4]. Hence, in spite of Na<sup>+</sup> having a similar ionic radius as Ca<sup>2+</sup>, its single charge does not manage to stabilize the symmetric folding of the crown ether backbone.

#### 4. Summary and conclusions

FT-ICR mass spectrometry and FEL-based IRMPD spectroscopy have been employed to provide new insights into the conformational characteristics of the gas-phase complexes formed by 18-crown-6 with the alkaline-earth cations Mg<sup>2+</sup>, Ca<sup>2+</sup>, Sr<sup>2+</sup> and Ba<sup>2+</sup>. The position and structure of the C–C and C–O stretching bands observed in the IRMPD spectra, in combination with B3LYP computations have served to support a conformational landscape dominated by symmetric molecular arrangements in the complexes. The most stable conformers evolve from compact D<sub>2</sub> geometries for the smaller cations, Mg<sup>2+</sup> and Ca<sup>2+</sup>, to a more open C<sub>2</sub> configuration for Sr<sup>2+</sup> and to a planar D<sub>3d</sub> structure for Ba<sup>2+</sup>. Further low lying conformers of C<sub>2</sub> and C<sub>1</sub> symmetry contribute to the present room temperature experiments.

Such trends and symmetry constraints are similar to those found in previous studies for the analogous complexes of 18c6 with the alkali cations [4]. When comparing the IRMPD spectra of the 18c6 complexes with alkaline-earth and alkali cations of similar ionic radius, coincidence is found for the position and width of the C–C stretching band, which can be related to the similar degree of folding undergone by the crown backbone. On the other hand, a pronounced red shift is found for the C–O stretching band of the alkaline-earth spectra with respect to the alkali counterparts, as a natural consequence of the tighter binding of the divalent alkaline-earth cations to the oxygen sites of the ether. The C–O and C–C stretching band positions are well reproduced by the B3LYP computations. The higher charge state of the alkaline-earth cations also enhances the stability of the folded D<sub>2</sub> arrangement, as follows from the comparison of the 18c6-Ca<sup>2+</sup> (most stable D<sub>2</sub> conformer) and 18c6-Na<sup>+</sup> (most stable C<sub>1</sub> conformer) complexes.

The open configuration of the quasi-planar D<sub>3d</sub> conformer found for 18c6-Ba<sup>2+</sup> is similar to the one displayed by the 18c6-K<sup>+</sup> complex [4]. Such conformation is of key relevance for the behavior of these complexes in solution, as it leads to a facile solvation of the cation. In contrast, the folded conformations adopted by the complexes of the lighter cations must be significantly distorted in order to provide access of the solvent to the cation. As a consequence, 18c6-Ba<sup>2+</sup> and 18c6-K<sup>+</sup> are the most stable complexes among the alkaline-earth and alkali cation series in polar solvents [15,37]. We note in closing that the open ether ring structures are as well suitable for the formation of selective ternary complexes, in which two crown ethers are bridged by one guest cation [21,33,56,57]. The investigation of these tweezer-like structures for 18-crown-6 mediated by alkaline-earth cations is currently underway in our group.

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