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Infrared multiple photon dissociation action spectroscopy of alkali metal cation–cyclen complexes: Effects of alkali metal cation size on gas-phase conformation



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Dedicated to the memory of Detlef Schröder a great gas phase ion chemist, mass spectrometrist, friend, and colleague.

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ABSTRACT

The gas-phase structures of alkali metal cationized complexes of cyclen (1,4,7,10-tetraazacyclododecane) are examined via infrared multiple photon dissociation (IRMPD) action spectroscopy and electronic structure theory calculations. The measured IRMPD action spectra of four M⁺(cyclen) complexes are compared to IR spectra predicted for the stable low-lying conformers of these complexes calculated at the B3LYP/def2-TZVPPD level of theory to identify the structures accessed in the experiments. The IRMPD yields of the M⁺(cyclen) complexes investigated increase as the size of the alkali metal cation increases, in accordance with the decrease in the strength of alkali metal cation binding. The IRMPD spectrum of the Na⁺(cyclen) complexes. New spectral features begin to appear for K⁺(cyclen) and become very obvious for the Rb⁺(cyclen) and Cs⁺(cyclen) complexes. The IRMPD action spectra predicted for the most stable conformations computed. Overall comparisons suggest that only the ground-state conformations of the M⁺(cyclen) complexes were accessed in the experiments for the complexes to Rb⁺ and Cs⁺.

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1. Introduction

Cyclen (1,4,7,10-tetraazacyclododecane), the aza analog of 12crown-4 (1,4,7,10-tetraoxacyclododecane) is extensively used in many applications ranging from biomedical imaging [1–4] to many different areas of chemistry including synthetic, analytical, and pharmaceutical chemistry [5–10]. For most applications, the backbone of cyclen is highly functionalized to effect very strong binding to transition metal cations. Recently, noncovalent interactions of cyclen with the alkali metal cations, Na⁺, K⁺, Rb⁺, and Cs⁺, were studied using guided ion beam tandem mass spectrometry techniques, where binding was found to be based primarily on electrostatic interactions [11]. The alkali metal cation–cyclen binding energies decrease as the size of the alkali metal cation increases, and the intact neutral cyclen ligand and alkali metal cation are observed as the only products of the CID process. Experimental bond dissociation energies (BDEs) were determined and exhibit good agreement with theoretical values predicted for binding in the ground-state $C_4(++++)$ conformations (where the nomenclature used here is described below). The $C_4(++++)$ conformers are calculated to lie well below all other conformations, such that quantitative measurements are sufficient to determine the conformation(s) accessed experimentally. Cyclen exhibits preferential binding to Na⁺, whereas K⁺, Rb⁺, and Cs⁺ bind to 12-crown-4 slightly more strongly [12], however the differences are smaller than the experimental error in these measurements. Similar trends are observed theoretically at both the B3LYP and MP2(full) levels of theory, but also suggest preferential binding of K⁺ to cyclen over 12cown-4. These binding trends are attributed to the selectivity that the nitrogen donor atoms of cyclen exhibit for hard metal cations.

IRMPD action spectroscopy has previously been used to investigate crown ether interactions with protons [13], metal cations [14–17], and small organic cations [18–21]. All of the IRMPD studies reported to date have involved crown ethers possessing oxygen donor atoms, and have primarily focused on the 18-membered ring, 18-crown-6, rather than the nitrogen analogs and smaller 12-membered ring of cyclen examined here. For the alkali metal cation complexes of 18-crown-6, the ground-state conformation

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changes as a function of the size of the alkali metal cation, and in most cases evidence for a small population of excited conformers is found in the IRMPD experiments [14]. For the 12-membered ring, 12-crown-4, Armentrout and co-workers investigated complexes with the dications, Zn^{2+} and Cd^{2+} [16]. In that study, results were compared to the interactions with 15-crown-5 and 18-crown-6 and showed that the conformation of the metal-crown ether complex is highly dependent on the size and charge of the metal cation as well as the flexibility of the crown ether.

In the present study, we measure IRMPD action spectra for the dissociation of four M⁺(cyclen) complexes, where M⁺ = Na⁺, K⁺, Rb⁺, and Cs⁺. Identification of the conformation(s) accessed in the experiments is achieved by comparison to linear IR spectra derived from quantum-chemical calculations of the stable low-lying structures of the M⁺(cyclen) complexes with structures optimized and vibrational frequencies determined at the B3LYP/def2-TZVPPD level of theory. Relative energies for these complexes are calculated at the B3LYP/def2-TZVPPD and MP2(full)/def2-TZVPPD levels of theory, and for the largest alkali metal cations, Rb⁺ and Cs⁺, an effective core potential (ECP) was used to describe the alkali metal cation.

2. Experimental and computational section

2.1. Mass spectrometry and photodissociation

IRMPD action spectra of four M⁺(cyclen) complexes were measured using a 4.7 T Fourier transform ion cyclotron resonance mass spectrometer (FT-ICR MS) coupled to the FELIX free electron laser (FEL) located at the FOM Institute for Plasma Physics, Rijnhuizen, but recently moved to the Radboud University of Nijmegen. The experimental setup used in these experiments has been described in detail elsewhere [22,23]. Cyclen was purchased from TCI Europe, whereas the alkali metal hydroxide salts used in the experiments were purchased from Sigma Aldrich. The M⁺(cyclen) complexes, where $M^+ = Na^+$, K^+ , Rb^+ , and Cs^+ , were formed by electrospray ionization (ESI) using a Micromass "Z-spray" source and solutions containing 1 mM of the corresponding alkali metal hydroxide salt and 1 mM of cyclen in an approximately 85-90%:15-10% CH₃CN:H₂O mixture. A solution flow rate of 10 µL/min was used and the electrospray needle was held at a voltage in the range between 2.0 and 2.8 kV. Ions emanating from the source were focused into a hexapole ion trap and accumulated for several seconds before being injected into the ICR cell via a quad bender and radiofrequency (rf) octopole ion guide through electrostatic switching of the dc bias on the octopole. This dc bias switching method allows ions to be captured in the ICR cell in the absence of a gas pulse, thus avoiding collisional heating of the ions as described in detail elsewhere [24]. Isolation of the precursor ions was achieved using stored waveform inverse Fourier transform (SWIFT) techniques prior to irradiation by the FEL at pulse energies of \sim 40 mJ per macropulse of 5 μ s duration at a repetition rate of 10 Hz. The number of photons required to effect efficient dissociation of the M⁺(cyclen) complexes varies inversely with the size of the alkali metal cation such that the irradiation time was varied between 2 and 5 s for the complexes investigated here, corresponding to interaction with 20-50 macropulses over the wavelength region extending from 16.7 μ m (600 cm⁻¹) to 6.3 μ m (1600 cm⁻¹).

2.2. Theoretical calculations

The stable low-energy conformers of cyclen and its complexes with Na⁺, K⁺, Rb⁺, and Cs⁺ were examined in detail in our previous work [11]. Simulated annealing using Amber force field methods was performed for 200 cycles at 1000 and 298 K for each initial structure subjected to annealing. The ground-state conformer of cyclen previously reported in the literature along with two additional low-energy structures were used as the starting structures for the simulated annealing [25–26]. Initially, a simulation temperature of 1000 K was employed, and then the 15 most stable structures found were subjected to a second stage of annealing at 298 K. This latter procedure was particularly helpful in eliminating imaginary frequencies associated with low-curvature transition states that were not adequately resolved in the initial structures due to minor steric interferences. The 15 lowest energy structures of cyclen found from all of the simulated annealing cycles performed were chosen for higher level geometry optimization.

Initial candidate structures for the M⁺(cyclen) complexes were generated using five of the low-energy neutral cyclen structures, i.e., those that were expected to provide the most favorable geometries for interaction with the alkali metal cation, and placing the alkali metal cation in various positions to exhaustively probe the range of geometries that allow interaction with one, two, three, and all four of the nitrogen donor atoms. In addition, structures analogous to the ground-state conformations of the M⁺(12-crown-4) complexes previously reported were also used [27–31].

Geometry optimizations of neutral cyclen and the M⁺(cyclen) complexes, where M⁺ = Na⁺, K⁺, Rb⁺, and Cs⁺, were performed using the def2 triple zeta valence basis sets of Rappoport and Furche, def2-TZVPPD, which include polarization and diffuse functions, and use an ECP for the rubidium and cesium atoms developed by Leininger et al. [32–33]. The def2-TZVPPD basis set was obtained from the EMSL basis set exchange [34–35]. All structures were optimized at the B3LYP/def2-TZVPPD level of theory using the Gaussian 03 suite of programs [36]. Theoretical linear IR spectra were generated using the calculated harmonic vibrational frequencies (scaled by a factor of 0.9704) and IR intensities. For comparison to the measured IRMPD action spectra, the theoretical linear IR spectra were convoluted using a 20 cm^{-1} full width at half maximum (fwhm) Gaussian line shape.

Single-point energies of the geometry optimized structures at the B3LYP and MP2(full) levels of theory using the def2-TZVPPD basis set were performed to determine the relative stabilities of the stable low-energy conformations and the alkali metal binding energies of cyclen. Zero point energy corrections were included using the calculated harmonic vibrational frequencies (scaled by a factor of 0.9804). Basis set superposition error corrections were also included in the computed alkali metal cation–cyclen binding energies. Thermal corrections using standard formulas (assuming harmonic oscillator and rigid rotor approximations) were performed to convert the 0 K enthalpies to enthalpies and Gibbs free energies at 298 K.

3. Results

3.1. IRMPD action spectroscopy

Photodissociation of $M^+(cyclen)$ results in loss of the intact neutral cyclen ligand and detection of the alkali metal cation. This fragmentation behavior is consistent with collision-induced dissociation (CID) results for these complexes [11]. The IRMPD yield for each complex was determined using Eq. (1):

IRMPD yield =
$$I_{M^+}/(I_{M^+(cyclen)} + I_{M^+})$$
 (1)

where the M⁺ fragment ion intensity (I_{M^+}) is divided by the total ion intensity ($I_{M^+(cyclen)} + I_{M^+}$) as determined from the mass spectrum recorded after laser irradiation. The IRMPD yield was not corrected for variations in the laser power as a function of the wavelength of the FEL because the uncorrected spectra provide a better match to the relative intensities of the linear IR spectra predicted. The IRMPD behavior was investigated over the range of wavelengths



Fig. 1. Measured infrared multiple photon dissociation action spectra of M^+ (cyclen) complexes, where $M^+ = Na^+$, K^+ , Rb^+ and Cs^+ .

extending from 6.3 μ m (1600 cm⁻¹) to 16.7 μ m (600 cm⁻¹) for all four M⁺(cyclen) complexes.

The IRMPD action spectra of the four alkali metal cation-cyclen complexes investigated here are compared in Fig. 1. As can be seen in the figure, the features observed for the Na⁺(cyclen) complex are retained for all of the other alkali metal cation-cyclen complexes. New spectral features appear in the IRMPD spectrum of K⁺(cyclen), and become very obvious in the spectra of the larger alkali metal cation-cyclen complexes, Rb⁺(cyclen) and Cs⁺(cyclen). The IRMPD yields for the M⁺(cyclen) complexes increase as the size of the alkali metal cation increases, consistent with the decrease

in the strength of binding. The IRMPD yield of the most intense spectral feature(s) increases by more than a factor of 10 from Na⁺(cyclen) to K⁺(cyclen), while increasing by a factor of three from K⁺(cyclen) to Rb⁺(cyclen), and 1.5 from Rb⁺(cyclen) to Cs⁺(cyclen). Small systematic shifts in the peak positions are observed across these systems, consistent with observations reported in previous studies of alkali metal cations interacting with a variety of amino acid and nucleobase ligands [37–46]. The spectral features that are retained throughout the IRMPD spectra of the four M⁺(cyclen) complexes examined here are increasingly blue shifted as the size of the alkali metal cation increases, except for the spectral feature centered at ~805 cm⁻¹, which does not shift appreciably for any of the M⁺(cyclen) complexes.

3.2. Theoretical results

Structures for the complexes of cyclen to the alkali metal cations, Na⁺, K⁺, Rb⁺, and Cs⁺ were calculated as described above. The nomenclature used to identify the different conformations is adopted from a previous study by Bosnich et al., where the symmetry of the complex is identified and (+) and (-) signs are used to designate the positions of the amine hydrogen atoms as lying above or below the plane of the ring [47]. A detailed discussion of the structures of cyclen and its complexes to Na⁺, K⁺, Rb⁺, and Cs⁺ has been published [11]. The optimized ground-state structures obtained for the M^+ (cyclen) complexes, where $M^+ = Na^+$, K^+ , Rb^+ , and Cs⁺, along with the calculated binding energies are shown in Fig. 2. Similar figures for the three most stable excited low-energy conformers are provided in the Supplementary data as Figures S1-S3. Relative enthalpies and Gibbs free energies as well as estimated populations for Maxwell-Boltzmann distributions at 298 K calculated at the B3LYP and MP2(full) levels of theory, using the B3LYP/def2-TZVPPD optimized geometries and the def2-TZVPPD basis set are given in Table 1. For both levels of theory, the relative enthalpies and Gibbs free energies at 298 K of these complexes vary with the size of the metal cation, see Table 1 and Fig. 3. Both B3LYP and MP2(full) theories find that for all four alkali metal cation-cyclen complexes, the $C_4(++++)$ conformer is the groundstate conformation, while the $C_{2v}(+-+-)$ conformer is the least stable among the four stable low-energy conformations computed. In contrast, the relative stabilities of the $C_{2v}(++++)$ and $C_s(+++-)$ conformers vary with the size of the alkali metal cation and the

Table 1

Relative enthalpies and Gibbs free energies (in kJ/mol) and Maxwell–Boltzmann populations (%) at 298 K of stable low-energy conformers of M⁺(cyclen).^a

Complex	Conformer	B3LYP/def2-TZVPPD ^b			MP2(full)/def2-TZVPPD ^c		
		ΔH_{298}	ΔG_{298}	Pop ₂₉₈	ΔH_{298}	ΔG_{298}	Pop ₂₉₈
Na ⁺ (cyclen)	C ₄ (++++)	0.0	0.0	100	0.0	0.0	100
	C _{2v} (++++)	21.9	18.8	<0.1	22.7	19.6	<0.1
	$C_{s}(+++-)$	31.2	26.4	<0.1	25.6	20.8	<0.1
	C _{2v} (+-+-)	53.6	45.4	<0.1	56.6	48.4	<0.1
K ⁺ (cyclen)	C ₄ (++++)	0.0	0.0	100	0.0	0.0	100
	C _{2v} (++++)	27.2	25.8	<0.1	27.1	25.7	<0.1
	$C_{s}(+++-)$	26.4	25.9	<0.1	19.3	18.8	<0.1
	C _{2v} (+-+-)	49.6	44.3	<0.1	46.7	41.4	<0.1
Rb ⁺ (cyclen)	C ₄ (++++)	0.0	0.0	100	0.0	0.0	98
	C _{2v} (++++)	28.6	21.9	<0.1	24.8	18.1	<0.1
	$C_{s}(+++-)$	24.5	20.1	<0.1	14.1	9.7	2.1
	C _{2v} (+-+-)	45.6	43.5	<0.1	34.3	32.1	<0.1
Cs ⁺ (cyclen)	C ₄ (++++)	0.0	0.0	100	0.0	0.0	90
	C _{2v} (++++)	28.8	21.0	<0.1	19.1	11.4	1.0
	$C_{s}(+++-)$	24.0	20.1	<0.1	10.2	6.3	8.9
	C _{2v} (+-+-)	43.9	42.9	<0.1	26.9	32.1	<0.1

^a Geometries optimized at the B3LYP/def2-TZVPPD level of theory. The ground-state conformations are indicated in boldface.

^b Calculated at B3LYP/def2-TZVPPD level of theory.

^c Calculated at the MP2(full)/def2-TZVPPD level of theory.



Fig. 2. B3LYP/def2-TZVPPD ground state $C_4(++++)$ conformers and B3LYP/def2-TZVPPD and *MP2(full)/def2-TZVPPD* (in red) Gibbs free energies of binding at 298 K (in kJ/mol) of M⁺(cyclen) complexes, where M⁺ = Na⁺, K⁺, Rb⁺, and Cs⁺.

level of theory employed. At the B3LYP level of theory, there is little variation in the relative Gibbs free energy as a function metal cation identity, Fig. 3a. In contrast, the MP2(full) level of theory predicts greater variation in the relative Gibbs free energies as a function of the metal cation identity, Fig. 3b, where the relative stabilities become closer as the size of the alkali metal cation increases.

For all of the alkali metal cation-cyclen complexes at both the B3LYP and MP2(full) levels of theory, the lowest energy structure is the $C_4(++++)$ conformation, where all four nitrogen donor atoms are oriented toward the metal cation (Fig. 2). For each alkali metal cation-cyclen complex, the four M⁺--N bond distances are equal and increase with the size of the alkali metal cation from 2.434 Å for Na⁺ to 3.190 Å for Cs⁺. The \angle NM⁺N bond angles decrease with the size of the cation from 76.4° to 57.7° for the complexes with Na⁺ through Cs⁺, consistent with the elongations of the M⁺-N bond distances. In concert with these changes, the ∠NCCN and \angle CNCC dihedral angles increase from 61.1° to 64.3° and -161.4° to -160.5° , respectively, for the complexes with Na⁺ through Cs⁺. For the $C_{2v}(++++)$ conformer of the Na⁺(cyclen) complex, all four M⁺-N bond distances are equal, whereas the four M⁺-N bond distances are split into two groups that differ by 0.07, 0.10, and 0.17 Å in length for the complexes with K⁺, Rb⁺, and Cs⁺, respectively, (Figures S1). In the $C_{2v}(+++)$ conformations, the $\angle NCCN$ dihedral angles alternate between positive and negative values. For the $C_s(+++-)$ conformations (Figure S2), one of the amino groups is further away from the metal cation than the other three, suggesting a weaker interaction with the fourth donor atom. In the $C_{2v}(+-+-)$



Fig. 3. Variation in the B3LYP/def2-TZVPPD (part a) and MP2(full)/def2-TZVPPD (part b) relative Gibbs free energies at 298 K (in kJ/mol) of the four most stable conformations of the M⁺(cyclen) complexes determined at the B3LYP/def2-TZVPPD level of theory as a function of the alkali metal cation.

conformers (Figure S3), the amine hydrogen atoms alternate up and down with respect to the position of the alkali metal cation, and the \angle NCCN dihedral angles alternate between positive and negative values. The four \angle NCCN dihedral angles of the C_{2v}(+-+-) conformer of Na⁺(cyclen) are equal, but are again split into two groups that differ by 0.10°, 7.0°, and 6.0° for the complexes to K⁺, Rb⁺, and Cs⁺, respectively.

4. Discussion

4.1. Comparison of experimental IRMPD and theoretical IR spectra of Na⁺(cyclen)

Fig. 4 compares the experimental IRMPD action spectrum with theoretical IR spectra for the four low-energy conformers found for the Na⁺(cyclen) complex. Because the experimental IRMPD yields are based on multiple photon processes, whereas the theoretical IR intensities are for a linear absorption process, the relative intensities predicted by theory do not always correspond well with the measured action spectrum. Good agreement between the IRMPD action spectrum and the calculated IR spectrum for the ground-state $C_4(++++)$ conformer is obtained for the few bands that are observed experimentally, suggesting that the ground-state $C_4(++++)$ conformer is accessed in the experiments. For the $C_4(++++)$ conformer, the bands centered at 812 and 933 cm⁻¹ are blue shifted by 7 cm⁻¹ relative to the measured IRMPD spectrum, whereas the band centered at 1366 cm⁻¹ is blue shifted by 21 cm⁻¹. The peak centered at 1068 cm⁻¹ in the theoretical spectrum for



Fig. 4. Comparison of the experimental IRMPD action spectrum of Na⁺(cyclen) with linear IR spectra for the four most stable conformations predicted at the B3LYP/def2-TZVPPD level of theory. B3LYP/def2-TZVPPD and *MP2(full)/def2-TZVPPD* (in red) relative Gibbs free energies at 298 K are also shown. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

the $C_4(++++)$ conformer is red shifted by 2 cm^{-1} relative to the measured IRMPD spectrum. However, many additional bands of lower intensity are predicted that are not observed, indicating that the IRMPD efficiency at these wavelengths is poor for the strongly bound Na⁺(cyclen) complex. For the $C_{2v}(++++)$ conformer, the bands centered at 814, 927, and 1355 cm⁻¹ are blue shifted by 9, 1, and 10 cm⁻¹, respectively, relative to the measured IRMPD spectrum. The peak centered at 1061 cm⁻¹ in the theoretical spectrum for the $C_{2v}(++++)$ conformer is red shifted by 9 cm^{-1} relative to the measured IRMPD spectrum. Because the computed spectra of the $C_4(++++)$ and $C_{2v}(++++)$ conformers are similar, the presence of the $C_{2v}(++++)$ conformer in the experiments is difficult to rule out. The C_{2v}(++++) conformer lies 18.9 and 19.6 kJ/mol higher in free energy than the ground-state $C_4(++++)$ conformer at the B3LYP and MP2(full) levels of theory, respectively. Assuming that the computed energies are reliable and that an equilibrium distribution at 298 K was present, the $C_{2v}(++++)$ conformer would comprise less than 0.05% of the reactant population. A broad spectral feature between 760 and $860 \, \text{cm}^{-1}$ is predicted in the theoretical IR spectrum of the $C_s(+++-)$ conformer instead of the relatively narrow band observed at 805 cm⁻¹ in the IRMPD action spectrum. The bands centered at 900, 1068, and 1357 cm⁻¹ in the theoretical spectrum of the $C_s(+++-)$ conformer are red shifted by 26, 2, and 12 cm⁻¹, respectively, relative to the measured IRMPD spectrum. The $C_s(+++-)$ conformer lies 26.4 and 20.8 kJ/mol above the ground state $C_4(++++)$ conformer at the B3LYP and MP2(full) levels of theory, and would thus comprise less than 0.1% of the reactant ion population in a 298 K Maxwell-Boltzmann distribution, suggesting that this conformer was not accessed in this experiments. The absence in the measured IRMPD spectrum of the very intense band centered at $674 \,\mathrm{cm}^{-1}$ in the predicted IR spectrum, moderate red shifts in most of the computed bands, and the relatively high free energy computed for this conformer are diagnostic for confirming that this conformer was not accessed in these experiments.

The agreement between the experimental IRMPD action spectrum and the theoretical IR spectrum for the ground-state $C_4(++++)$ conformer allows for a qualitative assignment of the vibrational features for the Na⁺(cyclen) complex (Table 2). The most intense band observed at 805 cm⁻¹ in the IRMPD spectrum for Na⁺(cyclen) corresponds to a delocalized mode comprising M⁺—N stretching, N—H bending, and CNC scissoring. The next most intense spectral feature, at 926 cm⁻¹, is doubly degenerate and corresponds to a mode of mixed character arising from N—H and CH₂ rocking. The very weak band observed at 1070 cm⁻¹, corresponds to a normal mode composed of CH₂ stretching and a C—N torsion that is doubly degenerate. The very weak band observed at 1345 cm⁻¹

4.2. Comparison of experimental IRMPD and theoretical IR spectra of K⁺(cyclen)

The IRMPD action spectrum of K⁺(cyclen) is similar to that of Na⁺(cyclen), see Fig. 1. However, the IRMPD yield has increased by more than an order of magnitude such that new bands are now evident at 835, 888, 1126, 1244, and 1451 cm⁻¹. This is primarily the result of enhanced sensitivity associated with more facile dissociation of this less strongly bound system. The K⁺-cyclen bond dissociation energy (BDE) is 176.4 ± 7.8 kJ/mol, substantially weaker than the Na⁺-cyclen BDE, 280.8 ± 11.5 kJ/mol [11]. On the basis of the measured BDEs, 63% fewer photons are needed to dissociate the K⁺(cyclen) complex as compared to the Na⁺(cyclen) complex.

Very good agreement between the measured IRMPD action spectrum and the calculated IR spectrum for the ground-state $C_4(++++)$ conformer is found, as can be seen in the comparison of Fig. 5. The band positions are well reproduced, suggesting that the ground-state structure is accessed in the experiments. In most cases, the bands in the theoretical IR spectrum for the $C_4(++++)$ conformer are slightly red shifted as compared to the measured IRMPD spectrum, e.g., the bands centered at 808, 888, 1075, 1126, and 1244 cm^{-1} in the measured spectrum are red shifted by 2, 6, 6, 15, and 5 cm⁻¹, respectively, in the calculated spectrum. In contrast, the bands that are centered at 835, 1354, and 1451 in the measured IRMPD spectrum are blue shifted in the predicted spectrum for the $C_4(++++)$ conformer by 4, 13, and 3 cm^{-1} , respectively. For the calculated spectrum of the $C_{2v}(++++)$ conformer, overlapping spectral features are also observed, but most of the spectral features are red shifted as compared to experiment. Bands centered at 793, 863, 1058, and 1432 cm^{-1} in the theoretical IR spectrum for the $C_{2v}(++++)$ conformer are red shifted by 17–25 cm⁻¹, bands centered at 928 and 1351 cm⁻¹ are red shifted by 9 and 3 cm⁻¹, respectively, and bands at 1134 and 1260 cm^{-1} are blue shifted by 8 and 16 cm^{-1} , respectively, relative to the measured IRMPD spectrum. Notably the strong band predicted at $860 \, \text{cm}^{-1}$ for the $C_{2\nu}(++++)$ conformer is absent in the experimental spectrum and the two bands on either side of 1100 cm^{-1} are split by too much. The $C_{2v}(++++)$ conformer lies 25.8 and 25.7 kJ/mol above the ground-state $C_4(++++)$ conformer at the B3LYP and MP2(full) levels of theory, respectively, an increase in the relative Gibbs free energy difference for the ground-state and first-excited conformers as compared to those of the Na⁺(cyclen) complex. The spectrum computed for the $C_{s}(+++-)$ conformer exhibits a very broad feature between 760 and 860 $\rm cm^{-1}$ that does not match well with the peak observed at 808 cm⁻¹ in the experimental IRMPD spectrum of the K⁺(cyclen) complex. Other

Table 2

Observed band positions (in cm⁻¹) of the vibrational modes of M⁺(cyclen) complexes in the IR fingerprint region^a

Vibrational mode	Degeneracy	Na ⁺ (cyclen)	K ⁺ (cyclen)	Rb ⁺ (cyclen)	Cs ⁺ (cyclen)
N—H bending, CH ₂ rocking	2	-	-	752	752
N—H wagging ^b	1	-	-	787	783
M ⁺ —N stretching, N—H bending, CNC scissoring	1	805	808	805	805
CH ₂ rocking, N—H bending	1	-	835	838	835
N—H bending, CH ₂ rocking	1	-	888	889	889
N—H bending, CH ₂ rocking	2	926	937	937	938
CH ₂ rocking, N—H wagging	1	-	-	1008	1008
CH ₂ stretching, C—N torsion	2	1070	1075	1075	1081
C—N stretching	1	-	1126	1121	1123
CH ₂ twisting, N—H wagging	2	-	1244	1241	1240
CH ₂ wagging	1	-	-	1284	1288
CH ₂ wagging	2	1345	1354	1357	1358
N—H wagging, CH ₂ scissoring	2	-	1451	1446	1447

^a Assignments based on comparison of the IRMPD action spectra and theoretical IR spectra of the ground-state C₄(++++) conformers optimized at the B3LYP/def2-TZVPPD level of theory, except as noted.

^b Assignments based on $C_{s}(+++-)$ conformers.



Fig. 5. Comparison of the experimental IRMPD action spectrum of K⁺(cyclen) with linear IR spectra for the four most stable conformations predicted at the B3LYP/def2-TZVPPD level of theory. B3LYP/def2-TZVPPD and *MP2(full)/def2-TZVPPD* (in red) relative Gibbs free energies at 298 K are also shown. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

features observed in the low frequency region between 600 and 1000 cm^{-1} are not reproduced or are blue shifted as compared to experiment for the C_s(+++-) conformer. The C_s(+++-) conformer lies 25.9 and 18.8 kJ/mol above the ground-state C₄(++++) conformer at the B3LYP and MP2(full) levels of theory, respectively, a decrease in the relative Gibbs free energy as compared to those of the Na⁺(cyclen) complex. On the basis of the relative Gibbs free energies, the C_{2v}(++++) and C_s(+++-) conformers would comprise less than 0.1% of the K⁺(cyclen) population at 298 K. The observed

spectral differences and relative stabilities suggest that these conformers are not accessed in the experiments. Although several spectral features predicted for the $C_{2v}(+-+-)$ conformer overlap with those observed, there are several intense spectral features predicted in the theoretical IR spectrum for the $C_{2v}(+-+-)$ conformer (i.e., the peaks centered at 640, 740, 1136, and 1483 cm⁻¹) that are not observed in the IRMPD action spectrum, suggesting that this conformer is not accessed in the experiments. This is consistent with the relative Gibbs free energies, 44.3 and 41.4 kJ/mol at the B3LYP and MP2(full) levels of theory, respectively.

Assignments for the bands observed in the K⁺(cyclen) IRMPD action spectrum based on comparison to the IR spectrum computed for the ground state $C_4(++++)$ conformer are consistent with those assigned for the Na⁺(cyclen) complex (see Table 2). The new minor spectral features observed at 835 and 888 cm⁻¹ correspond to CH₂ rocking coupled with N–H bending, and N–H bending coupled with CH₂ rocking, respectively. The peak centered at 1126 cm⁻¹ is the result of a doubly degenerate C–N stretch. The peak with the lowest IRMPD yield, at 1244 cm⁻¹, corresponds to a mode of mixed character comprised of doubly degenerate CH₂ twisting and N–H wagging. The feature at 1354 cm⁻¹ corresponds to doubly degenerate CH₂ wagging modes.

4.3. Comparison of experimental IRMPD and theoretical IR spectra of $Rb^+(cyclen)$

The experimental IRMPD action spectrum for the Rb⁺(cyclen) complex, shown in Fig. 6, is the most complicated spectrum thus far. Compared to the experimental IRMPD spectrum of K⁺(cyclen), the Rb⁺(cyclen) complex retains all the same bands, but new features are observed at 752 and 1008 cm⁻¹ and a very minor feature at 1284 cm⁻¹, Fig. 1. For the major feature centered at 805 cm⁻¹, there is the appearance of small shoulder at 787 cm⁻¹. In addition, there is a notable increase in the relative intensity of the peaks observed, more so in the frequency range between 1100 and 1600 cm⁻¹ where the intensities increase by approximately 2 orders of magnitude. As previously stated, the appearance of new bands could be the result of better sensitivity associated with more facile dissociation of this more weakly bound system, or could be evidence of additional conformers being accessed in the experiments. The Rb⁺-cyclen BDE, 146.7 ± 4.6 kJ/mol, is substantially weaker than that those of Na⁺(cyclen) and K⁺(cyclen) [11], such that only 52 and 83% as many photons are needed to dissociate the Rb⁺(cyclen) complex as compared to the Na⁺(cyclen) and K⁺(cyclen) complexes, respectively.



Fig. 6. Comparison of the experimental IRMPD action spectrum of Rb⁺(cyclen) with linear IR spectra for the four most stable conformations predicted at the B3LYP/def2-TZVPPD level of theory. B3LYP/def2-TZVPPD and *MP2(full)/def2-TZVPPD* (in red) relative Gibbs free energies at 298 K are also shown. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

Excellent agreement between the measured IRMPD action spectrum and the calculated IR spectrum for the ground-state $C_4(++++)$ conformer is found, as can be seen from the comparison in Fig. 6. The band positions are well reproduced and even the relative intensities correspond reasonably well (except for a higher predicted intensity of the 805 cm⁻¹ band), suggesting that the groundstate conformer is accessed in the experiments. The most intense spectral feature appears at 1075 cm⁻¹ and is red shifted by 6 cm⁻¹ in the calculated spectrum for the ground-state conformer. The bands centered at 805, 838, 889, 1008, 1075, 1121, 1241, and 1284 cm⁻¹ in the measured IRMPD spectrum are red shifted by less than 10 cm⁻¹, whereas the bands centered at 1357 and 1446 cm⁻¹ are blue shifted by less than 5 cm⁻¹ in the theoretical IR spectrum predicted for the $C_4(++++)$ conformer. As found for the $K^+(cyclen)$ complex, the predicted IR spectrum of the $C_s(+++-)$ conformer does not reproduce or substantially blue-shifts many of the spectral features observed in the low frequency region between 600 and 1000 cm⁻¹ as compared to experiment. The bands centered at 1075, 1121, and 1357 cm⁻¹ are in good agreement with the $C_s(+++-)$ conformer in position, but not in relative intensity, and are red or blue shifted by less than 3 cm^{-1} . The difference in the Gibbs free energy at the B3LYP level of theory, 20.1 kJ/mol, suggests the conformer would comprise less than 0.1% of the Rb⁺(cyclen) population at 298 K. In contrast, the difference in the Gibbs free energy at the MP2(full) level of theory, 9.7 kJ/mol, suggests that this conformer would comprise 2.1% of the Rb⁺(cyclen) population at 298 K. The absence of the intense band predicted at 703 cm⁻¹ in the IRMPD spectrum is probably the most diagnostic for ruling out a significant presence of the C_s(+++-) conformer in the experiments. However, the appearance of the shoulder at 787 cm⁻¹ in the measured IRMPD spectrum matches well with the feature observed at 789 cm⁻¹ in the predicted IR spectrum for the C_s(+++-) conformer, suggesting that a very small population of this conformation may have been accessed in the experiments.

For the calculated spectrum of the $C_{2v}(++++)$ conformer, overlapping spectral features are observed, but most of the spectral features in the ranges between 600 and 1000 cm⁻¹ and from 1200 to 1600 cm⁻¹ are red shifted as compared to experiment, similar to those observed for the K^+ (cyclen) complex. Bands centered at 805, 937, 1075, 1357, and 1446 cm⁻¹ in the measured IRMPD spectrum are red shifted by $6-20 \,\mathrm{cm}^{-1}$, whereas the bands observed at 838, 1121, and 1241 cm⁻¹ are blue shifted by 14–23 cm⁻¹ in the theoretical spectrum predicted for the $C_{2v}(++++)$ conformer. The $C_{2v}(++++)$ conformer lies 21.9 and 18.1 kJ/mol above the ground-state at the B3LYP and MP2(full) levels of theory, respectively, such that it would comprise less than 0.1% of the reactant ion population in a 298 K Maxwell-Boltzmann distribution. The spectral and energetic differences suggest that this conformer was not accessed in the experiments. The absence of the intense spectral features predicted at 623 and 735 cm⁻¹ and little similarity in the observed spectrum with that predicted for the $C_{2v}(+-+-)$ conformer indicates that this conformer is not accessed in the experiments. The large difference in the relative Gibbs free energies computed for the $C_{2v}(+-+-)$ conformer at both the B3LYP and MP2(full) levels of theory, 43.5 and 32.1 kJ/mol, respectively, also suggest that this conformer is not present

Assignments for the bands observed in the Rb⁺(cyclen) action spectrum based on comparison to the IR spectrum computed for the ground state $C_4(++++)$ conformer are consistent with those assigned for the Na⁺(cyclen) and K⁺(cyclen) complexes. The new spectral feature centered at 752 cm⁻¹ is a mixed character mode comprised of doubly degenerate N-H bending with contributions from CH_2 rocking. The feature at 787 cm⁻¹ can be attributed to a very minor population of the $C_s(+++-)$ conformer and this band is assigned as N-H wagging. This now completes the assignment of all the main bands observed in the experimental spectrum as summarized in Table 2. Vibrational modes that were previously more rigid because of stronger interactions with the smaller metal cations contribute more to the IRMPD yield. There is a change in the most intense peak as compared to the Na⁺(cyclen) and K⁺(cyclen) complexes, which now occurs at 1075 cm⁻¹ for Rb⁺(cyclen). Theory generally does a good job of reproducing the peak intensities as compared to the experimental IRMPD spectrum, but predicts the mixed character mode comprised of M⁺-N stretching, N-H bending, and CNC scissoring to be relatively more intense than the other spectral features in the IR spectrum of the $C_4(++++)$ conformer.

4.4. Comparison of experimental IRMPD and theoretical IR spectra of Cs⁺(cyclen)

Fig. 7 compares the experimental IRMPD action spectrum to the calculated IR spectra for the four most stable conformers found for the Cs⁺(cyclen) complex. Compared to the experimental spectrum of Rb⁺(cyclen), Cs⁺(cyclen) retains all the same bands, but overall the spectral features observed in the experimental spectrum of Cs⁺(cyclen) are slightly better resolved. In addition, there is a notable increase in the IRMPD yield of the peaks observed as compared to the M⁺(cyclen) complexes to the smaller alkali metal cations. The Cs⁺-cyclen BDE, 131.3 ± 5.6 kJ/mol, is substantially lower than that those of Na⁺(cyclen), K⁺(cyclen), and Rb⁺(cyclen) [11]. On the basis of the measured BDEs, only 47, 74 and 90% as many photons are needed to dissociate the Cs⁺(cyclen) complex



Fig. 7. Comparison of the experimental IRMPD action spectrum of Cs⁺(cyclen) with linear IR spectra for the four most stable conformations predicted at the B3LYP/def2-TZVPPD level of theory. B3LYP/def2-TZVPPD and *MP2(full)/def2-TZVPPD* (in red) relative Gibbs free energies at 298 K are also shown. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

as compared to the Na⁺(cyclen), K⁺(cyclen), and Rb⁺(cyclen) complexes, respectively.

Excellent agreement between the measured IRMPD action spectrum and the calculated IR spectrum for the ground-state $C_4(++++)$ conformer is evident in the comparison in Fig. 7. The band positions are well reproduced, suggesting that the ground-state conformer is accessed in the experiments. The most intense spectral feature appears at 805 cm⁻¹ in both the IRMPD spectrum and predicted IR spectrum. The bands centered at 752, 835, 889, 938, 1008, 1081, 1123, and 1240 cm⁻¹ in the measured IRMPD spectrum are red shifted by less than 10 cm⁻¹, whereas the bands centered at 1288, 1358 and 1447 cm^{-1} are blue shifted by less than 5 cm^{-1} in the theoretical IR spectrum predicted for the $C_4(++++)$ conformer. As found for the K⁺(cyclen) and Rb⁺(cyclen) complexes, the spectral features observed in the low frequency region between 600 and 1000 cm⁻¹ are not reproduced or, are blue shifted as compared to experiment in the IR spectrum of the $C_{s}(+++-)$ conformer. The two bands centered at 1081 and 1123 cm⁻¹ are in very good agreement with the $C_s(+++-)$ conformer in position and are red or blue shifted by less than 3 cm⁻¹. In contrast, the feature centered at 1358 cm⁻¹ is not well reproduced in shape or relative intensity. The bands predicted at 788 and 845 cm⁻¹ that contribute to the broad feature in the theoretical IR spectrum for the $C_s(+++-)$ conformer are only blue and red shifted by 5 and $10 \,\mathrm{cm}^{-1}$ as compared to the features in the experimental spectrum at 783 and $835 \,\mathrm{cm}^{-1}$, respectively, however, the central feature at 818 cm⁻¹ is much less intense and blue shifted by 13 cm^{-1} . The difference in the Gibbs free energy at the B3LYP level of theory, 20.1 kJ/mol, suggests the conformer would comprise less than 0.1% of the Cs⁺(cyclen) population at 298 K. In contrast, the difference in the Gibbs free energy at the MP2(full) level of theory, 6.3 kJ/mol, suggests the conformer would comprise 8.9% of the Cs⁺(cyclen) population at 298 K. The absence of the intense band predicted at 699 cm⁻¹ in the IRMPD spectrum is probably the most diagnostic for ruling out a significant presence of the $C_{s}(+++-)$ conformer in the experiments. However, the appearance of the shoulder at 783 cm⁻¹ in the measured IRMPD spectrum matches well with the feature at 788 cm⁻¹ in the predicted IR spectrum for the $C_s(+++-)$ conformer suggesting that a small population of this conformation may have been accessed in the experiments. For the calculated spectrum of the $C_{2v}(+++)$ conformer, overlapping spectral features are observed, but most of the spectral features in the ranges between 600 and 1000 cm⁻¹ and from 1200 to 1600 cm⁻¹ are red shifted as compared to experiment, similar to that observed for the K⁺(cyclen) and Rb⁺(cyclen) complexes. Bands centered at 805, 938, 1081, 1358, and 1447 cm⁻¹ in the measured IRMPD spectrum are red shifted by 8-23 cm⁻¹, while the bands observed at 835, 1123, and 1240 cm⁻¹ are blue shifted by 15–25 cm⁻¹ in the theoretical spectrum predicted for the $C_{2v}(++++)$ conformer. The $C_{2v}(++++)$ conformer lies 21.0 and 11.4 kJ/mol above the ground-state at the B3LYP and MP2(full) levels of theory, respectively, such that it would comprise less than 0.1 and 1.0% of the reactant ion population at 298 K, suggesting that a significant population of this conformer was not accessed in this experiments. The appearance of the shoulder at 783 cm⁻¹ in the measured IRMPD spectrum does match the intense feature at 788 cm⁻¹ in the predicted IR spectrum for the $C_{2v}(+++)$ conformer, potentially consistent with a very small population of this conformation in the experiments; however, this shoulder more likely arises from the presence of the $C_s(+++-)$ conformer. The absence of intense spectral features at 623 and 735 cm⁻¹ and little similarity in the predicted spectrum of the $C_{2v}(+-+-)$ conformer with the experimental spectrum indicates that this conformer is not accessed in the experiments. The large difference in the relative Gibbs free energies computed for this conformer at both the B3LYP and MP2(full) levels of theory, 42.9 and 25.8 kJ/mol, respectively, also suggest that the $C_{2v}(+-+-)$ conformer is not present.

Assignments for the bands observed in the Cs⁺(cyclen) IRMPD action spectrum based on comparison to the IR spectrum computed for the ground state $C_4(++++)$ conformer, and possibly a very minor contribution from the $C_s(+++-)$ conformer, exactly parallel those for Rb⁺(cyclen), Table 2.

4.5. Effects of alkali metal cation size of gas-phase conformation

On the basis of a comparison of the measured IRMPD action spectra for the M⁺(cyclen) complexes and calculated IR spectra and energetics for the stable low-energy conformations of these complexes, it is clear that the symmetry and mode of binding are not altered by the size of the alkali metal cation. The $C_4(++++)$ conformation is consistently the ground-state conformation for all four alkali metal cations and is the dominant species accessed in the experiments. However, as can be seen in Fig. 1, the strength of interaction between the alkali metal cation and cyclen does vary with the cation as evidenced by the systematic shifts in several of the spectral features observed in the IRMPD spectra of these complexes, in agreement with the measured M⁺-cyclen BDEs [11]. Indeed, the strength of binding and the shifting of the frequencies of the spectral features are strongly correlated with the size of the metal cation. The smaller the metal cation, the more closely it can

approach the cyclen ligand, resulting in stronger binding and larger spectral shifts to lower frequencies as compared to the complexes to the larger alkali metal cations as observed. The systematic variation in the M⁺−N bond lengths and the ∠NM⁺N bond angles is nicely illustrated in the ground-state $C_4(++++)$ conformers shown in Fig. 2. The cyclen ring is sufficiently small that even the Na⁺ cation is not quite able to insert itself in the ring, whereas the alkali metal cations of increasing size occupy sites further and further above the cyclen ring. To optimize the alkali metal cation-N donor binding interactions in these complexes, the N donor atoms of cyclen slightly curve toward the Na⁺ cation. However, as the size of the alkali metal cation increases, the cyclen ring becomes slightly flatter to accommodate the binding. This is easily seen from the comparison of the N1-N7 and N4-N10 distances, which increase from 4.268 Å for Na⁺ to 4.348 Å for Cs⁺, and the \angle NCCN dihedral angles that increase from 61.1° for Na⁺ to 64.3° for Cs⁺ The possible presence of a minor population of the first excited $C_s(+++-)$ conformers for Rb⁺ and Cs⁺ clearly indicates that the size of the alkali metal cation is important in determining the conformations accessed in the experiments, and suggest that larger, more flexible azacrown ether analogs may exhibit greater variation in the preferred alkali metal cation binding modes.

5. Conclusions

IRMPD action spectra of alkali metal cation-cyclen complexes in the region extending from 600 to 1600 cm⁻¹ have been obtained for four M^+ (cyclen) complexes where $M^+ = Na^+$, K^+ , Rb^+ , and Cs^+ . For all four complexes, the loss of the intact neutral cyclen ligand is the only dissociation pathway observed, consistent with simple CID fragmentation behavior [11]. The binding energies were found to decrease monotonically with the size of the alkali metal cation [11]. The IRMPD yields for the M⁺(cyclen) complexes increase as the size the alkali metal cation increases, in accordance with the trends in the strength of alkali metal cation binding in these systems [11]. Spectral features in the IRMPD action spectra observed for Na⁺(cyclen) are retained throughout the entire series, while new spectral features are observed for the complexes to the larger alkalimetal cations, again a consequence of the decreasing dissociation energies. Comparison with IR spectra calculated at the B3LYP/def2-TZVPPD level of theory allows the conformations present in the experiments to be identified. For the larger alkali metal cations K⁺, Rb⁺, and Cs⁺, the IRMPD action spectra are well reproduced by the calculated spectra for the most-stable conformation, $C_4(++++)$. Evidence for the presence of a minor population of an excited $C_s(+++-)$ conformation is observed for the complexes to Rb⁺ and Cs⁺. For the Na⁺(cyclen) complex, the lack of spectral features, which is a result of the low IRMPD yield, makes identifying the conformations accessed in the experiment less definitive, but trends for the larger metal cations suggest that only the ground state $C_4(++++)$ conformation was accessed in the experiments. This behavior is in sharp contrast to that found for the alkali and transition metal cation complexes to 15-crown-5 and 18-crown-6, where the conformation(s) accessed vary with the size of the metal cation. It is presently unclear whether this difference arises from the size of the crown (12 versus 15 and 18-membered rings) or the nature of the donor atoms (N versus O).

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.ijms.2013.08.004.

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