Infrared multiple photon dissociation spectroscopy of cationized methionine: effects of alkali-metal cation size on gas-phase conformation†

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The gas-phase structures of alkali-metal cation complexes of the amino acid methionine (Met) as well as protonated methionine are investigated using infrared multiple photon dissociation (IRMPD) spectroscopy utilizing light generated by a free electron laser. Spectra of Li^+(Met) and Na^+(Met) are similar and relatively simple, whereas the spectra of K^+(Met), Rb^+(Met), and Cs^+(Met) include distinctive new bands. Measured IRMPD spectra are compared to spectra calculated at the B3LYP/6-311+G(d,p) level of theory to identify the conformations present in the experimental studies. For Li^+ and Na^+ complexes, the only conformation present is a charge-solvated, tridentate structure that binds the metal cation to the amine and carbonyl groups of the amino acid backbone and the sulfur atom of the side chain, [N,CO,S]. In addition to the [N,CO,S] conformer, bands corresponding to alkali-metal cation binding to a bidentate zwitterionic structure, [CO_2^-], are clearly present for the K^+, Rb^+, and Cs^+ complexes. Theoretical calculations of the lowest energy conformations of Rb^+ and Cs^+ complexes suggest that the experimental spectra could also include contributions from two additional charge-solvated structures, tridentate [COOH,S] and bidentate [COOH]. For H^+(Met), the IRMPD action spectrum is reproduced by multiple low-energy [N,CO,S] conformers, in which the protonated amine group hydrogen bonds to the carbonyl oxygen atom and the sulfur atom of the amino acid side chain. These [N,CO,S] conformers only differ in their side-chain orientations.

Introduction

Fundamental interactions between biologically relevant metal ions and small molecules can have a profound effect on the function of complex biological processes. For example, the interactions between potassium ions and sulfur-containing amino acid methionine (Met) in the outer pore region of inward rectifying K^+ (Kir) ion channels are an important controlling factor in the selective passage of monocations.[1] Recently, the pairwise interactions between Met with the alkali-metal cations, Li^+, Na^+, and K^+, have been investigated using guided ion beam mass spectrometry.[2] Quantitative bond dissociation energies were determined and found to be consistent with theoretical values predicted for the ground state conformations, charge-solvated structures involving tridentate bonding of the metal ion to the amine and carbonyl groups of the amino acid backbone and the side-chain sulfur atom, [N,CO,S] (see nomenclature below), for Li^+ and Na^+. For Li^+(Met) and Na^+(Met), the [N,CO,S] ground state lies well below (> 10 kJ mol^{-1}) any other conformations such that quantitative measurements are sufficient to determine the identity of the complexes formed experimentally.[2] Calculations indicate that the energy differences between the ground state and higher energy conformations decrease as the metal cations become heavier. For example, MP2(full) calculations predict a ground state of [N,CO,S] for K^+ complexed to Met, but density functional theory calculations indicate the ground state is bidentate with K^+ bound to the carboxylate moiety of the zwitterionic [CO_2^-] conformation and the NH_3^+ group hydrogen bonds to the side-chain sulfur atom.[2] At both levels of theory, the [N,CO,S] and [CO_2^-] conformers are separated by less than 3 kJ mol^{-1}. Low-energy conformations are likely present for Rb^+ and Cs^+ complexed to Met as well. As such, threshold collision-induced dissociation measurements are unable to distinguish between small differences in conformational energy.

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† Electronic supplementary information (ESI) available: A description of the structures of Met and M^+(Met) for M^+ = Li^+, Na^+, K^+, Rb^+, and Cs^+. One figure (S1) depicting the Gibbs free energy at 298 K calculated at the B3LYP/6-311+G(2d,2p)//B3LYP/6-311+G(d,p) (M^+ = Li^+, Na^+, K^+) and B3LYP/HW*/6-311+G(2d,2p)//B3LYP/HW*6-311+G(d,p) (M^+ = Rb^+ and Cs^+) levels of theory. One table (S1) providing 0 K relative energies calculated at the **R**/HW*/6-311+G(2d,2p) and **R**/Def2TZVP levels of theory, where **R** = B3LYP, B3P86, and MP2(full), for eight conformations of Rb^+(Met) and Cs^+(Met). Two tables (S2 and S3) providing geometric parameters (bond lengths, bond angles, and dihedral angles) for low-energy structures of M^+(Met). Ten tables (S4–S13) providing the vibrational frequencies and IR intensities for various conformations of M^+(Met) calculated at the B3LYP/6-311+G(d,p) (M^+ = Li^+, Na^+, K^+) and B3LYP/HW*/6-311+G(d,p) (M^+ = Rb^+ and Cs^+) levels of theory. Two tables (S14 and S15) providing the vibrational frequencies and IR intensities for four [N,CO,S] and four [N,OH,S] conformers of H^+(Met) calculated at the B3LYP/6-311+G(d,p) level.

Infrared multiple photon dissociation (IRMPD) action spectroscopy can be used to examine the presence of specific conformations as a function of metal cation size. Previous IRMPD studies on M^+(Ser)[3] and M^+(Thr)[4] have found that the $M^+ = Li^+$ and Na^+ complexes are bound in a tridentate [N,CO,OH] conformer, whereas spectra for $M^+ = K^+$ and Rb^+ include evidence of bidentate [COOH] conformations. Additionally, the spectra for Cs^+ serine and threonine complexes also include contributions from a zwitterionic [CO_2^-] conformer. For M^+(Arg), the transition from ground state charge-solvated to zwitterionic conformation occurs at Na^+(Arg).[5] The IRMPD action spectra of M^+(Asn) maintain the charge-solvated tridentate [N,CO,CO] conformation throughout the alkali cation series, but also include spectral contributions from the [COOH,CO] conformer for K^+(Asn) to Cs^+(Asn).[6] A similar progression is seen in IRMPD studies of M^+(Gln),[7] M^+(Trp)[8] and M^+(Lys)[9] transition from tridentate to bidentate conformers as the metal ion becomes heavier, but still maintain charge-solvated complexes. In the present study, we examine whether such trends are influenced by having a side chain with a sulfur-containing functional group, which tends to bind metal cations at different angles compared to analogous ether functional groups.[2] Thus, we measure the IRMPD action spectra for dissociation of M^+(Met) complexes, where $M^+ = Li^+$, Na^+, K^+, Rb^+, Cs^+, and H^+. The conformations are identified by comparing the experimental action spectra to IR spectra predicted by quantum chemical calculations of the low-lying structures of the M^+(Met) complexes optimized at the B3LYP/6-311+G(d,p) level of theory.

Experimental and computational section

Mass spectrometry and photodissociation

A 4.7 T Fourier transform ion cyclotron resonance (FTICR) mass spectrometer was used in these experiments and has been described in detail elsewhere.[10–12] Tunable radiation for the photodissociation experiments is generated by the free electron laser for infrared experiments (FELIX).[13] For the present experiments, spectra were recorded over the wavelength range 19.4 μm (520 cm^{-1}) to 5.5 μm (1820 cm^{-1}). Pulse energies were around 50 mJ per macropulse of 5 μs duration, although they fell off to about 20 mJ toward the blue edge of the scan range. Complexes were irradiated for 2.5 seconds, which corresponds to interaction with approximately 12 macropulses. The fwhm bandwidth of the laser was typically 0.5% of the central wavelength. Methionine was obtained from Aldrich. Cationized amino acids were formed by electrospray ionization using a Micromass Z-Spray source and a solution of 1 mM Met and 1 mM alkali-metal chloride (or 1 mM acetic acid for H^+(Met)) in 70% : 30% MeOH : H_2O. Solution flow rates were about 10 μL min^{-1} and the electrospray needle was held at a voltage of 3250 V. Ions were accumulated in a hexapole trap for about 4 s prior to being injected into the ICR cell *via* an rf octopole ion guide. Electrostatic switching of the dc bias of the octopole, where a dc bias voltage is superimposed on the full length of all octopole rods, results in there being no change in the dc electric field along the axis of the ion guide.[12] This decelerates the ions exiting the octopole such that they can be captured in the ICR cell without a gas pulse and collisional heating of the ions is avoided.[12]

Computational details

In previous work,[2] Armentrout *et al.* examined likely conformers for Li^+(Met), Na^+(Met), and K^+(Met) using a simulated annealing procedure that combines annealing cycles with quantum chemical calculations.[14] The same procedure is used here for H^+(Met) complexes. Briefly, the AMBER program and the AMBER force field based on molecular mechanics[15] were used to search for possible stable structures in each system's conformational space. All possible structures identified this way were subsequently optimized using NWChem[16] at the HF/3-21G level.[17,18] Unique structures for each system within 50 kJ mol^{-1} of the lowest energy structure (~50 for each complex) were optimized using Gaussian 03[19] at the B3LYP/6-31G(d) level of theory[20,21] with the "loose" keyword (maximum step size 0.01 au and an RMS force of 0.0017 au) to facilitate convergence. Unique structures obtained from this procedure were then chosen for higher-level geometry optimization and frequency calculations using density functional theory (DFT) at the B3LYP/6-311G(d,p) level of theory.[22,23] This level of theory has been shown to provide a reasonable structural description of comparable metal–ligand systems.[3,4,6] Here, we have altered the results slightly by reoptimizing at the B3LYP/6-311+G(d,p) level of theory. Only small changes are observed as bond lengths typically change by <0.03 Å, bond angles by $<1°$, and relative energies of different conformers are within about 3 kJ mol^{-1}. Single point energy calculations were carried out for the 6–10 most stable structures at the B3LYP, B3P86, and MP2(full) levels using the 6-311+G(2d,2p) basis set.[22] Zero-point vibrational energy (ZPE) corrections were determined using vibrational frequencies calculated at the B3LYP/6-311+G(d,p) level scaled by a factor of 0.9804.[24]

For the Rb^+(Met) and Cs^+(Met) complexes studied here, all conformations considered previously for K^+(Met) were used as starting points for geometry and vibrational frequency calculations optimized at the B3LYP/HW*/6-311+G(d,p) level where HW* indicates that Rb^+ and Cs^+ were described using the effective core potentials (ECPs) and valence basis sets of Hay and Wadt[25] with a single d polarization function (exponents of 0.24 and 0.19, respectively) included.[26] Relative energies are determined using single point energies at the B3LYP, B3P86, and MP2(full) levels using the HW*/6-311+G(2d,2p) basis set. In previous work on serine complexes,[3] similar HW* calculations were performed for K^+(Ser) complexes (with an exponent of 0.48 for the d polarization function on K^+) in order to assess the accuracy of the Hay–Wadt ECP–valence basis sets. It was determined that vibrational frequencies calculated using the all-electron *vs.* HW* basis sets on K yield results that differ by an average of less than 0.03%. Therefore, we did not perform HW* calculations on K^+(Met) complexes and conclude that the use of the HW* basis sets for the Rb^+ and Cs^+ systems should yield equivalent results to the all-electron basis sets used for the smaller cations. In addition to using the HW* basis sets on

Rb^+ and Cs^+ complexes, we also performed geometry optimizations, frequency calculations, and single point energy calculations using the Def2TZVP basis sets of triple-ζ valence quality for all elements.[27] These basis sets for Rb and Cs are designed to be used with small core ECPs developed by Leininger *et al.*[28]

Vibrational frequencies and intensities were calculated using the harmonic oscillator approximation and analytical derivatives of the energy-minimized Hessian calculated at the levels of theory noted above. Frequencies were scaled by 0.975 as this scaling factor leads to good agreement between calculated and experimentally well-resolved peaks and is in accord with previous IRMPD studies as well.[6–8,29] For comparison to experiment, calculated vibrational frequencies are broadened using a 20 cm^{-1} fwhm Gaussian line shape.

Results and discussion

Theoretical results

The low-lying structures found for all M^+(Met) complexes are illustrated by those for Rb^+(Met) in Fig. 1. The nomenclature used to identify different structural isomers is identical to that described previously for the CID study of alkali-metal asparagine complexes[6] and differs somewhat from that utilized in the CID study of Met complexes.[2] Briefly, conformations of M^+(Met) are identified by their metal binding site (or protonation site) in brackets, followed by a description of the methionine orientation by a series of five dihedral angles. These dihedral angles start with the carboxylic acid hydrogen atom (or analogous proton attached to the NH_2 group for zwitterionic structures) to define the H–O–C–C dihedral angle and proceeds along the molecule to the terminal methyl group of the amino acid side chain (O–C–C–C, C–C–C–C, C–C–C–S, and C–C–S–C). The dihedral angles are distinguished as *cis* (c, for angles between 0° and 50°), *gauche* (g, 50°–135°) and *trans* (t, 135°–180°). Previously, we designated the conformations somewhat less completely by designating the HOCO angle followed by the last three side-chain dihedrals, C–C–C–C, C–C–C–S, and C–C–S–C. In all cases, the HOCO and HOCC bond angles are the inverse of one another, *i.e.*, c *versus* t, and the last three dihedral angles are identical. Descriptions of these structures have been provided for the cases of $M^+ = Li^+$, Na^+, and K^+ previously,[2] and the ESI† describes the variations among all five alkali-metal cations in more detail.

Relative energies including zero-point energy (ZPE) corrections with respect to the ground state calculated at three different levels of theory are given in Table 1 for the M^+(Met) complexes. Because the relative Gibbs free energies at 298 K may be more relevant in describing the experimental distributions, these values are also listed in Table 1 and used throughout the discussion below. The overall trends in relative Gibbs free energies at 298 K calculated at the MP2(full) level are shown in Fig. 2. Comparable figures for the relative Gibbs free energies at 298 K calculated at the B3LYP and B3P86 levels can be found in ESI†, Fig. S1. Conversion from 0 K bond energies to 298 K free energies is accomplished using the rigid rotor–harmonic oscillator approximation with rotational

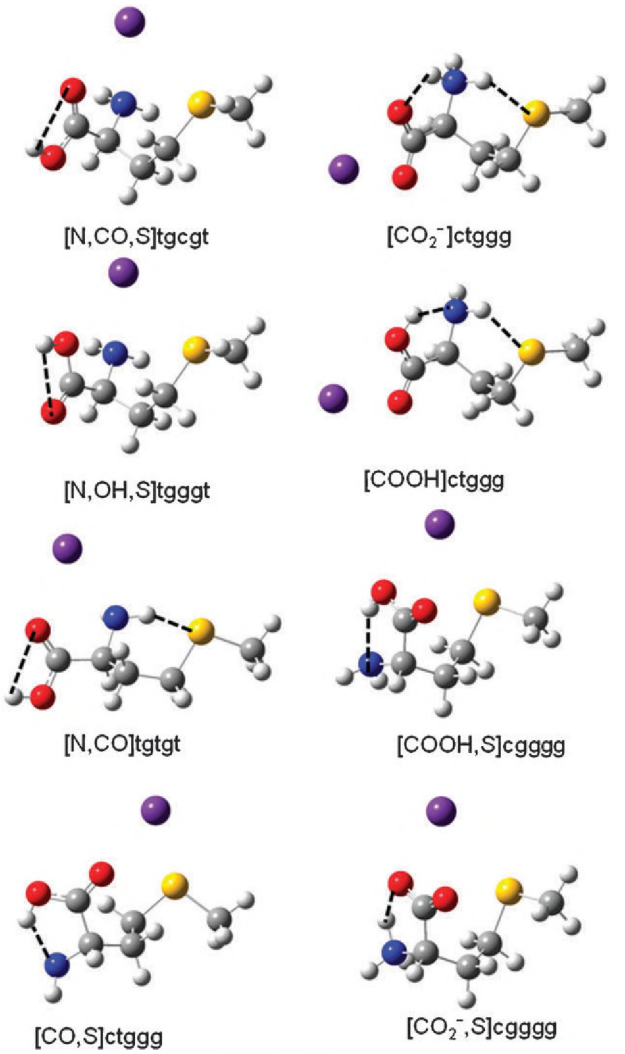

Fig. 1 Structures of the Rb^+(Met) complexes calculated at the B3LYP/HW*/6-311+G(d,p) level of theory. Hydrogen bonds are indicated by dashed lines.

constants and vibrational frequencies calculated at the B3LYP/6-311+G(d,p) and B3LYP/HW*/6-311+G(d,p) levels. In the previous CID study of M^+(Met) complexes,[2] three to four side-chain orientations were optimized for each distinct type of conformation, but only the lowest of these are plotted in Fig. 2. For the most part, the calculated IR spectra of the various side-chain orientations are very similar, such that a comparison with the lowest energy conformer is sufficient for identification; however, in the comparison between calculated and observed photodissociation spectra, spectral differences among these orientations will be discussed. Therefore, higher energy orientations that make up at least 1% of the ion population are included in Table 1. This corresponds to an excitation free energy of ~12 kJ mol^{-1} above the ground state.

The charge-solvated, tridentate [N,CO,S] conformation is the lowest energy conformation for Li^+(Met) and Na^+(Met). For K^+(Met), Rb^+(Met), and Cs^+(Met), the [N,CO,S] conformer is low-lying, 0–8, 1–10, and 5–13 kJ mol^{-1}, respectively, higher in energy than the calculated ground state conformer.

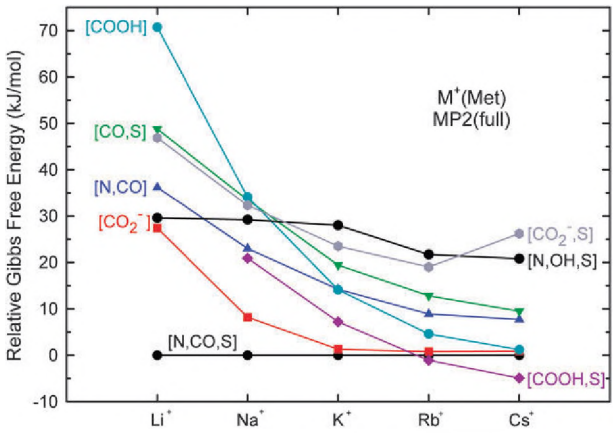

Fig. 2 298 K Gibbs free energies (kJ mol^{-1}) calculated at the MP2(full) level of theory (from Table 1) of eight conformations of M^+(Met) complexes as a function of the alkali-metal cation relative to the energy of the [N,CO,S] conformer. The relative energy of the [CO_2^-,S] structure is higher than expected for Cs^+ because the orientation preferred for Li^+ to Rb^+ collapses to a high energy [CO_2^-] structure.

The zwitterionic [CO_2^-] conformation lies >20 kJ mol^{-1} higher than the [N,CO,S] ground state for Li^+(Met), however, as the metal cation becomes larger, the energetic difference between the [N,CO,S] and [CO_2^-] conformers decreases to 2–8 kJ mol^{-1} at Na^+(Met) and the two structures become nearly isoenergetic with one another at K^+(Met) through Cs^+(Met), with excitation energies of 0–8, −1 to 10, and −1 to 13 kJ mol^{-1}, respectively, Fig. 2. The [COOH] conformer, the charge-solvated analogue of the zwitterionic [CO_2^-] structure, starts 58–71 kJ mol^{-1} higher than the ground state for Li^+(Met). As the metal cation becomes larger, the energy of the [COOH] conformer with respect to the ground state quickly decreases, but remains higher in energy than the [CO_2^-] conformation. For Li^+(Met), the [CO_2^-]–[COOH] difference is 38–43 kJ mol^{-1}, but decreases to 24–26, ~13, and ~4 kJ mol^{-1} for M^+(Met), M^+ = Na^+, K^+, and Rb^+, respectively. For Cs^+(Met), the difference drops to 0.3–1.9 kJ mol^{-1}. The charge-solvated, tridentate [COOH,S] conformation lies 19–23 kJ mol^{-1} above [N,CO,S] at Na^+(Met). For Li^+(Met), this structure collapses to the bidentate [CO,S]. At the MP2 level of theory, the [COOH,S] conformer becomes the lowest energy state for Rb^+(Met) and Cs^+(Met), lying 2 and 5 kJ mol^{-1}, respectively, below [CO_2^-], but the DFT calculations indicate the opposite order, with [COOH,S] lying 3–5 and 0–1 kJ mol^{-1}, respectively, above [CO_2^-]. Overall, the 298 K free energies of the [N,CO,S], [CO_2^-], [COOH], and [COOH,S] conformers all lie within 10 and 13 kJ mol^{-1} of one another for Rb^+(Met) and Cs^+(Met), respectively.

The [CO_2^-,S] conformer, the zwitterionic analogue of the charge-solvated [COOH,S] conformer, lies 11–14 kJ mol^{-1} above the [COOH,S] structure for Na^+(Met); however, as the metal cation becomes larger, the difference between these two tridentate structures increases eventually reaching a difference of 31–32 kJ mol^{-1} at Cs^+(Met). The charge-solvated, tridentate [N,OH,S] conformer lies 30–35 kJ mol^{-1} above the [N,CO,S] ground state for Li^+(Met) and remains fairly high in energy, only getting to within 21–30 kJ mol^{-1} of the [N,CO,S] conformer for Cs^+(Met). The charge-solvated bidentate [N,CO] conformer is 27–36 kJ mol^{-1} higher than the tridentate [N,CO,S] ground state at Li^+(Met), but the difference between these two types of complexes decreases with larger cations, differing by 1–8 kJ mol^{-1} at Cs^+(Met). Similar behavior is also observed for the charge-solvated, bidentate [CO,S] structure.

The [CO_2^-] and [COOH] conformers differ only in the position of the hydrogen atom shared by the carboxylic acid and amino groups, which moves only by 0.88 Å for Li^+(Met) to 0.75 Å for Cs^+(Met) for the ctggg orientation. Therefore, we also located the transition states (TSs) between these conformers using the synchronous transit-guided quasi-newton (STQN) method[30] at the B3LYP/6-311+G(d,p) (M^+ = Li^+, Na^+, and K^+) and B3LYP/HW*/6-311+G(d,p) (M^+ = Rb^+ and Cs^+) levels. Single point energies were calculated at the three levels listed above using the 6-311+G(2d,2p) basis set for M^+ = Na^+ and K^+ and HW*/6-311+G(2d,2p) basis set for M^+ = Rb^+ and Cs^+. 0 K energies for these TSs with ZPE corrections are 37–43, 18–24, 9–15, 3–7, and 1–5 kJ mol^{-1} higher in energy than the [CO_2^-] ctggg conformers for M^+ = Li^+, Na^+, K^+, Rb^+, and Cs^+, respectively. When compared to the energies of the [COOH] ctggg conformer, the TS is 3 kJ mol^{-1} lower for M^+ = Li^+, 4–8 kJ mol^{-1} lower for M^+ = Na^+, 2–7 kJ mol^{-1} lower for M^+ = K^+, 4 kJ mol^{-1} lower to 1 kJ mol^{-1} higher for M^+ = Rb^+, and 2 kJ mol^{-1} lower to 3 kJ mol^{-1} higher for M^+ = Cs^+. Therefore, once ZPEs are included, the [COOH] ctggg conformer of Li^+(Met), Na^+(Met), and K^+(Met) collapses to the lower energy zwitterionic [CO_2^-] ctggg with no barrier to proton transfer, whereas for Rb^+(Met) and Cs^+(Met), small barriers for proton transfer of ~1 and ~3 kJ mol^{-1}, respectively, are calculated at the B3LYP and MP2(full) levels, but no barrier is found at the B3P86 level.

In order to more completely evaluate the utility of the HW* basis sets for the heavier Rb^+ and Cs^+ metal cations, relative free energies at 298 K for their complexes with Met were also calculated utilizing the Def2TZVP basis sets at the B3LYP, B3P86, and MP2(full) levels of theory, Table 2. Relative 0 K energies utilizing the same basis set treatment are presented in ESI†, Table S1. Overall, the relative free energies using the Def2TZVP basis sets change very little compared to the results of the HW*/6-311+G(2d,2p) basis set. For Rb^+(Met), DFT energies from both treatments agree that the [CO_2^-] conformer is the lowest energy structure. MP2(full) calculations using the HW* and Def2TZVP basis sets predict that a [COOH,S] conformer is the lowest energy conformer. The MP2(full) energies using the HW* basis set predict that the [CO_2^-], [N,CO,S], and [COOH,S] conformers lie within 2 kJ mol^{-1} of one another for HW* and less than 0.5 kJ mol^{-1} with the Def2TZVP basis set. For all basis sets, [CO_2^-], [N,CO,S], [COOH], and [COOH,S] conformers lie within 10 kJ mol^{-1} of one another.

For Cs^+(Met), the B3P86 level of theory with the HW* basis set maintains that the [CO_2^-] structure is the lowest energy complex, whereas the B3LYP and MP2(full) levels of theory calculate a [COOH,S] conformer as the lowest energy state. Additionally, all levels of theory with the Def2TZVP basis set determine the [COOH,S] conformer to be the lowest

Table 1 Relative energies at 0 K and free energies at 298 K (kJ mol^{-1}) of low-lying conformers of cationized Met[a]

Complex	Structure	B3LYP	B3P86	MP2(full)
Li^+(Met)	[N,CO,S]tgcgt	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)
	[N,CO,S]tgcgg	6.1 (6.0)	6.3 (6.2)	5.2 (5.1)
	[N,CO,S]tgggt	11.2 (10.8)	11.2 (10.8)	11.6 (11.2)
	[N,CO,S]tgggg	12.9 (12.2)	12.9 (12.3)	12.4 (11.7)
	[CO_2^-]ctggg	27.4 (24.5)	23.1 (20.2)	30.3 (27.4)
	[N,CO]tgtgt	31.9 (28.1)	31.4 (27.5)	40.0 (36.2)
	[N,OH,S]tgggt	33.5 (32.9)	35.6 (35.0)	30.1 (29.6)
	[CO,S]ctggg	40.5 (37.3)	39.4 (36.2)	52.0 (48.8)
	[CO_2^-,S]cgggg	52.2 (51.9)	48.6 (48.4)	47.2 (46.9)
	TS[CO_2^-,COOH]	68.0 (64.5)	60.2 (56.7)	73.0 (69.5)
	[COOH]ctggg	70.6 (65.4)	63.6 (58.5)	75.8 (70.7)
	[COOH,S]cgggg[b]			
Na^+(Met)	[N,CO,S]tgcgt	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)
	[N,CO,S]tgcgg	7.3 (7.1)	7.6 (7.4)	6.8 (6.6)
	[N,CO,S]tgggt	8.7 (8.6)	8.6 (8.5)	8.1 (8.0)
	[CO_2^-]ctggg	10.1 (7.7)	4.6 (2.3)	10.5 (8.2)
	[CO_2^-]cgtgg	10.3 (7.9)	5.6 (3.2)	13.3 (10.9)
	[N,CO,S]tgggg	12.2 (11.9)	11.6 (11.3)	9.4 (9.1)
	[CO_2^-]ctggt	12.8 (10.3)	7.6 (5.1)	14.8 (12.3)
	[N,CO]tgtgt	23.3 (19.3)	21.8 (17.8)	27.1 (23.0)
	[COOH,S]cgcgg	29.3 (23.4)	25.2 (19.3)	26.8 (20.9)
	[CO,S]ctggg	29.3 (26.6)	26.8 (24.1)	36.2 (33.5)
	[N,OH,S]tgggt	32.6 (31.8)	34.3 (33.5)	29.9 (29.2)
	TS[CO_2^-,COOH]	33.3 (30.7)	23.0 (20.4)	34.3 (31.7)
	[COOH]ctggg	37.8 (33.2)	31.0 (26.5)	38.7 (34.1)
	[CO_2^-,S]cgggg	37.9 (37.3)	33.6 (32.9)	32.9 (32.3)
K^+(Met)	[CO_2^-]ctggg	0.0 (0.0)	0.0 (0.0)	1.7 (1.3)
	[CO_2^-]cgtgg	0.7 (0.4)	1.5 (1.2)	5.0 (4.2)
	[CO_2^-]ctggt	2.6 (0.9)	2.8 (1.2)	5.5 (3.5)
	[N,CO,S]tgcgt	2.7 (3.1)	7.8 (8.2)	0.0 (0.0)
	[N,CO,S]tgggt	9.3 (9.9)	14.4 (15.0)	5.4 (5.5)
	[N,CO,S]tgcgg	10.1 (10.3)	15.3 (15.6)	7.1 (7.0)
	[N,CO,S]tgggg	10.8 (12.7)	14.8 (16.6)	3.3 (4.7)
	[COOH,S]cgggt	12.6 (11.1)	15.1 (13.5)	10.0 (8.1)
	[COOH,S]cgcgg	13.0 (13.1)	15.3 (15.4)	8.5 (8.2)
	[COOH,S]cgggg	13.1 (13.0)	15.1 (14.9)	7.8 (7.2)
	TS[CO_2^-,COOH]	13.5 (13.0)	9.4 (8.9)	15.2 (14.3)
	[N,CO]tgtgt	15.2 (12.2)	19.9 (16.8)	17.6 (14.2)
	[COOH]ctggg	15.4 (12.6)	16.0 (13.2)	17.3 (14.1)
	[CO,S]ctggg	18.1 (15.5)	21.6 (19.0)	22.4 (19.4)
	[CO_2^-,S]cgggg	29.3 (28.6)	30.2 (29.6)	24.6 (23.5)
	[N,OH,S]tgggt	34.1 (33.4)	40.4 (39.7)	29.2 (28.0)
Rb^+(Met)	[CO_2^-]ctggg	*0.0 (0.0)*	*0.0 (0.0)*	*1.7 (1.9)*
	[CO_2^-]cgtgg	*0.9 (0.6)*	*1.8 (1.5)*	*5.3 (5.3)*
	[CO_2^-]ctggt	*2.5 (1.6)*	*2.8 (1.9)*	*5.8 (5.1)*
	[N,CO,S]tgcgt	*5.0 (4.9)*	*10.0 (9.9)*	*0.9 (1.1)*
	[COOH]ctggg	*6.4 (3.4)*	*7.5 (4.5)*	*8.4 (5.7)*
	[COOH]cgtgg	*6.5 (3.9)*	*7.8 (5.2)*	*10.6 (8.3)*
	[COOH,S]cgggt	*6.6 (2.7)*	*9.1 (5.2)*	*3.9 (0.4)*
	[COOH,S]cgcgg	*6.7 (5.7)*	*9.3 (8.3)*	*2.0 (1.3)*
	[COOH,S]cgggg	*7.2 (5.6)*	*9.4 (7.8)*	*1.4 (0.0)*
	TS[CO_2^-,COOH]	*7.4 (6.8)*	*3.3 (2.7)*	*8.8 (8.5)*
	[COOH]ctggt	*9.2 (5.7)*	*10.5 (7.0)*	*12.8 (9.7)*
	[N,CO,S]tgggg	*10.1 (11.7)*	*13.9 (15.5)*	*0.0 (1.9)*
	[N,CO,S]tgggt	*10.6 (10.7)*	*15.6 (15.7)*	*4.5 (4.9)*
	[N,CO,S]tgcgg	*12.3 (10.5)*	*17.5 (15.7)*	*8.2 (6.7)*
	[N,CO]tgtgt	*12.5 (8.8)*	*17.4 (13.7)*	*13.3 (10.0)*
	[CO,S]ctggg	*13.0 (10.2)*	*16.5 (13.7)*	*16.4 (13.9)*
	[CO_2^-,S]cgggg	*28.7 (24.8)*	*29.1 (25.2)*	*23.7 (20.1)*
	[N,OH,S]ttggg	*34.0 (36.7)*	*37.9 (40.5)*	*19.9 (22.8)*
Cs^+(Met)	[CO_2^-]ctggg	*0.0 (1.2)*	*0.0 (0.0)*	*3.2 (5.8)*
	[CO_2^-]cgtgg	*1.1 (4.2)*	*1.8 (3.6)*	*7.6 (11.9)*
	[COOH]cgtgg	*1.3 (1.6)*	*3.0 (2.1)*	*7.4 (9.0)*
	[COOH]ctggg	*1.5 (1.6)*	*3.1 (1.9)*	*4.7 (6.1)*
	[COOH,S]ctggt	*2.5 (0.0)*	*5.0 (1.3)*	*1.2 (0.0)*
	[CO_2^-]cgggt	*2.8 (4.3)*	*3.1 (3.3)*	*7.6 (10.4)*
	[COOH,S]cgcgg	*3.2 (4.7)*	*6.0 (6.3)*	*0.2 (3.0)*
	[COOH]ctggt	*4.0 (1.9)*	*5.9 (2.5)*	*9.3 (8.4)*
	[COOH,S]cgggg	*4.2 (4.8)*	*6.7 (6.0)*	*0.4 (2.4)*
	TS[CO_2^-,COOH]	*4.7 (6.5)*	*0.7 (1.3)*	*7.7 (10.9)*
	[N,CO,S]tgcgt	*7.2 (9.1)*	*12.2 (12.8)*	*3.7 (7.0)*

Table 1 (*continued*)

Complex	Structure	B3LYP	B3P86	MP2(full)
	[N,CO,S]tgggg	*9.3 (12.9)*	*13.2 (15.6)*	*0.0 (4.9)*
	[CO,S]ctgtg	*9.4 (9.2)*	*13.1 (11.7)*	*13.3 (14.4)*
	[N,CO]tgtgt	*11.0 (9.8)*	*16.2 (13.8)*	*12.5 (12.6)*
	[N,CO,S]tgggt	*11.6 (13.2)*	*16.6 (16.9)*	*6.3 (9.1)*
	[N,CO,S]tgcgg	*12.0 (10.4)*	*16.9 (14.0)*	*9.0 (8.7)*
	[CO_2^-,S]cgcgg	*30.1 (32.2)*	*31.1 (32.0)*	*27.7 (31.1)*
	[N,OH,S]ttggg	*32.9 (37.6)*	*36.7 (40.1)*	*19.8 (25.7)*
H^+(Met)	[N,CO,S]tgtgg	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)
	[N,CO,S]tgggg	2.6 (3.0)	2.0 (2.4)	0.4 (0.8)
	[N,CO,S]tgtgt	2.7 (1.9)	3.1 (2.3)	3.9 (3.1)
	[N,CO,S]tgggt	3.6 (3.3)	3.2 (2.9)	2.5 (2.2)
	[N,OH,S]tgtgg	15.4 (12.7)	16.6 (13.9)	14.5 (11.8)
	[N,OH,S]ttggg	17.2 (17.4)	17.7 (17.9)	13.7 (13.9)
	[N,OH,S]tgtgt	17.5 (13.9)	19.2 (15.6)	17.9 (14.2)
	[N,OH,S]ttggt	18.9 (17.9)	19.8 (18.8)	16.5 (15.5)

[a] Free energies in parentheses. All values calculated at the level of theory indicated using the 6-311+G(2d,2p) basis set with structures and zero-point energies calculated at the B3LYP/6-311+G(d,p) level of theory. Values in italics use the HW* basis set on the metal. [b] The [COOH,S] conformer for Li^+(Met) collapses to [CO,S].

Table 2 Relative free energies at 298 K (kJ mol^{-1}) of low-lying conformations of cationized Met calculated using different basis sets[a]

Complex	Structure	HW*/6-311+G(2d,2p)	Def2TZVP
Rb^+(Met)	[CO_2^-]ctggg	0.0, 0.0, 1.9	0.0, 0.0, 0.5
	[N,CO,S]tgcgt	4.9, 9.9, 1.1	2.5, 7.3, 0.2
	[COOH]ctggg	3.4, 4.5, 5.7	4.5, 5.3, 7.2
	[COOH,S]cgggt	2.7, 5.2, 0.4	4.1, 6.3, 0.0
	[COOH,S]cgggg	5.6, 7.8, 0.0	6.5, 8.4, 1.4
	[N,CO]tgtgt	8.8, 13.7, 10.0	7.8, 12.5, 11.1
	[CO,S]ctggg	10.2, 13.7, 13.9	9.4, 12.7, 13.7
	[CO_2^-,S]cgggg	24.8, 25.2, 20.1	23.3, 23.3, 15.4
	[N,OH,S]ttggg	36.7, 40.5, 22.8	35.7, 39.6, 24.8
Cs^+(Met)	[CO_2^-]ctggg	1.2, 0.0, 5.8	3.4, 1.1, 7.5
	[COOH]ctggg	1.6, 1.9, 6.1	5.6, 4.8, 11.8
	[COOH,S]ctggt	0.0, 1.3, 0.0	0.0, 0.0, 0.0
	[N,CO,S]tgcgt	9.1, 12.8, 7.0	9.0, 11.3, 8.7
	[CO,S]ctgtg	9.2, 11.7, 14.4	11.6, 13.0, 18.0
	[N,CO]tgtgt	9.8, 13.8, 12.6	11.6, 14.3, 17.8
	[CO_2^-,S]cgcgg	32.2, 32.0, 31.1	32.9, 31.3, 28.6
	[N,OH,S]ttggg	37.6, 40.1, 25.7	39.4, 40.9, 30.2

[a] Values listed are calculated at the B3LYP, B3P86, and MP2(full) levels of theory using the indicated basis set. For the Def2TZVP basis set on all elements, geometries and zero-point energies were calculated at the B3LYP/Def2TZVP level of theory.

energy structure. For both basis sets, all three levels of theory predict that the [N,CO,S] conformer lies 4–13 kJ mol^{-1} above the lowest energy conformation. The [COOH] conformer lies 0–4 kJ mol^{-1} above the [CO_2^-] conformer at all levels of theory.

The vibrational frequencies calculated using the HW*/6-311+G(d,p) and Def2TZVP basis sets are identical within about 2 cm^{-1} for the Rb^+(Met) and Cs^+(Met) complexes. These results further indicate that the HW*-calculations are adequate to describe relative energies and vibrational frequencies for the M^+(Met) set of systems.

Finally, all levels of theory predict that the [N,CO,S] tgtgg conformer is the lowest energy structure of the H^+(Met) system, Table 1. Additional [N,CO,S] orientations lie within ~3 kJ mol^{-1} of the tgtgg conformer. The [N,OH,S] analogues lie 11–16 kJ mol^{-1} higher with respect to the analogous [N,CO,S] conformers at all levels of theory.

IRMPD action spectroscopy

Photodissociation spectra of Met complexed with Li^+, Na^+, K^+, Rb^+, Cs^+, and H^+ were examined. For the Na^+, K^+, Rb^+, and Cs^+ complexes, photodissociation resulted in the loss of the intact ligand leaving the atomic metal cation. This result is consistent with collision-induced dissociation (CID) results for Na^+(Met) and K^+(Met).[2] For the complexes of K^+, Rb^+, and Cs^+, Fig. 3 shows IRMPD action spectra taken from the relative intensity of the M^+ product cation as a function of laser wavelength. For Na^+(Met), the results shown in Fig. 3 correspond to the depletion spectrum of the reactant complex as the Na^+ ion was difficult to collect in the FTICR and no other photodissociation products were observed for the Na^+(Met) system. Because of these difficulties, the Na^+(Met) spectrum only spans 900 to 1800 cm^{-1}.

For Li^+(Met), the CID spectra exhibit four low-energy channels corresponding to the loss of NH_3, NH_3 + CO, C_3H_8S, and C_3H_8S + H_2O.[2] The first two dissociation pathways were also observed in the IRMPD spectrum for Li^+(Met) and have the greatest intensity upon photodissociation. Two additional channels consisting of the loss of H_2O + CO and CH_3SH were also observed in the IRMPD spectrum, but these decomposition pathways encompass less than 10% of the photodissociation signal. The sum of these four decomposition pathways is shown as the IRMPD action spectrum in Fig. 3. For most bands, loss of NH_3 (deamination) is 2–3 times more intense than the loss of NH_3 + CO, which is expected as deamination is the lowest energy decomposition pathway in the CID spectra of Li^+(Met). However, these two dissociation pathways have the same intensity for bands at 1445 and 1595 cm^{-1}.

For H^+(Met), the IRMPD spectrum shown in Fig. 3 comprises the sum of the decomposition pathways corresponding to the loss of NH_3, H_2O + CO, H_2O + CO + NH_3, H_2O + CO + CH_3SH, and H_2O + CO + NH_3 + C_2H_2. All of these decomposition pathways are consistent with observed products in the CID spectra of H^+(Met) produced by electrospray ionization[31] and fast atom bombardment.[32] The deamination channel has about five times more intensity than the loss of H_2O + CO throughout the spectrum. The latter three

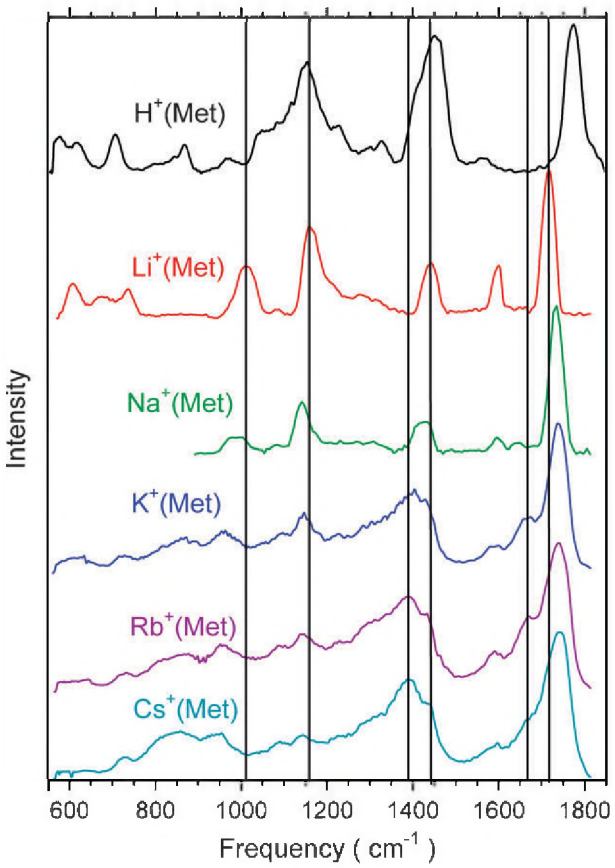

Fig. 3 Infrared multiple photon dissociation action spectra of M^+(Met) complexes, where $M^+ = Li^+$, Na^+, K^+, Rb^+, Cs^+, and H^+.

channels make up approximately 5% of the product intensities from photodissociation.

Comparison of the IRMPD spectra in Fig. 3 shows that the features observed in the Li^+(Met) spectrum are retained for all of the metal cation complexes, but that new spectral features begin to appear for K^+(Met). The major band at 1716 cm^{-1} shifts to the blue as the metal cation becomes heavier and the bands at 1160 and 1015 cm^{-1} shift to the red. Spectral features at 735, 1085, and 1595 cm^{-1} remain largely unchanged as the size of the metal ion increases. The band at 1445 cm^{-1} for Li^+(Met) red shifts to 1430 cm^{-1} in Na^+(Met), and the photodissociation signal in this frequency range increases substantially for K^+(Met), Rb^+(Met), and Cs^+(Met). A new band emerges at 1670 cm^{-1} for K^+(Met) and Rb^+(Met), but is less distinct for Cs^+(Met). These progressions suggest multiple conformers are now present in the IRMPD spectra for the K^+, Rb^+, and Cs^+ complexes. Of considerable interest here is that the spectra for K^+(Met), Rb^+(Met), and Cs^+(Met) are virtually identical. In contrast, the IRMPD action spectrum for H^+(Met) closely resembles a broadened version of the Li^+(Met) spectrum, with the exception that the highest frequency band blue shifts to 1770 cm^{-1} and there is a distinct peak at 865 cm^{-1}.

Comparison of experimental and theoretical IR spectra: Li^+(Met)

Fig. 4 shows the experimental IRMPD action spectrum along with calculated IR spectra for the seven distinct conformers of Li^+(Met). In making these comparisons, it should be remembered that the calculated IR intensities may not correspond exactly with the action spectrum because the latter is a multiple photon process, whereas the theoretical IR spectra are based on single photon absorption. Given this information, it is clear that the bands predicted by the [N,CO,S] conformer correspond well with the observed spectrum and have comparable relative intensities. All major bands are present with comparable theoretical and experimental frequencies. Alternative side-chain orientations of the [N,CO,S] conformer are sufficiently low in energy (Table 1) that they could also contribute to the experimental spectrum. According to the relative free energies in Table 1, the tgcgg conformer could comprise 8–11% with the other two conformers contributing less than 2% presuming an equilibrium distribution at room temperature. The calculated frequencies for these higher energy structures are included in ESI†. No other distinct conformers are predicted to be low enough in energy to contribute to the experimental spectrum.

The band observed at 1716 cm^{-1} corresponds to the carbonyl stretch, which explains its large intensity. The CO stretch predicted by the [N,CO,S]tgcgt conformer at 1705 cm^{-1} agrees with the observed band, but is red shifted by $\sim$10 cm^{-1}. The three higher energy [N,CO,S] conformers have comparable CO stretching frequencies at 1708 (tgcgg), 1712 (tgggt), and 1711 (tgggg) cm^{-1}. Interaction with the lithium cation results in a red shift of this band with respect to free Met, calculated as 1758 and 1782 cm^{-1} depending on the specific conformation. The observed band at 1595 cm^{-1} has the largest deviation with the calculated spectra for the [N,CO,S] tgcgt conformer, which has a band predicted at 1624 cm^{-1} (a frequency essentially invariant for the other orientations). This band describes the bending motion of the NH_2 group and its predicted position is largely unaffected compared to $\sim$1627 cm^{-1} band for neutral Met. Such deviations between experiment and theory have been observed for NH_2 bending modes in other systems[3,4,33,34] and are believed to result from strong anharmonic effects. The peaks observed at 1445, 1160, 1015, 740, 680, and 610 cm^{-1} are well represented by the spectra calculated for the [N,CO,S] conformer. The band at 1445 cm^{-1} is a conglomerate of vibrations corresponding to HCH bends in the amino acid side chain. The band at 1160 cm^{-1} is primarily associated with bending of the H–O–C angle of the carboxylic acid moiety. This is one of the few bands where the spectra of the various [N,CO,S] conformers differ somewhat. The observed band corresponds particularly well with the calculated ground state tgcgt conformer, as this has the most intensity at 1163 cm^{-1} with a shoulder at 1183 cm^{-1}. The shape of the band predicted for the tgcgg conformer is also similar to the observed spectra with a strong band at 1163 and shoulder at 1186 cm^{-1}. The tgggt orientation has a single strong band at 1173 cm^{-1} with a shoulder at 1148 cm^{-1} and the tgggg orientation has two bands of equal intensity at 1164 and 1174 cm^{-1}. The profiles of these latter two bands do not agree as well with the observed spectrum, consistent with them making only small contributions to the observed spectrum. The [N,CO,S] spectra have predicted bands at 1021–1033 cm^{-1}, the NH_2 wagging motion, which is slightly blue shifted with respect to an observed peak

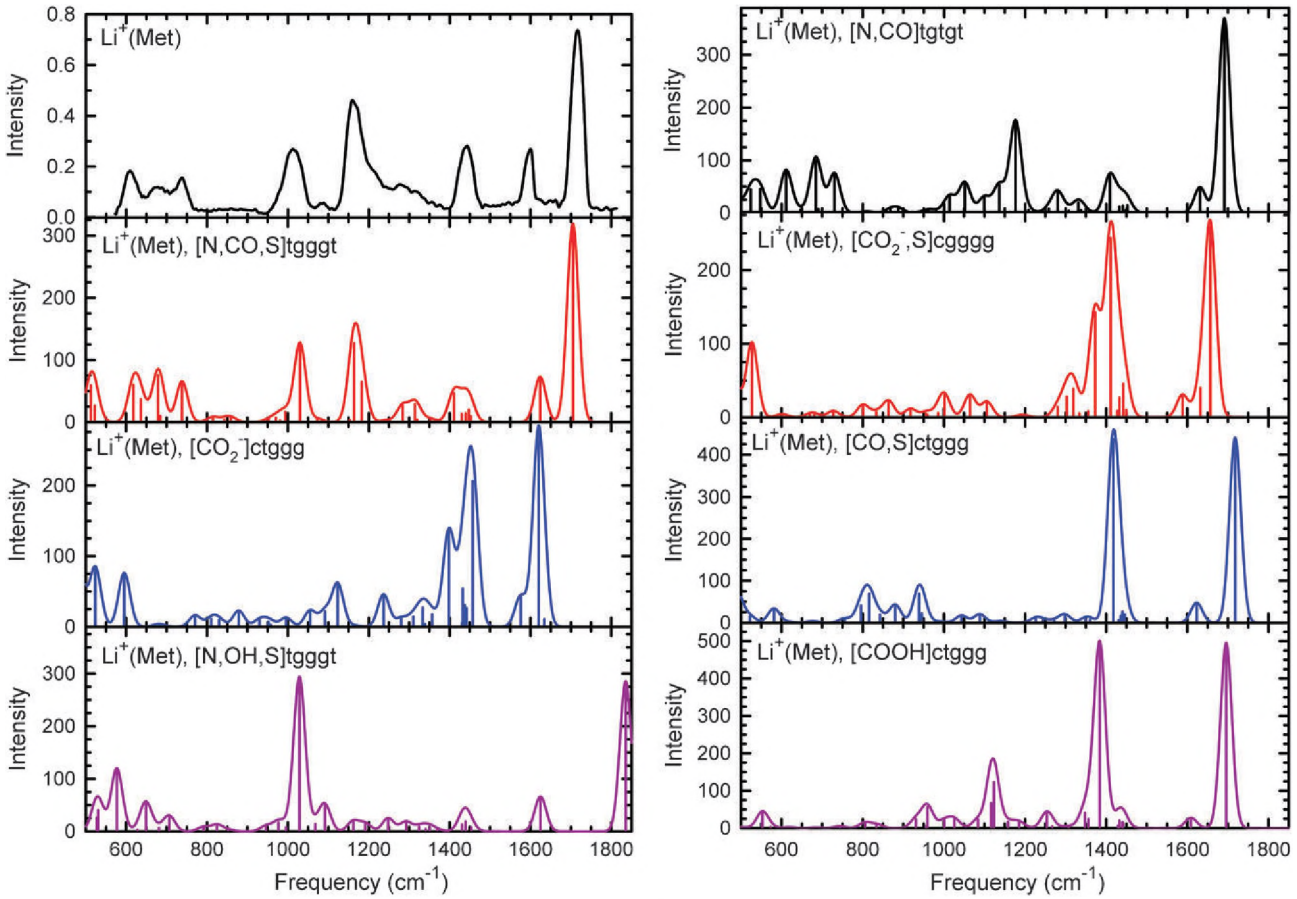

Fig. 4 Comparison of the experimental IRMPD action spectrum for Li^+(Met) with IR spectra predicted at the B3LYP/6-311+G(d,p) level of theory for seven conformations.

at 1015 cm^{-1}. Observed peaks at 610, 680, and 740 cm^{-1} correspond to wagging motions of the carboxylic acid hydrogen atom and match the predicted spectra for all [N,CO,S] conformers well. Broad and weak bands observed at 800–900 cm^{-1} and 1250–1350 cm^{-1} are also consistent with predicted bands in the [N,CO,S] spectra. Finally, there is a weak band observed at 1080 cm^{-1} that could correspond to a weak band in the [N,CO,S] calculated spectra associated with synchronous C–C and C–N bond stretches.

It is quite clear that the observed spectrum for Li^+(Met) does not include any contributions from the zwitterionic [CO_2^-] and [CO_2^-,S] conformers. The intense carbonyl stretch predicted at 1620 and 1656 cm^{-1}, respectively, is much lower in frequency compared to free Met and the observed spectrum. Additionally, the broad bands at 1250–1500 cm^{-1} in the predicted zwitterionic spectra are inconsistent with the experimental spectrum. There does not appear to be any contribution from the [N,OH,S] tgggt conformer either. Compared to the [N,CO,S] calculated spectrum, this conformation has minimal diagnostic bands. The CO stretch (1835 cm^{-1}) is considerably blue shifted with respect to the observed band at 1716 cm^{-1}, but lies beyond the frequency range for the experimental spectrum. The major band predicted at 1029 cm^{-1} overlaps with the predicted band at 1030 cm^{-1} in the [N,CO,S] spectrum. Therefore, the bands at 577, 649, and 707 cm^{-1} corresponding to the wagging motion of the acid hydrogen atom are the most diagnostic bands and do not match the observed spectrum. Although the predicted spectrum for the [N,CO] tgtgt conformer has a number of similarities to that for [N,CO,S] tgcgt, we can dismiss any contribution from the [N,CO] tgtgt conformation for Li^+(Met). First, the carbonyl stretch of the bidentate conformation (1690 cm^{-1}) is red shifted with respect to the observed band at 1716 cm^{-1} and calculated frequency of 1705–1712 cm^{-1} in the [N,CO,S] conformation. Second, the predicted spectrum shows a low frequency shoulder for the band at 1160 cm^{-1}, which is not observed. Finally, the predicted profile for the observed band at 1015 cm^{-1} matches that predicted for the NH_2 wagging motion in the [N,CO,S] tgcgt and tgcgg conformations at 1030–1033 cm^{-1}, with a weaker low frequency shoulder and a steep profile at higher frequencies, in contrast to the relative intensities of these bands in the [N,CO] tgtgt spectrum. Similarly, the [CO,S] and [COOH] spectra do not reproduce the experimental spectrum with any fidelity. Overall, the experimental IRMPD action spectrum can be explained completely by the calculated spectra of the ground state [N,CO,S] tgcgt and tgcgg conformers.

Comparison of experimental and theoretical IR spectra: Na^+(Met)

The Na^+(Met) spectrum is very similar to the Li^+(Met) spectrum over the available range of 900 to 1800 cm^{-1},

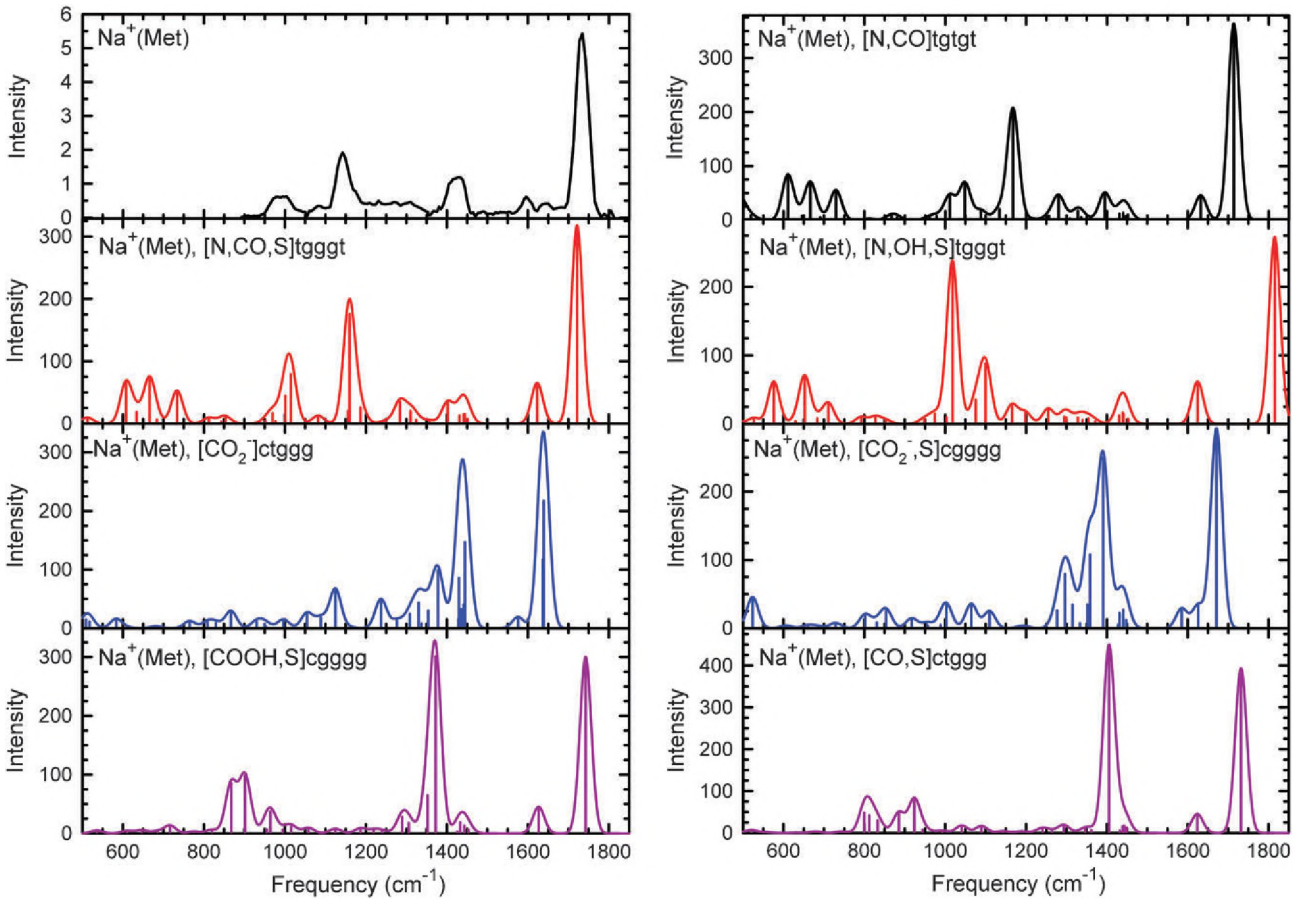

Fig. 5 Comparison of the experimental IRMPD action spectrum for Na^+(Met) with IR spectra predicted at the B3LYP/6-311+G(d,p) level of theory for seven conformations.

Fig. 3. Subtle differences with respect to the action spectrum of Li^+(Met) are present and include a blue shift in the band at 1716 cm^{-1} to 1734 cm^{-1} and bands that red shift from 1015 cm^{-1} to 1000 cm^{-1}, 1160 cm^{-1} to 1140 cm^{-1}, and 1445 cm^{-1} to 1430 cm^{-1}. Bands located at 1080 and 1595 cm^{-1} are unaffected. Comparison of the experimental spectrum with the theoretical spectra for Na^+(Met) is shown in Fig. 5. As for Li^+(Met), the predicted [N,CO,S] tgcgt spectrum shows a close correspondence to the limited observed spectrum for Na^+(Met). Notably, the predicted carbonyl stretch frequency shifts to higher frequency by 16 cm^{-1} from Li^+(Met) to Na^+(Met), in agreement with the experimental observation. Likewise the NH_2 bending band at 1595 cm^{-1} is predicted not to shift from Li^+(Met) to Na^+(Met), consistent with experiment. Overall, the predicted spectra for the [N,CO,S] conformers of Li^+(Met) and Na^+(Met) accurately represent the changes observed with metal cation identity.

The major peaks observed in the Na^+(Met) depletion spectrum at 1735, 1430, 1140, and 1000 cm^{-1} were also observed in the Na^+ product ion spectrum (not shown); however, the weak bands observed at 1650, 1595, and 1080 cm^{-1} in the depletion spectrum were not present in the Na^+ product ion spectrum. The weak band at 1650 cm^{-1} cannot be described by the [N,CO,S] tgcgt conformer, but could correspond to the carbonyl stretch (really an antisymmetric carboxylate stretch) for the zwitterionic [CO_2^-] ctggg and cgtgg conformers calculated to lie at 1639 cm^{-1}. It is possible that the experimental spectrum could contain the [CO_2^-]ctggg and cgtgg conformers, which are calculated to lie 2–11 kJ mol^{-1} above the [N,CO,S] tgcgt ground state, Table 1. One might anticipate that the presence of the [CO_2^-] conformer would also lead to a signal increase near 1440 cm^{-1}; however, the low intensity of the 1650 cm^{-1} band suggests that this would be hidden by the spectral features already present from [N,CO,S]. If the relative intensities of the bands at 1734 and 1650 cm^{-1} are reliable indicators of the relative populations of the two conformers (and this may not be the case for the reasons noted above), then the [CO_2^-] conformer would represent ~7% of the signal present (consistent with an excitation energy of 6.4 kJ mol^{-1} at 298 K).

Comparison of experimental and theoretical IR spectra: K^+(Met) and Rb^+(Met)

Fig. 6 and 7 show the experimental IRMPD action spectrum of K^+(Met) and Rb^+(Met) compared with theoretical predictions for the seven lowest energy distinct conformations. Compared to the experimental spectra for Li^+(Met) and Na^+(Met), the IRMPD spectrum of K^+(Met) retains the same bands, but new features are present, Fig. 3. The spectrum for Rb^+(Met) is very similar to that for K^+(Met), having the same number of new bands compared to the Li^+(Met) and

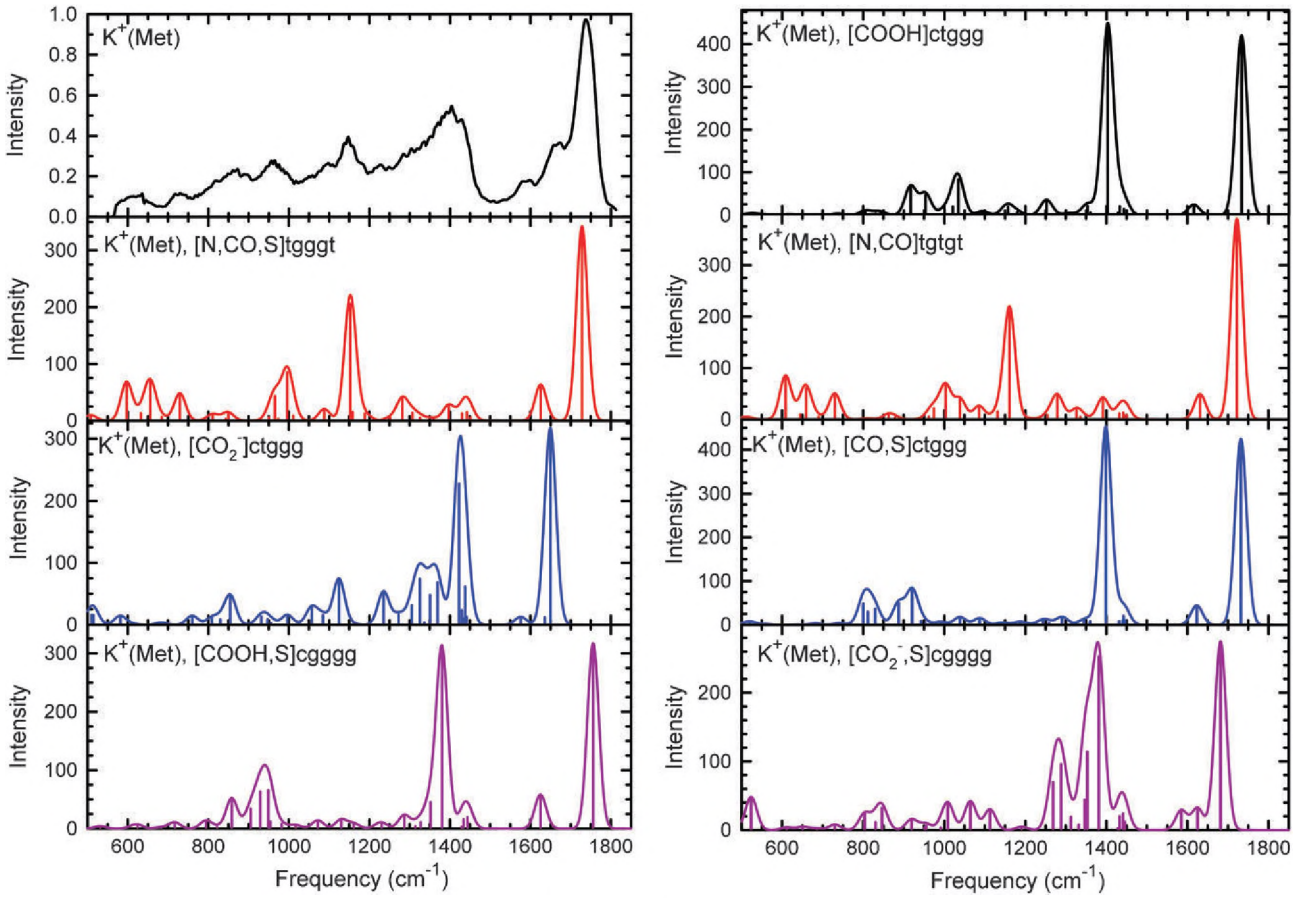

Fig. 6 Comparison of the experimental IRMPD action spectrum for K^+(Met) with IR spectra predicted at the B3LYP/6-311+G(d,p) level of theory for seven conformations.

Na^+(Met) spectra. These new bands could be attributed to new conformers present or could be attributed to improved sensitivity by more facile dissociation from this weakly bound system. However, in no case do the new experimental bands correspond to previously unobserved peaks in the predicted spectrum for [N,CO,S]. Hence, there is no indication that enhanced sensitivity can explain the new features.

New bands in the observed spectrum of K^+(Met) [Rb^+(Met)] occur at 875 [880], 960 [955], 1225 [1230], 1405 [1395], and 1670 [1670] cm^{-1}. The band at 1430 [1430] cm^{-1} has grown in intensity with respect to Na^+(Met) and a broad low frequency shoulder is now present. Overall, a comparison between the K^+(Met) and Rb^+(Met) spectra with those of Li^+(Met) and Na^+(Met) shows a considerable increase in photodissociation in the region from 750 to 1400 cm^{-1}. The [N,CO,S] conformers may still be present as the predicted carbonyl stretch of 1724–1730 [1731–1737] cm^{-1} agrees well with the corresponding band observed at 1735 [1742] cm^{-1}; however, carbonyl stretches of the [COOH] (1733 [1743] cm^{-1}) and [CO,S] (1732 [1739] cm^{-1}) conformers are equally consistent. The frequencies for the bending mode of the NH_2 group in the [N,CO,S] spectra (1618–1626 [1618–1624] cm^{-1}) are still blue shifted by $\sim$30 cm^{-1} with respect to the observed band at $\sim$1595 [1590] cm^{-1}, consistent with observations for Li^+(Met) and Na^+(Met). The intense calculated band at 1149–1152 [1143–1148] cm^{-1} corresponding to the C–O–H bending mode of the [N,CO,S] conformer matches the observed spectrum for K^+(Met) [Rb^+(Met)] well. Likewise, the wagging motions of the acidic hydrogen atom at 730 [735] and below 700 cm^{-1} in the observed K^+(Met) [Rb^+(Met)] spectrum are also well characterized in the calculated spectra for the [N,CO,S] conformer. These bands demonstrate the presence of the [N,CO,S] conformer as it and the higher energy [N,CO] are the only conformers with bands in this frequency range. Bands observed at 960 [955], 1100 [1090], and the shoulder at 1430 [1430] cm^{-1} could also have contributions from the [N,CO,S] conformer.

A prominent new peak at 1670 [1670] cm^{-1} in the observed spectra for K^+(Met) [Rb^+(Met)] indicates the presence of the zwitterionic [CO_2^-] conformer. Calculated spectra for these conformers indicate this band appears at 1649–1650 [1660–1661] cm^{-1} for K^+(Met) [Rb^+(Met)]. The appearance of this new peak is accompanied by the band observed at 1405 [1395] cm^{-1} along with a broad shoulder to the red. These new bands can be attributed to the intense band calculated at 1417–1423 [1408–1413] cm^{-1} in the predicted spectra for the three [CO_2^-] conformers along with several bands extending from 1225 [1230] to 1405 [1395] cm^{-1}. Bands observed at 875 [880] and 1100 [1090] cm^{-1} can also be described by bands calculated in all [CO_2^-] spectra.

Overall, the experimental spectra for K^+(Met) and Rb^+(Met) are adequately represented by contributions from

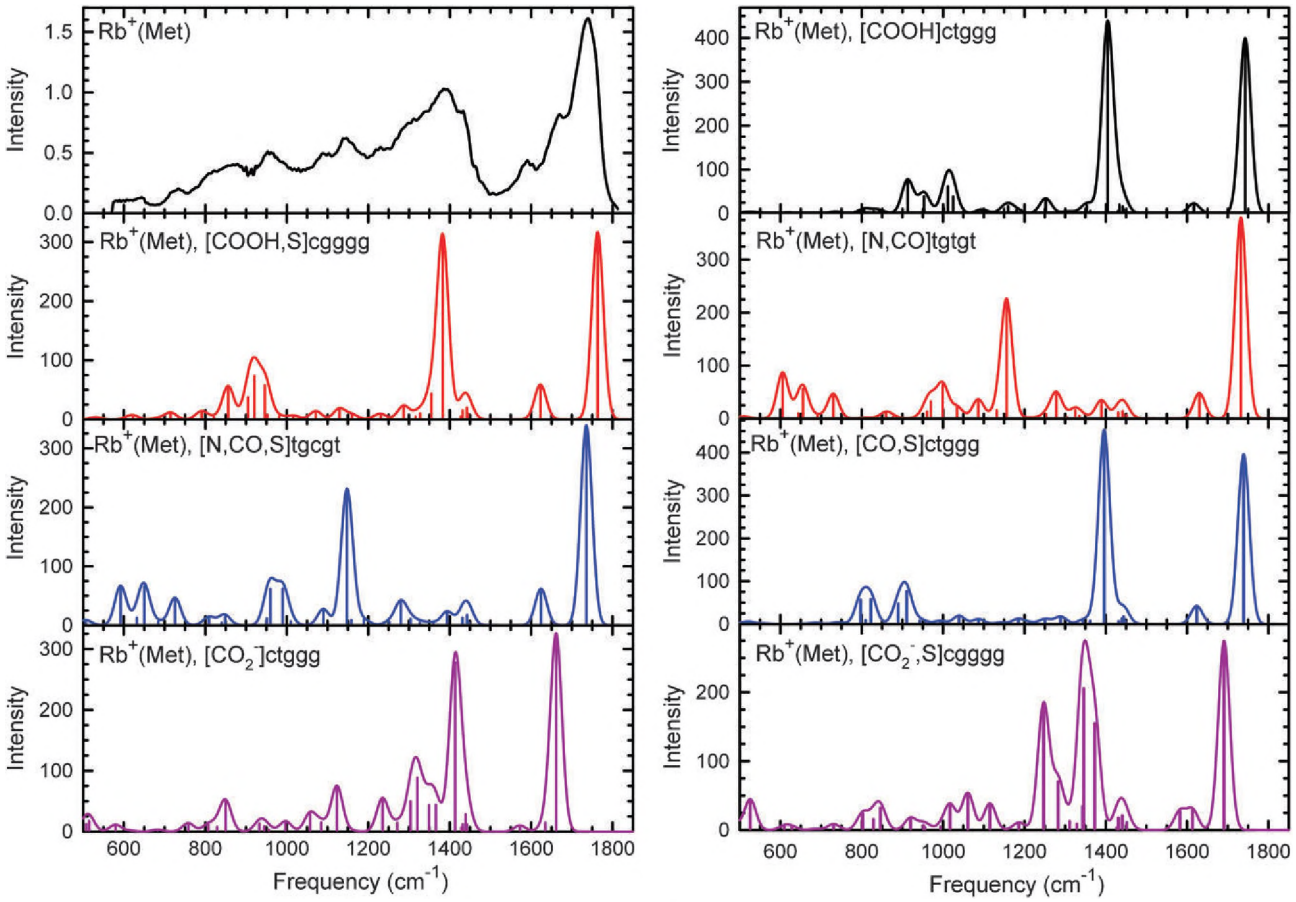

Fig. 7 Comparison of the experimental IRMPD action spectrum for Rb^+(Met) with IR spectra predicted at the B3LYP/6-311+G(d,p) level of theory for seven conformations.

the [N,CO,S] and [CO_2^-] conformers. This is consistent with calculations for K^+(Met), which indicate that any other conformers lie at least 7 kJ mol^{-1} higher in energy, Table 1. Thus, at 298 K, contributions from [COOH,S] conformations are calculated to be $<6\%$ and those for any other conformer are $<1\%$. For Rb^+(Met), both the [COOH,S] and [COOH] conformers lie low enough in energy (0–8 and 3–10 kJ mol^{-1}, respectively, Table 1) to potentially contribute to the ion population. Indeed, the broad band observed at 1405 [1395] cm^{-1} for K^+(Met) [Rb^+(Met)] could have contributions from the intense bands at 1378–1386 [1374–1389] cm^{-1} for the [COOH,S] conformers, which are attributed to the C–O–H bending mode. The relative intensities of the peaks observed at 875 [880] and 960 [955] cm^{-1} are also consistent with similar bands in the calculated spectra of the [COOH,S] cgggg and cgggt conformations, but notably not of the highest energy cgcgg orientation. Discounting the presence of the [COOH,S] conformers is the fact that the calculated carbonyl stretches (1750–1756 [1756–1763] cm^{-1}) are blue shifted by 15–20 cm^{-1} with respect to the observed band at 1735 [1742] cm^{-1}, in contrast to the red shift of $\sim$15 cm^{-1} observed for this band in the Li^+(Met) and Na^+(Met) spectra. There are no high frequency shoulders in this region of the observed spectra that would be consistent with the presence of considerable amounts of both the [N,CO,S] and [COOH,S] conformers, although minor amounts of the latter would lead to simple broadening of this peak, which is possibly consistent with the data. In contrast, the carbonyl stretches at 1733–1735 [1743–1745] cm^{-1} for the [COOH] conformers agree well with the CO stretch observed in the IRMPD spectra and would simply overlap the contribution from the [N,CO,S] conformer present. These three [COOH] conformers lie within 4 kJ mol^{-1} of one another for K^+(Met) and Rb^+(Met), Table 1. These conformers also have an intense peak predicted at 1403 [1404–1410] cm^{-1} that could correspond to the observed peak at 1405 [1395] cm^{-1}. The [COOH] conformer has no additional distinctive bands that allow its presence to be verified. In conclusion, we can confidently attribute the observed spectra of K^+(Met) and Rb^+(Met) to dissociation from [N,CO,S] and [CO_2^-] conformers, but cannot rule out contributions from [COOH,S] and [COOH] conformers.

Comparison of experimental and theoretical IR spectra: Cs^+(Met)

Fig. 8 shows the IRMPD action spectrum of Cs^+(Met) with theoretical predictions for seven low-energy distinct conformers. All of the spectral features for K^+(Met) and Rb^+(Met) are still present in the Cs^+(Met) spectrum, Fig. 3, with the only differences being increases in relative intensity between 700–900 and 1200–1400 cm^{-1}. Therefore, all of the comparisons between the observed spectrum and the predicted

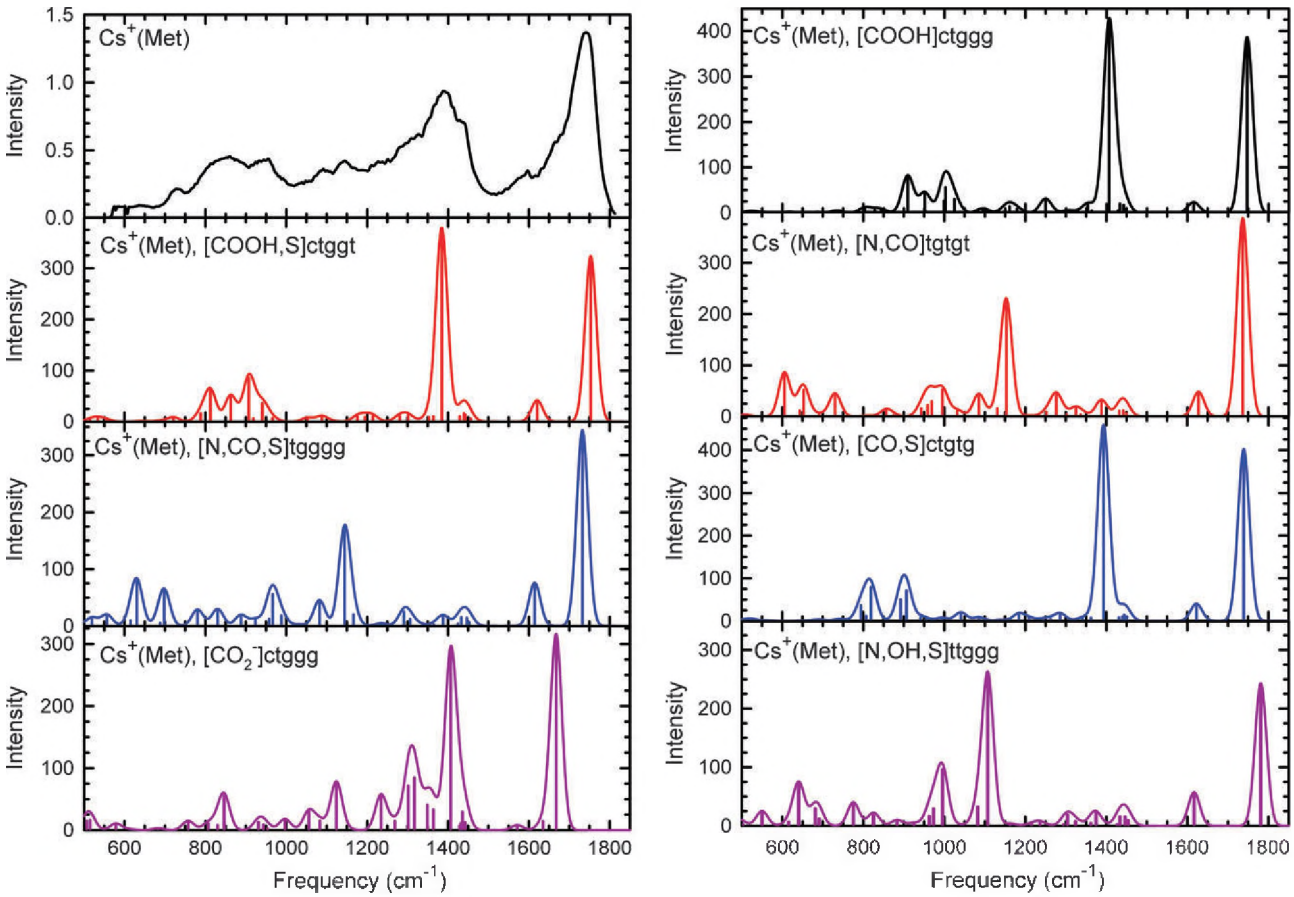

Fig. 8 Comparison of the experimental IRMPD action spectrum for Cs^+(Met) with IR spectra predicted at the B3LYP/HW*/6-311+G(d,p) level of theory for seven conformations.

spectra mentioned in the previous section are still viable. Both [N,CO,S] tgcgt and [CO_2^-] conformers appear to contribute to the observed spectra with intensity changes indicating that there is more [CO_2^-] compared to [N,CO,S], consistent with the changes in the relative energies calculated as a function of metal cation. The presence of [COOH] and [COOH,S] conformers is again possible, although the peak corresponding to the carbonyl stretch provides no strong indications that these latter conformers are present.

Comparison of experimental and theoretical IR spectra: H^+(Met)

Fig. 9 shows the IRMPD action spectrum of H^+(Met) with theoretical predictions for three low-energy conformations. The H^+(Met) complex is unique among all the systems investigated here as the proton is covalently bound to the amine group of the amino acid backbone. Only two spectra are shown for the four low-energy [N,CO,S] conformations described in Table 1 as the calculated IR spectra are identical for tgtgg and tgtgt orientations and for tgggg and tgggt orientations. The calculated spectrum for the [N,OH,S] tgtgg conformation is also shown for comparison. The experimental spectrum exhibits bands at 1775, 1560, 1455, 1330, 1230, 1155, 1050, 975, 865, 710, 620, and 580 cm^{-1}. The observed peak at 1775 cm^{-1} corresponds to the carbonyl stretch. The peaks at 1560 and 1455 cm^{-1} correspond to the NH_3 bending and NH_3 umbrella motions, respectively. Observed bands at 1330 and 1230 cm^{-1} correspond to wagging motions of the alpha carbon hydrogen atom and CH_2 groups of the amino acid side chain. The H–O–C bending motion is represented by the peak observed at 1155 cm^{-1}. The peak at 975 corresponds to elongation of the C–C and C–N bonds in the backbone, while the band at 865 cm^{-1} corresponds to the NH_2 rocking motion. The three peaks at 710, 620, and 580 cm^{-1} are wagging motions of the acidic hydrogen atom.

The IRMPD action spectrum is well described by the [N,CO,S] calculated spectra. The H^+(Met) carbonyl stretch in the observed spectrum (1775 cm^{-1}) is reproduced extremely well by the [N,CO,S] spectra (1768–1770 cm^{-1}), whereas the CO stretch is blue shifted nearly 45 cm^{-1} (1820 cm^{-1}) for the [N,OH,S] tgtgg conformer. Therefore, it is unlikely that the observed spectrum includes any contribution from the [N,OH,S] conformers, consistent with their calculated relative energies (Table 1), which would predict $<0.5\%$ population at 298 K. This peak is red shifted compared to the neutral ligand by much less than any of the metal cation complexes, consistent with a more delocalized charge in the H^+(Met) complex. The bending and umbrella motions of the NH_3 group in the calculated spectra for H^+(Met) are blue shifted with respect to the observed peaks at 1455 and 1560 cm^{-1}. This further illustrates that the single photon calculations cannot

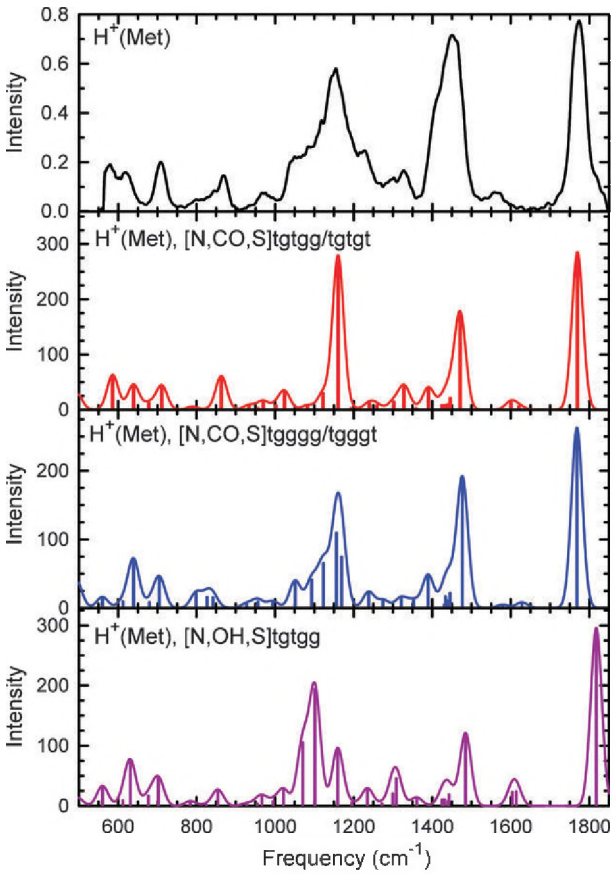

Fig. 9 Comparison of the experimental IRMPD action spectrum for H^+(Met) with IR spectra for two of the four lowest energy [N,CO,S] conformers and the lowest energy [N,OH,S] conformer predicted at the B3LYP/6-311+G(d,p) level of theory.

adequately describe the multiple photon spectra for umbrella or bending motions of the amine group. The broad peak spanning 1375–1500 cm^{-1} in the observed spectrum is a conglomerate of the bands corresponding to the umbrella motions at 1470–1475 cm^{-1} for the [N,CO,S] conformations, as well as the band at 1390 cm^{-1}. The calculated spectra predict a band associated with the H–O–C bending mode at 1160 cm^{-1}, which agrees with the 1155 cm^{-1} peak in the observed spectrum. The large shoulder located at frequencies below the 1155 cm^{-1} peak is reproduced by the shoulder of the tgggg/tgggt calculated spectrum, which indicates that these higher energy orientations are definitely present. The observed spectrum from 580 to 1000 cm^{-1} is reproduced quite well by the [N,CO,S] calculated spectra. The band at 865 cm^{-1} with a low frequency shoulder is consistent with the presence of both tgtgg/tgtgt and tgggg/tgggt orientations. The largest discrepancy in the low frequency region is the calculated band at 640 cm^{-1} is blue shifted with respect to the observed peak at 620 cm^{-1}. As noted above, the 865 cm^{-1} band in the H^+(Met) spectrum, which corresponds to the rocking motion of the NH_2 group, does not appear in the Li^+(Met) spectrum, Fig. 3. This is because the strong tridentate interaction of the lithium ion effectively quenches this rocking motion from occurring, whereas the bidentate interactions of the proton allow it.

Overall comparison

We can now provide a more global comparison of the main features in all five spectra in Fig. 3. The predicted frequencies for the CO stretch of the [N,CO,S]tgcgt conformer change from 1705 cm^{-1} for Li^+(Met), 1721 cm^{-1} for Na^+(Met), 1728 cm^{-1} for K^+(Met), 1736 cm^{-1} for Rb^+(Met), and 1739 cm^{-1} for Cs^+(Met) (1732 cm^{-1} for the tgggg orientation), in agreement with the observed blue shift in the experimental spectra from 1716 cm^{-1} for Li^+(Met), 1734 cm^{-1} for Na^+(Met), 1735 cm^{-1} for K^+(Met), and 1742 cm^{-1} for both Rb^+(Met) and Cs^+(Met). The CO stretch of the [COOH] conformers shows a similar shift with metal cation, changing from 1733–1735 cm^{-1} for K^+, 1743–1745 cm^{-1} for Rb^+, and 1746–1749 cm^{-1} for Cs^+; however, because these bands are blue shifted compared to the [N,CO,S] conformer, appreciable contributions of the [COOH] conformers would be expected to lead to larger blue shifts in the experimental spectrum than observed. Likewise, the CO stretch for the [COOH,S] conformers, 1750–1756 cm^{-1} for K^+, 1747–1763 cm^{-1} for Rb^+, and 1753–1764 cm^{-1} for Cs^+, is blue shifted even further, again suggesting that this species does not make major contributions to the experimental spectrum. The observed band at 1158 cm^{-1} in the Li^+(Met) spectrum red shifts to 1145 cm^{-1} for Cs^+(Met). This shift is consistent with that predicted for the in-plane COH bending motion of [N,CO,S]tgcgt conformers with predicted frequencies of 1168 cm^{-1} for Li^+(Met), 1160 cm^{-1} for Na^+(Met), 1152 cm^{-1} for K^+(Met), 1148 cm^{-1} for Rb^+(Met), and 1145 cm^{-1} for Cs^+(Met). Although the band at 1595 cm^{-1} is not accurately predicted because of its anharmonicity, this band does not shift with metal cation identity, in agreement with the predictions for the [N,CO,S] tgcgt conformers. No shifts are predicted for the broad band at 1430 cm^{-1}, which becomes a high frequency shoulder in the spectra for K^+(Met)–Cs^+(Met). Likewise the bands at about 730 cm^{-1} observed in all the spectra are predicted to red shift somewhat, from 738 to 724 cm^{-1} in going from Li^+(Met) to Cs^+(Met). The good agreement in these trends provides further evidence that the [N,CO,S] tgcgt conformer is present for all the IRMPD action spectra in Fig. 3.

The antisymmetric CO stretch of the [CO_2^-] conformers first appears in the IRMPD action spectrum for Na^+(Met) at 1650 cm^{-1} and blue shifts to 1670 cm^{-1} for both K^+(Met) and Rb^+(Met). This band is not as well defined for Cs^+(Met), but the photodissociation signal at similar frequencies can only be described by the presence of [CO_2^-] conformations. The predicted bands of all [CO_2^-] conformers agree well with the observed bands and are predicted to shift from 1639 to 1661 cm^{-1} in going from Na^+(Met) to Rb^+(Met). The umbrella motions of the NH_3 group in the [CO_2^-] conformers are predicted at 1417–1426 cm^{-1} for K^+(Met), 1408–1417 cm^{-1} for Rb^+(Met), and 1402–1411 cm^{-1} for Cs^+(Met). This decrease in frequencies with heavier metal ion is consistent with the IRMPD action spectra for K^+(Met), Rb^+(Met), and Cs^+(Met) with peaks located at 1405, 1395, and 1390 cm^{-1}, respectively, Fig. 3, with a consistent shift to lower frequencies compared to experiment of $\sim$15 cm^{-1}.

The theoretical results for Rb^+(Met) and Cs^+(Met) indicate that the [COOH,S] and [COOH] conformers are low-energy

structures and could be present in the IRMPD action spectra. These conformers have intense bands predicted near 1400 cm^{-1}, corresponding to the C–O–H bending motion, which are the most diagnostic bands in their calculated spectra. This motion is largely unaffected with increasing cation size for both conformers. For the [COOH,S] conformers, this motion is predicted at 1378–1386 cm^{-1} for K^+(Met), 1374–1389 cm^{-1} for Rb^+(Met), and 1377–1386 cm^{-1} for Cs^+(Met). These predicted frequencies do lie closer to the observed peaks at 1405, 1395, and 1390 cm^{-1} for K^+(Met), Rb^+(Met), and Cs^+(Met), respectively, than the frequencies corresponding to the umbrella motion of the NH_3 group in the [CO_2^-] conformers, but the frequencies increase as the metal gets heavier for the cgggg orientation and change very little for cgggt and cgcgg orientations instead of the red shift experimentally observed. Likewise, the C–O–H bending modes of the [COOH] conformers are predicted to occur at 1403 cm^{-1} for K^+(Met), 1404–1410 cm^{-1} for Rb^+(Met), and 1405–1407 cm^{-1} for Cs^+(Met). Because the observed bands at ~1400 cm^{-1} are broad in these three spectra, contributions from these two conformations cannot be eliminated.

Conclusion

The IRMPD action spectra of cationized methionine in the region of 550–1800 cm^{-1} have been obtained for complexes with Li^+, Na^+, K^+, Rb^+, Cs^+, and H^+. Comparison of these experimental spectra with IR spectra calculated at the B3LYP/6-311+G(d,p) and B3LYP/HW*/6-311+G(d,p) levels of theory allow the conformations likely to be present in the experiment to be identified. For the H^+(Met) system, the IRMPD spectrum is characterized by four [N,CO,S] conformers that differ only in their side-chain orientation and therefore little in energy (within 4 kJ mol^{-1}). For the alkali-metal cationized systems, these comparisons suggest that the charge-solvated [N,CO,S] conformer is the only structure present in the IRMPD action spectrum for Li^+(Met) and Na^+(Met), consistent with it being the clear ground state conformation according to theory. This species remains a contributor for all metal cations studied. Contributions from the [CO_2^-] conformer, which becomes the ground state according to DFT calculations as the metal cation gets heavier, clearly manifest themselves for K^+(Met), Rb^+(Met), and Cs^+(Met). Theory suggests that [COOH,S], the ground state conformer for Rb^+(Met) and Cs^+(Met) according to MP2(full) calculations, and [COOH] conformers should also be present for Rb^+(Met) and Cs^+(Met). The experimental IRMPD action spectra cannot eliminate the presence of these conformers, but do not require their presence to be reproduced. The photodissociation spectra of K^+(Met), Rb^+(Met), and Cs^+(Met) have very similar spectral features and are considerably more complex than IRMPD spectra of K^+, Rb^+, and Cs^+ bound to other amino acids.[3–8]

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