Supplementary Material (ESI) for *PCCP*

Supporting Information for

Infrared Multiple Photon Dissociation Spectroscopy of Cationized Methionine: Effects of Alkali-Metal Cation Size on Gas-Phase Conformation

By D. R. Carl, T. E. Cooper, J. Oomens, J. D. Steill, and P. B. Armentrout

A description of the structures of Met and M^+(Met) for M^+ = Li^+, Na^+, K^+, Rb^+, and Cs^+. Two figures (S1a and S1b) depicting the 298 K Gibbs free energies calculated at the **R**/6-311+G(2d,2p)//B3LYP/6-311+G(d,p) (M^+ = Li^+, Na^+, K^+) and **R**/HW*/6-311+G(2d,2p)// B3LYP/HW*6-311+G(d,p) (M^+ = Rb^+ and Cs^+) levels, where **R** = B3LYP (S1a) and B3P86 (S1b) for eight distinct conformations. 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). Vibrational frequencies and IR intensities are calculated for M^+(Met) 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. Four tables (S4–S7) providing the vibrational frequencies and IR intensities for the [N,CO,S] tgcgt, tgcgg, tgggt, and tgggg conformers for all M^+(Met). Two tables (S8 and S10) providing vibrational frequencies and IR intensties for the [CO_2^-] ctggg and [COOH] ctggg conformers for all M^+(Met). Two tables (S9 and S11) providing vibrational frequencies and IR intensities for the [CO_2^-] cgtgg and ctggt and [COOH] cgtgg and ctggt conformers for K^+(Met) to Cs^+(Met). One table (S12) providing vibrational frequencies and IR intensities for the [COOH,S] cgggg conformers for Na^+(Met) to Cs^+(Met). One table (S13) providing vibrational frequencies and IR intensities for the [COOH,S] cgggt and cgcgg conformers for K^+(Met) to Cs^+(Met). 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.

Supplementary Material (ESI) for *PCCP*

Theoretical Results – Structures. The lowest energy conformations found for neutral methionine have been described in detail elsewhere and are of two types. The N1 conformations have side-chain orientations of tgttg and tgtgt with NH···OC hydrogen bonds (2.564 and 2.521 Å, respectively) and OH···OC hydrogen bonds (2.302 and 2.298 Å, respectively). The N2 type conformation has a COH···N hydrogen bond (1.883 Å) with the lowest energy ctggt side-chain orientation having an additional NH···S hydrogen bond (2.479 Å). Because the methionine side chain is quite flexible, four additional structures for neutral methionine are within 10 kJ/mol of these lowest energy structures. An additional N1 type conformer with a tgttt side-chain orientation is identical to the tgttg orientation except that the side chain is further extended. The N2 cttgt conformer maintains both COH···N and NH···S hydrogen bonds but is a full angstrom longer than the ctggt structure. The side-chain orientations of two additional N2 conformers, ctttg and cgggg, do not allow the NH···S hydrogen bond to form such that only the COH···N hydrogen bond is present.

The low-lying structures found for all M^+(Met) complexes are illustrated by those for Rb^+(Met) in Figure 1 of the main text. Several important geometric parameters for the M^+(Met) complexes are provided in Tables S2 and S3. For completeness, Table S2 also includes geometric parameters calculated at the B3LYP/Def2TZVP level of theory for Rb^+(Met) and Cs^+(Met). In general compared to B3LYP/HW*/6-311+G(d,p) geometries, metal ligand bond lengths are shorter by 0.07 – 0.21 Å and 0.16 – 0.38 Å for Rb^+ and Cs^+, respectively, and bond angles are within 5º. In the comparisons below, B3LYP/HW*/6-311+G(d,p) calculations are used throughout.

For Li^+(Met) and Na^+(Met), the ground state structure is the tridentate charge-solvated [N,CO,S] conformation with a tgcgt orientation. This orientation remains the lowest energy [N,CO,S] conformation for K^+(Met) and Rb^+(Met) but the CCCC dihedral angle crosses the arbitrary 50º cis-gauche limit to become a tgggt orientation for K^+(Met) through Cs^+(Met), Table S3. For convenience, we will retain the tgcgt designation for this orientation for all metal cations in order to distinguish it from an alternative [N,CO,S]tgggt orientation. DFT calculations for

Cs^+(Met) predict that the tgcgt orientation is the lowest energy [N,CO,S] conformer, whereas MP2(full) energies calculate the tgggg orientation as the lowest [N,CO,S] conformer, Table 1. [N,CO,S] tgcgg and tgggt orientations were also identified as unique structures. Dihedral parameters for the four [N,CO,S] conformers are shown in Table S3. [N,CO,S] tgcgg, tgggt, and tgggg conformers for the Li^+(Met), Na^+(Met), and K^+(Met) complexes are higher in energy by 5 – 12, 7 – 12, and 5 – 10 kJ/mol, respectively, compared to the [N,CO,S] tgcgt conformers, Table 1. The differences drop to 1 – 7 kJ/mol for Rb^+(Met), and all four orientations are within 4 kJ/mol of one another for Cs^+(Met).

In all [N,CO,S] conformers, a single hydrogen bond between the carboxylic hydrogen atom and carbonyl oxygen atom is present, Figure 2. For the tgcgt orientation, the M^+-OC, M^+-N, and M^+-S distances increase from 1.938 to 3.106 Å, 2.068 to 3.445 Å, and 2.439 to 3.781 Å, respectively, as the size of the metal cation increases from Li^+ to Cs^+, Table S2. Similar differences in these bond distances are found for the tgcgg, tgggt, and tgggg orientations. These changes directly reflect the increase in the ionic radius of the metal cation (0.70 Å for Li^+, 0.98 Å for Na^+, 1.33 Å for K^+, 1.49 Å for Rb^+, and 1.69 Å for Cs^+)[1] coupled with the resultant decreasing charge density, which weakens the electrostatic interaction with methionine. The $\angle NM^+O$, $\angle NM^+S$, and $\angle OM^+S$ angles decrease as the metal cation becomes heavier, consistent with an elongation of the M^+-OC, M^+-N, and M^+-S distances, Table S2. Because of the small M^+-OC, M^+-N, and M^+-S distances in Li^+(Met) and Na^+(Met), the position of the terminal methyl group in the [N,CO,S] orientations is an important factor in establishing the relative energies, whereas in the larger M^+(Met) systems (M^+ = K^+, Rb^+, and Cs^+), the methyl group position isn't as critical because these bond distances are larger. The terminal methyl group points away from the metal binding site in all orientations except for the tgggg orientation, such that the methyl group begins to interact repulsively with the carboxylic acid moiety.

For the zwitterionic [CO_2^-] conformer, a ctggg orientation is the lowest energy structure, Table 1. The protonated amine group forms hydrogen bonds with the sulfur of the amino acid side chain and the carboxylate oxygen atom, Figure 2. The NH···S hydrogen bond increases

from 2.209 to 2.234 Å, whereas the NH···OC interaction decreases from 1.816 to 1.758 Å for K^+(Met) to Cs^+(Met). The M^+-O bond lengths are similar to each other, but the oxygen interacting with the NH_3^+ group is longer by 0.02 – 0.05 Å, Table S2. These bond lengths increase as the metal cation gets heavier, in proportion to the cation sizes noted above, reflecting the weaker metal cation binding as the metal gets larger. The [COOH] conformation is the charge-solvated analogue of the zwitterionic [CO_2^-], with the only difference being the position of the proton shared between the amine nitrogen atom and the carboxylate group, Figure 2. As for [CO_2^-], all levels of theory for the [COOH] conformation prefer a ctggg side chain orientation. The neutral NH_2 group now hydrogen bonds to the sulfur atom of the amino acid chain and the acidic hydrogen atom of the carboxylic acid. Compared to [CO_2^-] conformers, the M^+-OC bond distances are similar (0.01 – 0.04 Å longer), whereas the M^+-OH bond distances increase substantially (0.10 – 0.18 Å longer). From K^+(Met) to Cs^+(Met), the OH···N and NH···S hydrogen bonds increase by 0.033 and 0.025 Å, respectively. Alternate cgtgg and ctggt orientations were also found for [CO_2^-] and [COOH] conformers for all M^+. These structures are nearly isoenergetic with the ctggg orientations for DFT energies regardless of the cation size, whereas MP2(full) results predict slightly larger energetic differences between the structures, Table 1. For all metal cations, the geometrical parameters of the amino acid side chain are similar for the analogous [CO_2^-] and [COOH] conformers, Table S3.

Another low-energy structure for the K^+(Met), Rb^+(Met), and Cs^+(Met) complexes is the charge-solvated, tridentate [COOH,S] conformation, in which the metal ion interacts with the sulfur of the amino acid side chain in addition to both oxygen atoms of the carboxylic acid moiety, Figure 2. For K^+(Met) and Rb^+(Met), the lowest energy [COOH,S] conformer is a cgggt orientation for DFT calculations, Table 1, whereas a cgggg orientation is preferred at the MP2(full) level of theory. The cgggt orientation in K^+(Met) and Rb^+(Met) progresses into a ctggt orientation for Cs^+(Met), which is the lowest energy [COOH,S] orientation at all levels of theory, but only because the OCCC dihedral angle has increased over the arbitrary 135º gauche-trans limit, Table S2. For consistency, this set of structures will be identified as the

[COOH,S]cgggt orientation for Cs^+(Met) as well as the lighter metals. The ligand structure changes very little with metal cations for the cgggg orientation, Table S2, whereas the OCCC, CCCC, and CCCS dihedral angles in the cgggt orientations change appreciably from K^+(Met) to Cs^+(Met), Table S2. The cgggg and cgggt orientations differ primarily in the position of the terminal methyl group, which is located much closer to the carboxylic acid moiety in the cgggg orientation than in the cgggt orientation. Table S2 shows that the cgggg conformer allows shorter M^+-OH bonds (by 0.10 – 0.20 Å) by compensating with longer M^+-OC bonds (by 0.03 – 0.06 Å) and variable M^+-S bond lengths (longer for K^+ by 0.03 Å, comparable for Rb^+, and shorter for Cs^+ by 0.20 Å) with respect to the [COOH,S] cgggt conformer.

Four additional high energy conformations were identified for M^+(Met). If the carboxylic acid moiety in the [N,CO,S] conformation is rotated by 180º, the result is a charge-solvated, tridentate [N,OH,S] conformation. This structure was not included in the previous theoretical results for the CID study of M^+(Met) with $M^+ = Li^+$, Na^+, and K^+, because it is always higher in energy than the [N,CO,S] conformer and could not correspond to the ground state. Only the lowest energy [N,OH,S] orientations, either tgggt or ttggt, are presented in Tables 1 and 3, and are analogous to the tgcgt and tgggg orientations of the [N,CO,S] conformer. Compared to the cation-oxygen interaction of the [N,CO,S] conformers, the metal cation interaction with the hydroxyl oxygen atom of the [N,OH,S] conformers is weaker; therefore, the M^+-O distances are longer in the latter and compensated by shorter M^+-N and M^+-S distances.

If the metal cation interaction with the side chain is lost from [N,CO,S], the charge-solvated bidentate [N,CO] conformation is obtained, and this has a tgtgt side-chain orientation. The loss of the M^+-S interaction is partially compensated by allowing the amine group to form a hydrogen bond with the side-chain sulfur atom, Figure 2. As expected, the M^+-O and M^+-N distances in the bidentate [N,CO] conformation are shorter than those in the tridentate [N,CO,S] conformation. An additional high energy conformer is charge-solvated and binds in a bidentate fashion to the carbonyl oxygen atom of the backbone and the sulfur atom of the side chain, [CO,S]. The side chain has a ctggg orientation for Li^+(Met) to Rb^+(Met) and a ctgtg orientation

for Cs^+(Met), as the CCCS dihedral progresses smoothly from 106º to 117º to 121º to 130º to 140º from Li^+(Met) to Cs^+(Met). Because the carboxylic hydrogen is trans with respect to the carbonyl oxygen atom, the hydroxyl group hydrogen bonds to the nitrogen atom of the amine group. Because the metal cation is no longer constrained to bind to the other oxygen, the M^+-OC bond lengths are the shortest of any conformation, Table S2.

The final high-energy conformations are the [CO_2^-,S] cgggg conformations, tridentate zwitterionic analogues of charge-solvated [COOH,S] cgggg conformations. Minimal comparisons can be made between these zwitterionic and charge-solvated conformers for Li^+(Met) as the [COOH,S] cgggg structure collapses to a [CO,S] structure and the [CO_2^-,S] cgggg conformer for Cs^+(Met) collapses to the a high energy [CO_2^-] conformer with CCCS and CCSC dihedral angles that position the terminal methyl group closer to the metal binding site. For M^+ = Na^+, K^+, and Rb^+, the zwitterionic [CO_2^-,S] cgggg structure has shorter M^+-OC (by 0.01 – 0.03 Å) and M^+-O (by 0.14 – 0.15 Å) distances and longer M^+-S distances than the analogous [COOH,S] conformations.

Finally, the protonated methionine complex, H^+(Met), has a set of low energy structures, [N,CO,S], in which the protonated amine group hydrogen bonds to both the carbonyl oxygen atom (NH···OC) and the sulfur atom of the amino acid side chain (NH···S). A third hydrogen bond is also present between the hydroxyl group and the carbonyl oxygen atom. Four structures having this bonding motif vary in the side-chain orientations: tgtgg, tgtgt, tgggg, and tgggt. The NH···OC hydrogen bond is longer by 0.085 Å for the tgtgg (tgtgt) structures compared to the tgggg (tgggt) orientations. A second set of structures were identified with the carboxylic acid group rotated by ~ 180º such that a hydrogen bond forms between the hydrogen atom on the amine group and hydroxyl group oxygen atom, [N,OH,S]. The [N,OH,S] tgtgg, ttggg, tgtgt, and ttggt orientations are direct analogues of the [N,CO,S] tgtgg, tgggg, tgtgt, and tgggt orientations.

One final observation regarding the structures in which the metal cation binds to the sulfur side chain is the ∠M-C-S-C dihedral angle. For most of the [N,CO,S] conformers, these dihedral angles are near 120°, indicating that the metal ion prefers to bind in a tetrahedral-like

geometry as opposed to a planar geometry that would be favored by aligning with the local dipole moment of the sulfur group. As the metal ion gets larger, these dihedral angles do increase for the tgcgg and tgggg orientations, reaching 171° and 153° respectively. For the [COOH,S] conformers, the tetrahedral-like geometry is also preferred for the metal cations with the cgggg orientation; however, for the cgggt and cgcgg orientations, these dihedral angles also increase as the metal cation size increases, reaching 167º and 151º, respectively. Notably such tetrahedral-like side-chain geometries differ from those calculated for oxygen side-chains (serine and threonine) which favor a much more planar dihedral angle,[2,3] even though the longer side-chain length of Met allows greater flexibility in its coordination geometry.

(1) Wilson, R. G.; Brewer, G. R. *Ion Beams with Applications to Ion Implantation*; Wiley: New York, 1973.

(2) Armentrout, P. B.; Rodgers, M. T.; Oomens, J.; Steill, J. D. *J. Phys. Chem. A* **2008**, *112*, 2248.

(3) Rodgers, M. T.; Armentrout, P. B.; Oomens, J.; Steill, J. D. *J. Phys. Chem. A* **2008**, *112*, 2258.

Figure Caption

Figure S1. 298 K Gibbs free energies (kJ/mol) calculated at the B3LYP (a) and B3P86 (b) levels 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.

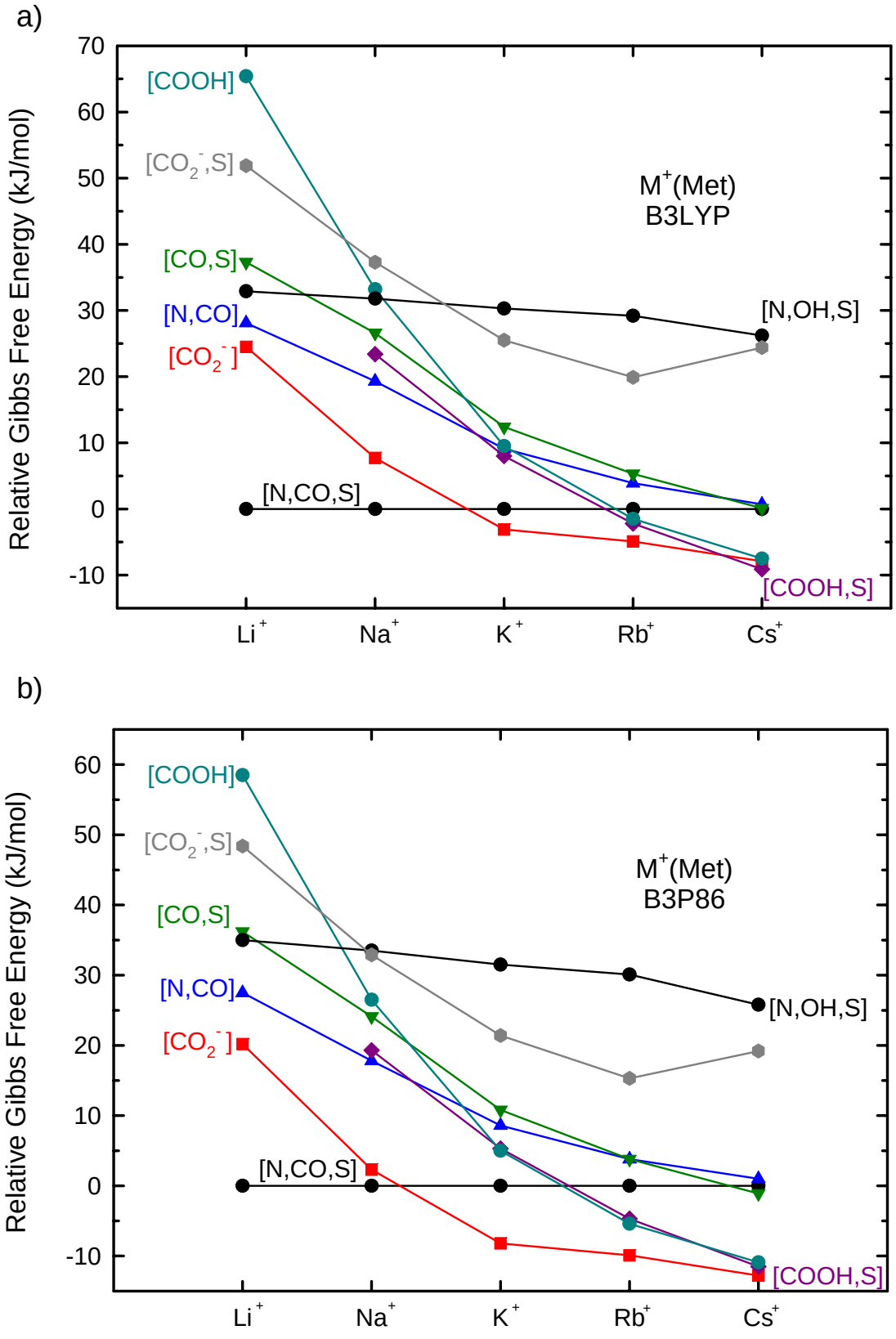
a)
Relative Gibbs Free Energy (kJ/mol)
70
60
50
40
30
20
10
0
-10
[COOH]
[CO2-,S]
[CO,S]
[N,CO]
[CO2-]
[N,CO,S]
M+(Met)
B3LYP
[N,OH,S]
[COOH,S]
Li+
Na+
K+
Rb+
Cs+
b)
Relative Gibbs Free Energy (kJ/mol)
60
50
40
30
20
10
0
-10
[COOH]
[CO2-,S]
[CO,S]
[N,CO]
[CO2-]
[N,CO,S]
M+(Met)
B3P86
[N,OH,S]
[COOH,S]
Li+
Na+
K+
Rb+
Cs+

Figure S1

TABLE S1: Relative energies at 0 K (kJ/mol) 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**, 1.7	**0.0**, **0.0**, 0.2
	[N,CO,S]tgggt	5.0, 10.0, 0.9	2.6, 7.4, **0.0**
	[COOH]ctggg	6.4, 7.5, 8.4	7.4, 8.2, 9.8
	[COOH,S]cgggt	6.6, 9.1, 3.9	6.2, 8.3, 3.0
	[COOH,S]cgggg	7.2, 9.4, 1.4	7.3, 9.1, 1.9
	[N,CO,S]tgggg	10.1, 13.9, **0.0**	8.3, 12.0, 0.4
	[N,CO]tgtgt	12.5, 17.4, 13.3	11.2, 16.0, 14.2
	[CO,S]ctggg	13.0, 16.5, 16.4	12.3, 15.5, 16.3
	[CO_2^-,S]cgggg	28.7, 29.1, 23.7	27.4, 27.4, 19.3
	[N,OH,S]ttggg	34.0, 37.9, 19.9	33.1, 37.0, 21.9
	[N,OH,S]tgggt	35.2, 41.2, 28.6	33.5, 39.3, 29.3
Cs^+(Met)	[CO_2^-]ctggg	**0.0**, **0.0**, 3.2	**0.0**, **0.0**, 0.4
	[COOH]ctggg	1.5, 3.1, 4.7	4.6, 6.2, 7.1
	[COOH,S]ctggt	2.5, 5.0, 1.2	4.4, 6.6, 0.6
	[COOH,S]cgggg	4.2, 6.7, 0.4	6.3, 8.5, 0.5
	[N,CO,S]tgggt	7.2, 12.2, 3.7	5.4, 9.9, 1.4
	[N,CO,S]tgggg	9.3, 13.2, **0.0**	9.3, 13.1, **0.0**
	[CO,S]ctgtg	9.4, 13.1, 13.3	11.4, 15.1, 14.0
	[N,CO]tgtgt	11.0, 16.2, 12.5	11.1, 16.1, 13.6
	[CO_2^-,S]cgggg	30.1, 31.1, 27.7	29.0, 29.7, 21.0
	[N,OH,S]ttggg	32.9, 36.7, 19.8	33.6, 37.3, 20.7
	[N,OH,S]tgggt	36.0, 41.7, 30.8	35.2, 40.6, 29.9

[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.

TABLE S2: Geometric parameters for low-energy structures of M^+(Met) [a]

conformer orientation	$r(M^+$-O) (Å)					$r(M^+$-X) (Å)					$r(M^+$-S) (Å)				
	Li	Na	K	Rb	Cs	Li	Na	K	Rb	Cs	Li	Na	K	Rb	Cs
[N,CO,S][b]	1.938	2.293	2.631	*2.888*	*3.106*	2.068	2.462	2.885	*3.178*	*3.445*	2.439	2.802	3.229	*3.516*	*3.781*
tgcgt				**2.825**	**2.991**				**3.116**	**3.301**				**3.433**	**3.623**
[N,CO,S][b]	1.941	2.299	2.634	*2.887*	*3.084*	2.054	2.443	2.858	*3.149*	*3.419*	2.451	2.811	3.254	*3.549*	*3.934*
tgcgg				**2.828**	**2.981**				**3.088**	**3.264**				**3.454**	**3.694**
[N,CO,S][b]	1.926	2.279	2.612	*2.859*	*3.079*	2.090	2.485	2.933	*3.249*	*3.521*	2.464	2.826	3.265	*3.548*	*3.806*
tgggt				**2.794**	**2.957**				**3.185**	**3.366**				**3.467**	**3.661**
[N,CO,S][b]	1.923	2.275	2.608	*2.862*	*3.082*	2.085	2.483	2.941	*3.255*	*3.550*	2.448	2.835	3.273	*3.566*	*3.795*
tgggg				**2.800**	**2.959**				**3.191**	**3.396**				**3.473**	**3.642**
[N,OH,S][b]	1.974	2.349	2.750	*3.021*	*3.287*	2.027	2.413	2.815	3.103	3.358	2.419	2.770	3.181	3.468	3.720
tgggt				**2.989**	**3.186**				**3.040**	**3.219**				**3.381**	**3.563**
[N,OH,S][b]	1.975	2.362	2.760	*3.044*	*3.328*	2.040	2.429	2.851	*3.142*	*3.412*	2.447	2.811	3.219	*3.476*	*3.697*
ttggg				**2.998**	**3.209**				**3.082**	**3.274**				**3.339**	**3.547**
[N,CO][b]	1.871	2.250	2.608	*2.869*	*3.092*	2.022	2.411	2.839	*3.130*	*3.385*					
tgtgt				**2.806**	**2.972**				**3.061**	**3.235**					
[CO_2^-][c]	1.927	2.286	2.620	*2.886*	*3.111*	1.950	2.308	2.672	*2.936*	*3.154*					
ctggg				**2.811**	**2.951**				**2.871**	**3.039**					
[CO_2^-][c]	1.923	2.280	2.618	*2.882*	*3.085*	1.952	2.314	2.673	*2.943*	*3.189*					
ctggt				**2.801**	**2.936**				**2.881**	**3.060**					
[CO_2^-][c]	1.920	2.277	2.611	*2.872*	*3.090*	1.957	2.314	2.682	*2.953*	*3.168*					
cgtgg				**2.795**	**2.937**				**2.888**	**3.049**					
[COOH][d]	1.919	2.292	2.648	*2.906*	*3.149*	2.064	2.410	2.826	*3.108*	*3.313*					
ctggg				**2.830**	**2.985**				**3.064**	**3.273**					
[COOH][d]	1.906	2.290	2.639	2.905	3.129	2.080	2.411	2.832	3.111	3.367					
ctggt				**2.825**	**2.972**				**3.074**	**3.315**					
[COOH][d]	1.913	2.282	2.630	2.906	3.124	2.076	2.431	2.848	3.116	3.349					
cgtgg				**2.823**	**2.968**				**3.067**	**3.317**					
[COOH,S][d]	[e]	2.316	2.655	*2.912*	*3.130*	[e]	2.476	2.822	*3.055*	*3.283*	[e]	2.921	3.433	*3.796*	*4.125*
cgggg				**2.834**	**2.981**				**3.026**	**3.241**				**3.657**	**3.864**
[CO_2^-,S][c]	1.964	2.303	2.629	*2.891*	[f]	1.989	2.331	2.680	*2.921*	[f]	2.580	3.063	3.529	*4.121*	[f]
cgggg				**2.814**	[f]				**2.864**	[f]				**3.908**	[f]
[COOH,S][d]	[e]	2.266	2.628	*2.877*	*3.098*	[e]	2.715	2.929	3.207	*3.451*	[e]	2.880	3.366	*3.672*	*3.919*
cgcgg				**2.802**	**2.961**				**3.253**	**3.415**				**3.547**	**3.727**
[CO_2^-,S][c]	1.949	2.292	2.608	*2.860*	*3.067*	2.018	2.364	2.722	*3.000*	*3.239*	2.580	3.030	3.530	*3.855*	*4.090*
cgcgg				**2.785**	**2.920**				**2.941**	**3.131**				**3.729**	**3.902**

[COOH,S][d,]	[e]	2.287	2.620	*2.872*	*3.066*	[e]	2.574	2.918	*3.151*	*3.475*	[e]	2.902	3.401	*3.806*	*4.326*
cgggt				**2.799**	**2.915**				**3.117**	**3.480**				**3.641**	**3.944**
[CO_2^-,S][c]	1.949	2.290	2.604	*2.857*	[f]	2.014	2.361	2.713	*2.964*	[f]	2.583	3.029	3.568	*4.179*	[f]
cgggt				**2.783**	[f]				**2.901**	[f]				**4.010**	[f]
[CO,S]	1.780	2.156	2.505	*2.765*	*2.994*						2.429	2.835	3.337	*3.681*	*3.991*
ctggg				**2.703**	**2.875**									**3.561**	**3.768**

conformer orientation	∠XMO (º)					∠XMS (º)					∠OMS (º)				
	Li	Na	K	Rb	Cs	Li	Na	K	Rb	Cs	Li	Na	K	Rb	Cs
[N,CO,S][b]	84.6	71.1	60.3	*54.5*	*50.0*	90.1	76.3	64.1	*58.1*	*53.0*	109.9	99.1	86.2	*80.0*	*74.7*
tgggt				**55.7**	**52.2**				**59.2**	**55.6**				**81.1**	**76.8**
[N,CO,S][b]	87.7	71.2	60.6	*54.9*	*51.1*	98.5	849	70.2	*62.7*	*53.0*	103.5	94.2	82.9	*77.3*	*71.5*
tgcgg				**56.1**	**53.1**				**64.6**	**58.5**				**78.6**	**74.7**
[N,CO,S][b]	84.0	70.2	59.0	*53.1*	*48.7*	98.6	86.3	73.9	*67.4*	*62.7*	96.8	84.1	72.2	*65.7*	*61.3*
tgggt				**54.3**	**50.9**				**68.7**	**65.1**				**67.2**	**63.9**
[N,CO,S][b]	84.7	70.5	58.6	*52.6*	*48.0*	96.7	85.0	72.8	*66.8*	*62.1*	106.1	91.4	77.5	*70.6*	*64.8*
tgggg				**53.7**	**50.3**				**68.2**	**64.4**				**72.1**	**68.0**
[N,OH,S][b]	82.6	69.2	58.2	*52.7*	*47.9*	92.8	79.4	66.8	*60.1*	*55.1*	110.5	99.6	87.4	*80.9*	*76.7*
tgggt				**53.3**	**49.8**				**61.8**	**57.6**				**82.8**	**79.1**
[N,OH,S][b]	81.1	67.5	56.8	*51.3*	*46.8*	98.7	86.6	74.2	*68.3*	*63.3*	106.0	92.4	78.3	*71.7*	*66.1*
ttggg				**52.2**	**48.7**				**69.8**	**65.8**				**73.6**	**69.0**
[N,CO][b]	87.8	73.0	61.3	*55.4*	*51.0*										
tgtgt				**56.7**	**53.3**										
[CO_2^-][c]	69.8	58.3	50.2	*45.5*	*42.4*										
ctggg				**46.6**	**44.1**										
[CO_2^-][c]	69.9	58.3	50.2	*45.5*	*42.1*										
ctggt				**46.6**	**44.0**										
[CO_2^-][c]	69.9	58.4	50.3	*45.6*	*42.2*										
cgtgg				**46.6**											
[COOH][d]	66.9	56.1	47.6	*43.2*	*40.2*										
ctggg				**44.0**	**41.3**										
[COOH][d]	66.9	56.1	47.7	*43.2*	*39.8*										
ctggt				**44.0**	**40.9**										
[COOH][d]	66.8	55.9	47.6	*43.2*	*40.0*										
cgtgg				**44.1**	**40.9**										
[COOH,S][d]	[e]	54.9	47.7	*43.7*	*40.5*	[e]	80.9	69.6	*62.8*	*57.8*	[e]	83.2	70.5	*63.8*	*58.3*
cgggg				**44.4**	**41.6**				**64.5**	**61.0**				**66.6**	**62.6**
[CO_2^-,S][c]	68.7	58.0	50.2	*45.7*	[f]	93.8	79.8	69.4	*60.9*	[f]	93.8	78.6	68.4	*57.2*	[f]

cgggg				**46.8**	[f]				**63.8**	[f]				**60.9**	[f]
[COOH,S][d]	[e]	51.8	46.7	*42.4*	*39.2*	[e]	86.2	75.8	*69.2*	*64.4*	[e]	76.5	64.3	*58.4*	*54.3*
cgcgg				**42.2**	**39.9**				**70.7**	**67.0**				**60.6**	**57.2**
[CO_2^-,S][c]	68.5	57.7	50.0	*45.2*	*41.9*	100.2	86.7	75.7	*69.7*	*65.8*	86.4	72.1	60.9	*54.9*	*51.5*
cgcgg				**46.3**	**43.6**				**72.0**	**68.6**				**57.2**	**54.3**
[COOH,S][d,]	[e]	53.8	46.9	*43.0*	*39.1*	[e]	82.9	71.3	*64.0*	*56.4*	[e]	80.2	67.5	*59.6*	*51.3*
cgggt				**43.7**	**39.4**				**66.5**	**60.3**				**62.5**	**56.4**
[CO_2^-,S][c]	68.5	57.8	50.1	*45.6*	[f]	95.9	82.6	70.9	*61.0*	[f]	89.1	75.5	63.9	*53.8*	[f]
cgggt				**46.6**	[f]				**63.4**	[f]				**56.2**	[f]
[CO,S]											105.3	90.4	76.5	*71.2*	*68.6*
ctggg														**73.2**	**70.1**

[a] Values calculated at the B3LYP/6-311+G(d,p) (roman), B3LYP/HW*/6-311+G(d,p) (italics), or B3LYP/Def2TZVP (bold) levels of theory for the lowest energy structure of a given conformer of each metal. The O atom for the M^+-O bond distances and the XMO and OMS bond angles refers to the carbonyl oxygen atom, except for [N,OH,S] conformers. [b] X = amino nitrogen. [c] X = carboxylate oxygen atom bound to NH_3^+ by a hydrogen bond. [d] X = hydroxyl oxygen atom. [e] The [COOH,S] conformer for Li^+(Met) collapses to a [CO,S] conformer. [f] [CO_2^-,S]cgg.gg conformer for Cs^+(Met) converges to a [CO_2^-] conformer.

Table S3: Side-chain dihedral angles (°) for the [N,CO,S], [CO_2^-], and [COOH] conformers for Li^+(Met) to Cs^+(Met) and the [COOH,S] conformers for Na^+(Met) to Cs^+(Met)[a]

Complex	Conformer	Orientation	∠ (HOCC)	∠ (OCCC)	∠ (CCCC)	∠ (CCCS)	∠ (CCSC)
Li^+(Met)	[N,CO,S]	tgcgt	177.9	-81.6	-45.6	-63.3	-179.0
Na^+(Met)		tgcgt	178.1	-77.8	-49.6	-67.4	-167.9
K^+(Met)		tgcgt	178.6	-73.5	-52.0	-67.9	-159.8
Rb^+(Met)		tgcgt	*178.9*	*-71.6*	*-53.6*	*-69.8*	*-154.3*
Cs^+(Met)		tgcgt	*179.2*	*-70.2*	*-55.8*	*-70.0*	*-148.0*
Li^+(Met)	[N,CO,S]	tgcgg	177.9	-80.8	-40.1	-59.2	-68.6
Na^+(Met)		tgcgg	178.4	-76.4	-41.0	-65.3	-66.7
K^+(Met)		tgcgg	178.7	-72.5	-44.4	-67.3	-69.2
Rb^+(Met)		tgcgg	*178.7*	*-71.9*	*-47.8*	*-70.2*	*-75.5*
Cs^+(Met)		tgcgg	*177.9*	*-74.4*	*-56.7*	*-70.3*	*-92.0*
Li^+(Met)	[N,CO,S]	tgggt	178.2	-75.1	-90.2	59.0	180.0
Na^+(Met)		tgggt	179.5	-68.2	-86.1	61.4	167.9
K^+(Met)		tgggt	-179.7	-63.7	-82.4	62.9	159.0
Rb^+(Met)		tgggt	*-179.6*	*-62.3*	*-80.5*	*63.6*	*151.1*
Cs^+(Met)		tgggt	*-179.3*	*-60.6*	*-79.3*	*64.9*	*148.1*
Li^+(Met)	[N,CO,S]	tgggg	179.3	-76.8	-95.6	55.3	67.0
Na^+(Met)		tgggg	-177.3	-64.3	-89.2	57.4	63.8
K^+(Met)		tgggg	-174.3	-53.4	-81.4	58.4	69.4
Rb^+(Met)		tgggg	*-173.8*	*-51.6*	*-78.9*	*60.2*	*70.2*

Cs^+(Met)		tgggg	*-173.9*	*-51.5*	*-77.5*	*61.5*	*71.8*
Li^+(Met)	[CO_2^-]	ctggg	-3.5	137.6	-57.4	-65.8	-77.4
Na^+(Met)		ctggg	-3.9	137.2	-57.6	-67.0	-76.9
K^+(Met)		ctggg	-3.6	135.5	-58.6	-68.3	-76.5
Rb^+(Met)		ctggg	*-4.2*	*136.1*	*-57.8*	*-68.1*	*-76.8*
Cs^+(Met)		ctggg	*-4.1*	*135.9*	*-57.2*	*-68.2*	*-76.8*
Li^+(Met)	[CO_2^-]	ctggt	-2.8	136.6	-62.3	-75.1	159.5
Na^+(Met)		ctggt	-3.3	136.5	-62.4	-76.2	160.5
K^+(Met)		ctggt	-3.6	136.1	-62.5	-76.6	160.4
Rb^+(Met)		ctggt	*-3.8*	*136.0*	*-62.5*	*-76.9*	*161.0*
Cs^+(Met)		cgggt	*-3.0*	*134.5*	*-62.4*	*-77.3*	*160.9*
Li^+(Met)	[CO_2^-]	cgtgg	-0.1	110.3	175.2	68.5	77.9
Na^+(Met)		cgtgg	1.2	109.7	176.0	69.7	76.3
K^+(Met)		cgtgg	1.5	110.9	176.8	70.6	76.9
Rb^+(Met)		cgtgg	*1.7*	*111.1*	*176.9*	*71.0*	*77.6*
Cs^+(Met)		cgtgg	*1.8*	*112.0*	*178.0*	*71.3*	*77.4*
Li^+(Met)	[COOH]	ctggg	-2.1	135.0	-59.2	-66.1	-76.9
Na^+(Met)		ctggg	-2.3	136.7	-58.8	-66.4	-76.8
K^+(Met)		ctggg	-2.3	137.6	-58.0	-66.0	-76.8
Rb^+(Met)		ctggg	*-2.5*	*138.1*	*-59.1*	*-67.0*	*-76.0*
Cs^+(Met)		ctggg	*-2.6*	*139.3*	*-56.3*	*-65.1*	*-76.9*
Li^+(Met)	[COOH]	cgggt	-2.0	134.7	-66.2	-77.2	172.3
Na^+(Met)		ctggt	-2.5	137.8	-65.8	-76.5	173.4

K^+(Met)		ctggt	-2.5	138.2	-66.0	-77.2	173.6
Rb^+(Met)		ctggt	*-2.5*	*138.3*	*-66.0*	*-77.7*	*173.6*
Cs^+(Met)		ctggt	*-2.4*	*139.0*	*-64.4*	*-76.7*	*173.2*
Li^+(Met)	[COOH]	cgtgg	1.5	118.3	177.0	75.5	80.0
Na^+(Met)		cgtgg	1.7	117.4	174.0	75.8	80.3
K^+(Met)		cgtgg	1.7	116.8	173.7	76.2	79.8
Rb^+(Met)		cgtgg	*2.4*	*115.4*	*172.2*	*75.3*	*80.0*
Cs^+(Met)		cgtgg	*1.9*	*117.0*	*173.3*	*76.8*	*79.1*
Na^+(Met)	[COOH,S]	cgggg	6.6	107.1	-60.4	-81.9	68.5
K^+(Met)		cgggg	4.7	111.2	-63.3	81.0	71.3
Rb^+(Met)		cgggg	*4.1*	*112.1*	*-65.0*	*80.7*	*73.3*
Cs^+(Met)		cgggg	*2.9*	*114.5*	*-66.5*	*79.2*	*73.6*
Na^+(Met)	[COOH,S]	cgggt	5.7	109.5	-59.5	87.3	176.6
K^+(Met)		cgggt	2.7	117.3	-64.5	82.4	176.1
Rb^+(Met)		cgggt	*0.7*	*124.3*	*-69.0*	*76.6*	*179.9*
Cs^+(Met)		ctggt	*-2.6*	*139.7*	*-77.9*	*62.5*	*-174.6*
Na^+(Met)	[COOH,S]	cgcgg	10.2	94.1	48.2	-86.1	-71.5
K^+(Met)		cgcgg	8.6	97.1	47.8	-87.6	-77.5
Rb^+(Met)		cgcgg	*8.3*	*98.6*	*47.9*	*-88.3*	*-78.7*
Cs^+(Met)		cgcgg	*7.5*	*99.4*	*47.8*	*-88.3*	*-80.2*

[a] Values calculated at the B3LYP/6-311+G(d,p) (roman) and B3LYP/HW*/6-311+G(d,p) (italics) levels of theory .

Table S4. Vibrational frequencies (cm^{-1}) scaled by 0.975 and IR intensities (kM/mole) for the [N,CO,S] tgcgt conformer of M^+(Met) calculated at B3LYP/6-311+G(d,p) (M^+ = Li^+, Na^+, and K^+) and B3LYP/HW*/6-311+G(d,p) (M^+ = Rb^+ and Cs^+) levels of theory[a]

Li^+(Met)		Na^+(Met)		K^+(Met)		Rb^+(Met)		Cs^+(Met)	
54	1	46	1	40	1	37	0.5	37	0.3
88	1	75	1	64	0.4	57	1	50	1
140	1	106	7	78	5	65	3	56	2
146	3	120	4	100	4	88	2	78	6
158	3	149	3	113	10	90	7	79	3
176	0.3	161	10	144	3	119	8	103	5
195	1	178	1	152	7	131	3	124	2
279	9	187	4	164	16	152	0.5	151	0.5
286	14	216	12	173	3	173	0.1	170	0.2
325	8	216	26	202	2	209	1	212	2
351	44	287	5	271	16	254	27	245	32
371	29	308	2	301	2	296	4	293	3
415	18	341	15	328	19	325	18	326	21
453	58	401	43	369	28	358	15	355	8
512	59	461	12	454	7	453	7	453	7
522	27	512	10	508	10	507	9	508	9
618	**60**	608	66	**597**	**68**	**592**	**67**	**589**	**65**
636	**37**	634	18	**633**	**13**	**632**	**13**	**630**	**13**
679	**76**	666	72	**656**	**69**	**650**	**66**	**647**	**63**
684	**10**	684	6	**684**	**7**	**684**	**6**	**684**	**7**
738	**66**	734	53	**729**	**48**	**725**	**47**	**724**	**46**
814	**8**	812	9	**811**	**12**	**809**	**14**	**806**	**18**
843	**4**	843	3	**843**	**3**	**840**	**4**	**839**	**5**
858	**7**	853	10	**850**	**12**	**849**	**14**	**847**	**17**
952	**4**	**952**	**4**	**950**	**6**	**951**	**12**	**949**	**60**
970	**7**	**969**	**17**	**965**	**43**	**960**	**62**	**953**	**34**
981	**2**	**977**	**4**	**973**	**3**	**972**	**2**	**970**	**4**
993	**17**	**1001**	**45**	**996**	**85**	**990**	**62**	**986**	**35**
1030	**127**	**1015**	**79**	**1011**	**9**	**1010**	**7**	**1009**	**8**
1072	**6**	**1082**	**13**	**1088**	**21**	**1090**	**28**	**1092**	**35**
1153	**3**	**1155**	**20**	**1152**	**206**	**1148**	**225**	**1145**	**235**
1163	**127**	**1159**	**176**	**1159**	**16**	**1158**	**9**	**1158**	**5**
1183	**65**	**1186**	**26**	**1189**	**13**	**1189**	**10**	**1188**	**8**
1244	**3**	**1249**	**4**	**1252**	**5**	**1252**	**6**	**1251**	**7**
1284	**27**	**1284**	**36**	**1282**	**39**	**1280**	**39**	**1279**	**39**
1314	**29**	**1310**	**20**	**1307**	**14**	**1304**	**11**	**1303**	**9**
1320	**4**	**1324**	**6**	**1326**	**5**	**1327**	**4**	**1327**	**4**
1340	**1**	**1340**	**1**	**1339**	**1**	**1339**	**2**	**1338**	**2**
1353	**5**	**1357**	**5**	**1359**	**4**	**1360**	**4**	**1361**	**4**
1411	**46**	**1402**	**34**	**1397**	**28**	**1394**	**23**	**1392**	**21**
1430	**13**	**1431**	**13**	**1430**	**13**	**1431**	**13**	**1431**	**13**
1440	**14**	**1441**	**15**	**1442**	**13**	**1443**	**18**	**1443**	**15**
1447	**20**	**1444**	**15**	**1442**	**15**	**1443**	**10**	**1443**	**11**
1452	**10**	**1451**	**8**	**1451**	**6**	**1448**	**4**	**1448**	**4**

1624	**73**	**1623**	**65**	**1626**	**64**	**1624**	**62**	**1624**	**61**
1705	**319**	**1721**	**318**	**1728**	**342**	**1736**	**339**	**1739**	**350**
2969	2	2963	3	2951	8	2942	11	2936	13
2974	14	2971	12	2968	11	2967	11	2968	12
2978	5	2973	13	2971	17	2970	20	2970	19
2984	5	2976	5	2973	8	2972	8	2972	10
3012	3	3010	3	3010	4	3010	5	3011	6
3026	4	3022	5	3019	7	3019	8	3020	9
3067	2	3063	2	3057	3	3055	4	3053	4
3071	1	3068	1	3064	2	3062	3	3060	3
3392	18	3395	10	3396	6	3399	4	3402	3
3456	20	3458	15	3461	11	3466	9	3470	8
3627	152	3637	138	3644	128	3649	120	3653	115

[a] Bold indicates the region of the IR spectrum included in the present experimental study.

Table S5. Vibrational frequencies (cm^{-1}) scaled by 0.975 and IR intensities (kM/mole) for the [N,CO,S] tgcgg conformer of M^+(Met) calculated at B3LYP/6-311+G(d,p) (M^+ = Li^+, Na^+, and K^+) and B3LYP/HW*/6-311+G(d,p) (M^+ = Rb^+ and Cs^+) levels of theory[a]

Li^+(Met)		Na^+(Met)		K^+(Met)		Rb^+(Met)		Cs^+(Met)	
56	1	50	2	47	1	30	2	19	2
87	0.4	73	0.1	58	0.1	49	0.4	36	2
112	1	89	3	75	2	61	2	44	1
144	1	119	5	90	6	66	2	58	0.2
146	2	128	3	117	7	94	6	84	6
164	2	160	2	134	2	116	7	102	6
232	2	179	14	147	4	130	7	118	4
300	7	202	13	160	8	135	3	136	2
306	4	215	23	165	21	159	1	157	5
320	17	240	5	235	1	237	10	235	37
348	39	303	1	285	24	272	27	261	5
384	37	314	3	296	3	290	2	281	5
419	18	337	16	320	13	319	11	314	15
461	60	403	40	363	16	355	6	351	2
503	47	461	7	455	4	451	3	443	5
523	32	504	10	501	11	502	11	509	14
599	**13**	594	16	**593**	**38**	**594**	**48**	**599**	**59**
628	**78**	616	62	**612**	**39**	**614**	**30**	**614**	**20**
679	**78**	663	68	**655**	**65**	**652**	**61**	**653**	**53**
682	**11**	681	10	**686**	**12**	**685**	**13**	**684**	**14**
736	**64**	728	55	**724**	**48**	**721**	**45**	**722**	**42**
806	**8**	803	10	**805**	**11**	**805**	**12**	**797**	**14**
827	**9**	823	10	**822**	**9**	**822**	**9**	**826**	**11**
862	**7**	853	7	**847**	**12**	**843**	**20**	**837**	**26**
934	**0.3**	**933**	**0.2**	**933**	**1**	**933**	**10**	**918**	**85**
953	**3**	**955**	**3**	**952**	**3**	**952**	**3**	**951**	**18**
990	**17**	**993**	**44**	**981**	**112**	**963**	**115**	**954**	**11**

1002	**7**	**1004**	**4**	**1008**	**24**	**1005**	**4**	**1004**	**3**
1033	**131**	**1019**	**101**	**1009**	**5**	**1010**	**3**	**1009**	**1**
1074	**8**	**1081**	**15**	**1087**	**26**	**1090**	**38**	**1093**	**51**
1163	**120**	**1158**	**186**	**1152**	**211**	**1147**	**224**	**1146**	**251**
1175	**23**	**1176**	**7**	**1176**	**7**	**1173**	**7**	**1159**	**7**
1186	**51**	**1193**	**24**	**1194**	**13**	**1191**	**9**	**1187**	**3**
1247	**4**	**1253**	**5**	**1255**	**5**	**1255**	**6**	**1252**	**9**
1287	**22**	**1285**	**27**	**1281**	**30**	**1278**	**32**	**1270**	**28**
1318	**25**	**1312**	**20**	**1308**	**12**	**1307**	**9**	**1305**	**4**
1324	**5**	**1328**	**6**	**1329**	**6**	**1328**	**7**	**1326**	**11**
1338	**1**	**1340**	**2**	**1340**	**4**	**1339**	**4**	**1336**	**4**
1355	**7**	**1355**	**6**	**1358**	**4**	**1358**	**3**	**1358**	**1**
1413	**46**	**1402**	**30**	**1396**	**25**	**1392**	**20**	**1387**	**17**
1431	**7**	**1428**	**6**	**1428**	**5**	**1429**	**4**	**1431**	**16**
1438	**17**	**1434**	**20**	**1433**	**18**	**1433**	**19**	**1432**	**6**
1439	**13**	**1441**	**9**	**1442**	**9**	**1443**	**11**	**1440**	**13**
1454	**19**	**1445**	**16**	**1445**	**15**	**1445**	**12**	**1443**	**10**
1621	**69**	**1624**	**62**	**1621**	**58**	**1622**	**54**	**1617**	**50**
1708	**319**	**1724**	**317**	**1730**	**343**	**1737**	**340**	**1738**	**349**
2966	4	2960	6	2951	8	2948	9	2961	4
2976	11	2970	5	2964	7	2966	7	2971	13
2982	6	2975	14	2972	16	2971	18	2973	16
2985	2	2981	4	2978	6	2978	6	2982	5
3005	5	3003	7	3000	8	3001	10	3003	11
3029	3	3024	4	3021	6	3021	7	3027	6
3061	6	3059	6	3054	7	3053	6	3058	4
3068	0.4	3064	1	3063	1	3062	2	3064	2
3392	14	3394	8	3399	4	3406	3	3414	8
3461	15	3461	11	3469	8	3478	7	3489	27
3625	159	3635	142	3643	131	3648	122	3650	112

[a] Bold indicates the region of the IR spectrum included in the present experimental study.

Table S6. Vibrational frequencies (cm^{-1}) scaled by 0.975 and IR intensities (kM/mole) for the [N,CO,S] tgggt conformer of M^+(Met) calculated at B3LYP/6-311+G(d,p) ($M^+ = Li^+$, Na^+, and K^+) and B3LYP/HW*/6-311+G(d,p) ($M^+ = Rb^+$ and Cs^+) levels of theory[a]

Li^+(Met)		Na^+(Met)		K^+(Met)		Rb^+(Met)		Cs^+(Met)	
51	0.2	46	0.1	45	0.01	41	0.1	31	0.4
91	1	79	1	67	2	57	2	50	1
124	2	97	3	73	3	69	2	67	6
136	1	115	4	98	3	80	8	68	1
163	3	153	14	105	14	88	4	76	5
165	1	154	4	127	9	105	3	92	1
236	3	180	5	157	1	136	6	118	4
249	0.5	183	12	172	14	155	0.4	154	0.4
287	15	224	19	186	6	188	2	187	2
311	2	234	6	215	1	210	1	209	1
336	52	258	2	254	5	253	9	248	14

370	39	321	5	296	15	290	12	287	10
405	18	323	16	325	8	326	8	324	8
458	73	407	29	383	18	376	13	371	8
504	45	470	13	462	10	462	9	462	9
558	25	542	15	531	15	527	15	523	16
608	**72**	588	56	**573**	**51**	**566**	**51**	**561**	**49**
642	**18**	640	10	**634**	**70**	**627**	**70**	**622**	**69**
665	**60**	647	65	**639**	**4**	**637**	**2**	**636**	**1**
683	**9**	683	7	**685**	**8**	**685**	**9**	**686**	**9**
723	**76**	716	62	**711**	**60**	**709**	**57**	**707**	**56**
784	**18**	779	18	**779**	**19**	**778**	**20**	**778**	**20**
846	**9**	847	10	**845**	**13**	**845**	**16**	**843**	**21**
893	**10**	895	15	**892**	**21**	**890**	**27**	**889**	**31**
942	**3**	**939**	**4**	**939**	**4**	**938**	**4**	**937**	**4**
965	**4**	**962**	**5**	**959**	**5**	**957**	**4**	**955**	**4**
971	**2**	**971**	**5**	**970**	**15**	**967**	**28**	**963**	**44**
1021	**74**	**1012**	**106**	**999**	**91**	**992**	**70**	**987**	**45**
1033	**53**	**1031**	**6**	**1030**	**2**	**1030**	**3**	**1029**	**5**
1063	**12**	**1072**	**16**	**1074**	**20**	**1077**	**25**	**1078**	**28**
1148	**30**	**1147**	**73**	**1143**	**105**	**1143**	**138**	**1142**	**156**
1173	**160**	**1169**	**134**	**1166**	**108**	**1165**	**80**	**1165**	**63**
1211	**9**	**1220**	**10**	**1219**	**4**	**1221**	**4**	**1222**	**3**
1222	**2**	**1223**	**1**	**1224**	**7**	**1227**	**6**	**1228**	**6**
1294	**23**	**1294**	**28**	**1294**	**31**	**1292**	**31**	**1292**	**31**
1310	**20**	**1308**	**24**	**1305**	**21**	**1304**	**21**	**1305**	**20**
1320	**13**	**1323**	**7**	**1324**	**6**	**1324**	**5**	**1324**	**5**
1339	**0.2**	**1339**	**0.3**	**1337**	**1**	**1336**	**1**	**1336**	**1**
1360	**3**	**1364**	**3**	**1365**	**4**	**1366**	**4**	**1366**	**4**
1412	**60**	**1401**	**37**	**1397**	**28**	**1395**	**23**	**1395**	**21**
1430	**13**	**1430**	**12**	**1431**	**12**	**1430**	**12**	**1430**	**12**
1440	**16**	**1441**	**16**	**1441**	**18**	**1442**	**17**	**1441**	**16**
1453	**7**	**1451**	**6**	**1446**	**3**	**1445**	**2**	**1445**	**4**
1456	**7**	**1452**	**9**	**1449**	**9**	**1447**	**11**	**1448**	**10**
1621	**74**	**1621**	**69**	**1620**	**70**	**1619**	**67**	**1617**	**67**
1712	**327**	**1725**	**318**	**1728**	**341**	**1734**	**336**	**1736**	**345**
2970	1	2949	7	2931	11	2921	13	2913	15
2975	20	2971	8	2965	8	2961	11	2959	13
2978	2	2975	12	2972	18	2971	18	2970	19
2982	8	2979	15	2976	18	2980	19	2982	19
3017	1	3017	1	3016	2	3018	1	3020	1
3028	5	3029	6	3030	7	3031	9	3033	10
3066	2	3062	2	3057	3	3056	4	3054	4
3072	1	3069	1	3065	2	3064	2	3062	3
3396	17	3397	11	3396	7	3398	5	3399	4
3460	18	3459	13	3460	9	3463	7	3465	6
3630	160	3641	143	3649	131	3655	121	3658	115

[a] Bold indicates the region of the IR spectrum included in the present experimental study.

Table S7. Vibrational frequencies (cm^{-1}) scaled by 0.975 and IR intensities (kM/mole) for the [N,CO,S] tgggg conformer of M^+(Met) calculated at B3LYP/6-311+G(d,p) (M^+ = Li^+, Na^+, and K^+) and B3LYP/HW*/6-311+G(d,p) (M^+ = Rb^+ and Cs^+) levels of theory[a]

Li^+(Met)		Na^+(Met)		K^+(Met)		Rb^+(Met)		Cs^+(Met)	
46	1	43	1	57	2	56	3	42	3
84	2	72	2	74	1	62	4	53	4
119	2	97	5	78	5	67	2	66	1
138	0.1	116	7	94	14	81	5	82	2
146	2	140	7	108	4	92	3	82	3
182	1	145	2	125	8	106	3	106	4
233	1	170	9	154	0.2	147	5	131	3
278	8	200	14	170	3	158	0.1	155	0.03
302	8	223	23	184	16	169	1	167	1
311	1	247	0.2	243	2	238	4	232	5
334	61	285	1	286	1	289	12	283	24
366	29	319	7	301	21	292	12	289	1
400	15	323	15	330	4	334	4	331	5
463	72	404	34	391	18	383	13	377	10
505	52	470	12	476	12	475	11	474	11
569	18	552	12	531	12	522	15	520	15
597	**11**	580	36	**562**	**23**	**558**	**21**	**556**	**20**
620	**74**	611	18	**615**	**8**	**616**	**9**	**615**	**10**
665	**59**	648	70	**641**	**84**	**633**	**83**	**630**	**79**
683	**7**	685	6	**687**	**5**	**689**	**6**	**688**	**5**
719	**75**	706	63	**701**	**67**	**699**	**61**	**698**	**62**
780	**20**	777	20	**780**	**26**	**782**	**28**	**781**	**29**
833	**13**	832	17	**832**	**23**	**831**	**26**	**830**	**30**
878	**6**	882	9	**887**	**14**	**888**	**17**	**888**	**19**
933	**4**	**930**	**6**	**929**	**9**	**927**	**10**	**924**	**12**
956	**2**	**958**	**3**	**955**	**3**	**955**	**5**	**958**	**13**
974	**17**	**973**	**27**	**971**	**41**	**970**	**53**	**966**	**56**
1025	**83**	**1012**	**93**	**1001**	**57**	**995**	**35**	**988**	**19**
1028	**39**	**1032**	**1**	**1032**	**1**	**1032**	**2**	**1032**	**3**
1069	**16**	**1080**	**27**	**1082**	**35**	**1083**	**42**	**1082**	**45**
1164	**90**	**1155**	**149**	**1149**	**150**	**1146**	**165**	**1144**	**172**
1174	**94**	**1170**	**45**	**1166**	**41**	**1165**	**26**	**1166**	**20**
1210	**7**	**1219**	**4**	**1216**	**1**	**1216**	**0.5**	**1216**	**0.3**
1226	**2**	**1231**	**2**	**1232**	**4**	**1234**	**4**	**1235**	**5**
1294	**21**	**1293**	**26**	**1293**	**27**	**1292**	**27**	**1291**	**25**
1309	**15**	**1309**	**14**	**1306**	**12**	**1306**	**12**	**1306**	**12**
1320	**7**	**1322**	**3**	**1324**	**2**	**1325**	**2**	**1324**	**2**
1338	**3**	**1338**	**3**	**1335**	**2**	**1336**	**1**	**1336**	**1**
1359	**5**	**1362**	**5**	**1363**	**3**	**1364**	**3**	**1365**	**3**
1410	**53**	**1395**	**28**	**1388**	**23**	**1387**	**19**	**1388**	**18**
1430	**2**	**1429**	**2**	**1427**	**3**	**1426**	**4**	**1425**	**4**
1436	**21**	**1435**	**19**	**1433**	**18**	**1435**	**15**	**1433**	**16**
1438	**11**	**1442**	**12**	**1447**	**14**	**1446**	**14**	**1447**	**15**
1459	**6**	**1458**	**7**	**1456**	**8**	**1455**	**8**	**1453**	**7**

1625	**78**	**1622**	**73**	**1618**	**79**	**1617**	**76**	**1614**	**76**
1711	**315**	**1725**	**306**	**1724**	**333**	**1731**	**336**	**1732**	**344**
2969	2	2942	7	2913	11	2903	14	2896	16
2978	5	2967	6	2959	11	2956	13	2954	15
2981	10	2978	9	2976	10	2974	12	2974	13
2988	6	2986	10	2986	12	2986	14	2985	15
3013	2	3015	1	3018	0.5	3019	1	3020	1
3030	4	3029	6	3033	7	3034	8	3035	9
3066	5	3064	4	3062	3	3059	3	3059	3
3069	1	3068	1	3067	2	3065	2	3064	2
3397	18	3398	12	3398	8	3400	5	3401	4
3463	19	3462	14	3463	10	3465	8	3468	7
3630	150	3641	134	3648	122	3653	113	3657	107

[a] Bold indicates the region of the IR spectrum included in the present experimental study.

Table S8. Vibrational frequencies (cm^{-1}) scaled by 0.975 and IR intensities (kM/mole) for the [CO_2^-] ctggg conformer of M^+(Met) calculated at B3LYP/6-311+G(d,p) (M^+ = Li^+, Na^+, and K^+) and B3LYP/HW*/6-311+G(d,p) (M^+ = Rb^+ and Cs^+) levels of theory[a]

Li^+(Met)		Na^+(Met)		K^+(Met)		Rb^+(Met)		Cs^+(Met)	
45	2	36	4	36	5	29	4	17	3
69	3	58	5	58	7	49	6	47	6
83	1	79	5	76	4	72	7	67	7
116	5	91	10	82	8	77	4	72	3
151	0.4	125	22	106	16	96	11	89	10
162	68	152	7	130	12	112	6	99	3
220	37	159	15	143	1	152	16	141	19
237	31	221	35	185	35	163	6	146	1
269	13	252	22	226	31	220	32	215	29
300	18	269	7	262	4	260	4	256	5
336	29	308	36	305	14	301	14	300	12
343	26	315	15	311	41	315	34	314	29
389	5	344	43	342	38	346	45	343	55
481	98	401	15	406	10	405	6	412	5
518	1	509	15	510	16	507	13	507	15
523	84	518	12	514	15	515	18	515	17
595	**75**	584	16	**581**	**14**	**579**	**11**	**579**	**11**
613	**1**	612	1	**613**	**1**	**614**	**2**	**611**	**2**
681	**4**	681	3	**683**	**3**	**683**	**3**	**683**	**3**
770	**16**	765	12	**760**	**15**	**758**	**14**	**757**	**15**
810	**11**	809	11	**809**	**11**	**807**	**11**	**807**	**11**
830	**10**	830	9	**830**	**8**	**829**	**8**	**830**	**8**
878	**23**	867	30	**854**	**47**	**850**	**50**	**846**	**56**
930	**10**	**930**	**12**	**931**	**13**	**933**	**13**	**931**	**13**
952	**7**	**950**	**8**	**947**	**9**	**945**	**9**	**943**	**9**
958	**3**	**954**	**2**	**955**	**3**	**956**	**3**	**954**	**3**
995	**13**	**996**	**15**	**996**	**16**	**997**	**17**	**997**	**18**

1055	**23**	**1055**	**26**	**1057**	**28**	**1057**	**30**	**1056**	**31**
1091	**22**	**1088**	**18**	**1085**	**15**	**1084**	**15**	**1083**	**15**
1123	**61**	**1125**	**67**	**1124**	**75**	**1123**	**75**	**1124**	**78**
1163	**2**	**1161**	**2**	**1159**	**1**	**1158**	**1**	**1157**	**1**
1237	**46**	**1237**	**50**	**1235**	**54**	**1235**	**55**	**1235**	**57**
1280	**12**	**1277**	**14**	**1273**	**17**	**1271**	**15**	**1269**	**15**
1310	**15**	**1308**	**25**	**1305**	**32**	**1304**	**50**	**1302**	**72**
1333	**27**	**1330**	**44**	**1326**	**74**	**1321**	**89**	**1317**	**85**
1339	**4**	**1337**	**8**	**1337**	**4**	**1336**	**2**	**1334**	**2**
1357	**18**	**1354**	**30**	**1351**	**48**	**1349**	**44**	**1349**	**41**
1398	**136**	**1378**	**99**	**1369**	**68**	**1366**	**44**	**1364**	**33**
1430	**6**	**1428**	**16**	**1423**	**228**	**1413**	**278**	**1407**	**287**
1432	**54**	**1430**	**86**	**1430**	**23**	**1429**	**7**	**1428**	**7**
1437	**31**	**1435**	**32**	**1433**	**10**	**1432**	**12**	**1432**	**11**
1442	**26**	**1441**	**40**	**1438**	**62**	**1439**	**29**	**1436**	**30**
1457	**207**	**1444**	**147**	**1442**	**13**	**1443**	**12**	**1442**	**13**
1576	**43**	**1576**	**19**	**1576**	**12**	**1573**	**10**	**1571**	**8**
1620	**277**	**1637**	**118**	**1636**	**12**	**1635**	**15**	**1635**	**15**
1634	**11**	**1639**	**218**	**1650**	**310**	**1661**	**324**	**1667**	**315**
2835	962	2895	869	2935	805	2959	407	2923	351
2970	4	2967	7	2966	7	2965	210	2962	22
2974	15	2974	15	2974	15	2969	476	2972	56
2990	4	2989	5	2988	5	2973	48	2985	677
3003	0.1	3006	0.5	3006	7	2988	6	2987	27
3013	2	3013	2	3012	1	3007	1	3008	16
3037	3	3036	3	3026	326	3011	5	3011	3
3058	5	3057	6	3035	7	3035	5	3035	5
3067	1	3066	1	3056	6	3054	7	3054	7
3169	201	3102	258	3065	1	3065	1	3064	1
3419	83	3422	77	3427	75	3429	71	3431	69

[a] Bold indicates the region of the IR spectrum included in the present experimental study.

Table S9. Vibrational frequencies (cm^{-1}) scaled by 0.975 and IR intensities (kM/mole) for the $[CO_2^-]$ cgtgg and ctggt conformers of M^+(Met) calculated at B3LYP/6-311+G(d,p) ($M^+ = K^+$) and B3LYP/HW*/6-311+G(d,p) ($M^+ = Rb^+$ and Cs^+)[a]

$[CO_2^-]$ cgtgg						$[CO_2^-]$ ctggt					
K^+(Met)		Rb^+(Met)		Cs^+(Met)		K^+(Met)		Rb^+(Met)		Cs^+(Met)	
36	1	30	2	31	2	25	0.4	25	0.3	23	0.2
56	8	52	8	53	3	51	5	51	6	49	7
65	7	61	2	59	3	62	14	58	7	54	4
86	4	78	7	73	9	88	4	77	5	67	7
122	21	106	7	93	5	115	17	109	13	97	7
147	8	124	18	118	15	141	10	117	7	108	9
155	14	147	3	151	4	150	8	147	11	143	11
179	14	174	12	174	13	187	41	171	18	167	13
204	29	199	27	196	21	196	7	195	15	192	17
230	12	217	1	216	1	230	12	226	6	226	5

299	5	298	8	299	8	295	18	293	14	293	13
323	53	320	58	331	62	309	23	308	25	307	31
351	11	356	17	356	21	338	39	337	45	336	47
357	14	357	5	362	2	400	22	404	18	406	15
435	55	434	50	431	52	511	30	511	29	510	31
519	28	520	26	520	28	522	1	520	1	520	2
616	**1**	**616**	**1**	**618**	**1**	**581**	**15**	**580**	**12**	**582**	**11**
651	**12**	**650**	**10**	**649**	**10**	**635**	**0.3**	**634**	**0.3**	**634**	**0.3**
684	**3**	**684**	**3**	**686**	**3**	**688**	**5**	**690**	**5**	**690**	**4**
756	**7**	**754**	**7**	**754**	**9**	**761**	**12**	**759**	**11**	**757**	**12**
793	**3**	**792**	**3**	**792**	**3**	**813**	**13**	**812**	**13**	**812**	**13**
831	**1**	**831**	**2**	**830**	**3**	**847**	**15**	**843**	**29**	**840**	**42**
882	**92**	**879**	**96**	**877**	**102**	**860**	**41**	**857**	**31**	**857**	**25**
931	**11**	**931**	**10**	**929**	**10**	**940**	**2**	**941**	**2**	**940**	**3**
956	**3**	**956**	**3**	**954**	**3**	**951**	**13**	**950**	**13**	**950**	**12**
961	**14**	**961**	**15**	**960**	**14**	**961**	**3**	**962**	**2**	**961**	**2**
1003	**7**	**1003**	**7**	**1005**	**7**	**986**	**24**	**985**	**26**	**986**	**28**
1030	**26**	**1031**	**27**	**1035**	**27**	**1059**	**21**	**1059**	**23**	**1059**	**25**
1078	**23**	**1076**	**26**	**1077**	**34**	**1083**	**20**	**1082**	**19**	**1080**	**18**
1115	**89**	**1115**	**91**	**1116**	**96**	**1127**	**63**	**1126**	**64**	**1127**	**68**
1185	**9**	**1185**	**11**	**1186**	**13**	**1138**	**12**	**1139**	**13**	**1138**	**12**
1231	**28**	**1231**	**29**	**1231**	**29**	**1237**	**49**	**1237**	**50**	**1237**	**50**
1256	**21**	**1254**	**21**	**1252**	**26**	**1269**	**22**	**1267**	**23**	**1266**	**24**
1295	**13**	**1294**	**14**	**1296**	**18**	**1304**	**41**	**1302**	**55**	**1301**	**65**
1322	**132**	**1315**	**168**	**1308**	**181**	**1326**	**68**	**1320**	**79**	**1316**	**79**
1335	**3**	**1335**	**4**	**1332**	**41**	**1334**	**5**	**1335**	**4**	**1335**	**4**
1346	**99**	**1339**	**76**	**1335**	**32**	**1353**	**39**	**1350**	**44**	**1348**	**44**
1371	**49**	**1368**	**29**	**1368**	**22**	**1369**	**69**	**1365**	**43**	**1365**	**35**
1417	**199**	**1407**	**218**	**1402**	**234**	**1426**	**176**	**1417**	**249**	**1411**	**269**
1428	**12**	**1427**	**9**	**1428**	**8**	**1431**	**71**	**1431**	**22**	**1431**	**19**
1433	**19**	**1433**	**16**	**1434**	**14**	**1440**	**16**	**1437**	**31**	**1437**	**26**
1442	**18**	**1442**	**15**	**1442**	**14**	**1441**	**53**	**1441**	**18**	**1441**	**17**
1447	**12**	**1447**	**11**	**1446**	**13**	**1453**	**10**	**1453**	**8**	**1454**	**7**
1589	**12**	**1587**	**10**	**1589**	**8**	**1578**	**11**	**1578**	**6**	**1576**	**5**
1629	**36**	**1629**	**21**	**1628**	**16**	**1633**	**8**	**1632**	**8**	**1632**	**8**
1650	**336**	**1661**	**363**	**1667**	**352**	**1649**	**307**	**1660**	**325**	**1666**	**317**
2959	6	2957	5	2945	285	2935	831	2961	385	2924	333
2973	212	2973	18	2956	8	2966	6	2964	191	2963	16
2978	422	2979	8	2973	16	2973	13	2971	317	2972	51
2981	33	2994	80	2980	11	2978	10	2974	212	2978	33
3007	2	3006	4	3005	4	3007	5	2979	64	2984	729
3025	16	3024	853	3023	24	3020	0.2	3008	1	3010	9
3029	5	3026	63	3028	6	3030	292	3020	2	3019	2
3058	3	3028	64	3036	764	3030	31	3030	7	3030	7
3066	1	3057	10	3056	13	3058	6	3058	6	3056	7
3068	424	3065	1	3065	1	3067	1	3067	2	3066	2
3414	73	3418	71	3420	69	3424	81	3427	77	3429	76

[a] Bold indicates the region of the IR spectrum included in the present experimental study.

Table S10. Vibrational frequencies (cm^{-1}) scaled by 0.975 and IR intensities (kM/mole) for the [COOH] ctggg conformer of M^+(Met) calculated at B3LYP/6-311+G(d,p) (M^+ = Li^+, Na^+, and K^+) and B3LYP/HW*/6-311+G(d,p) (M^+ = Rb^+ and Cs^+) levels of theory[a]

Li^+(Met)		Na^+(Met)		K^+(Met)		Rb^+(Met)		Cs^+(Met)	
40	4	32	6	26	5	23	4	20	3
62	7	47	7	43	9	38	5	40	4
83	17	75	8	68	4	57	7	55	5
107	21	80	8	71	11	66	1	65	0.4
136	120	100	19	83	2	80	1	79	1
146	4	133	11	120	8	98	6	85	5
155	58	153	3	153	6	145	13	141	10
193	20	182	13	171	24	160	2	154	1
253	30	228	24	192	9	190	8	188	8
264	34	268	17	261	8	262	6	262	7
301	37	292	36	292	18	291	12	295	10
332	17	321	16	324	13	324	12	323	10
453	108	368	14	372	18	372	17	377	17
466	13	429	16	425	16	418	16	419	16
503	2	503	1	504	1	504	1	504	2
553	44	532	4	528	4	526	4	526	3
573	**4**	564	2	**561**	**2**	**559**	**2**	**557**	**2**
619	**3**	618	2	**619**	**2**	**619**	**2**	**617**	**3**
685	**2**	685	2	**685**	**2**	**686**	**2**	**686**	**2**
743	**5**	742	3	**738**	**4**	**736**	**4**	**735**	**5**
806	**15**	807	11	**805**	**11**	**805**	**10**	**804**	**11**
833	**8**	833	3	**830**	**3**	**829**	**4**	**828**	**5**
839	**2**	841	5	**843**	**6**	**843**	**6**	**844**	**6**
931	**24**	**920**	**58**	**917**	**68**	**913**	**77**	**910**	**82**
955	**5**	**952**	**3**	**951**	**4**	**953**	**39**	**951**	**41**
959	**56**	**954**	**51**	**953**	**47**	**953**	**8**	**953**	**4**
1001	**21**	**1000**	**16**	**1000**	**13**	**1001**	**13**	**999**	**27**
1026	**25**	**1021**	**18**	**1021**	**20**	**1011**	**62**	**1003**	**56**
1084	**24**	**1057**	**86**	**1034**	**83**	**1024**	**39**	**1025**	**31**
1117	**67**	**1091**	**9**	**1094**	**9**	**1095**	**9**	**1095**	**10**
1123	**123**	**1146**	**19**	**1150**	**6**	**1149**	**6**	**1150**	**7**
1158	**17**	**1150**	**23**	**1157**	**19**	**1160**	**17**	**1161**	**14**
1185	**17**	**1179**	**6**	**1180**	**7**	**1180**	**8**	**1179**	**9**
1254	**42**	**1252**	**37**	**1252**	**35**	**1252**	**34**	**1250**	**31**
1267	**5**	**1267**	**3**	**1268**	**1**	**1268**	**1**	**1268**	**0**
1307	**5**	**1307**	**4**	**1307**	**5**	**1307**	**5**	**1307**	**6**
1336	**3**	**1335**	**2**	**1333**	**1**	**1335**	**1**	**1335**	**1**
1348	**41**	**1351**	**26**	**1353**	**21**	**1353**	**18**	**1354**	**18**
1357	**24**	**1359**	**8**	**1361**	**6**	**1362**	**6**	**1364**	**5**
1384	**496**	**1394**	**466**	**1403**	**445**	**1404**	**434**	**1407**	**422**
1428	**6**	**1430**	**7**	**1429**	**5**	**1429**	**5**	**1429**	**5**
1432	**21**	**1434**	**19**	**1433**	**20**	**1433**	**20**	**1433**	**20**
1439	**16**	**1440**	**18**	**1443**	**14**	**1441**	**16**	**1442**	**17**
1441	**15**	**1442**	**11**	**1443**	**14**	**1443**	**10**	**1444**	**9**

1609	**28**	**1613**	**25**	**1616**	**24**	**1616**	**23**	**1615**	**24**
1696	**496**	**1724**	**428**	**1733**	**420**	**1743**	**399**	**1747**	**387**
2444	663	2779	658	2902	633	2961	3	2961	2
2965	5	2962	6	2962	9	2968	12	2968	14
2970	12	2969	13	2969	15	2972	48	2971	18
2974	8	2973	10	2972	11	2975	6	2977	8
2975	11	2975	13	2975	15	2983	552	3003	1
3009	5	3007	7	3005	10	3005	22	3019	350
3021	9	3020	11	3020	13	3019	18	3022	251
3052	6	3050	7	3049	7	3048	7	3048	8
3063	1	3062	2	3061	2	3061	2	3060	2
3283	244	3312	191	3329	166	3335	159	3345	134
3483	61	3489	54	3492	51	3492	48	3495	47

[a] Bold indicates the region of the IR spectrum included in the present experimental study.

Table S11. Vibrational frequencies (cm^{-1}) scaled by 0.975 and IR intensities (kM/mole) for the [COOH] cgtgg and ctggt conformers of M^+(Met) calculated at B3LYP/6-311+G(d,p) ($M^+ = K^+$) and B3LYP/HW*/6-311+G(d,p) ($M^+ = Rb^+$ and Cs^+)[a]

[COOH] cgtgg						[COOH] ctggt					
K^+(Met)		Rb^+(Met)		Cs^+(Met)		K^+(Met)		Rb^+(Met)		Cs^+(Met)	
31	3	29	1	28	2	27	3	22	1	16	1
50	6	43	4	39	3	48	2	47	2	38	2
53	6	51	4	50	2	59	8	53	5	46	7
68	13	63	7	63	6	67	15	57	10	51	4
99	3	89	3	81	4	91	2	88	1	84	2
132	15	108	9	101	5	129	9	103	7	87	5
137	11	131	8	130	8	138	17	132	11	132	11
165	4	161	4	159	4	172	4	170	4	169	1
197	11	195	9	193	8	187	13	175	5	173	6
221	13	209	2	206	1	210	4	208	1	206	1
302	5	300	3	299	3	285	23	285	16	287	14
351	6	349	1	348	10	325	17	325	15	323	14
355	26	357	27	350	10	368	18	367	17	367	17
391	12	385	14	370	18	412	8	404	8	399	7
431	1	431	1	430	1	511	1	512	1	512	1
540	5	537	3	536	4	528	5	526	4	524	4
623	**2**	**623**	**1**	**622**	**2**	**562**	**2**	**561**	**2**	**558**	**2**
632	**4**	**633**	**5**	**631**	**4**	**644**	**0.3**	**645**	**0.4**	**644**	**0.4**
687	**2**	**687**	**2**	**689**	**2**	**693**	**3**	**693**	**3**	**693**	**3**
726	**5**	**724**	**5**	**724**	**5**	**741**	**4**	**739**	**4**	**737**	**5**
790	**1**	**791**	**1**	**790**	**1**	**805**	**6**	**805**	**6**	**805**	**6**
850	**12**	**849**	**13**	**849**	**16**	**835**	**7**	**835**	**8**	**833**	**10**
878	**1**	**877**	**1**	**876**	**1**	**870**	**4**	**872**	**4**	**870**	**3**
937	**5**	**936**	**8**	**937**	**9**	**923**	**91**	**920**	**97**	**915**	**105**
952	**27**	**952**	**42**	**951**	**61**	**948**	**22**	**948**	**21**	**947**	**19**
965	**87**	**964**	**75**	**961**	**60**	**966**	**5**	**965**	**5**	**964**	**4**
983	**19**	**982**	**18**	**982**	**22**	**998**	**4**	**998**	**4**	**997**	**16**

1018	**20**	**1015**	**18**	**1007**	**42**	**1019**	**35**	**1012**	**52**	**1001**	**53**
1035	**82**	**1025**	**80**	**1022**	**47**	**1038**	**75**	**1022**	**55**	**1020**	**39**
1081	**7**	**1081**	**9**	**1082**	**9**	**1097**	**6**	**1098**	**6**	**1097**	**6**
1123	**7**	**1123**	**9**	**1124**	**10**	**1133**	**5**	**1133**	**7**	**1133**	**7**
1172	**27**	**1171**	**24**	**1172**	**22**	**1158**	**21**	**1158**	**15**	**1159**	**12**
1206	**2**	**1206**	**1**	**1205**	**1**	**1174**	**10**	**1175**	**12**	**1175**	**13**
1262	**15**	**1262**	**16**	**1263**	**21**	**1255**	**40**	**1255**	**39**	**1254**	**39**
1271	**35**	**1272**	**30**	**1270**	**24**	**1265**	**7**	**1263**	**5**	**1262**	**3**
1306	**5**	**1305**	**5**	**1305**	**4**	**1304**	**4**	**1303**	**4**	**1304**	**5**
1329	**16**	**1330**	**14**	**1331**	**13**	**1334**	**3**	**1334**	**3**	**1333**	**3**
1334	**0**	**1335**	**0**	**1335**	**1**	**1356**	**18**	**1356**	**15**	**1356**	**13**
1352	**3**	**1353**	**3**	**1354**	**3**	**1358**	**5**	**1360**	**5**	**1361**	**6**
1403	**497**	**1410**	**480**	**1406**	**469**	**1403**	**442**	**1405**	**428**	**1405**	**415**
1425	**7**	**1424**	**6**	**1426**	**6**	**1432**	**13**	**1432**	**13**	**1432**	**13**
1434	**12**	**1434**	**12**	**1434**	**12**	**1440**	**22**	**1441**	**18**	**1440**	**20**
1442	**11**	**1442**	**11**	**1442**	**11**	**1441**	**10**	**1442**	**14**	**1441**	**12**
1449	**12**	**1449**	**12**	**1449**	**10**	**1453**	**6**	**1454**	**6**	**1453**	**6**
1634	**18**	**1634**	**19**	**1635**	**19**	**1621**	**22**	**1624**	**23**	**1622**	**23**
1735	**490**	**1745**	**467**	**1749**	**457**	**1733**	**424**	**1743**	**402**	**1746**	**393**
2902	695	2952	22	2954	2	2892	635	2953	8	2954	18
2953	12	2961	405	2965	5	2952	32	2962	29	2962	3
2967	12	2966	30	2966	28	2963	16	2966	20	2965	21
2967	19	2968	238	2974	9	2967	20	2972	501	2975	11
2976	8	2975	9	3002	133	2976	8	2977	99	3007	13
3002	13	3001	17	3006	531	3007	11	3008	13	3012	37
3022	6	3022	7	3021	7	3012	7	3013	13	3018	561
3046	8	3046	9	3044	9	3047	7	3045	7	3044	8
3060	2	3060	2	3059	3	3063	2	3061	3	3061	3
3337	189	3344	174	3350	164	3327	182	3334	166	3343	148
3468	47	3468	46	3472	46	3490	55	3491	52	3492	51

[a] Bold indicates the region of the IR spectrum included in the present experimental study.

Table S12. Vibrational frequencies (cm^{-1}) scaled by 0.975 and IR intensities (kM/mole) for the [COOH,S] cgggg conformer of M^+(Met) calculated at B3LYP/6-311+G(d,p) ($M^+ = Li^+$, Na^+, and K^+) and B3LYP/HW*/6-311+G(d,p) ($M^+ = Rb^+$ and Cs^+) levels of theory[a]

Na^+(Met)		K^+(Met)		Rb^+(Met)		Cs^+(Met)	
49	5	45	3	37	5	29	5
82	1	62	4	41	4	35	1
93	13	63	15	51	3	50	4
106	14	80	10	69	6	70	4
124	15	101	2	88	0.4	83	1
142	1	124	2	110	4	100	6
166	1	161	4	138	10	127	5
180	6	169	16	154	0.3	152	0.2
219	20	188	10	180	2	180	2
243	30	218	12	217	11	219	10

287	1	287	14	275	20	266	19
301	23	291	6	287	1	290	1
330	16	331	18	327	17	329	17
378	1	381	1	375	2	376	2
460	2	464	3	462	2	466	2
534	4	531	4	530	4	530	4
603	3	**610**	**2**	**612**	**2**	**611**	**2**
636	6	**624**	**6**	**622**	**6**	**619**	**5**
682	3	**683**	**3**	**684**	**2**	**686**	**2**
718	11	**716**	**11**	**715**	**11**	**714**	**12**
799	14	**794**	**14**	**791**	**14**	**789**	**13**
820	2	**821**	**3**	**821**	**4**	**821**	**3**
862	43	**858**	**52**	**856**	**56**	**854**	**61**
905	**38**	**905**	**34**	**905**	**37**	**905**	**40**
930	**66**	**929**	**64**	**920**	**74**	**918**	**72**
953	**68**	**949**	**66**	**946**	**58**	**944**	**50**
956	**17**	**954**	**12**	**953**	**8**	**951**	**8**
983	**12**	**982**	**8**	**981**	**6**	**980**	**4**
1011	**4**	**1017**	**6**	**1016**	**6**	**1021**	**7**
1070	**14**	**1072**	**14**	**1071**	**14**	**1072**	**15**
1131	**16**	**1130**	**16**	**1129**	**18**	**1131**	**17**
1167	**9**	**1161**	**9**	**1160**	**8**	**1159**	**9**
1216	**3**	**1214**	**2**	**1213**	**1**	**1213**	**1**
1232	**11**	**1230**	**10**	**1230**	**9**	**1230**	**9**
1289	**24**	**1287**	**23**	**1287**	**23**	**1287**	**22**
1314	**8**	**1314**	**4**	**1316**	**5**	**1317**	**3**
1327	**9**	**1327**	**11**	**1328**	**10**	**1328**	**10**
1337	**1**	**1336**	**1**	**1336**	**1**	**1335**	**3**
1354	**75**	**1352**	**46**	**1355**	**44**	**1356**	**34**
1378	**274**	**1380**	**308**	**1383**	**308**	**1386**	**316**
1428	**4**	**1429**	**3**	**1427**	**5**	**1428**	**5**
1432	**16**	**1434**	**16**	**1432**	**15**	**1432**	**15**
1442	**19**	**1444**	**20**	**1442**	**20**	**1443**	**19**
1445	**14**	**1445**	**11**	**1445**	**10**	**1445**	**9**
1624	**57**	**1625**	**58**	**1623**	**59**	**1623**	**60**
1753	**306**	**1756**	**317**	**1763**	**317**	**1764**	**318**
2963	6	2961	7	2957	9	2956	10
2975	9	2971	12	2969	14	2968	16
2985	5	2982	6	2979	8	2978	8
2989	4	2986	6	2984	8	2982	10
3020	3	3018	3	3016	3	3015	3
3033	3	3029	5	3027	6	3026	8
3062	1	3056	4	3053	5	3050	5
3063	3	3058	3	3056	4	3054	4
3172	412	3178	431	3200	415	3212	416
3429	15	3433	12	3433	10	3435	9
3499	26	3503	25	3503	23	3504	23

[a] Bold indicates the region of the IR spectrum included in the present experimental study.

Table S13. Vibrational frequencies (cm^{-1}) scaled by 0.975 and IR intensities (kM/mole) for the [[COOH,S] cgggt and cgcgg conformers of M^+(Met) calculated at B3LYP/6-311+G(d,p) (M^+ = K^+) and B3LYP/HW*/6-311+G(d,p) (M^+ = Rb^+ and Cs^+)[a]

[COOH,S] cgggt						[COOH,S] cgcgg					
K^+(Met)		Rb^+(Met)		Cs^+(Met)		K^+(Met)		Rb^+(Met)		Cs^+(Met)	
45	5	24	1	15	3	51	9	40	8	35	7
50	3	41	8	26	8	59	8	47	7	42	5
61	9	46	5	47	3	68	11	55	0.3	55	0.2
74	20	54	5	55	2	86	7	74	3	69	2
99	4	81	2	83	4	95	1	86	1	83	1
105	1	100	1	94	1	115	3	101	2	94	2
156	3	140	14	123	11	165	0.3	146	12	131	9
172	11	161	1	152	1	179	14	154	1	154	1
184	17	175	2	174	2	181	19	176	8	173	7
228	0.3	229	0.3	237	1	224	8	222	7	222	6
251	8	253	3	271	11	308	4	303	11	301	12
273	19	262	19	306	11	316	12	310	3	310	2
328	22	329	19	327	14	323	12	320	16	321	16
378	0.2	375	1	366	4	350	13	347	9	346	9
477	3	487	3	514	5	435	2	435	2	434	2
532	6	532	5	534	7	531	5	529	4	527	4
610	**4**	**590**	**4**	**555**	**4**	**619**	**4**	**622**	**4**	**624**	**4**
634	**1**	**636**	**1**	**642**	**2**	**645**	**5**	**641**	**5**	**640**	**5**
686	**3**	**688**	**2**	**690**	**2**	**688**	**3**	**687**	**3**	**688**	**2**
727	**11**	**724**	**10**	**721**	**9**	**714**	**13**	**713**	**14**	**712**	**14**
798	**14**	**794**	**11**	**788**	**17**	**772**	**4**	**769**	**4**	**768**	**5**
829	**8**	**822**	**23**	**812**	**62**	**818**	**5**	**815**	**5**	**814**	**6**
869	**71**	**864**	**70**	**863**	**52**	**873**	**88**	**866**	**90**	**866**	**90**
909	**13**	**910**	**7**	**907**	**85**	**909**	**92**	**898**	**98**	**897**	**98**
933	**74**	**923**	**86**	**919**	**7**	**934**	**6**	**934**	**3**	**935**	**4**
953	**32**	**948**	**38**	**941**	**36**	**957**	**11**	**955**	**9**	**953**	**6**
961	**26**	**960**	**11**	**957**	**1**	**965**	**34**	**965**	**29**	**965**	**30**
968	**6**	**965**	**1**	**966**	**7**	**996**	**6**	**995**	**7**	**995**	**7**
1032	**5**	**1040**	**6**	**1053**	**8**	**1016**	**13**	**1018**	**13**	**1018**	**12**
1071	**8**	**1077**	**8**	**1088**	**11**	**1057**	**10**	**1058**	**11**	**1058**	**12**
1126	**8**	**1123**	**4**	**1114**	**1**	**1125**	**9**	**1125**	**10**	**1125**	**10**
1166	**12**	**1167**	**15**	**1176**	**10**	**1181**	**11**	**1178**	**10**	**1178**	**11**
1209	**2**	**1206**	**4**	**1195**	**9**	**1218**	**4**	**1216**	**4**	**1217**	**3**
1230	**17**	**1227**	**17**	**1214**	**11**	**1240**	**2**	**1239**	**1**	**1240**	**1**
1287	**24**	**1286**	**22**	**1280**	**11**	**1288**	**24**	**1285**	**25**	**1286**	**25**
1312	**3**	**1310**	**5**	**1302**	**13**	**1308**	**15**	**1310**	**18**	**1309**	**16**
1332	**14**	**1336**	**4**	**1337**	**1**	**1321**	**1**	**1322**	**3**	**1323**	**3**
1339	**1**	**1343**	**10**	**1353**	**9**	**1338**	**2**	**1336**	**2**	**1335**	**1**
1355	**32**	**1357**	**22**	**1364**	**11**	**1355**	**20**	**1353**	**25**	**1353**	**19**
1386	**325**	**1389**	**345**	**1385**	**374**	**1378**	**353**	**1374**	**348**	**1377**	**352**
1429	**11**	**1430**	**11**	**1429**	**11**	**1428**	**4**	**1426**	**5**	**1426**	**5**
1442	**16**	**1442**	**11**	**1440**	**17**	**1434**	**17**	**1433**	**15**	**1432**	**15**
1444	**18**	**1442**	**22**	**1443**	**13**	**1444**	**11**	**1443**	**11**	**1443**	**11**

1452	**9**	**1451**	**7**	**1456**	**6**	**1451**	**7**	**1454**	**6**	**1454**	**6**
1624	**58**	**1621**	**57**	**1621**	**42**	**1624**	**46**	**1625**	**45**	**1624**	**45**
1750	**325**	**1756**	**322**	**1753**	**324**	**1752**	**311**	**1757**	**306**	**1758**	**310**
2968	11	2960	20	2954	21	2954	10	2953	12	2951	12
2971	15	2968	15	2966	8	2972	13	2971	14	2969	14
2972	11	2969	10	2968	19	2974	5	2972	7	2970	9
2982	4	2981	5	2976	8	2991	3	2990	3	2988	4
3017	2	3011	6	3008	7	3001	14	3001	17	2999	18
3022	6	3019	5	3021	5	3045	1	3044	2	3044	2
3054	3	3050	4	3049	5	3056	4	3053	5	3051	6
3061	3	3059	4	3060	4	3062	2	3059	3	3058	3
3179	425	3195	417	3238	392	3219	394	3267	364	3269	365
3437	11	3441	7	3440	4	3427	11	3428	9	3428	8
3507	28	3512	31	3516	29	3499	22	3500	21	3501	20

[a] Bold indicates the region of the IR spectrum included in the present experimental study.

Table S14. Vibrational frequencies (cm^{-1}) scaled by 0.975 and IR intensities (kM/mole) for H^+(Met) [N,CO,S] conformers calculated at B3LYP/6-311+G(d,p) levels of theory[a]

[N,CO,S]tgtgg		[N,CO,S]tgggg		[N,CO,S]tgtgt		[N,CO,S]tgggt	
44	5	47	2	39	2	35	2
63	1	67	1	63	0.2	58	1
92	6	79	1	76	5	92	4
147	2	125	1	147	2	143	3
160	7	151	0.5	166	3	157	2
185	1	230	35	189	14	213	19
214	11	256	3	198	3	238	15
281	10	281	18	251	5	275	20
321	29	299	25	308	43	294	17
337	27	341	6	320	6	327	5
355	2	374	3	360	15	376	9
424	46	474	40	426	46	474	42
494	30	496	30	496	25	502	31
586	**63**	**560**	**16**	**588**	**63**	**560**	**18**
617	**2**	**612**	**10**	**633**	**28**	**633**	**13**
639	**45**	**639**	**71**	**642**	**21**	**637**	**65**
678	**12**	**679**	**8**	**683**	**9**	**683**	**6**
711	**44**	**705**	**45**	**710**	**47**	**705**	**47**
790	**6**	**799**	**22**	**798**	**7**	**803**	**24**
836	**1**	**827**	**16**	**851**	**2**	**838**	**25**
863	**61**	**842**	**16**	**866**	**56**	**853**	**3**
933	**8**	**928**	**6**	**938**	**9**	**939**	**1**
957	**3**	**954**	**3**	**957**	**7**	**959**	**15**
970	**14**	**957**	**9**	**974**	**3**	**964**	**4**
1002	**8**	**994**	**10**	**1002**	**17**	**985**	**14**
1024	**33**	**1051**	**40**	**1029**	**28**	**1055**	**27**
1083	**8**	**1093**	**42**	**1075**	**2**	**1091**	**48**

1122	**30**	**1123**	**65**	**1116**	**35**	**1129**	**66**
1160	**279**	**1156**	**109**	**1161**	**267**	**1147**	**21**
1194	**3**	**1169**	**75**	**1181**	**14**	**1162**	**158**
1240	**13**	**1238**	**24**	**1246**	**13**	**1244**	**20**
1260	**8**	**1275**	**12**	**1257**	**4**	**1273**	**17**
1302	**15**	**1305**	**1**	**1298**	**20**	**1305**	**4**
1328	**41**	**1321**	**14**	**1331**	**38**	**1322**	**13**
1336	**2**	**1336**	**1**	**1337**	**6**	**1338**	**4**
1359	**3**	**1352**	**11**	**1360**	**3**	**1356**	**9**
1391	**40**	**1390**	**48**	**1390**	**42**	**1392**	**41**
1425	**8**	**1431**	**5**	**1429**	**10**	**1431**	**11**
1432	**8**	**1434**	**17**	**1438**	**15**	**1439**	**15**
1438	**10**	**1439**	**11**	**1446**	**12**	**1444**	**17**
1446	**21**	**1445**	**22**	**1451**	**13**	**1454**	**12**
1471	**173**	**1477**	**190**	**1477**	**162**	**1484**	**191**
1600	**15**	**1580**	**5**	**1599**	**28**	**1579**	**4**
1620	**6**	**1628**	**8**	**1620**	**4**	**1628**	**8**
1770	**285**	**1768**	**263**	**1771**	**290**	**1767**	**258**
2729	1195	2713	1177	2745	1227	2704	1229
2964	3	2973	2	2962	1	2971	2
2977	8	2976	12	2975	15	2978	12
2984	4	2987	5	2978	4	2982	7
3008	1	3003	0	3013	0	3004	1
3021	1	3014	2	3023	1	3021	1
3034	1	3035	2	3034	2	3036	2
3063	4	3061	4	3067	3	3069	2
3070	1	3069	1	3072	1	3072	1
3264	133	3228	145	3266	140	3242	126
3392	90	3416	99	3393	84	3413	106
3630	181	3630	179	3631	183	3632	173

[a] Bold indicates the region of the IR spectrum included in the present experimental study.

Table S15. Vibrational frequencies (cm^{-1}) scaled by 0.975 and IR intensities (kM/mole) for H^+(Met) [N,OH,S] conformers calculated at B3LYP/6-311+G(d,p) levels of theory[a]

[N,OH,S]tgtgg		[N,OH,S]ttggg		[N,OH,S]tgtgt		[N,OH,S]ttggt	
22	1	48	2	22	2	36	3
44	7	53	3	41	3	46	2
80	4	82	1	66	7	77	5
146	10	134	3	140	4	150	2
152	3	157	0.4	164	14	159	3
193	2	234	37	188	1	209	20
214	9	257	7	195	3	237	18
280	8	289	4	252	2	281	3
313	23	304	13	306	36	300	8
341	17	341	10	324	2	333	10
361	3	362	2	362	13	366	13
423	27	472	34	426	25	471	29

496	14	505	24	495	12	508	30
560	33	520	15	561	37	521	14
612	**9**	**609**	**7**	**627**	**85**	**624**	**57**
631	**74**	**624**	**82**	**635**	**2**	**632**	**30**
677	**17**	**678**	**13**	**683**	**11**	**682**	**8**
702	**46**	**697**	**40**	**701**	**50**	**696**	**43**
784	**8**	**791**	**20**	**793**	**11**	**794**	**25**
825	**2**	**819**	**11**	**837**	**0.3**	**835**	**5**
855	**27**	**836**	**5**	**857**	**26**	**838**	**4**
928	**4**	**921**	**5**	**932**	**7**	**937**	**1**
955	**4**	**945**	**9**	**956**	**8**	**948**	**15**
967	**15**	**958**	**3**	**972**	**2**	**961**	**8**
995	**8**	**992**	**14**	**994**	**18**	**980**	**10**
1021	**28**	**1049**	**20**	**1026**	**30**	**1053**	**8**
1070	**105**	**1078**	**138**	**1066**	**49**	**1076**	**143**
1101	**194**	**1105**	**121**	**1094**	**230**	**1107**	**131**
1160	**96**	**1150**	**93**	**1156**	**102**	**1147**	**44**
1196	**6**	**1171**	**13**	**1185**	**15**	**1153**	**41**
1235	**29**	**1239**	**33**	**1242**	**29**	**1246**	**32**
1272	**4**	**1279**	**14**	**1270**	**2**	**1276**	**9**
1300	**21**	**1295**	**22**	**1298**	**19**	**1291**	**32**
1309	**46**	**1320**	**12**	**1309**	**54**	**1323**	**8**
1335	**1**	**1339**	**1**	**1336**	**4**	**1338**	**5**
1357	**0**	**1348**	**1**	**1360**	**1**	**1352**	**1**
1361	**14**	**1371**	**5**	**1362**	**14**	**1372**	**5**
1425	**11**	**1430**	**6**	**1428**	**10**	**1430**	**11**
1431	**11**	**1432**	**22**	**1438**	**15**	**1436**	**23**
1440	**8**	**1438**	**13**	**1443**	**12**	**1439**	**16**
1443	**19**	**1442**	**20**	**1449**	**10**	**1457**	**8**
1485	**121**	**1486**	**154**	**1488**	**115**	**1489**	**152**
1604	**23**	**1591**	**28**	**1600**	**33**	**1592**	**24**
1614	**24**	**1625**	**15**	**1614**	**34**	**1622**	**33**
1818	**296**	**1816**	**255**	**1817**	**295**	**1816**	**250**
2687	1218	2671	1178	2734	1184	2708	1146
2959	5	2970	6	2958	3	2970	6
2975	9	2975	13	2977	14	2979	8
2986	4	2996	2	2979	3	2992	5
3002	1	2997	1	3005	1	2995	1
3014	1	3015	1	3019	1	3021	1
3037	1	3044	1	3036	2	3043	2
3060	4	3060	4	3068	2	3069	2
3070	0.4	3070	0.4	3073	1	3073	1
3353	87	3333	103	3350	90	3336	97
3407	80	3409	85	3405	81	3405	93
3633	176	3636	178	3633	178	3637	170

[a] Bold indicates the region of the IR spectrum included in the present experimental study.