Supporting Information for

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

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Figure Captions

Figure S1: Infrared multiple photon dissociation action spectra of M^+(Gly) complexes where M^+ = K^+, Rb^+, and Cs^+ taken on the FTICR (black trace) and QIT (red trace).

Figure S2. Relative Gibbs energies (kJ/mol) at 298 K calculated at the Level/6-311+G(2d,2p) or Level/def2TZVPP level of theory for six distinct structures of M^+(Gly), where M^+ = Li^+, Na^+, K^+, Rb^+, and Cs^+ as a function of the alkali-metal cation relative to the energy of the most stable structure. Level includes B3LYP, B3LYP-GD3BJ, B3P86, and MP2(full).

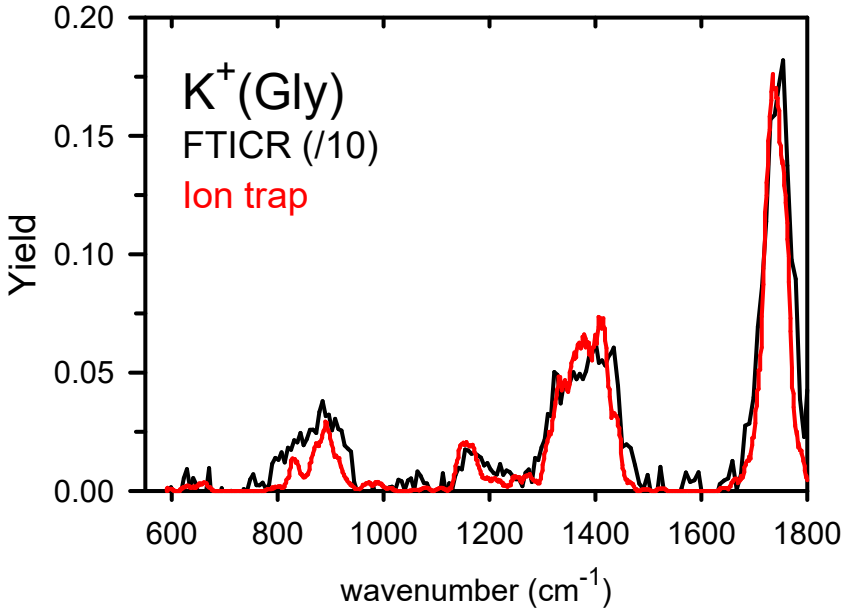
Figure S3: Relaxed potential energy surface scans of the MOC bond angle in M^+(Gly) calculated at the B3LYP, B3LYP-GD3BJ, and MP2(full) levels of theory for M = Li, Na, K (6-311+G(d,p) basis set) and M = Rb, Cs (def2TZVP basis set). Horizontal lines indicate the relative energies including zero-point energies of the stationary states.

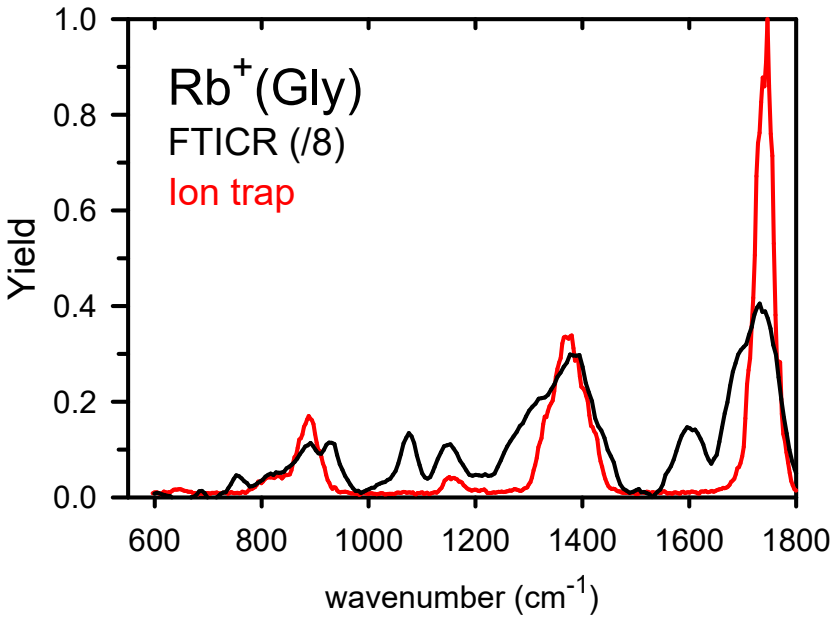
Figure S4: Comparison of the experimental IRMPD action spectrum for Rb^+(Gly) and Cs^+(Gly) (dashed line) with harmonic IR spectra for five structures predicted at the B3LYP/def2TZVP level except for [CO,OH]cc, which were calculated at the MP2/def2TZVP level. Relative Gibbs energies (kJ/mol) at 298 K are provided at the B3LYP, B3LYP-GD3BJ, B3P86, and MP2 levels.

Table S1: 0 K Relative Gibbs Energies (kJ/mol) of Low-Lying Conformers of M^+(Gly) Calculated at B3LYP, B3LYP-GD3BJ, B3P86, and MP2(full) Levels of Theory[a]

Structure	Li^+(Gly)	Na^+(Gly)	K^+(Gly)	Rb^+(Gly)	Cs^+(Gly)
[N,CO]tt	**0.0, 0.0, 0.0, 0.0**	**0.0, 0.0, 0.0, 0.0**	3.9, 0.2, 6.4, 2.8 (1.4)	7.8, 4.1, 10.7, 6.4	11.3, 7.5, 13.4, 7.9
[CO_2^-]cc	21.5.0, 23.7, 18.6, 17.0	10.5, 13.5, 7.4, 7.6	12.1, 11.1, 10.9, 9.9	19.4, 18.3, 17.6, 14.5	22.0, 20.5, 19.3, 14.4
[N,CO]ct	22.3, 21.8, 22.2, 22.7	21.5, 21.2, 21.3, 21.8	23.8, 19.9, 26.4, 23.2	26.9, 23.0, 29.6, 26.5	28.9, 25.1, 31.0, 26.2
[CO]cc	29.2, 31.5, 25.6, 32.2	10.4, 13.7, 6.2, 11.8	**0.0,** 0.1, **0.0,** 2.6 (2.1)	**0.0, 0.0, 0.0**, 2.1 (0.8)	**0.0, 0.0, 0.0**, 0.7 (**0.0**)
[CO,OH]cc	41.3,[b] 41.9,[b] 35.8,[b] 38.4[b]	10.7, 13.7, 6.5, 9.1	0.6, **0.0**, 0.3, **0.0 (0.0)**	4.2,[b] 0.1,[b] 2.4,[b] **0.0**[b] (**0.0**)	4.7,[b] 0.4,[b] 2.7,[b] **0.0**[b] (0.6)
[N,OH]tc	45.5, 43.2, 47.7, 39.1	41.3, 39.4, 42.9, 35.7	41.9, 36.0, 45.8, 35.7	45.0, 39.1, 49.1, 39.3	47.6, 41.5, 51.0, 40.8
[CO]tc	70.6, 73.5, 71.0, 75.7	49.0, 53.1, 48.5, 51.6	35.3, 36.0, 39.0, 38.8	36.7, 40.2,[c] 41.2, 40.1	33.2, 33.7, 37.3, 36.2
[CO]ct	72.5, 75.1, 72.5, 77.3	50.0, 53.7, 49.4, 52.6	37.4, 37.7, 40.9, 40.7	36.3, 36.5, 39.7, 41.2	34.8, 35.0, 38.5, 37.5
[N]tt	87.0, 86.9, 84.4, 81.8	61.5, 62.5, 60.0, 57.6	50.6, 48.0, 52.8, 47.5	49.1, 46.7, 51.7, 47.1	47.9, 45.1, 50.3, 47.0

[a] B3LYP, B3LYP-GD3BJ, B3P86, and MP2 (full) (CCSD(T,full)) values calculated using the 6-311+G(2d,2p) or def2-TZVPP basis set with the structures and zero-point energies calculated at the B3LYP/6-311+G(d,p) or B3LYP/def2-TZVP level of theory. Bold indicates the ground state. [b] Collapses to [CO]cc. Values are single point calculations using MP2(full)/6-311+G(d,p) or MP2(full)/def2-TZVP structures and zero-point energies. [c] Collapses to [N,CO]tt. Value is single point calculation using B3LYP/def2-TZVP structure and zero-point energy.


K+(Gly)
FTICR (/10)
Ion trap
Yield
wavenumber (cm-1)


Rb+(Gly)
FTICR (/8)
Ion trap
Yield
wavenumber (cm-1)

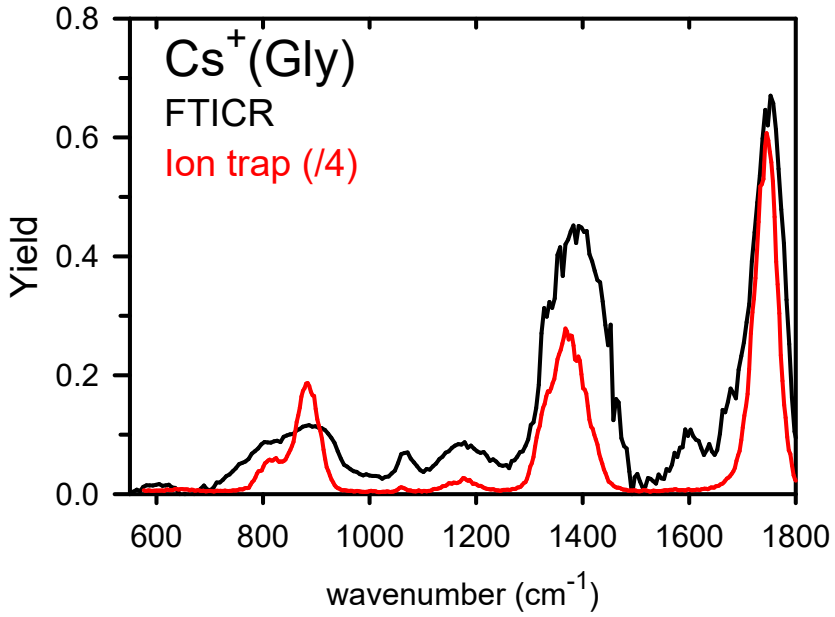

Cs+(Gly)
FTICR
Ion trap (/4)
Yield
wavenumber (cm-1)

Figure S1

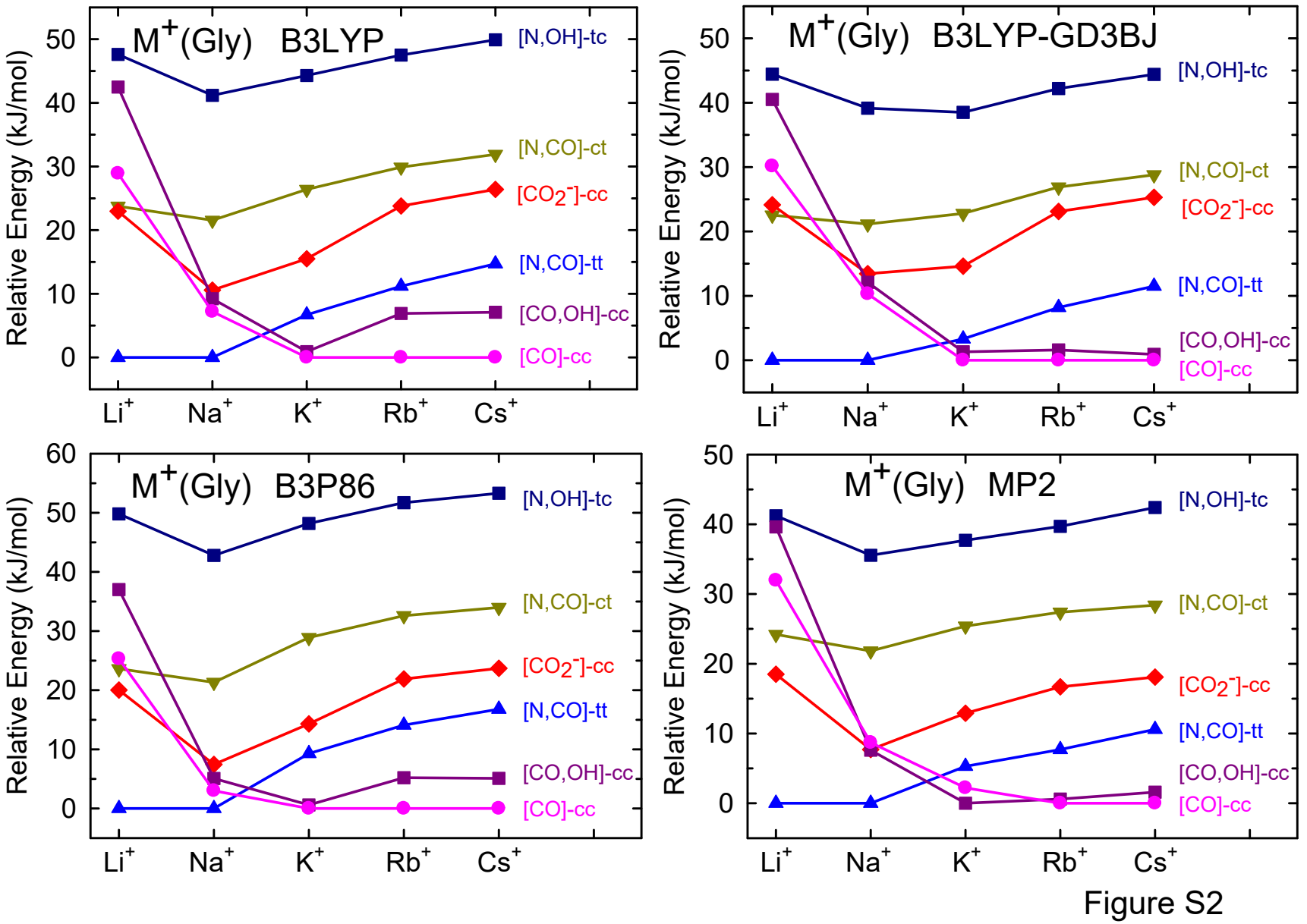

M+(Gly) B3LYP
M+(Gly) B3LYP-GD3BJ
M+(Gly) B3P86
M+(Gly) MP2
Relative Energy (kJ/mol)
[N,OH]-tc
[N,CO]-ct
[CO2-]-cc
[N,CO]-tt
[CO,OH]-cc
[CO]-cc
Li+
Na+
K+
Rb+
Cs+

Figure S2

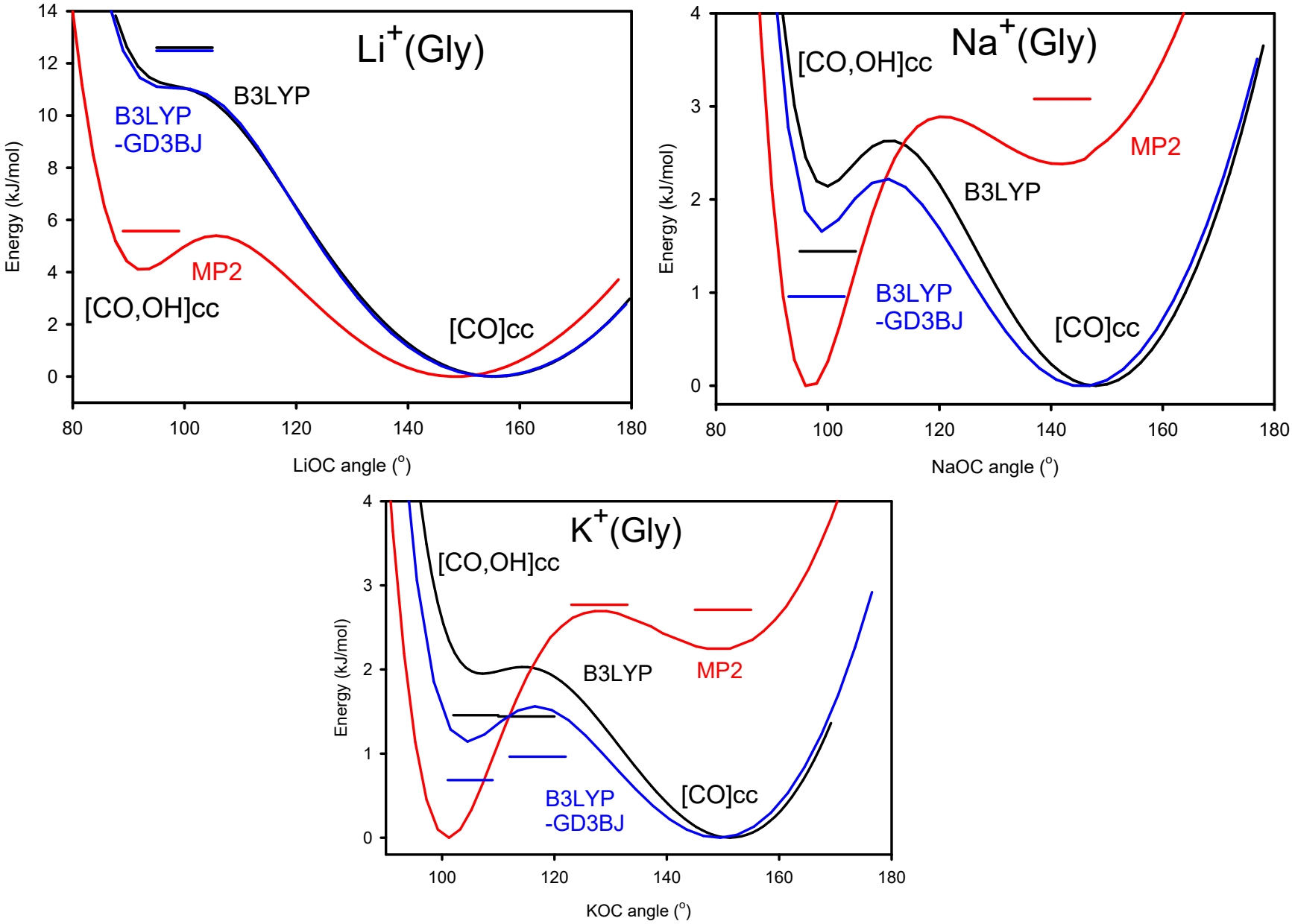

Li+(Gly)
B3LYP
B3LYP
-GD3BJ
MP2
[CO,OH]cc
[CO]cc
Energy (kJ/mol)
LiOC angle (°)
Na+(Gly)
[CO,OH]cc
MP2
B3LYP
B3LYP
-GD3BJ
[CO]cc
Energy (kJ/mol)
NaOC angle (°)
K+(Gly)
[CO,OH]cc
B3LYP
MP2
B3LYP
-GD3BJ
[CO]cc
Energy (kJ/mol)
KOC angle (°)

Figure S3

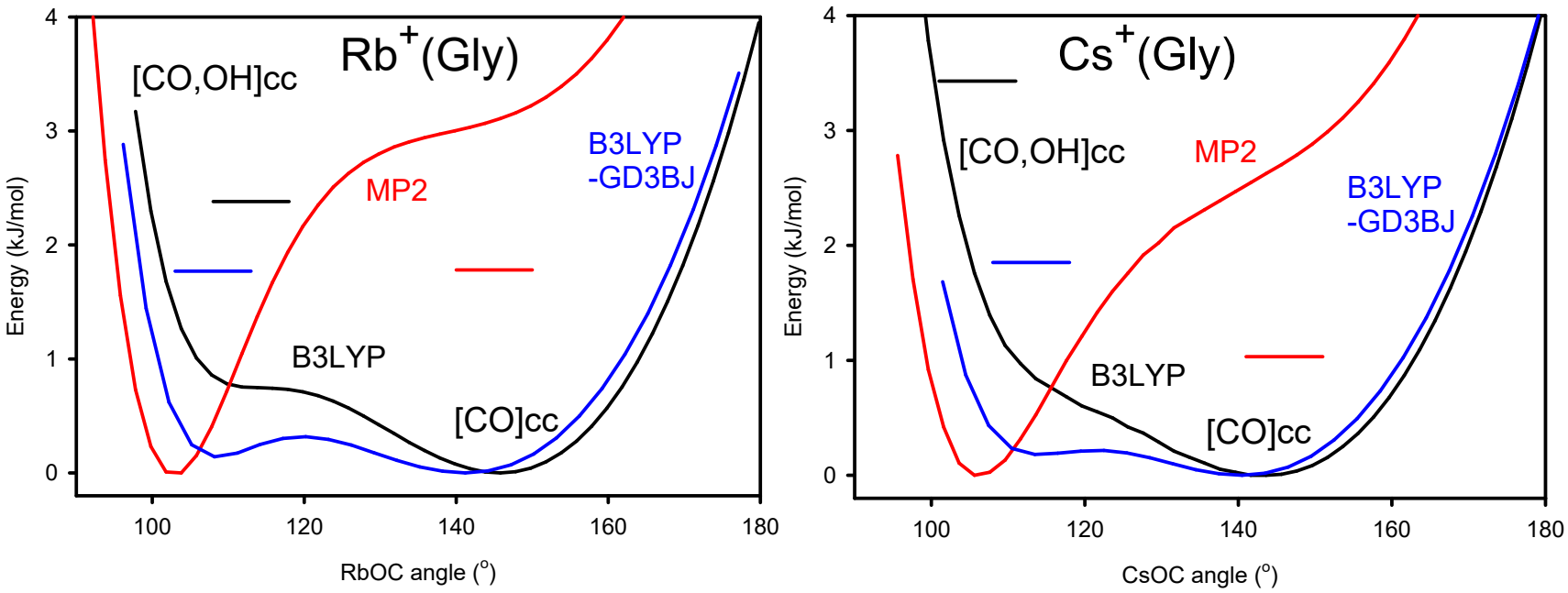

Rb+(Gly)
[CO,OH]cc
MP2
B3LYP
-GD3BJ
B3LYP
[CO]cc
Energy (kJ/mol)
RbOC angle (°)
Cs+(Gly)
[CO,OH]cc
MP2
B3LYP
-GD3BJ
B3LYP
[CO]cc
Energy (kJ/mol)
CsOC angle (°)

Figure S3

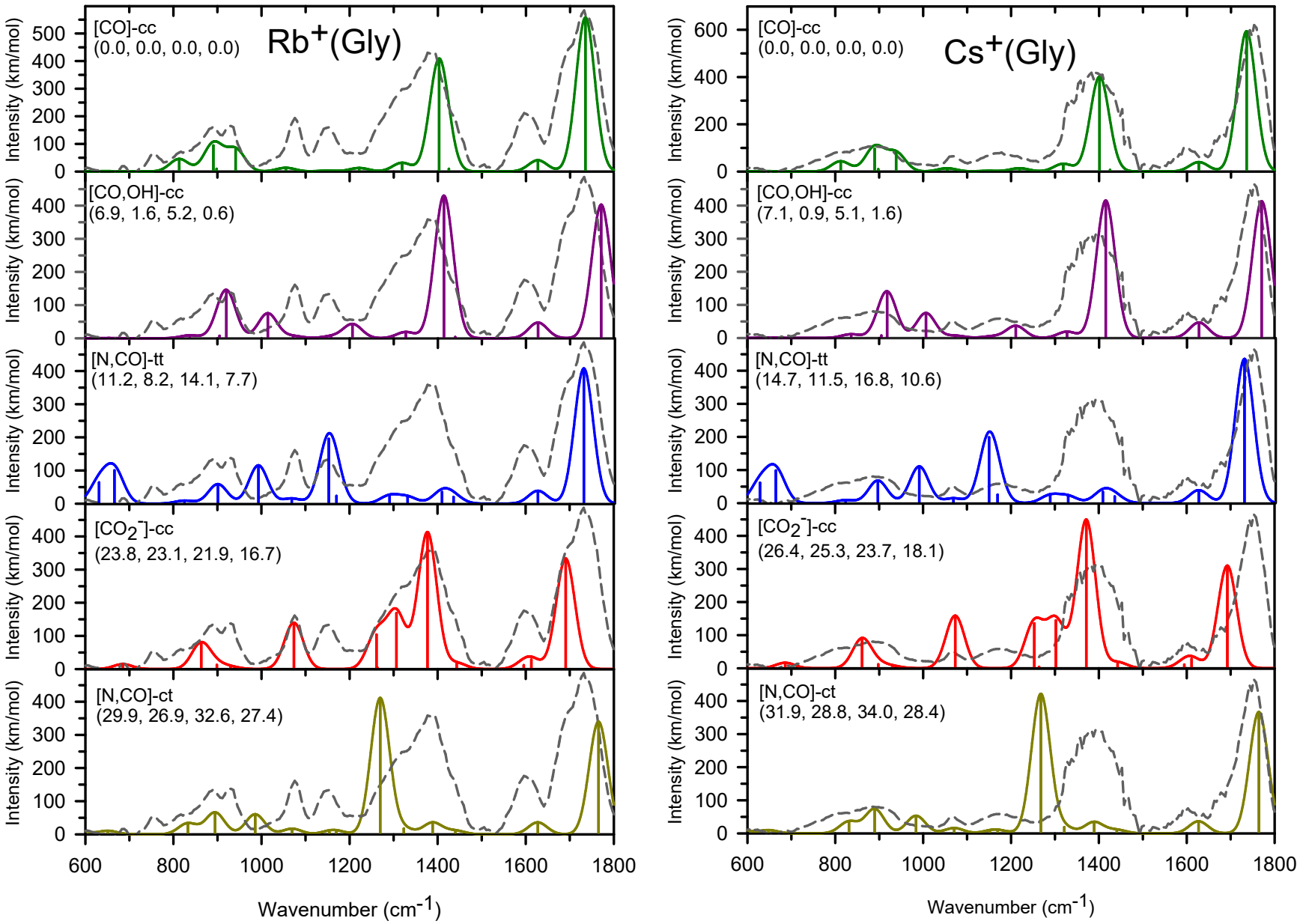

Rb+(Gly)
Cs+(Gly)
[CO]-cc
(0.0, 0.0, 0.0, 0.0)
[CO,OH]-cc
(6.9, 1.6, 5.2, 0.6)
(7.1, 0.9, 5.1, 1.6)
[N,CO]-tt
(11.2, 8.2, 14.1, 7.7)
(14.7, 11.5, 16.8, 10.6)
[CO2-]-cc
(23.8, 23.1, 21.9, 16.7)
(26.4, 25.3, 23.7, 18.1)
[N,CO]-ct
(29.9, 26.9, 32.6, 27.4)
(31.9, 28.8, 34.0, 28.4)
Intensity (km/mol)
Wavenumber (cm-1)

Figure S4