Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Potassium and Sodium Ions Complexes with a Partial Peptide of the Selectivity Filter in K+ Channels Studied by Cold Ion Trap Infrared Spectroscopy: Effect of Hydration

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Supporting information

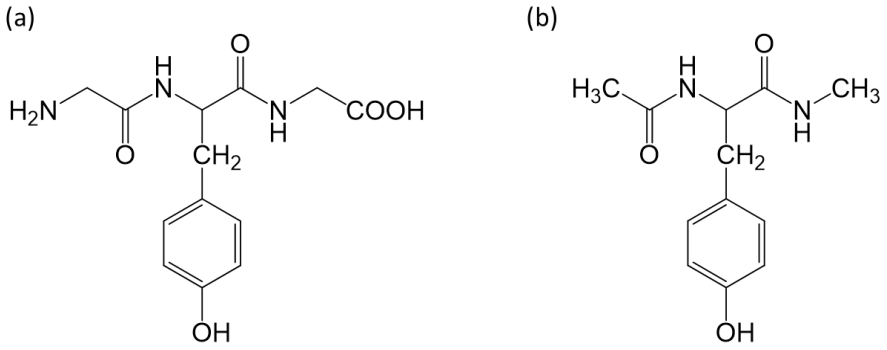

Figure S1 Structures of (a) GYG and (b) Ac-tyrosine-NHMe. The replacement of N-(-NH_2) and C-terminus (-COOH) with hydrogen atoms gives the dipeptide Ac-tyrosine-NHMe.

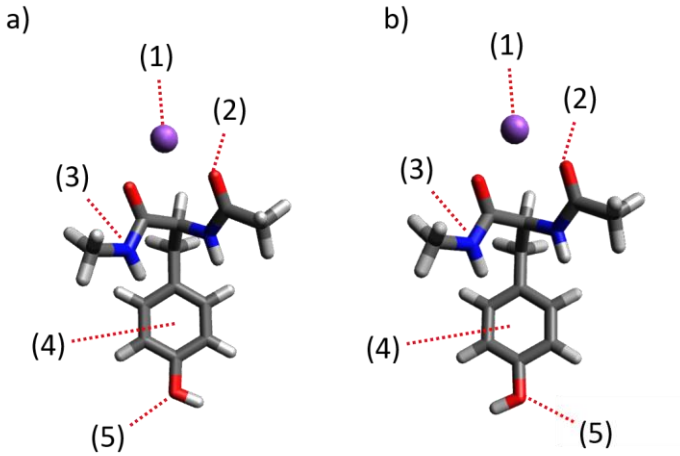

Figure S2 Five water binding sites of K^+GYG for a) O/O conformer and b) its tyrosine-OH rotamer. The conformers obtained from the initial structures are named as 1) metal ion, 2) carbonyl, 3) NH, 4) aromatic, and 5) tyrosine OH.

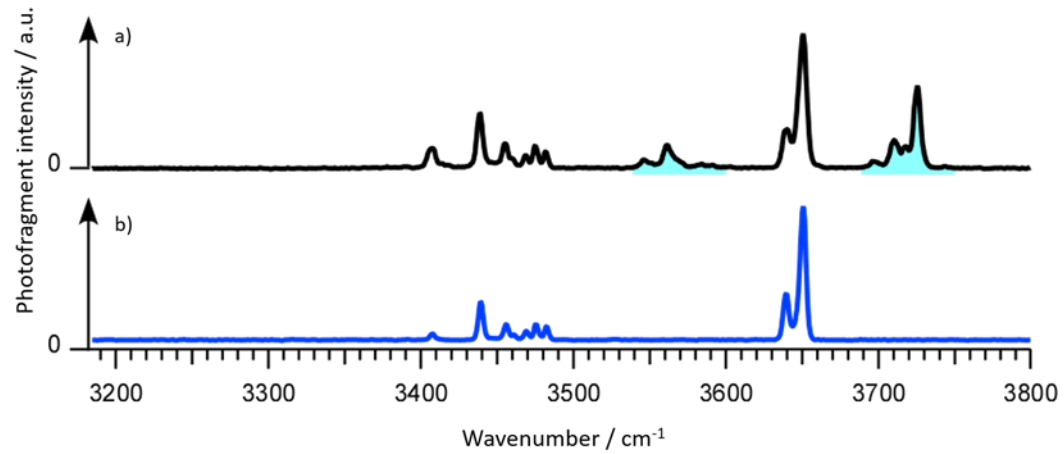

Figure S3 IRPD spectra of a) $K^+GYG(H_2O)$ and b) $K^+GYG(D_2O)$. The bands observed in 3540-3600 and 3690-3740 cm^{-1} in $K^+GYG(H_2O)$ are ascribed to vibrational modes of H_2O.

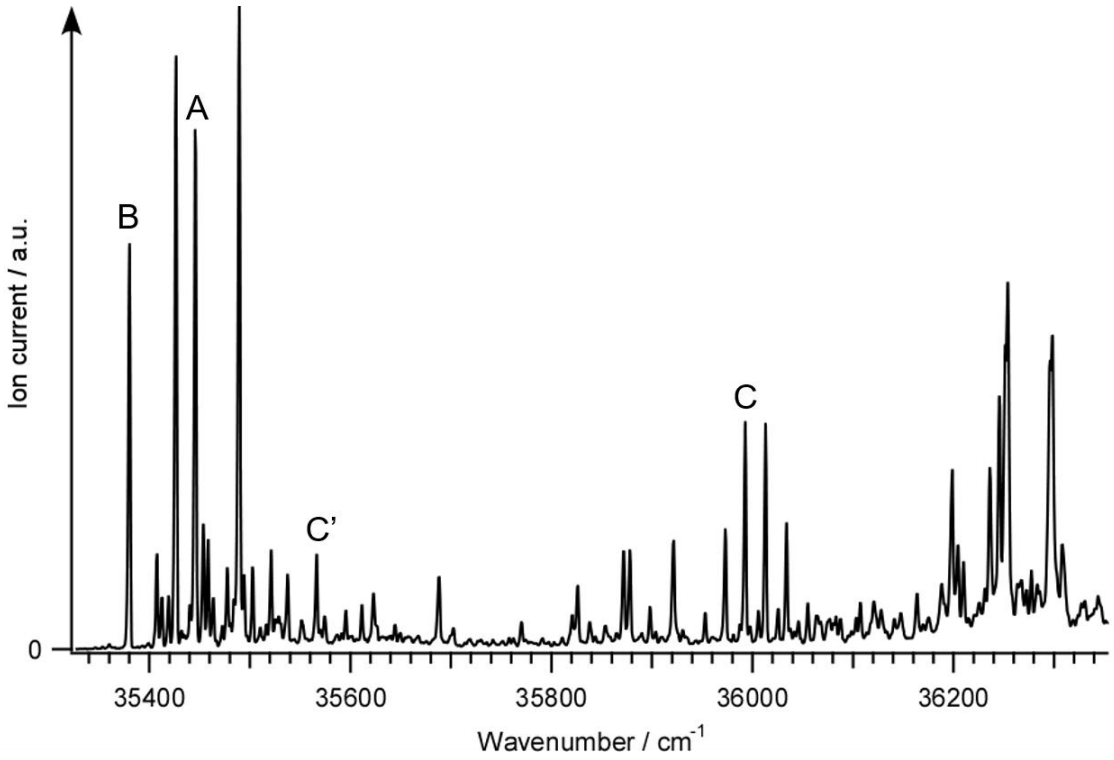

Figure S4 UVPD spectrum of $K^+GYG(H_2O)$. The IR-UV spectra of conformer A, B, C, and C' were measured by probing the bands at 35445, 35380, 35993, and 35567 cm^{-1}, respectively.

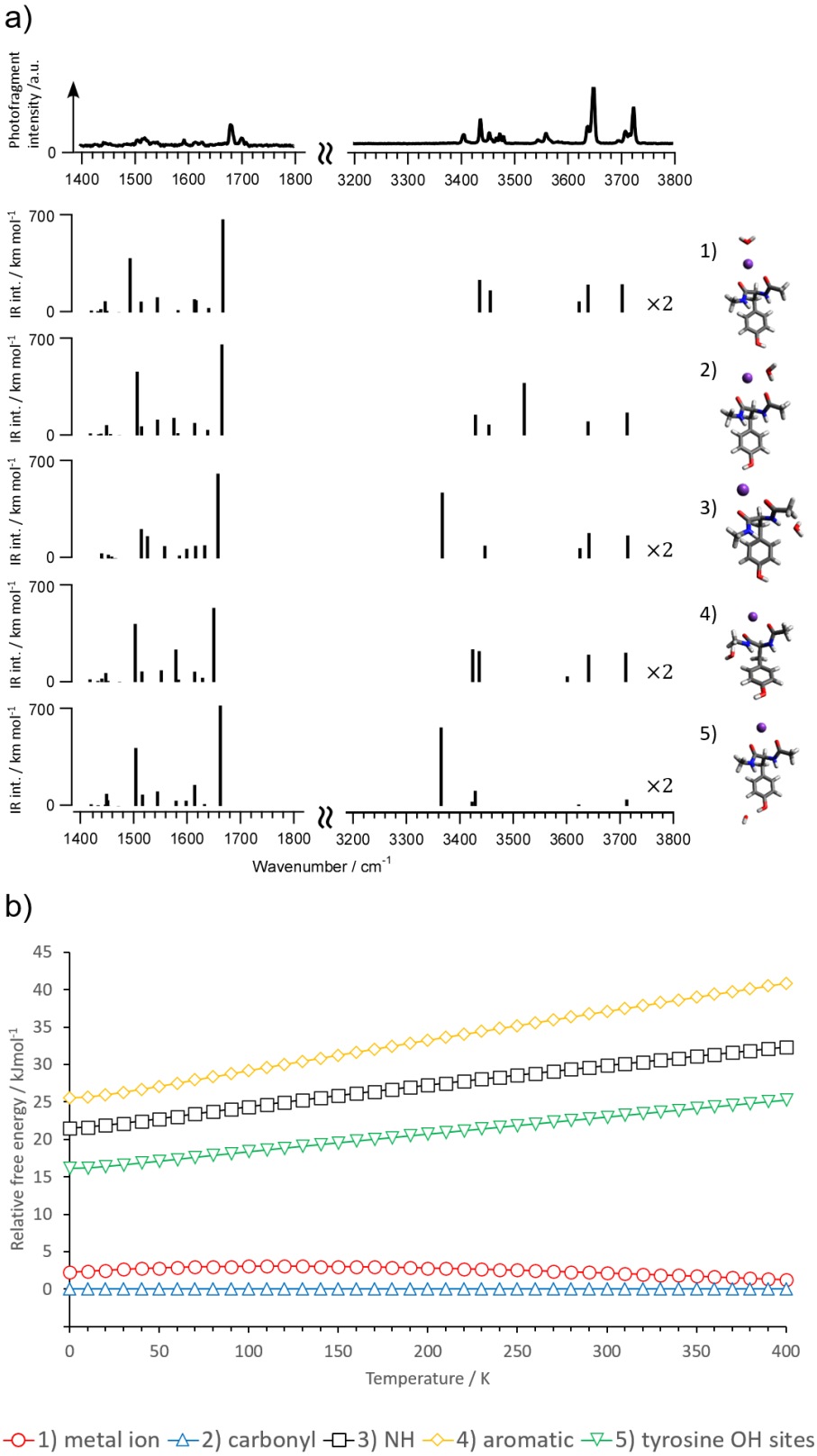

Figure S5 a) Calculated structures, IR intensities, and b) relative Gibbs free energies of O/O-type conformers of $K^+GYG(H_2O)$. More stable rotamer is shown.

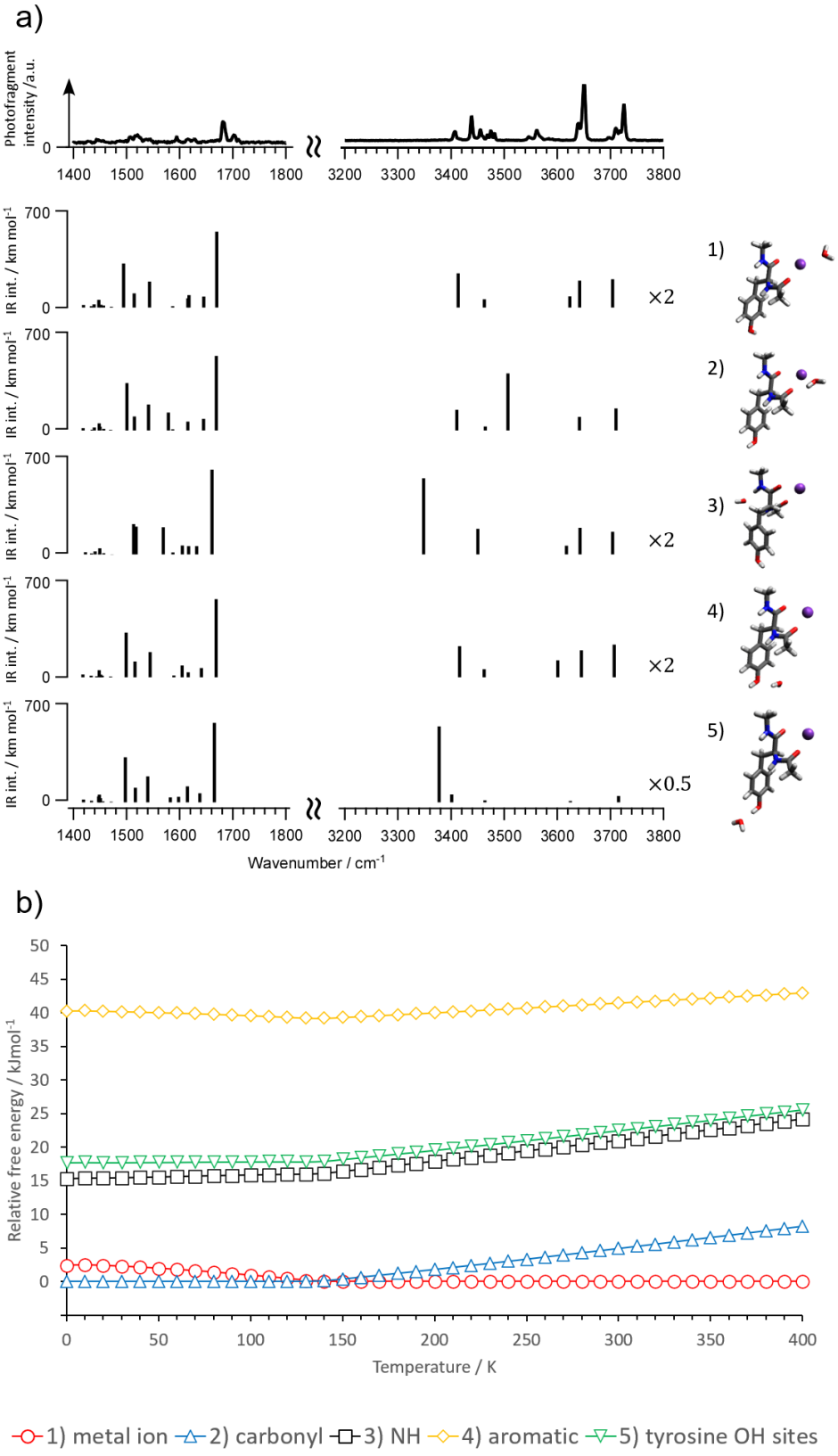

Figure S6 a) Calculated structures, IR intensities, and b) relative Gibbs free energies of O/O'-type conformers of $K^+GYG(H_2O)$. More stable rotamer is shown.

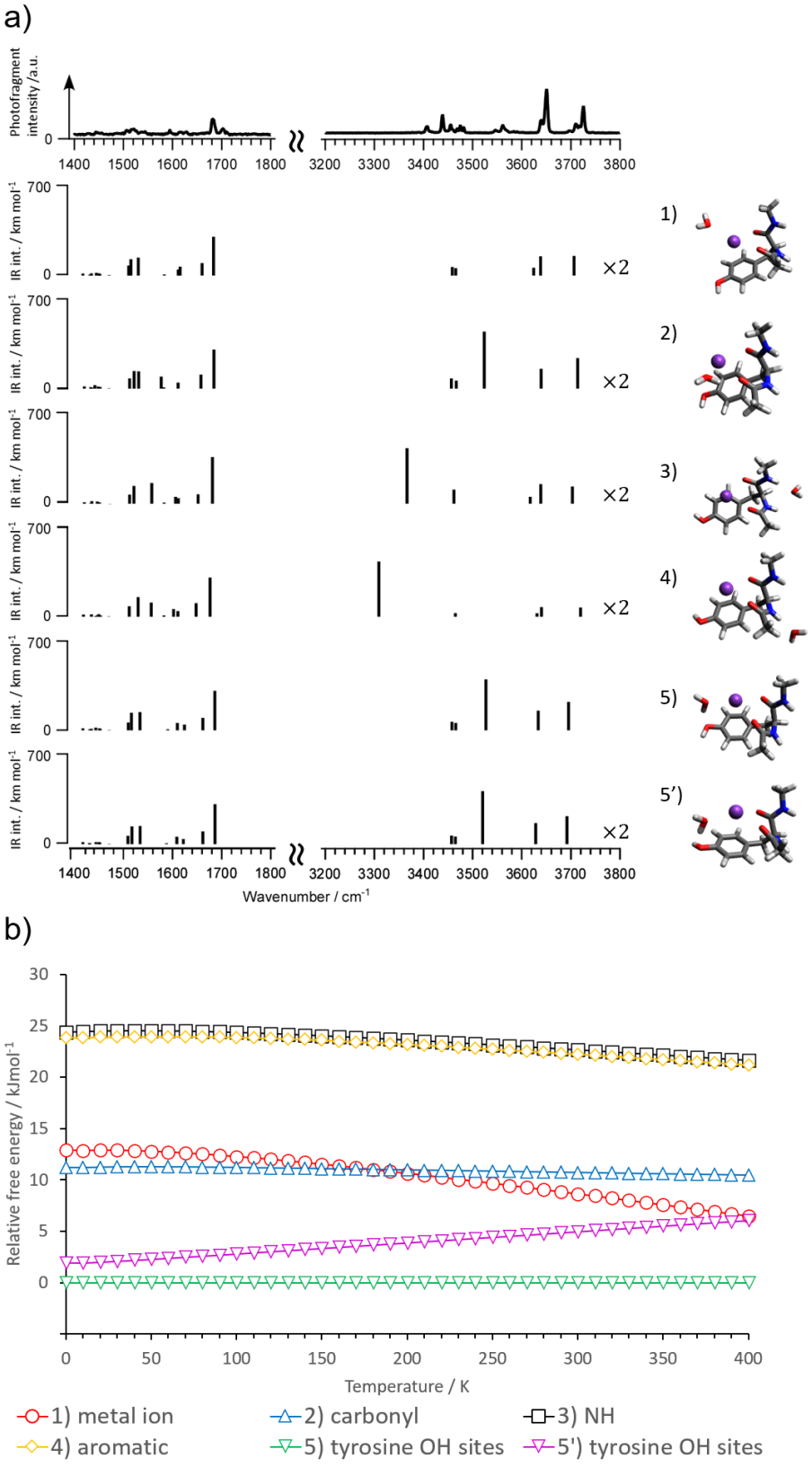

Figure S7 a) Calculated structures, IR intensities, and b) relative Gibbs free energies of O/O/R-type conformers of $K^+GYG(H_2O)$. More stable rotamer is shown.

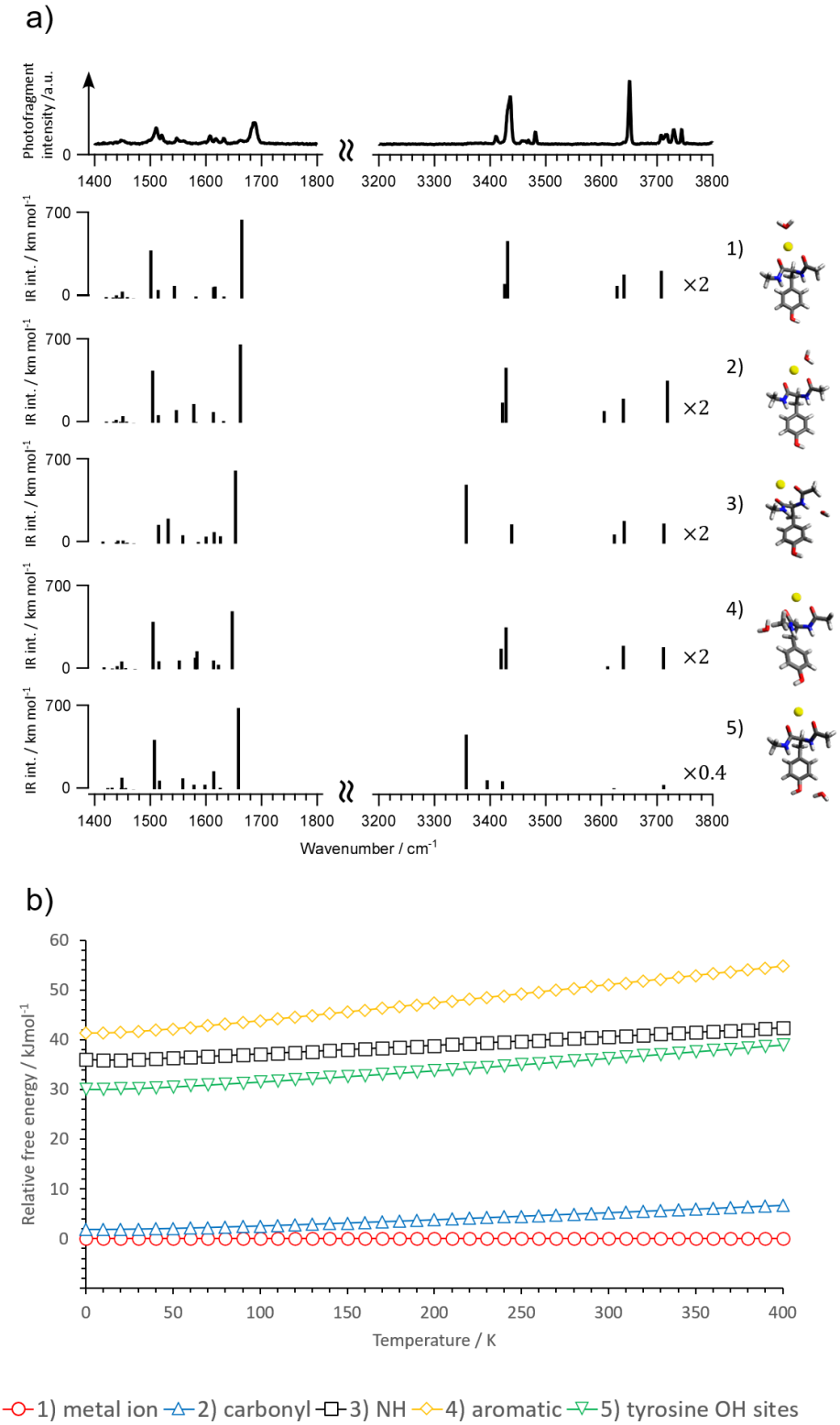

Figure S8 a) Calculated structures, IR intensities, and b) relative Gibbs free energies of O/O-type conformers $Na^{+}GYG(H_2O)$. More stable rotamer is shown.

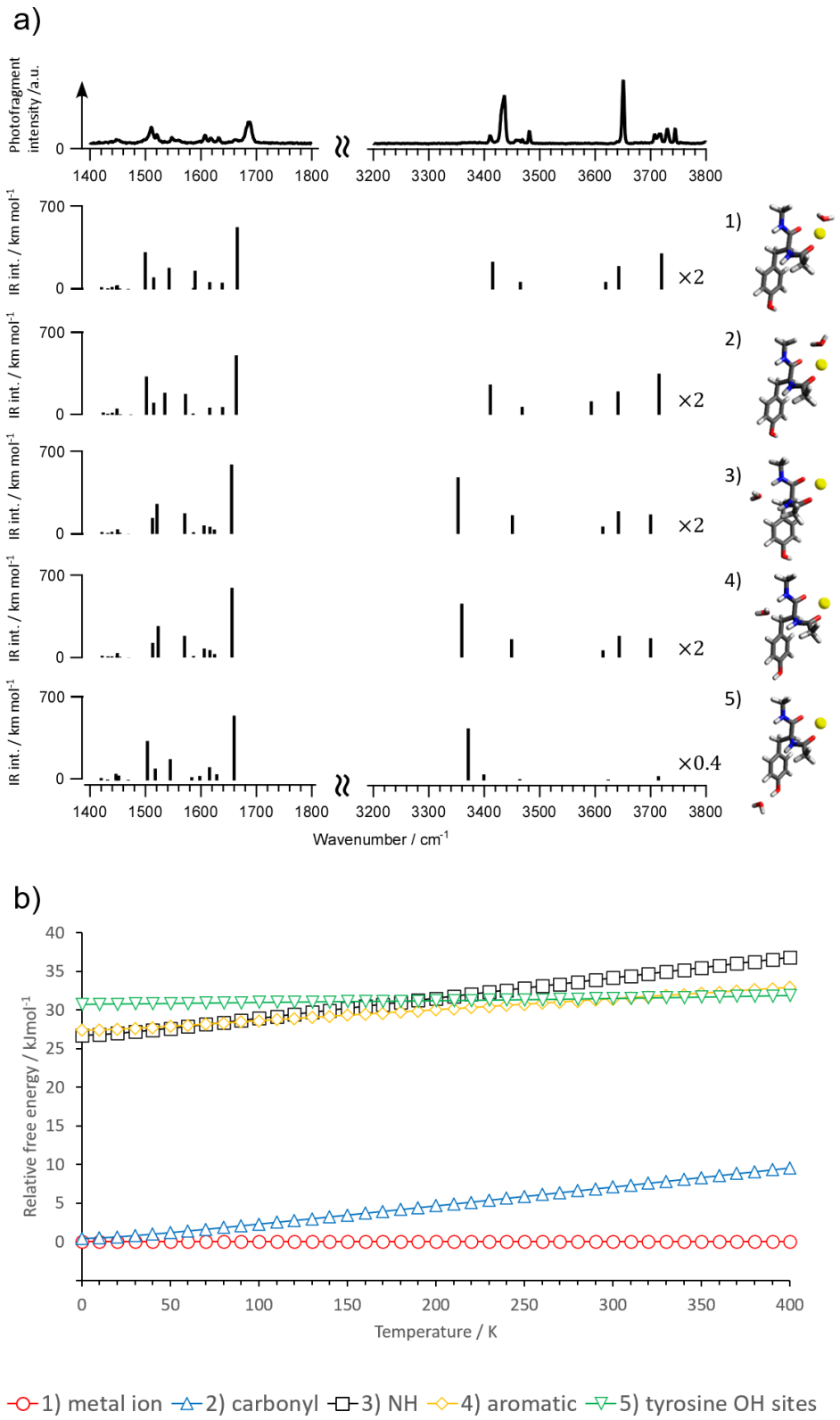

Figure S9 a) Calculated structures, IR intensities, and b) relative Gibbs free energies of O/O'-type conformers of $Na^+GYG(H_2O)$. More stable rotamer is shown.

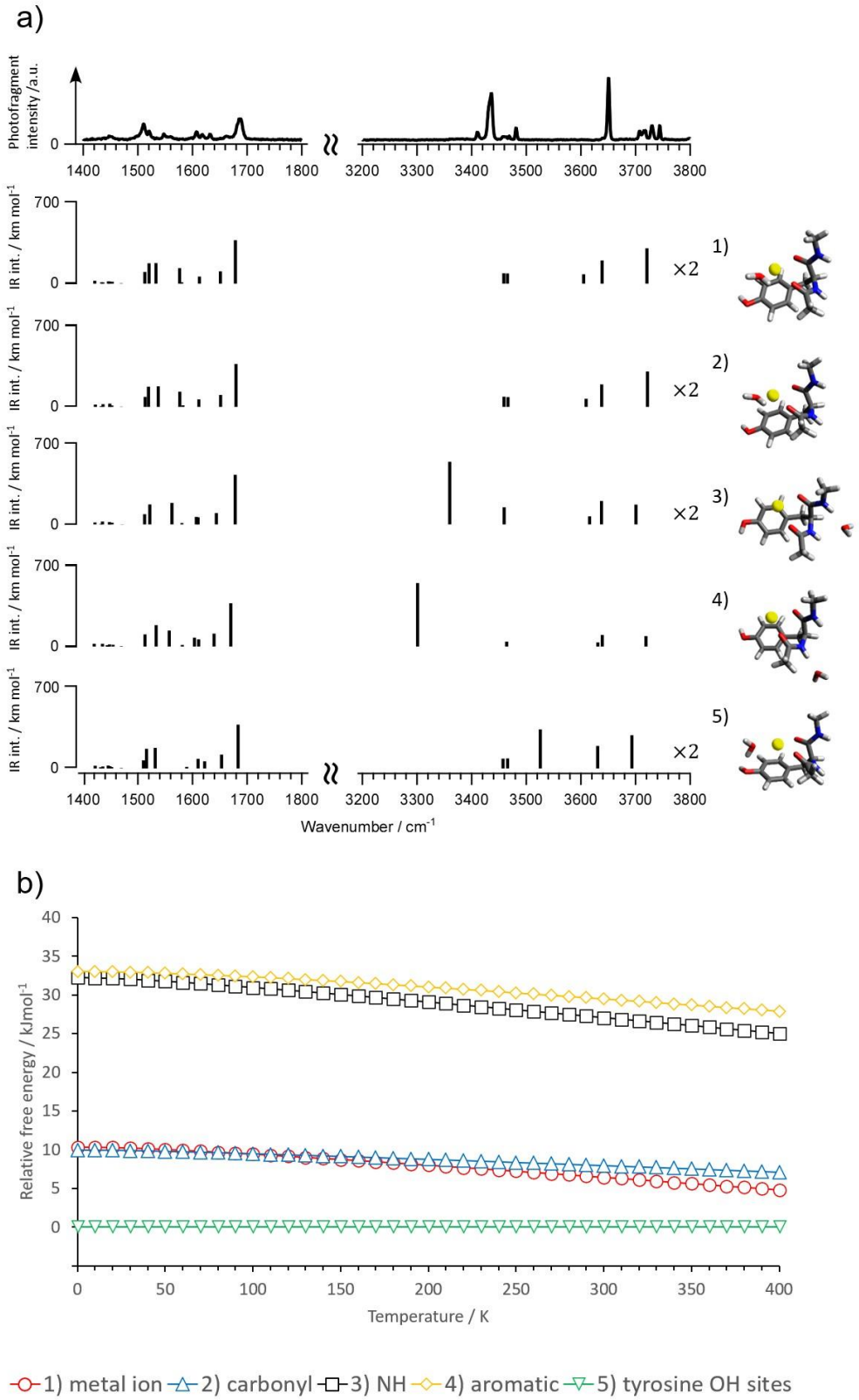

Figure S10 a) Calculated structures, IR intensities, and b) relative Gibbs free energies of O/O/R-type conformers of $Na^{+}GYG(H_2O)$. More stable rotamer is shown. Note that the initial structure of the metal ion-hydrated cluster (#1) converged to the carbonyl-hydrated structure (#2) after the geometry optimization.

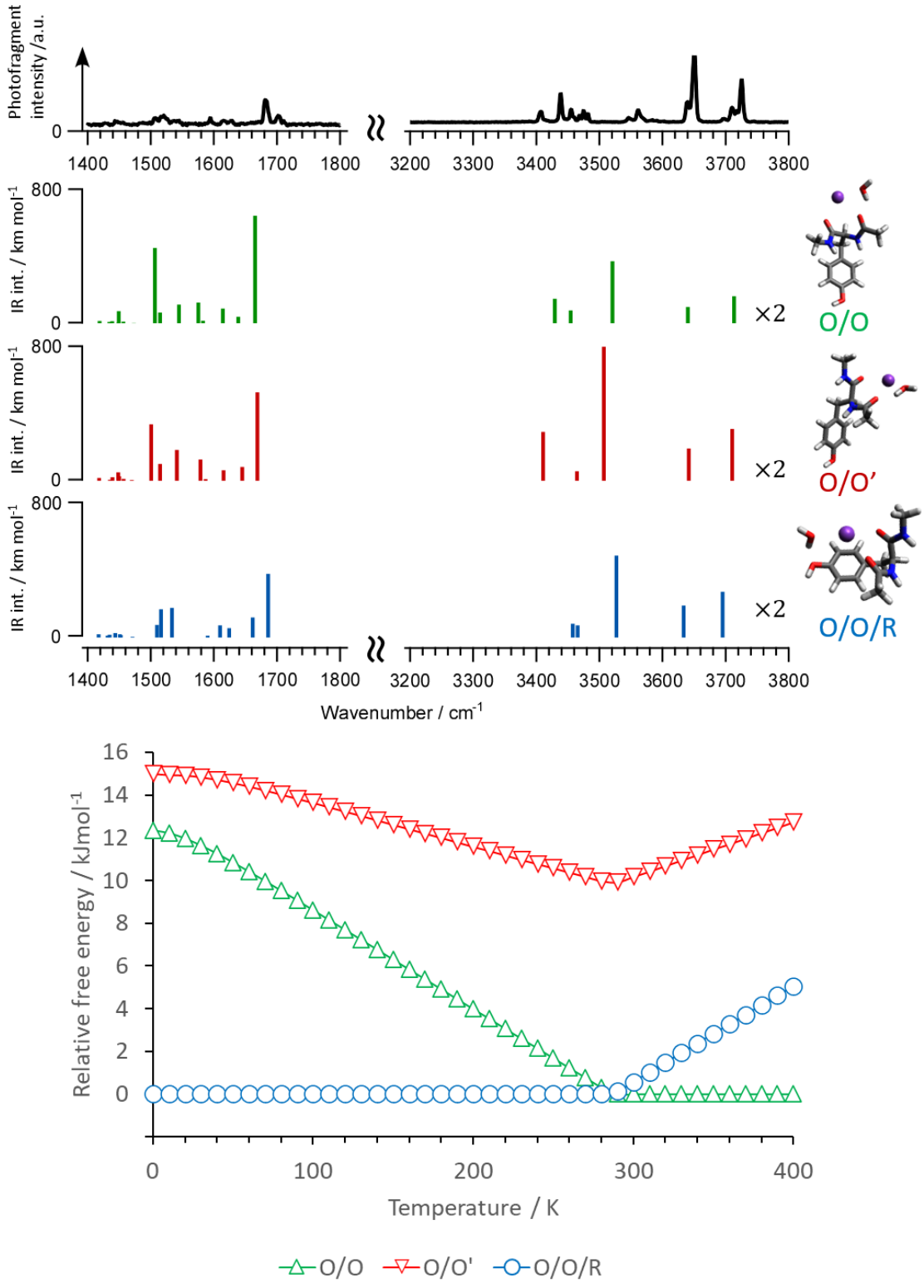

Figure S11 Experimental and calculated IR spectra of the observed conformers of $K^+GYG(H_2O)$ and their relative Gibbs free energies as a function of temperature.

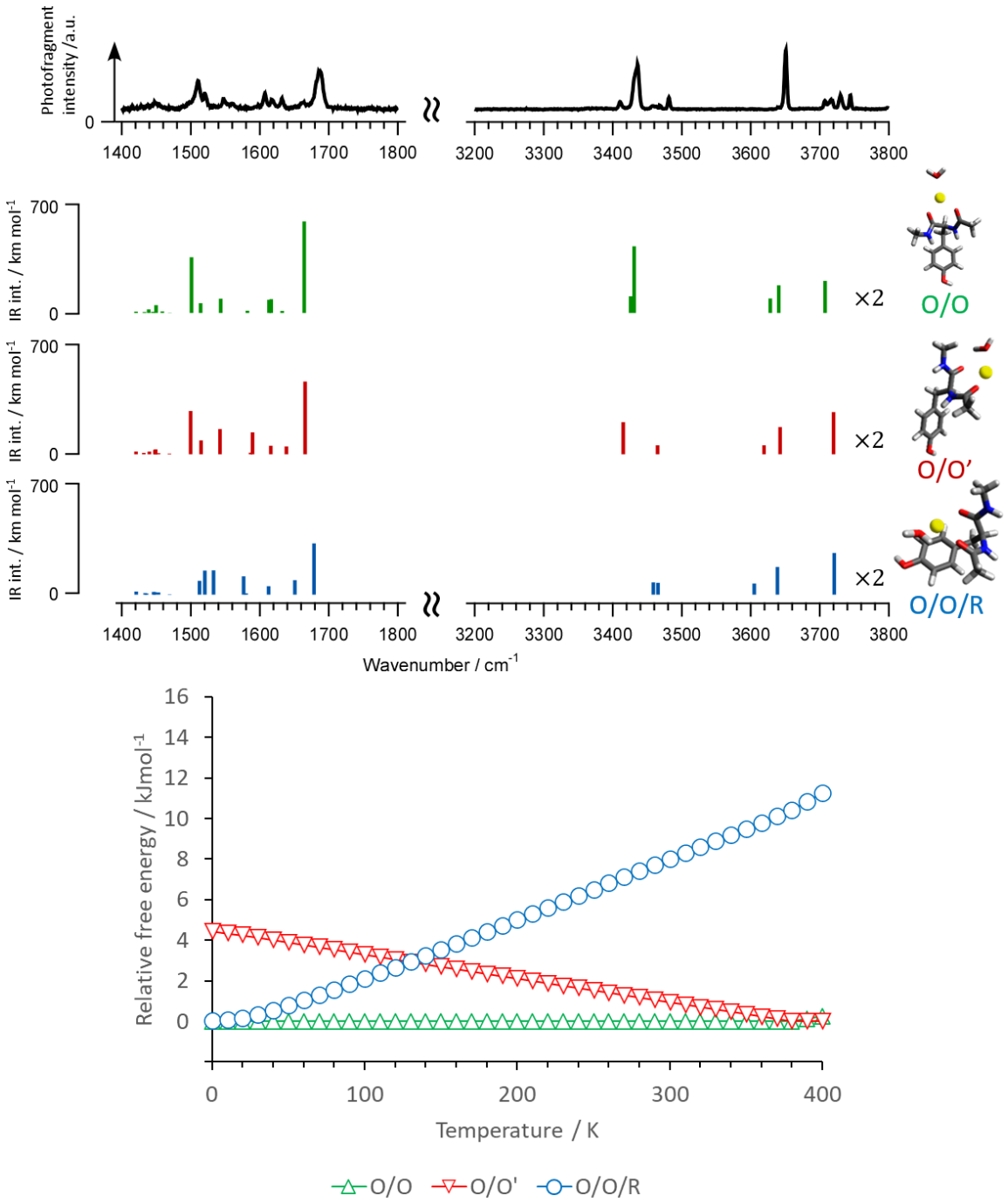

Figure S12 Experimental and calculated IR spectra of the observed conformers of $Na^+GYG(H_2O)$ and their relative Gibbs free energies as a function of temperature.

Table S1 Observed and calculated vibrational frequencies of $M^+GYG(H_2O)$ (M = Na, K) and their assignments.

	obs.					calc.					Isomer assignment
	OH str.	NH str. (NH_a)	NH str. (NH_b)	CO str. (sym)	CO str. (anti)	OH str.	NH str. (NH_a)	NH str. (NH_b)	CO str. (sym)	CO str. (anti)	
$Na^+GYG(H_2O)$	3651	3436	3436	1686	N.D.	3640	3426	3455	1664	1632	O/O
	3651	3411	3482	1686	N.D.	3642	3415	3465	1665	1638	O/O'
	3641	3459	3468	N.D.	N.D.	3639	3466	3459	1678	1651	O/O/R
$K^+GYG(H_2O)$	3650	3439	3455	1682	N.D.	3639	3429	3455	1665	1639	O/O
	3650	3407	3475	1682	N.D.	3641	3411	3465	1669	1645	O/O'
	3640	3468	3482	1703	N.D.	3639	3466	3459	1684	1660	O/O/R

	obs.		calc.		Isomer assignment
	Free OH str.	H-bonded OH str.	Free OH str.	H-bonded OH str.	
$Na^+GYG(H_2O)$	3707-3745	N.D.	3707	N.D.	O/O
		N.D.	3720	N.D.	O/O'
		N.D.	3721	N.D.	O/O/R
$K^+GYG(H_2O)$	3726	3539-3603	3713	3521	O/O
	3726	3539-3603	3710	3505	O/O'
	3710	N.D.	3706	N.D.	O/O/R

Table S2 Experimentally obtained conformer abundance of $M^+GYG(H_2O)$ (M = Na, K).

	K^+	Na^+
	Abundance	Abundance
O/O	57	65
O/O'	34	22
O/O/R	9	13