Supporting Information

Structural Versatility and Energy Difference of Salt-water Complex $NaCl(H_2O)$ encoded in Cryogenic Photoelectron Spectroscopy

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The structures of $NaCl^-$, NaCl, $NaCl(H_2O)^-$, and $NaCl(H_2O)$ were optimized with density functional theory (DFT) using the hybrid B3LYP functional with the dispersion D3 correction. The basis set def2-QZVPP was used for all the atoms. The vibration analysis was conducted using the same method.

$NaCl^-$ anion: R_{NaCl}= 2.5276 Å Vibrational frequency: 253 cm^{-1}
NaCl neutral: R_{NaCl}= 2.3765 Å Vibrational frequency: 354 cm^{-1}

Table S1 Geometry of A– isomer of anion $NaCl(H_2O)^-$ optimized at B3LYP-D3/def2-QZVPP (Å)

	X	Y	Z
Na	-0.7542	1.3475	0.0055
Cl	1.3742	-0.2289	0.0050
O	-1.5780	-1.0611	-0.1036
H	-1.8475	-1.3426	0.7754
H	-0.5927	-1.0996	-0.0909

Vibrational frequency at B3LYP-D3/def2-QZVPP (cm^{-1})

v_1	v_2	v_3	v_4	v_5	v_6	v_7	v_8	v_9
3824	3356	1632	765	358	295	227	162	93.5

Table S2 Geometry of A1 isomer of neutral $NaCl(H_2O)$ optimized at B3LYP-D3/def2-QZVPP (Å)

	X	Y	Z
Na	0.6020	1.2223	0.0079
Cl	-1.3517	-0.2763	0.0016
O	1.6728	-0.7716	-0.0455
H	2.2314	-1.4817	0.2748
H	0.7430	-1.0929	-0.0255

Vibrational frequency at B3LYP-D3/def2-QZVPP (cm^{-1})

v_1	v_2	v_3	v_4	v_5	v_6	v_7	v_8	v_9
3885	3413	1623	650	486	315	248	161	118

Table S3 Geometry of A2 isomer of neutral $NaCl(H_2O)$ optimized at B3LYP-D3/def2-QZVPP (Å)

	X	Y	Z
Na	-0.6029	1.2201	0.0055
Cl	1.3533	-0.2761	0.0011
O	-1.6722	-0.7662	-0.0307
H	-2.2497	-1.5002	0.1840
H	-0.7464	-1.0977	-0.0179

Vibrational frequency at B3LYP-D3/def2-QZVPP (cm^{-1})

ν_1	ν_2	ν_3	ν_4	ν_5	ν_6	ν_7	ν_8	ν_9
3889	3421	1620	630	496	315	248	159	56.6

Table S4 Geometry of B– isomer of anion $NaCl(H_2O)^-$ optimized at B3LYP-D3/def2-QZVPP (Å)

	X	Y	Z
Na	-0.4909	0.0003	0.1185
Cl	1.9953	-0.0000	-0.0350
O	-2.7412	0.0001	-0.1153
H	-3.2945	-0.7731	0.1068
H	-3.2957	0.7722	0.1063

Vibrational frequency at B3LYP-D3/def2-QZVPP (cm^{-1})

ν_1	ν_2	ν_3	ν_4	ν_5	ν_6	ν_7	ν_8	ν_9
3515	3485	1554	335	302	204	159	50.7	38.6

Table S5 Geometry of B isomer of neutral $NaCl(H_2O)$ optimized at B3LYP-D3/def2-QZVPP (Å)

	X	Y	Z
Na	0.0000	0.4306	0.0000
Cl	-0.0051	-1.9695	0.0000
O	0.0082	2.7583	0.0000
H	-0.7555	3.3422	0.0000
H	0.7765	3.3363	0.0000

Vibrational frequency at B3LYP-D3/def2-QZVPP (cm^{-1})

ν_1	ν_2	ν_3	ν_4	ν_5	ν_6	ν_7	ν_8	ν_9
3892	3804	1651	363	354	237	186	29.4	15.8

Table S6 Geometry of C– isomer of anion $NaCl(H_2O)^-$ optimized at B3LYP-D3/def2-QZVPP (Å)

	X	Y	Z
Na	1.6804	-1.0840	-0.0000
Cl	0.2974	1.0643	0.0000
O	-2.4721	-0.5923	0.0001
H	-2.0500	-1.4547	-0.0010
H	-1.7128	0.0237	0.0002

Vibrational frequency at B3LYP-D3/def2-QZVPP (cm^{-1})

ν_1	ν_2	ν_3	ν_4	ν_5	ν_6	ν_7	ν_8	ν_9
3851	3523	1655	614	346	238	160	25.5	15.1

Isomer	**S**	**ΔG**							
		300K	250K	200K	150K	100K	80K	50K	15K
A⁻	81.95	1.67	1.24	0.83	0.43	0.05	0.00	0.00	0.00
B⁻	80.14	1.77	1.54	1.30	1.05	0.80	0.78	0.81	0.78
C⁻	83.79	0.00	0.00	0.00	0.00	0.00	0.09	0.27	0.41

Table S7. Calculated entropies (S, cal mol^{-1} K^{-1}) at room temperature and relative Gibbs free energies (ΔG, kcal mol^{-1}) at different temperatures of $NaCl(H_2O)^-$ isomers

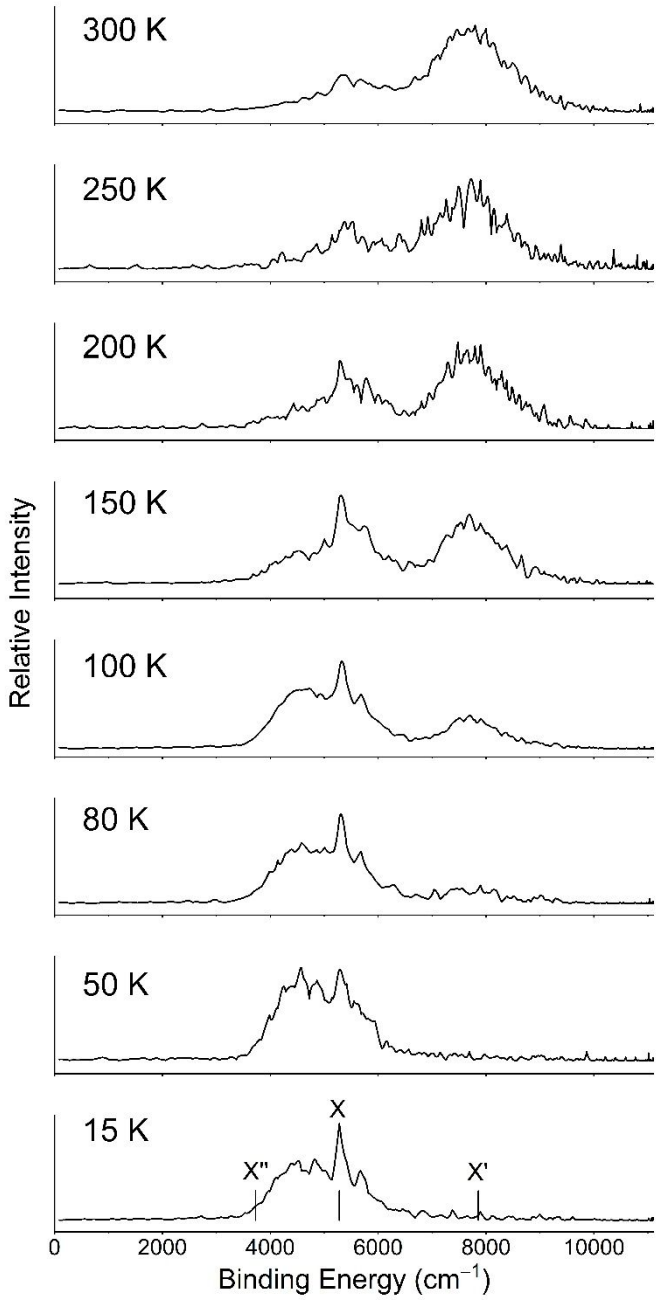

Fig.S1 Photoelectron spectra for NaCl(H2O)$^-$ at a series of temperatures at photon energy $h\nu$=11097 cm^{-1}.

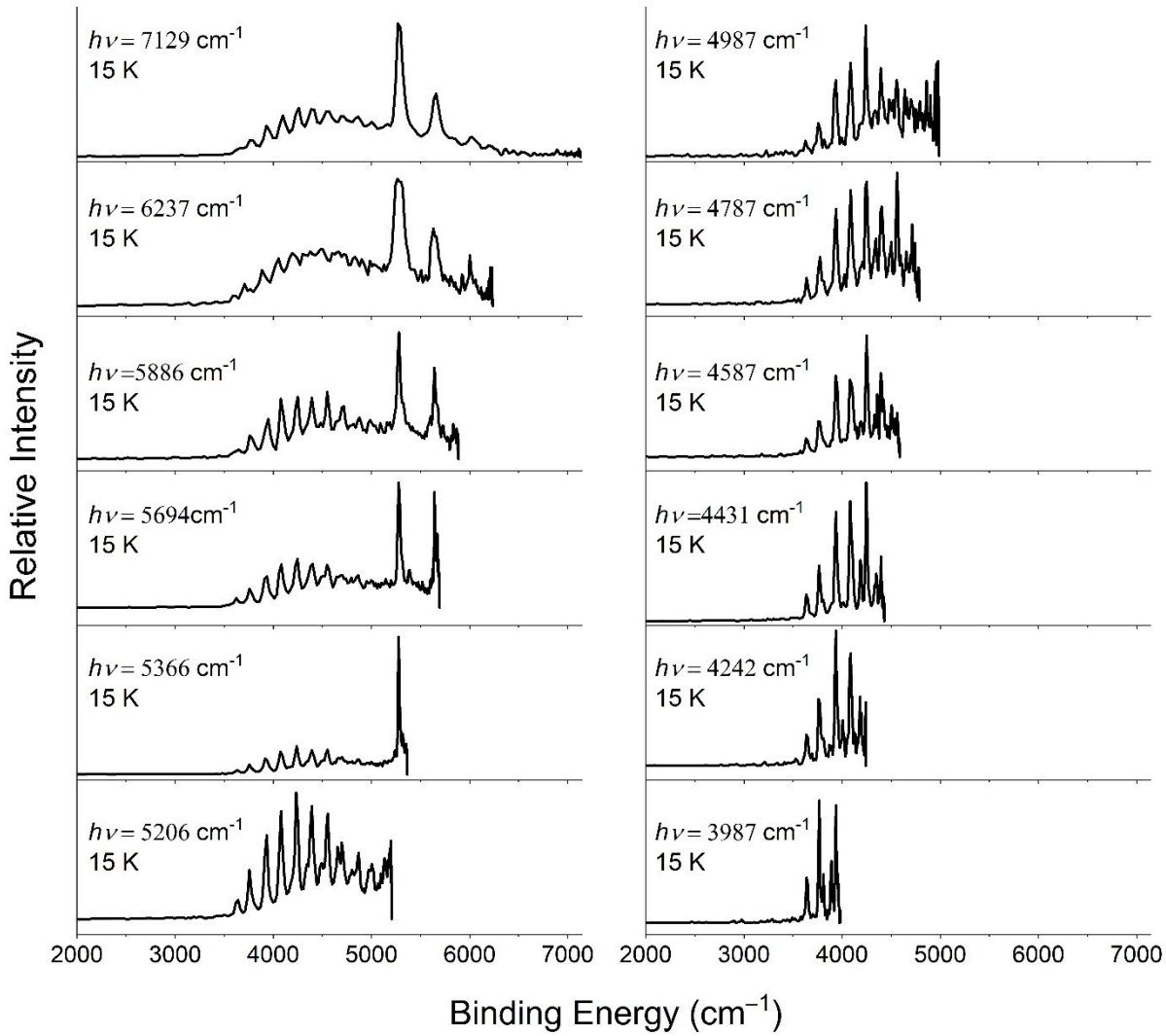

Fig.S2 Photoelectron spectra at a series of photon energies used to generate the combined high-resolution spectra in Fig.2.

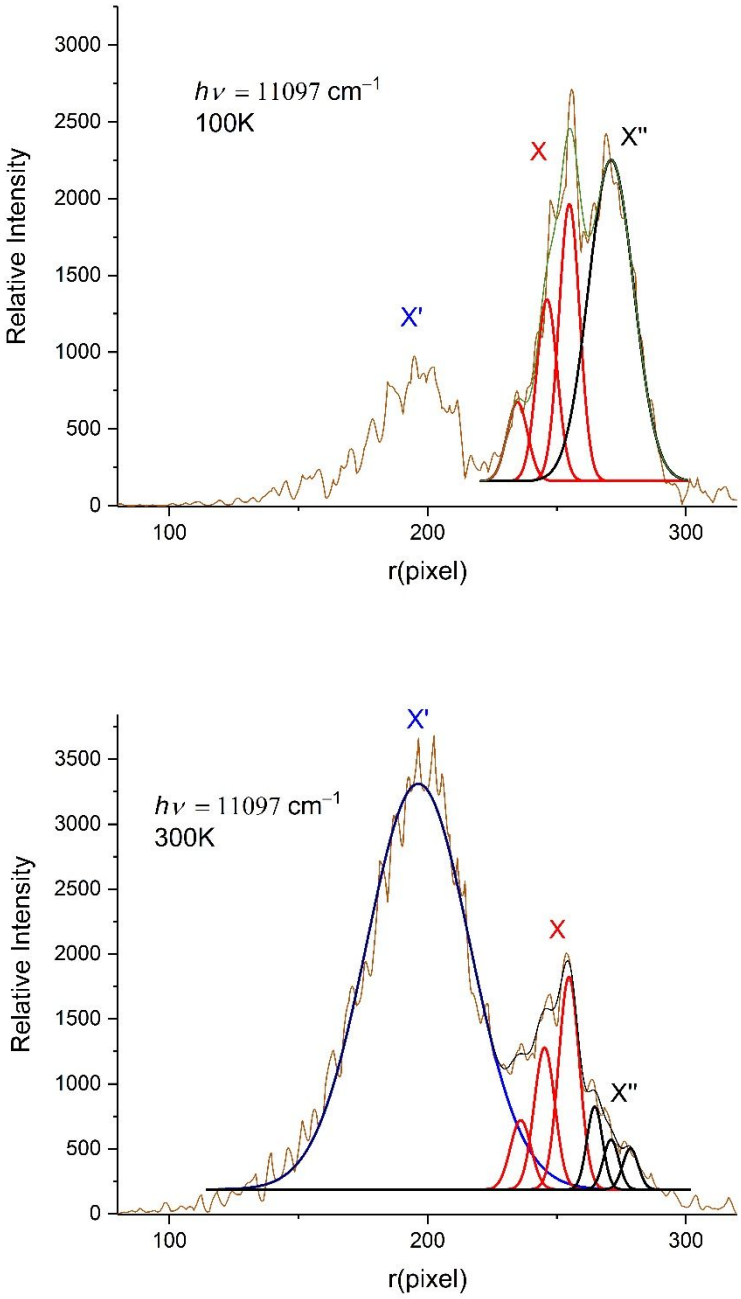

Fig.S3 Multipeak fitting used to extract the integral intensity of the overlapped features at 100 K and 300 K. Three Gaussian functions were used to fit the feature X, which is the key to separate the contributions of X′, X, and X″. The x axis is the radius r of the projected photoelectron sphere in the unit of pixel. The binding energy BE=$h\nu-\alpha r^2$, where $h\nu$ is the photon energy, and α is the calibration coefficient of energy.