

Structural Versatility and Energy Difference of Salt–Water Complex NaCl(H₂O) Encoded in Cryogenic Photoelectron Spectroscopy

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ABSTRACT: A weakly bound complex usually has multiple structural isomers with small energy differences. The sophisticated ab initio calculations are the main workhorse for providing theoretical results of different isomers. In contrast, the experimental determination of the energy difference is very rare. We report the energy-difference measurement of a model complex: salt–water complex NaCl(H₂O). We measured the energy difference among the structural isomers of the negatively charged NaCl(H₂O) complex and the neutral counterpart using cryogenic photoelectron spectroscopy. The temperature-dependent photoelectron spectra (15–300 K) revealed that the negatively charged NaCl(H₂O) and the neutral counterpart both have three isomers. The two higherlying isomers are 186(22) and 481(48) cm⁻¹, respectively, above the most stable isomer for the negatively charged and 123(10) and 1821(24) cm⁻¹ for the neutral. These results provide a benchmark for the development of theoretic methods of weakly bound complexes. The experimental technique demonstrated here can be employed to investigate other weakly bound complexes with multiple isomers.



 ${\displaystyle S}$ olvation effects can profoundly alter the structure and property of matter. Understanding the microscopic behavior of salts in solution is one of the most fundamental questions in physical chemistry.¹⁻²⁰ The salt-water complex $NaCl(H_2O)$ is a basic model system for understanding the solvation of salts in water at a molecular level. Recently, many theoretic and experimental studies have been performed on $NaCl(H_2O)_n$ clusters, such as ab initio calculations,²¹⁻²⁹ argon-matrix infrared spectroscopy,³⁰ helium-nanodroplet infrared spectroscopy,³¹ Fourier transform microwave spectroscopy,^{32,33} and anion photoelectron spectroscopy.³⁴ These studies have shown that small clusters $NaCl(H_2O)_n$ usually have several isomers close in energy due to the weak noncovalent interactions. For example, Hou et al. found that the negatively charged complex $NaCl(H_2O)^-$ has three isomers via a joint investigation of theoretical calculations and anion photoelectron spectroscopy.³⁴ Their ab initio calculations showed that the structure of the most stable isomer was cyclic, with Na, Cl, O, and H forming a nearly planar four-membered ring. The other two isomers were 0.029 and 0.034 eV, respectively, above the ground state. In addition, they found two isomers for the neutral complex $NaCl(H_2O)$. The most stable isomer was also cyclic, and the higher-lying isomer was 0.228 eV above the ground state.³⁴

Although previous studies have shown the structural versatility of salt—water complexes, the energy differences among different isomers were dominantly provided by theoretical calculations, which usually depend on specific methods. The experimental technique that can measure energy differences or barrier heights between different isomers is very rare.^{35,36} There is a substantial need for experimental data on the energy difference to assist in the development of theoretical methods for noncovalent interactions. Temperature-dependent photoelectron spectroscopy is a powerful tool to investigate the structural versatility of molecules.³⁷ Here we employ cryogenic photoelectron spectroscopy to determine the proportion of different isomers of NaCl(H₂O)⁻ over a series of temperatures. The effective energy differences and barrier heights of the negatively charged isomers were extracted from the population measurements, and the energy differences of the neutral isomers were obtained from the high-resolution photoelectron spectra.

The experiment was carried out on our slow-electron velocity-map imaging (SEVI) apparatus equipped with a cryogenically controlled ion trap.³⁸ The NaCl(H₂O)⁻ anions were generated in a laser ablation ion source, in which a NaCl salt disk was ablated by a pulsed 532 nm Nd:YAG laser, while helium carrier gas seeded with water vapor was delivered by a pulsed valve. The generated anions were guided into the radio frequency ion trap by a hexapole ion guide and then cooled through collisions with the buffer gas (20% H₂ and 80% He) in the trap. The buffer gas was injected by a pulsed valve. After

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sufficient collisions for 45 ms, the trapped anions were in thermal equilibrium with the buffer gas. The temperature of the ion trap is controllable in a range of 5-300 K. This is an important advantage compared with the generic molecular beam experiment, in which it is hard to define a temperature since it is not in thermal equilibrium. Moreover, the cold ion trap can significantly lessen thermal broadening. At a temperature ~10 K, molecular anions are almost all in their vibrational ground state and are partially populated in a few rotationally excited states. Thus, the spectra become very sharp and clean at a cryogenically low temperature. The SEVI technique features a very high energy resolution for low kinetic energy electrons.^{38–40} It can achieve an energy resolution of a few cm⁻¹ at a threshold photodetachment. Our group has taken this feature to resolve the complicated electronic structures of atomic anions of transitional, lanthanide, and actinide elements.^{41–47} The combination of the cryogenic ion trap and the SEVI method make cryo-SEVI a powerful tool to resolve the condensed vibrational states of the neutral species after photodetachment. The vibrationally resolved spectra are very helpful to determine the molecular structure. After cooling for 45 ms, anions were pulsed out from the ion trap and selected via a time-of-flight mass spectrometer. NaCl $(H_2O)^$ anions were photodetached in the interaction zone of a velocity-map-imaging setup. The detachment laser was the idler light of an optical parameter oscillator (OPO, 710-2750 nm for the idler light and line width $\sim 5 \text{ cm}^{-1}$) pumped by a Quanta-Ray lab 190 Nd:YAG laser. Chlorine has two stable isotopes ³⁵Cl (abundance 76%) and ³⁷Cl (24%). The isotope ³⁵Cl was selected in the present experiment. The maximum entropy Legendre expanded image reconstruction (MELEXIR) method was used to reconstruct the photoelectron distribution from the projected images.⁴⁸

Figure 1 shows the photoelectron energy spectrum of $NaCl(H_2O)^-$ in comparison with that of NaCl⁻. The well resolved peaks in Figure 1a are the vibrational progression of Na-Cl. The adiabatic detachment energy (ADE) of NaClwas determined to be 5867(14) cm⁻¹, and the vibrational frequency of NaCl was measured as 362(10) cm⁻¹. There are three features in the spectrum of $NaCl(H_2O)^-$ at temperature 100 K, which are labeled as X", X, and X', respectively. This is consistent with the observation of Hou et al. in a molecular beam experiment.³⁴ Feature X has two peaks related to the vibration progression of Na-Cl, but the broad features X" and X' barely have visible vibrational structure. To obtain a highresolution spectrum, we collected the spectrum at a lower temperature of 15 K. Interestingly, feature X' disappeared at the temperature of 15 K, as shown in Figure 1c. To further resolve the structures of features X" and X, we collected the spectra at a series of photon energies and then combined the lower-kinetic-energy part of each spectrum to form a highresolution spectrum. As shown in Figure 2, many sharp peaks were resolved with this method. Hou et al. assigned X", X, and X' to three different isomers of $NaCl(H_2O)^{-.34}$ The most stable isomer was cyclic, with Na, Cl, O, and H forming a nearly planar four-membered ring. The other two isomers were 0.029 and 0.034 eV higher than the ground state according to their calculations.³⁴

To measure the energy difference among the three isomers, we collected the spectra at a series of temperatures in the range of 15-300 K. As shown in Figure 3a, the normalized intensity of X' increases as the temperature goes up. In contrast, the normalized intensity of X" decreases as the temperature



Figure 1. Photoelectron spectra (a) for NaCl⁻ at photon energy $h\nu = 8319 \text{ cm}^{-1}$ and temperature T = 15 K, (b) for NaCl(H₂O)⁻ at $h\nu = 11097 \text{ cm}^{-1}$ and T = 100 K, and (c) for NaCl(H₂O)⁻ at $h\nu = 11097 \text{ cm}^{-1}$ and T = 15 K.



Figure 2. Combined photoelectron spectra at a series of photon energies. The vertical bars at the top indicated the vibrational progression of Na-Cl.

increases. Their intensities dramatically change as the temperature is tuned from 15 to 300 K. X'' is dominant at 15 K, while X' becomes dominant at 300 K. The normalized intensity of feature X does not change so dramatically. In thermal equilibrium, the populations of different isomers are given by the Boltzmann distribution. In Figure 3b, the intensity ratio of



Figure 3. (a) Normalized intensity of features X", X, and X' versus temperature T at photon energy $h\nu = 11097 \text{ cm}^{-1}$. (b) Intensity ratio X/X" versus the reciprocal temperature 1/T. The solid line is the fitting curve using eq 1. (c) Intensity ratio X'/X" versus the reciprocal temperature 1/T. The solid line is the fitting curve using eq 1. It should be noted that the temperature is the nominal temperature measured by the silicon diode thermometer attached on the wall of the ion trap. The temperature of trapped ions may be slightly higher than the nominal temperature.

X to X" at photon energy $h\nu = 11097 \text{ cm}^{-1}$ was plotted versus the reciprocal temperature 1/T. To extract the energy difference, the measured ratio was fitted using the following equation

$$y = y_0 + A \exp(-\Delta E/T) \tag{1}$$

where *y* defines the intensity ratio X/X'' and y_0 is the expected ratio as $T \rightarrow 0$ due to population trapping. The higher-lying isomer cannot get enough collision energy to surmount the transition barrier at a lower temperature. Thus, the transition from the higher-lying isomer to the ground isomer is stuck at a certain point as the temperature drops. The critical point reflects the effective height of the barrier. A is a constant related to the photodetachment cross sections and populations of two isomers. ΔE is the effective energy difference between two isomers in the unit of measure of K. As shown in Figure 3b, the experimental results can be well described using the equation. The energy difference between the two isomers was determined to be 186(22) cm⁻¹. The experimental ratio becomes a constant 0.40 at temperature T = 80 K and has no notable decline as the temperature decreases from 80 to 15 K. Therefore, the effective barrier height is estimated as 80 K or 56 cm⁻¹. Similarly, the energy difference between X' and X" can be determined to be 481(48) cm⁻¹ from the fitting of the experimental ratio X'/X" using the equation. The intensity of X' is almost zero at 50 and 15 K but notable at 80 K. This means that the transition still went on at T = 80 K and all molecular anions at the higher-lying isomer related to X' were completely transformed into X'' at T = 50 K. Therefore, it is

reasonable to estimate that the effective barrier height for the transition is less than 80 K (56 cm^{-1}).

To further understand the observed results, we conducted theoretical calculations on NaCl⁻ and NaCl(H₂O)⁻ anions and their neutral counterparts to compare with the experimental results. The structures were optimized with density functional theory (DFT) using the hybrid B3LYP functional⁴⁹ with the dispersion D3 correction.⁵⁰ The basis set def2-QZVPP was used for all the atoms.⁵¹ The vibration analysis was conducted using the same method. More accurate single-point energies were obtained using the high-level coupled-cluster CCSD(T)⁵² calculations with the same basis set. All calculations were implemented in the Gaussian program package.⁵³

The adiabatic detachment energy (ADE) with zero-point energy correction of NaCl⁻ was calculated to be 5744 cm⁻¹, which agrees well with the experimental value 5867(14) cm⁻¹ obtained in the present work. The calculated vibrational frequency of NaCl is 354 cm⁻¹, which agrees well with the experimental value 362(10) cm⁻¹. Figure 4 shows the



Figure 4. Low lying isomers of $NaCl(H_2O)^-$ and $NaCl(H_2O)$. The labels are the bond lengths in angstroms.

optimized structures of NaCl(H₂O)⁻ and the neutral counterparts. The detailed geometric data and vibrational frequencies can be found in the Supporting Information. The three stable isomers of $NaCl(H_2O)^-$ we obtained are similar to the predictions by Hou et al.³⁴ The most stable isomer A⁻ is cyclic, with Na, Cl, O, and H forming a nearly planar four-membered ring. For isomer B^- , H_2O is bound to atom Na via the O-Na bond. The total energy corrected with the zero-point energy of isomer B^- is 51 cm⁻¹ higher than that of A^- , while the experimental effective energy difference is 186(22) cm⁻¹. For isomer C^- , H_2O is bound to atom Cl via the H…Cl bond. Isomer C⁻ is theoretically predicted to be 330 cm⁻¹ higher in energy than A⁻, while the experiment determined the energy difference to be 481(48) cm⁻¹. It should be pointed out that the order of isomers B^- and C^- in energy by Hou et al. is opposite to our observation in the temperature-dependent photoelectron spectroscopy.³⁴ We found two isomers A1 and A2 for neutral counterparts of A⁻. Their structures are similar, and both are cyclic. The main difference is that isomer A1 has a slightly longer O-Na bond, a shorter H…Cl bond, and a negative dihedral angle $D(CINaO1H) = -114.5^{\circ}$, while A2 has a shorter O-Na bond, a longer H…Cl bond, and a positive dihedral angle $D(ClNaO1H) = 124.9^{\circ}$. Isomer A2 is 88 cm⁻¹ higher than A1 in energy. This is supported by the highresolution spectra in Figure 2. There are two series of vibrational progression for isomer A⁻. The experimental energy difference between A1 and A2 is 123(10) cm⁻¹. The calculated ADE of isomer A^- is 3726 cm⁻¹, and its experimental ADE is 3643(10) cm⁻¹. The calculated/experimental ADE of isomer B^- is 5279/5278(17) cm⁻¹. The experimental energy difference between isomers A1 and B can be obtained from the experimental ADEs of isomers A⁻ and B⁻ and the energy difference between A⁻ and B⁻. The theoretical/experimental energy difference between isomers A1 and B is 1604/1821(24) cm⁻¹. Our optimized geometric structure of isomer C⁻ has a docking position of H₂O different from that by Hou et al.³⁴ The angle ∠NaCl2H they obtained is close to 180°, but we determined it to be 95.4°. This difference might be due to the fact that isomer C⁻ is at a very shallow local minimum, which is revealed by the two lowest vibration frequencies of isomer C^- of 25.5 and 15.1 cm⁻¹, the rock and swing modes of the H_2O molecule as a whole. As a result, H_2O can occupy a large phase space at room temperature. This can partly explain why the intensity ratio X'/X'' = 15.5 at T = 300 K, though A⁻ is the global minimum. The neutral counterpart of C⁻ is a transition state, not a local minimum on the multidimensional potential surface. This is consistent with the observed broad feature X' in the spectra. We cannot observe any sharp peaks in feature X' at the photodetachment threshold with the cryo-SEVI method. The calculated vertical detachment energy (VDE) of C⁻ is 7857 cm⁻¹, which agrees well with the experimental value 7680(200) cm^{-1} . The theoretical results in comparison with the experimental values were summarized in Table 1. The

Table 1. Theoretical and Experimental Energy Difference, Adiabatic Detachment Energy (ADE), and Na–Cl Vibrational Frequency for Different Isomers of the NaCl(H_2O) Complex (in the Unit of Measure of cm⁻¹)

negatively charged complex NaCl(H ₂ O) ⁻					
isomer	A^-	B	C-		
relative energy (theo/expt)	0	51/186(22)	330/481(48)		
adiabatic detachment	3726/3643(22)	5279/5278(17)	7857/7680(200) ^a		
energy (theo/expt)					
neutral complex NaCl(H ₂ O)					
isomer	A1	A2	В		
relative energy (t expt)	heo/ 0	88/123(10)	1604/1821(24)		
Na-Cl vibration frequency (the expt)	al 315/294 o/	(10) 315/319(10) 363/365(10)		

^{*a*}Vertical detachment energy (VDE) for isomer C^- since its neutral counterpart is a transition state.

theoretical energy is the total energy at the level of CCSD(T)/def2-QZVPP corrected with the vibrational zero-point energy, not the generally used Gibbs free energy since it depends on the temperature.

In summary, we found three isomers for the negatively charged salt—water complex $NaCl(H_2O)$ and three isomers for the neutral counterpart using the cryo-SEVI method. The energy differences among different isomers were measured through the temperature-dependent photoelectron energy spectroscopy. As demonstrated here for the model complex $NaCl(H_2O)$, this method can be used to investigate other

species with multiple isomers close in energy. Moreover, the experimental data can provide a benchmark for the development of theoretical methods for the weakly bound noncovalent complex.

ASSOCIATED CONTENT

G Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpclett.2c01028.

Geometric data and vibrational analysis for isomers of the NaCl(H₂O) complex (Tables S1–S6), entropies and Gibbs free energy for three isomers of NaCl(H₂O)⁻ (Table S7), photoelectron spectra for NaCl(H₂O)⁻ at a series of temperatures at photon energy $h\nu = 11097$ cm⁻¹ (Figure S1), photoelectron spectra at a series of photon energies used to generate the combined highresolution spectra (Figure S2), and multipeak fitting used to extract the intensity of the overlapped features (Figure S3) (PDF)

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Notes

The authors declare no competing financial interest.

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