# Structures, Energetics, and Spectra of $Cl^-(H_2O)_n$ Clusters, $n = 1-6$: Ab Initio Study

**M. Masamura***

*Department of Preventive Dentistry, Okayama University Dental School, Shikata-cho 2-5-1, Okayama, 700-8525 Japan*

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$Cl^-(H_2O)_n$ ($n = 1-6$) clusters have been studied using ab initio calculations. The structures of the various $Cl^-(H_2O)_n$ isomers differed considerably from those of the corresponding $F^-(H_2O)_n$ isomers for $n = 2$ and 4−6, and especially so for $n = 6$. The relative stability of the $Cl^-(H_2O)_n$ isomers is also much different from that of the corresponding $F^-(H_2O)_n$ isomers at 0 and 298 K. The relative stability of the $Cl^-(H_2O)_n$ isomers at 298 K is different from that at 0 K, because of the entropy effect. The ionization potential, charge-transfer-to-solvent (CTTS) energy, and the OH stretching vibrational spectra are reported to facilitate future experimental work.

## I. Introduction

The hydration of ions is a subject of interest in solute and biochemistry.[1] The structures of aqua-halide anion clusters in regard to the internal or surface state of the halide anion have long been the subject of controversy.[2−22] The various structures of the $F^-(H_2O)_n$ cluster (where $n = 1-6$) have been examined using MP2/6-311++G(d,p) and BLYP/6-311++G(d,p) calculations,[23] and the various structures of $I^-(H_2O)_n$ for $n = 1-6$ have also been examined using extensive ab initio calculations.[24] For $Cl^-(H_2O)_n$, the structures that water molecules form around the chloride ion ($Cl^-$) in gas-phase clusters reflect the competition between solvation of the ion vs. hydrogen bonding among the water molecules. If hydrogen bonding to the ion dominates, then the $Cl^-$ ion will move to the interior of a solvation shell. If hydrogen bonding among the waters dominates, then the $Cl^-$ ion will move to the surface of a neutral water cluster.[25] Molecular dynamics[26−38] and ab initio calculations[4,5,10,39−41] both predict that the surface states dominate in $Cl^-(H_2O)_n$ clusters, even for large values of $n$. However, the effects of temperature and of the zero-point energy maintain the possibility of interior structures.[4,8,31,36,37]

Reference 41 contains the most extensive ab initio study on $Cl^-(H_2O)_n$. However, the structures of only the most stable isomers for $Cl^-(H_2O)_n$ ($n = 1-6$) at 0 K were discussed. Therefore, the various low-lying energy structures of $Cl^-(H_2O)_n$ were calculated using ab initio methods in the present work. The available experimental results can be grouped into three sets of data: formation enthalpies,[42−44] photodetachment energies,[3,40] and vibrational spectra.[25]

The purpose of this paper is (1) to show that the structures of the various $Cl^-(H_2O)_n$ isomers differ considerably from those of the corresponding $F^-(H_2O)_n$ isomers for $n = 2$ and 4−6, and especially so for $n = 6$; (2) to show that the relative stability of the $Cl^-(H_2O)_n$ isomers is significantly different from that of the corresponding $F^-(H_2O)_n$ isomers at 0 and 298 K; (3) to show that the relative stability of the $Cl^-(H_2O)_n$ isomers at 298 K is markedly different from that at 0 K owing to the entropy effect; (4) to calculate the ionization potentials (IPs); and (5) to calculate the OH stretching infrared (IR) spectra.

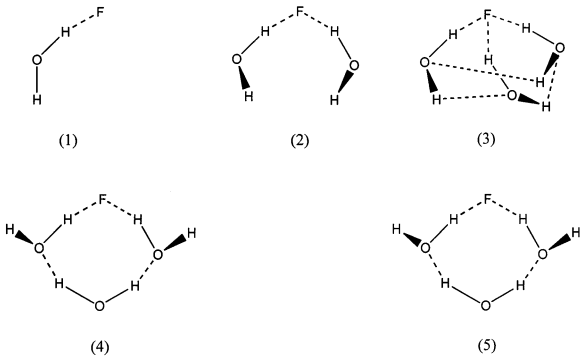


**Figure 1.** Sketches of the optimized structures of $F^-(H_2O)_n$ ($n = 1-3$).

## II. Computation Methods

We used the Gaussian 94[45] and Gaussian 98[46] programs, operating on the SX-5, VPP5000, and SGI2800 computers located at the Research Center for Computational Science.

For $F^-(H_2O)_n$ ($n = 1-4$), we considered the isomers discussed in ref 47 (see Figures 1 and 2). For $F^-(H_2O)_n$ ($n = 5$ and 6), we considered the isomers discussed in ref 23 (see Figures 3 and 4). For $Cl^-(H_2O)_n$ ($n = 1-6$), we substituted Cl for F in the above structures, and then optimized the resulting structures. Also, we optimized the structures of the isomers discussed in ref 41, (28′) and (29′) (see Figures 5−8).

MP2/aug-cc-pVDZ calculations could not be carried out owing to the large CPU time required. Therefore, we carried out full geometry optimizations using the MP2/6-31++G(2d,-2p) method for $Cl^-(H_2O)_n$ ($n = 1-6$). We also performed vibrational analysis for all of the clusters having the optimized structures to confirm that all of the vibrational frequencies are real. Also, we calculated the energies of those isomers at the MP4SDTQ/6-311++G(2d,2p)//MP2/6-31++G(2d,2p) levels. The zero-point energies were evaluated at the MP2/6-31++G-(2d,2p) level. The core electrons were frozen, and for the reason described in ref 48, the keyword "VeryTight" in the Gaussian 94 and Gaussian 98 programs was not used, i.e., standard optimization convergence criteria were used.

* E-mail address: tokin@mx3.tiki.ne.jp. Fax number: 81-86-235-6714. Telephone: 81-86-235-6712.

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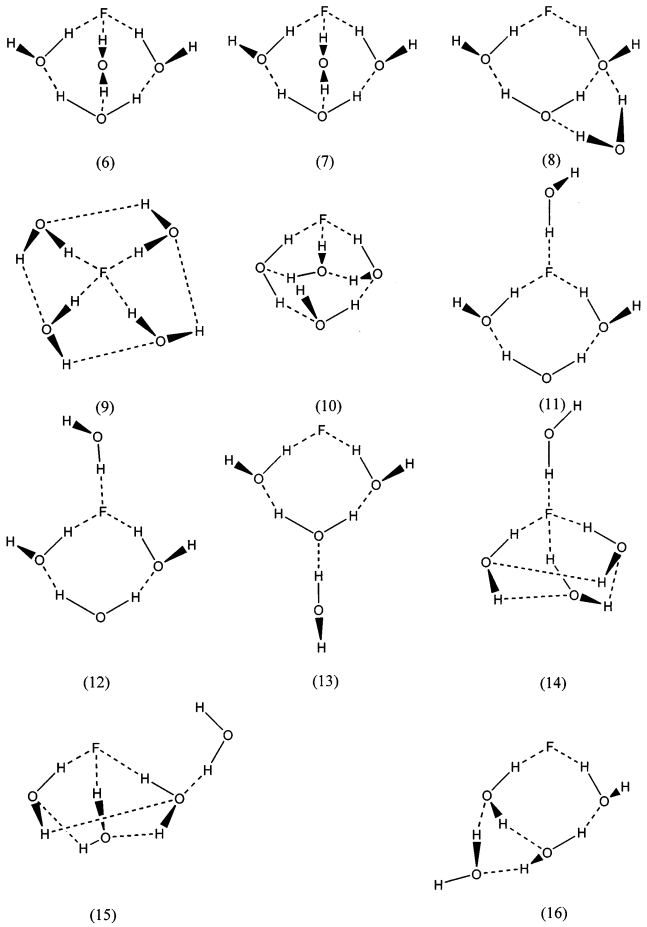


**Figure 2.** Sketches of the optimized structures of $F^-(H_2O)_4$.

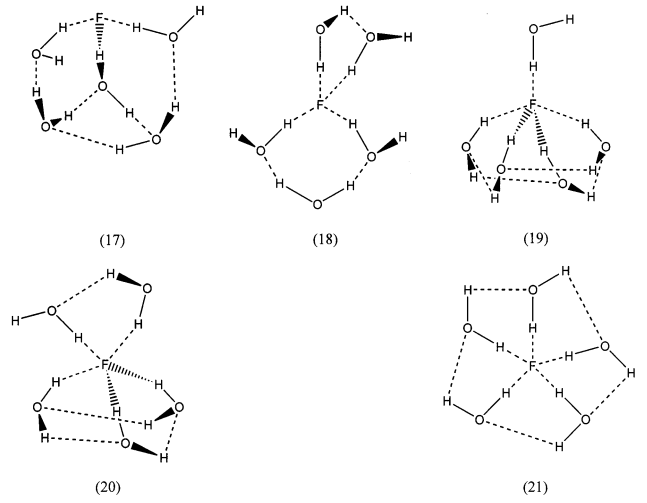


**Figure 3.** Sketches of the optimized structures of $F^-(H_2O)_5$.

The conversion of the computed energies to enthalpies for comparison with experimental data was represented by

$$\Delta H^{298\mathrm{K}} = \Delta E_e^\circ + \Delta E_v^\circ + \Delta(\Delta E_v^{298\mathrm{K}}) + \Delta E_r^{298\mathrm{K}} + \Delta E_t^{298\mathrm{K}} + \Delta(\mathrm{PV})$$

where $\Delta E_e^\circ$ is the electronic energy change, $\Delta E_v^\circ$ is the change in the zero-point energy, $\Delta(\Delta E_v^{298\mathrm{K}})$ is the vibrational energy change for the thermodynamic path from 0 to 298 K, and the remaining quantities are for the changes in rotational and translational energy, and for the work term, which were treated

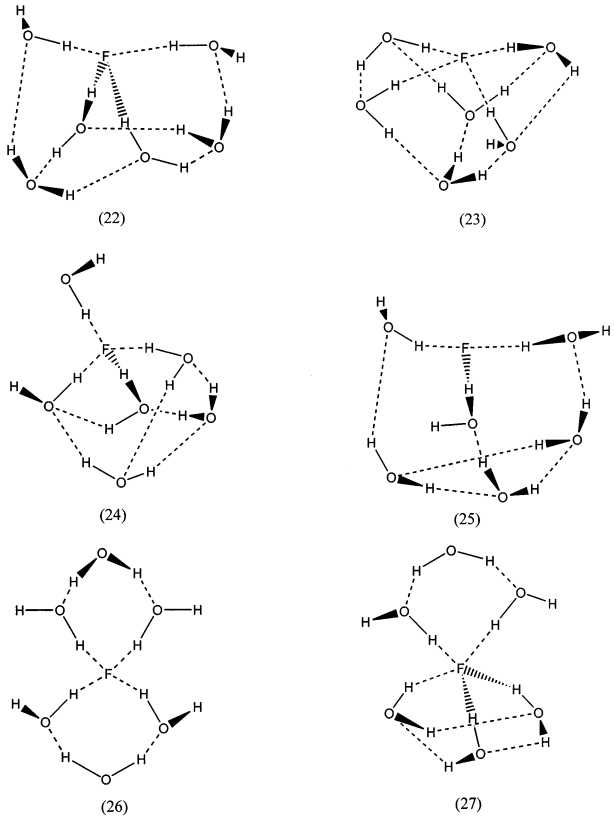


**Figure 4.** Sketches of the optimized structures of $F^-(H_2O)_6$.

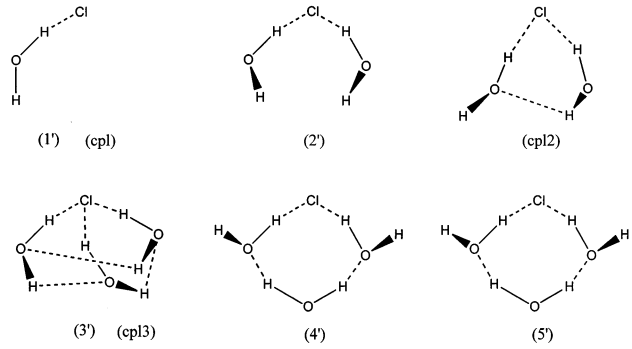


**Figure 5.** Sketches of the optimized structures of $Cl^-(H_2O)_n$ ($n = 1-3$). The isomers (cpl2) and (cpl3) are the isomers from ref 41.

classically. The enthalpy change of $Cl^-(H_2O)_n$ ($\Delta H_{n-1,n}^{298K}$) was calculated using the following formula:

$$\Delta H^{298K}{}_{n-1,n} = \mathrm{H}(\mathrm{Cl}^-(\mathrm{H_2O})_n) - \mathrm{H}(\mathrm{Cl}^-(\mathrm{H_2O})_{n-1}) - \mathrm{H}(\mathrm{H_2O})$$

Thermal corrections were evaluated using the MP2/6-31++G-(2d,2p) results. The basis set superposition error (BSSE) was corrected using the counterpoise method.[49,50]

For $Cl^-(H_2O)$, when the basis set is smaller, the counterpoise-uncorrected intermolecular interaction energies are closer to the CBS limit than the counterpoise-corrected intermolecular interaction energies at the MP2 and MP4 levels (Figure 9).[51] Also, the counterpoise-uncorrected $-\Delta H_{n-1,n}^{298K}$ are more reliable than the counterpoise-corrected $-\Delta H_{n-1,n}^{298K}$ evaluated at the MP2/6-31++G(2d,2p) level for $CH_3S^-(H_2O)_n$ ($n = 1-3$).[52] A similar trend was found for $F^-(H_2O)_n$ ($n = 1-6$).[23] Therefore, we used the counterpoise-uncorrected $-\Delta H_{n-1,n}^{298K}$ evaluated at the MP4/6-311++G(2d,2p)//MP2/6-31++G(2d,2p) level.

When certain frequencies are very low ($<10$ cm$^{-1}$), a serious error in the Gibbs free energy can arise owing to an overesti-

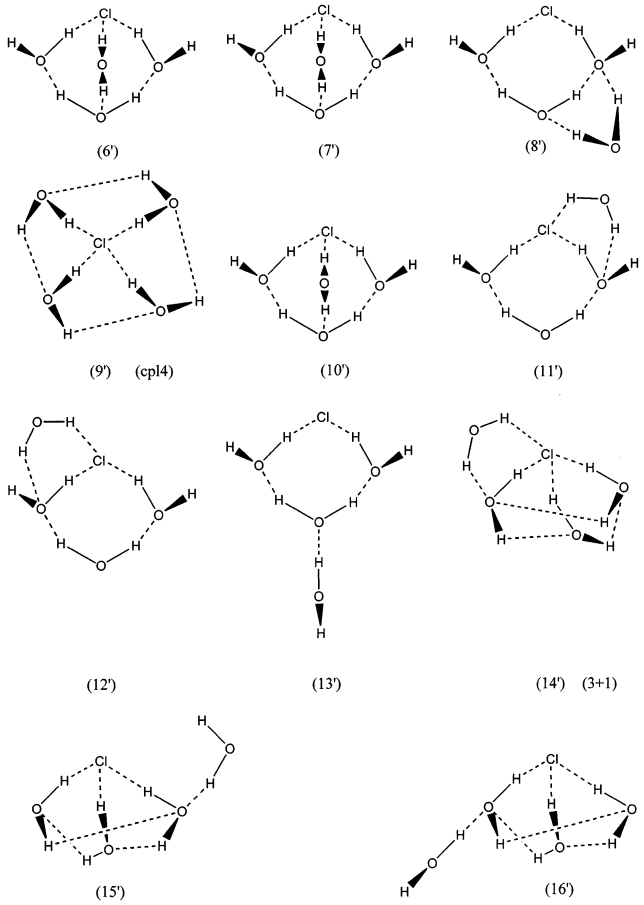


**Figure 6.** Sketches of the optimized structures of $Cl^-(H_2O)_4$. Isomer (cpl4) is the isomer from ref 41 and isomer (3 + 1) is the isomer from ref 10.

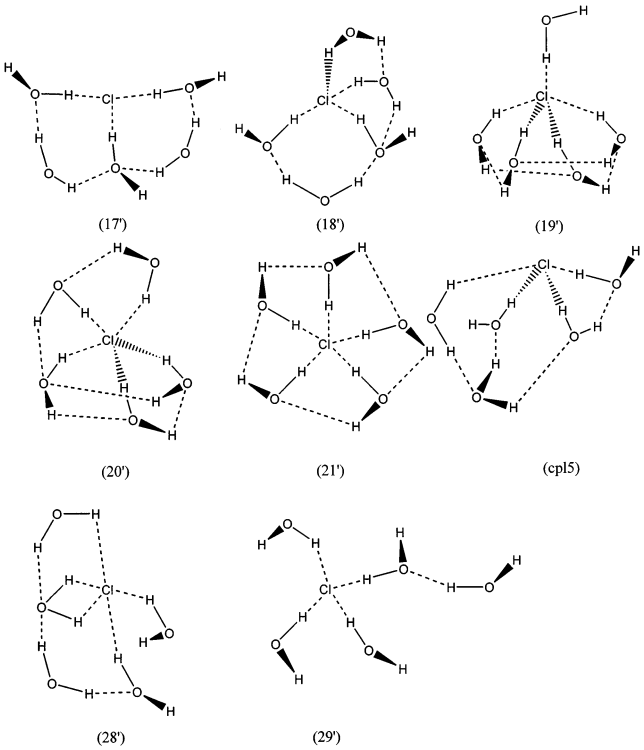


**Figure 7.** Sketches of the optimized structures of $Cl^-(H_2O)_5$. Isomer (cpl5) is the isomer from ref 41.

mated entropy corresponding to these low frequencies.[24] However, for our $Cl^-(H_2O)_n$ calculations, no such error arose.

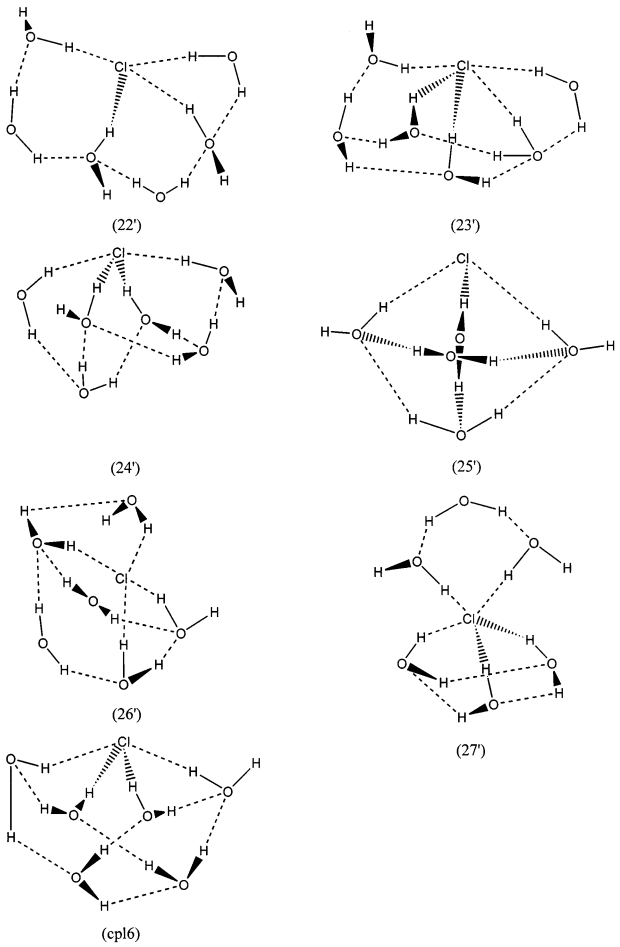


**Figure 8.** Sketches of the optimized structures of $Cl^-(H_2O)_6$. Isomer (cpl6) is the isomer from ref 41.

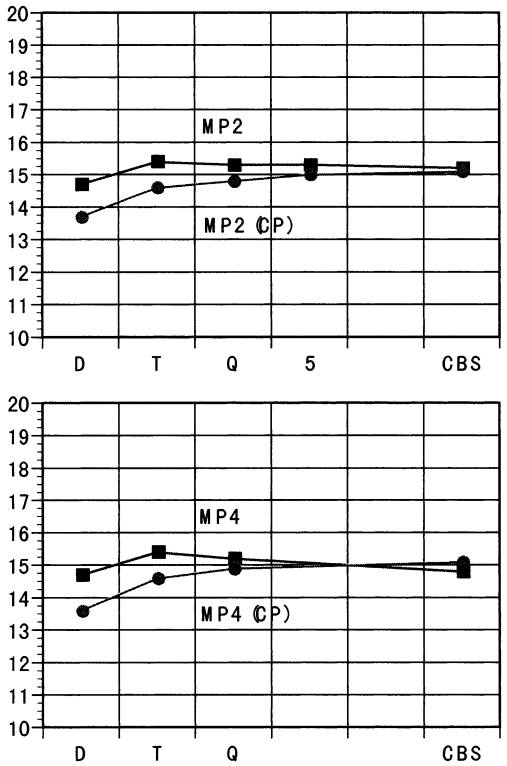


**Figure 9.** Calculated intermolecular interaction energies of $Cl^-(H_2O)$ as a function of the correlation consistent basis set (aug-cc-pVxZ ($x$ = D,T,Q,5) used. The counterpoise-corrected values are denoted by CP. The complete basis set (CBS) limit was estimated based on ref 55.

**TABLE 1: Calculated Energies of the $Cl^-(H_2O)_n$ ($n = 0-6$) Clusters[a]**

| n | isomer | MP2/6-31++G(2d,2p) | MP4/6-311++G(2d,2p) |
|---|---|---|---|
| 0 | | −459.69791 | −459.74752 |
| 1 | 1′ | −535.98541 | −536.08140 |
| 2 | cp12 | −612.27327 | −612.41533 |
| | 2′ | −612.27242 | −612.41475 |
| 3 | 3′ | −688.56251 | −688.75078 |
| | 4′ | −688.55913 | −688.74704 |
| | 5′ | −688.55947 | −688.74740 |
| 4 | 6′ | −764.84334 | −765.07719 |
| | 7′ | −764.84744 | −765.08141 |
| | 8′ | −764.84200 | −765.07571 |
| | 9′ | −764.84911 | −765.08294 |
| | 10′ | −764.84766 | −765.08167 |
| | 11′ | −764.84249 | −765.07640 |
| | 12′ | −764.84300 | −765.07694 |
| | 13′ | −764.84201 | −765.07509 |
| | 14′ | −764.84504 | −765.07924 |
| | 15′ | −764.84378 | −765.07751 |
| | 16′ | −764.84314 | −765.07684 |
| 5 | cp15 | −841.13190 | −841.41187 |
| | 17′ | −841.12612 | −841.40587 |
| | 18′ | −841.12867 | −841.40861 |
| | 19′ | −841.12898 | −841.40861 |
| | 20′ | −841.12785 | −841.40776 |
| | 21′ | −841.12913 | −841.40808 |
| | 28′ | −841.12951 | −841.40939 |
| | 29′ | −841.12923 | −841.40857 |
| 6 | cp16 | −917.42016 | −917.74563 |
| | 22′ | −917.40683 | −917.73252 |
| | 23′ | −917.41456 | −917.74013 |
| | 24′ | −917.41553 | −917.74077 |
| | 25′ | −917.41534 | −917.74082 |
| | 26′ | −917.41277 | −917.73843 |
| | 27′ | −917.40847 | −917.73394 |

[a] Eh.

**TABLE 2: Reliability of MP2/6-31++G(2d,2p) and MP4/6-311++G(2d,2p) Calculations[a]**

| | | $-\Delta H^{298K}_{n-1,n}$ (kcal/mol) | | |
|---|---|---|---|---|
| n | isomer | MP2/6-31++G(2d,2p) | MP4/6-311++G(2d,2p) | MP2/aug-cc-pVDZ[b] |
| 1 | 1′ | 14.5 (13.4) | 15.1 (13.3) | 14.4 (13.4) |
| 2 | cpl2 | 13.4 (12.0) | 13.8 (11.9) | 13.4 (12.0) |
| 3 | 3′ | 13.9 (12.0) | 14.4 (11.9) | 14.2 (12.4) |
| | 4′ | 12.1 (10.3) | 12.4 (10.2) | 12.0 (10.5) |
| 4 | 9′ | 12.2 (10.1) | 12.3 (9.5) | 12.1 (10.2) |
| | 14′ | 10.1 (8.8) | 10.4 (8.8) | 10.4 (9.0) |

[a] $-\Delta H^{298K}_{n-1,n}$ for the two isomers of the $n = 4$ cluster were computed with respect to isomer (3′). The numbers in parentheses indicate the BSSE-corrected values. [b] From ref 10.

According to ref 24, in the case of imaginary frequencies, the vibrational entropy, which is often treated as zero, is given by 10.5 cal/mol K.

## III. Results and Discussion

The optimized $Cl^-(H_2O)_n$ structures are shown in Figures 5 to 8. The initial structures of the (1′), (2′), (3′), ···, and (27′) clusters are the structures from the substituted Cl for F in the (1), (2), (3), ···, and (27) isomers, respectively. All of the present clusters, except for isomer (2′), have real vibrational frequencies and correspond to the equilibrium structures. Isomer (2′) is a transition state structure with one imaginary frequency. Table 1 shows the calculated energies for $Cl^-(H_2O)_n$.

MP4/6-311++G(2d,2p)//MP2/6-31++G(2d,2p) calculations for $SH^-(H_2O)_n$ are known to be reliable,[53] and therefore it is expected that MP4/6-311++G(2d,2p)//MP2/6-31++G(2d,2p) calculations for $Cl^-(H_2O)_n$ are also reliable. In fact, Table 2 shows that the MP2/6-31++G(2d,2p) and MP4/6-311++G(2d,2p) results agree with the MP2/aug-cc-pVDZ results from ref 10.

**TABLE 3: Relative Stability of Various Isomers of $Cl^-(H_2O)_n$ Clusters for $n = 2-6$ at 0 and 298 K, respectively[a]**

| | | relative energy | | relative Gibbs free energy | |
|---|---|---|---|---|---|
| n | isomer | MP2/6-31++G(2d,2p) | MP4/6-311++G(2d,2p) | MP2/6-31++G(2d,2p) | MP4/6-311++G(2d,2p) |
| 2 | cpl2 | 0.0 (0.0) | 0.0 (0.0) | 0.0 | 0.0 |
| | 2′ | 0.5 (0.2) | 0.4 (0.0) | −2.3 | −2.4 |
| 3 | 3′ | 0.0 (0.0) | 0.0 (0.0) | 0.0 | 0.0 |
| | 5′ | 1.9 (1.3) | 2.1 (1.5) | 0.2 | 0.4 |
| | 4′ | 2.1 (1.4) | 2.3 (1.7) | −0.2 | 0.0 |
| 4 | 9′ | 0.0 (0.0) | 0.0 (0.0) | 0.0 | 0.0 |
| | 10′ | 0.9 (0.5) | 0.8 (0.4) | −0.7 | −0.8 |
| | 7′ | 1.1 (0.7) | 1.0 (0.6) | −0.4 | −0.5 |
| | 14′ | 2.6 (1.5) | 2.3 (1.2) | −0.6 | −0.9 |
| | 15′ | 3.3 (2.3) | 3.4 (2.4) | −0.5 | −0.4 |
| | 6′ | 3.6 (2.4) | 3.6 (2.4) | 0.6 | 0.6 |
| | 16′ | 3.7 (2.6) | 3.8 (2.7) | −0.4 | −0.3 |
| | 12′ | 3.8 (2.2) | 3.8 (2.2) | −0.9 | −0.9 |
| | 11′ | 4.2 (2.5) | 4.1 (2.4) | −0.5 | −0.6 |
| | 8′ | 4.5 (3.2) | 4.5 (3.2) | 0.9 | 0.9 |
| | 13′ | 4.5 (3.0) | 4.9 (3.4) | −0.2 | 0.2 |
| 5 | cpl5 | 0.0 (0.0) | 0.0 (0.0) | 0.0 | 0.0 |
| | 28′ | 1.5 (0.9) | 1.6 (1.0) | −0.3 | −0.2 |
| | 29′ | 1.7 (1.3) | 2.1 (1.7) | −0.2 | 0.2 |
| | 21′ | 1.7 (1.5) | 2.4 (2.2) | 0.7 | 1.4 |
| | 19′ | 1.8 (0.9) | 2.1 (1.2) | −2.8 | −2.5 |
| | 18′ | 2.0 (1.2) | 2.0 (1.2) | −0.4 | −0.4 |
| | 20′ | 2.5 (1.7) | 2.6 (1.8) | 0.1 | 0.2 |
| | 17′ | 3.6 (2.2) | 3.8 (2.4) | −0.4 | −0.2 |
| 6 | cpl6 | 0.0 (0.0) | 0.0 (0.0) | 0.0 | 0.0 |
| | 24′ | 2.9 (1.9) | 3.0 (2.0) | 0.5 | 0.6 |
| | 25′ | 3.0 (2.2) | 3.0 (2.2) | 1.4 | 1.4 |
| | 23′ | 3.5 (2.6) | 3.5 (2.6) | 0.7 | 0.7 |
| | 26′ | 4.6 (3.3) | 4.5 (3.2) | 0.9 | 0.8 |
| | 27′ | 7.3 (5.0) | 7.3 (5.0) | −1.0 | −1.0 |
| | 22′ | 8.4 (5.6) | 8.2 (5.4) | 0.8 | 0.6 |

[a] kcal/mol.Parentheses indicate the relative energy including the zero-point energy.

Figures 1 to 8 show that the conformation of the optimized structures of the isomers for $Cl^-(H_2O)_n$ is different from that of $F^-(H_2O)_n$. For the isomers (cpl2), (10), (10′), (11), (11′), (12), (12′), (14), (14′), (18), (18′), (20), and (20′), the conformation of the $Cl^-(H_2O)_n$ isomer structures is slightly different from that of the corresponding $F^-(H_2O)_n$ isomers. This is because the intermolecular interaction between $Cl^-$ and the water molecules is much weaker than that between $F^-$ and the water molecules. Therefore, the water molecules in $Cl^-(H_2O)_n$ tend to form hydrogen bonds with the other water molecules in the cluster.

For isomers (16), (16′), (17), (17′), (cpl5), (28′), (29′), (22), (22′), (23), (23′), (24), (24′), (25), (25′), (26), (26′), and (cpl6), the conformation of the $Cl^-(H_2O)_n$ isomers is very different from that of the corresponding $F^-(H_2O)_n$ isomers. Three- and four-point hydrogen bonds are important in the stabilization of these isomers. The ionic radius of $Cl^-$ is larger than that of $F^-$, and thus the position of the water molecules around $Cl^-$ is different from those around $F^-$. For three-point hydrogen bonds and four-point hydrogen bonds, the intermolecular distances between water molecules are very important. As a result, the conformation in $Cl^-(H_2O)_n$, where three- and four-point hydrogen bonds form, is different from that in $F^-(H_2O)_n$. Thus, the conformation

**TABLE 4: NBO Charge of $Cl^-(q_{cl})$, the Vertical Ionization Potential (IP), the Integral ($dIP_v$), and Differential ($DIP_v$) Shifts, and the Charge-Transfer-to-Solvent Energy ($E_{CTTS}$) for $Cl^-(H_2O)_n$ Clusters at the MP2/6-31++G(2d,2p) Level[a]**

| *n* | isomer | $q_{cl}$ | $IP_v$ (eV) | $dIP_v$ (eV) | $DIP_v$ (eV) | $E_{CTTS}$ (eV) | expt. $IP_v$ (eV)[b] |
|---|---|---|---|---|---|---|---|
| 0 | | −1.00 | 3.46(4.09) | | | | 3.61 |
| 1 | 1′ | −0.94 | 4.30(4.81) | 0.84(0.72) | 0.84(0.72) | 5.04 | 4.37 |
| 2 | cpl2 | −0.91 | 4.93(5.45) | 1.47(1.36) | 0.63(0.64) | 5.21 | 4.97 |
| | 2′ | −0.90 | 4.93(5.47) | 1.47(1.38) | 0.63(0.66) | 5.26 | |
| 3 | 3′ | −0.90 | 5.38(6.06) | 1.92(1.97) | 0.45(0.61) | 5.45 | 5.50 |
| | 4′ | −0.88 | 5.39(5.95) | 1.93(1.86) | 0.46(0.50) | 5.31 | |
| | 5′ | −0.88 | 5.39(5.95) | 1.93(1.86) | 0.46(0.50) | 5.33 | |
| 4 | 6′ | −0.86 | 5.78(6.45) | 2.32(2.46) | 0.40(0.39) | 5.39 | 5.92 |
| | 7′ | −0.87 | - - -[c](6.43) | - - -[c](2.34) | - - -[c](0.37) | 5.47 | |
| | 8′ | −0.86 | 5.57(6.25) | 2.11(2.16) | 0.19(0.19) | 5.35 | |
| | 9′ | −0.90 | 5.73(6.51) | 2.27(2.42) | 0.35(0.45) | 5.58 | |
| | 10′ | −0.87 | 5.73(6.45) | 2.27(2.36) | 0.35(0.39) | 5.50 | |
| | 11′ | −0.86 | 5.82(6.52) | 2.36(2.43) | 0.44(0.46) | 5.46 | |
| | 12′ | −0.85 | 5.82(6.53) | 2.36(2.44) | 2.36(2.44) | 5.48 | |
| | 13′ | −0.86 | 5.66(6.21) | 2.20(2.12) | 0.28(0.15) | 5.32 | |
| | 14′ | −0.88 | 5.91(6.61) | 2.45(2.52) | 0.53(0.55) | 5.59 | |
| | 15′ | −0.88 | 5.75(6.42) | 2.29(2.33) | 0.37(0.36) | 5.48 | |
| | 16′ | −0.88 | 5.69(6.37) | 2.23(2.28) | 0.31(0.31) | 5.47 | |
| 5 | cpl5 | −0.86 | 6.21(6.88) | 2.75(2.79) | 0.48(0.37) | 5.68 | 6.21 |
| | 17′ | −0.84 | 6.36(6.97) | 2.90(2.88) | 0.63(0.46) | 5.56 | |
| | 18′ | −0.87 | 6.26(7.01) | 2.80(2.92) | 0.53(0.50) | 5.62 | |
| | 19′ | −0.89 | 6.28(7.03) | 2.82(2.94) | 0.55(0.52) | 5.62 | |
| | 20′ | −0.88 | 6.38(7.10) | 2.92(3.01) | 0.65(0.59) | 5.70 | |
| | 21′ | −0.89 | 6.20(6.87) | 2.74(2.78) | 0.47(0.36) | 5.67 | |
| | 28′ | −0.85 | 6.28(6.95) | 2.82(2.86) | 0.55(0.44) | 5.61 | |
| | 29′ | −0.88 | 6.06(6.84) | 2.60(2.75) | 0.33(0.33) | 5.61 | |
| 6 | cpl6 | −0.85 | 6.42(7.07) | 2.96(2.98) | 0.21(0.19) | 5.62 | 6.58 |
| | 22′ | −0.83 | 6.82(7.45) | 3.36(3.36) | 0.61(0.57) | 5.68 | |
| | 23′ | −0.86 | 6.67(7.35) | 3.21(3.26) | 0.46(0.47) | 5.77 | |
| | 24′ | −0.83 | 6.41(7.19) | 2.95(3.10) | 0.20(0.31) | 5.67 | |
| | 25′ | −0.85 | 6.44(7.07) | 2.98(2.98) | 0.23(0.19) | 5.66 | |
| | 26′ | −0.84 | 6.55(7.27) | 3.09(3.18) | 0.34(0.39) | 5.67 | |
| | 27′ | −0.87 | 6.77(7.49) | 3.31(3.40) | 0.56(0.61) | 5.71 | |

[a] $IP_v$, $dIP_v$, $DIP_v$ were obtained by the energy difference of the ionic and neutral species keeping the geometry unchanged, while their values in parentheses were obtained using Koopman's theorem. [b] From ref 3. [c] Values cannot be calculated.

of the $Cl^-(H_2O)_n$ isomers is very different from that of the corresponding $F^-(H_2O)_n$ isomers.

For $Cl^-(H_2O)_n$ at 0 K, Table 3 shows that: (1) for $n = 2$, isomer (cpl2) is a local minima, and isomer (2′) is a transition state structure, only being 0.4 kcal/mol above the local minimum energy; (2) for $n = 3$, isomer (3′) is the most stable isomer, and isomers (4′) and (5′) are less stable than isomer (3′) by 2 kcal/mol. The stability of isomer (4′) is close to that of isomer (5′); (3) for $n = 4$, isomer (9′) surface structure is the most stable, with isomer (10′) surface structure being less stable than isomer (9′) by 0.8 kcal/mol. Isomer (7′) surface structure is less stable than isomer (10′) by only 0.2 kcal/mol. The other isomers are considerably less stable than isomer (7′); (4) for $n = 5$, isomer (cpl5) surface structure is the most stable, with the other isomers being considerably less stable than isomer (cpl5); (5) for $n = 6$, isomer (cpl6) surface structure is the most stable, with the other isomers being considerably less stable than isomer (cpl6).

For $Cl^-(H_2O)_n$ ($n = 2-6$) clusters, our prediction for the most stable isomers agrees with the results shown in refs 10, 25, 41. For the $F^-(H_2O)_2$ cluster, isomer (2) is the most stable. For the $F^-(H_2O)_3$ cluster, isomer (3) is the most stable, with isomers (4) and (5) being less stable than isomer (3) by 1.2−1.4 kcal/mol. For the $F^-(H_2O)_4$, $F^-(H_2O)_5$, and $F^-(H_2O)_6$ clusters, isomer (6) surface structure, isomer (17) surface structure, and isomers (22) surface structure and (24) internal structure are the most stable, respectively.

The cause of the difference between the stability of the isomers for the $Cl^-(H_2O)_n$ and $F^-(H_2O)_n$ clusters is as follows. The interaction between $Cl^-$ and water molecules is much weaker than that between $F^-$ and water molecules. Further, the conformation of the $Cl^-(H_2O)_n$ isomers is very much different from that of the corresponding $F^-(H_2O)_n$ isomers.

For $Cl^-(H_2O)_n$ at 298 K, Table 3 shows that: (1) for $n = 2$, isomer (2′) is considerably more stable than isomer (cpl2); (2) for $n = 3$, isomers (3′), (4′), and (5′) are the most stable; (3) for $n = 4$, isomers (10′) surface structure, (12′) surface structure, and (14′) surface structure are the most stable; (4) for $n = 5$, isomer (19′) internal structure is the most stable, with the other isomers being considerably less stable than isomer (19′); (5) for $n = 6$, isomer (27′) internal structure is the most stable, with the other isomers being considerably less stable than isomer (27′).

At the MP4/6-311++G(2d,2p)//MP2/6-31++G(2d,2p) level, the $-\Delta H^{298K}_{n-1,n}$ ($n = 1-6$) of the minimum energy conformers [(1′), (cpl2), (3′), (9′), (cpl5), (cpl6)] are 15.1, 13.8, 14.4, 12.3, 10.8, and 13.3 kcal/mol, while $-\Delta H^{298K}_{n-1,n}$ ($n = 1-6$) of the conformers [(1′), (2′), ((3′), (4′) and (5′)), ((10′), (12′) and (14′)), (19′), (27′)] are 15.1, 14.1, 12.8, 11.8, 10.7, and 8.7 kcal/mol. The latter conformers are in better agreement with the experimental $-\Delta H^\circ_{n-1,n}$ values[42] (14.7, 13.0, 11.8, 10.6, 9.5, and 8.8). This indicates that the latter conformers are more populated than the former conformers at room temperature.

According to ref 23 for $F^-(H_2O)_n$ at 298 K, for $n = 2$, isomer (2) is the most stable. For $n = 3$, isomer (3) is the most stable. For $n = 4$, isomer (14) internal structure is most stable. For $n = 5$, isomer (18) internal structure is most stable. For $n = 6$, isomer (24) internal structure is most stable.

The relative stability of the $Cl^-(H_2O)_n$ isomers is much different from that of the corresponding $F^-(H_2O)_n$ isomers at

**TABLE 5: Shift of the OH Harmonic Frequencies for $Cl^-(H_2O)_n$ ($n = 1-6$) Clusters at the MP2/6-31++G(2d,2p) Level[a]**

| 1′ | δω | intensity | 2′ | δω | intensity | 19′ | δω | intensity | 20′ | δω | intensity |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | −525 | 1059 | | −441 | 291 | | −294 | 704 | | −317 | 177 |
| | +9 | 35 | | −402 | 1122 | | −286 | 15 | | −298 | 430 |
| | | | | −19 | 73 | | −252 | 346 | | −228 | 93 |
| | | | | −17 | 28 | | −250 | 328 | | −221 | 205 |
| cpl2 | δω | intensity | 3′ | δω | intensity | | −227 | 17 | | −176 | 205 |
| | −576 | 673 | | −322 [2] | 122 | | −185 | 54 | | −161 | 283 |
| | −258 | 400 | | −294 | 772 | | −176 | 252 | | −141 | 241 |
| | −99 | 163 | | −114 | 242 | | −173 | 200 | | −110 | 199 |
| | 0 | 41 | | −127 [2] | 168 | | −151 | 619 | | −92 | 201 |
| 4′ | δω | intensity | 5′ | δω | intensity | | +15 | 59 | | −53 | 108 |
| | −550 | 758 | | −551 | 761 | 21′ | δω | intensity | 28′ | δω | intensity |
| | −506 | 1191 | | −507 | 1197 | | −245 | 49 | | −628 | 947 |
| | −252 | 237 | | −253 | 237 | | −237 [2] | 321 | | −300 | 284 |
| | −174 | 481 | | −177 | 482 | | −226 [2] | 0 | | −276 | 166 |
| | 0 | 27 | | −3 | 77 | | −156 [2] | 0 | | −251 | 108 |
| | 1 | 67 | | −2 | 21 | | −156 [2] | 424 | | −189 | 501 |
| 6′ | δω | intensity | 7′ | δω | intensity | | −139 | 628 | | −180 | 394 |
| | −547 | 631 | | −565 | 926 | | | | | −169 | 340 |
| | −503 | 1071 | | −330 | 411 | | | | | −118 | 173 |
| | −280 | 256 | | −302 | 201 | | | | | −58 | 154 |
| | −215 | 169 | | −272 | 108 | | | | | −11 | 55 |
| | −196 | 493 | | −210 | 606 | 29′ | δω | intensity | cpl6 | δω | intensity |
| | −125 | 362 | | −174 | 432 | | −392 | 977 | | −621 | 886 |
| | +2 | 14 | | −134 | 183 | | −341 | 279 | | −408 | 38 |
| | +3 | 84 | | −1 | 51 | | −283 | 22 | | −357 | 721 |
| 8′ | δω | intensity | 9′ | δω | intensity | | −263 | 161 | | −319 | 496 |
| | −665 | 1221 | | −276 | 139 | | −254 | 190 | | −283 | 236 |
| | −524 | 1034 | | −267 [2] | 199 | | −227 | 360 | | −282 | 371 |
| | −286 | 325 | | −259 | 0 | | −182 | 324 | | −233 | 334 |
| | −197 | 372 | | −184 | 371 | | −172 | 438 | | −201 | 20 |
| | −176 | 219 | | −180 | 9 | | −128 | 180 | | −179 | 311 |
| | −80 | 205 | | −176 | 9 | | +17 | 55 | | −166 | 731 |
| | −1 | 51 | | | | | | | | −85 | 153 |
| | +3 | 51 | | | | | | | | +2 | 58 |
| 10′ | δω | intensity | 11′ | δω | intensity | 22′ | δω | intensity | 23′ | δω | intensity |
| | −551 | 873 | | −597 | 941 | | −494 | 746 | | −406 | 561 |
| | −341 | 413 | | −448 | 894 | | −459 | 1010 | | −359 | 242 |
| | −308 | 206 | | −235 | 238 | | −351 | 632 | | −298 | 503 |
| | −279 | 139 | | −192 | 239 | | −218 | 183 | | −280 | 120 |
| | −210 | 606 | | −147 | 410 | | −205 | 254 | | −252 | 123 |
| | −186 | 479 | | −69 | 160 | | −153 | 169 | | −220 | 81 |
| | −106 | 138 | | −6 | 50 | | −128 | 397 | | −209 | 623 |
| | −6 | _52 | | +1 | 56 | | −113 | 327 | | −179 | 591 |
| 12′ | δω | intensity | 13′ | δω | intensity | | −59 | 195 | | −167 | 132 |
| | −603 | 945 | | −599 | 719 | | −8 | 79 | | −131 | 192 |
| | −449 | 888 | | −548 | 1554 | | −6 | 58 | | −52 | 173 |
| | −234 | 241 | | −441 | 916 | | +3 | 61 | | −6 | 66 |
| | −202 | 262 | | −324 | 170 | 24′ | δω | intensity | 25′ | δω | intensity |
| | −148 | 397 | | −269 | 718 | | −600 | 867 | | −584 | 926 |
| | −70 | 157 | | −1 | 36 | | −447 | 690 | | −371 | 267 |
| | −4 | 62 | | 0 | 65 | | −330 | 472 | | −354 | 351 |
| | −2 | 46 | | +16 | 45 | | −292 | 115 | | −300 | 579 |
| | | | | | | | −267 | 219 | | −279 | 168 |
| 14′ | δω | intensity | 15′ | δω | intensity | | −235 | 255 | | −213 | 517 |
| | −359 | 277 | | −442 | 901 | | −209 | 520 | | −203 | 288 |
| | −312 | 392 | | −372 | 355 | | −167 | 323 | | −178 | 157 |
| | −254 | 243 | | −345 | 437 | | −140 | 370 | | −131 | 170 |
| | −198 | 260 | | −289 | 394 | | −106 | 304 | | −110 | 175 |
| | −151 | 258 | | −182 | 271 | | −9 | 67 | | −67 | 246 |
| | −134 | 192 | | −139 | 201 | | 0 | 58 | | +5 | 59 |
| | −79 | 32 | | −71 | 95 | 26′ | δω | intensity | 27′ | δω | intensity |
| | −67 | 216 | | +14 | 52 | | −612 | 887 | | −358 | 393 |
| 16′ | δω | intensity | cpl5 | δω | intensity | | −341 | 389 | | −333 | 1131 |
| | −420 | 922 | | −409 | 385 | | −274 | 217 | | −235 | 75 |
| | −355 | 435 | | −342 | 341 | | −246 | 467 | | −224 | 169 |
| | −342 | 297 | | −337 | 433 | | −232 | 77 | | −214 | 117 |
| | −298 | 444 | | −274 | 438 | | −215 | 162 | | −194 | 140 |
| | −186 | 287 | | −252 | 48 | | −162 | 365 | | −141 | 387 |
| | −136 | 190 | | −186 | 339 | | −154 | 380 | | −137 | 209 |
| | −81 | 108 | | −158 | 389 | | −111 | 224 | | −133 | 171 |
| | 21 | 52 | | −147 | 273 | | −79 | 236 | | −124 | 467 |
| | | | | −105 | 149 | | −76 | 140 | | +2 | 100 |
| | | | | −40 | 88 | | +2 | 61 | | +4 | 37 |
| 17′ | δω | intensity | 18′ | δω | intensity | | | | | | |
| | −544 | 848 | | −388 | 665 | | | | | | |
| | −420 | 1260 | | −336 | 444 | | | | | | |
| | −385 | 363 | | −250 | 94 | | | | | | |
| | −227 | 83 | | −244 | 296 | | | | | | |
| | −225 | 377 | | −224 | 199 | | | | | | |
| | −143 | 498 | | −151 | 423 | | | | | | |
| | −128 | 317 | | −138 | 77 | | | | | | |
| | −8 | 61 | | −131 | 385 | | | | | | |
| | −1 | 76 | | −94 | 154 | | | | | | |
| | +2 | 43 | | +1 | 62 | | | | | | |

[a] The shifts are given with respect to the corresponding mean of the symmetric and asymmetric OH stretch in water (3913 $cm^{-1}$). The frequency shifts are given in $cm^{-1}$ and the IR intensities in km/mol. The numbers in square brackets denote degeneracy.

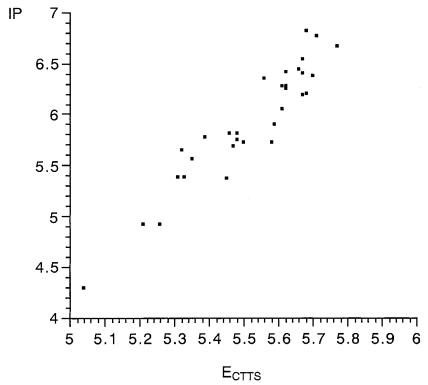


**Figure 10.** A plot of IP vs. $E_{CTTS}$ for $Cl^-(H_2O)_n$ using MP2/6-31++G-(2d,2p) results.

298 K. The relative stability of the $Cl^-(H_2O)_n$ isomers at 298 K is different from that at 0 K, because of the entropy effect.

We have represented the vertical ionization potentials of $Cl^-$ and the $Cl^-(H_2O)_n$ cluster as $IP_v(Cl^-)$ and $IP_v[Cl^-(H_2O)_n]$, respectively, and the integral shift $dIP_v(n)$ and the differential shifts $DIP_v(n)$ for the $n$th $Cl^-(H_2O)_n$ cluster are represented by $dIP_v(n) = IP_v[Cl^-(H_2O)_n] - IP_v(Cl^-)$ and $DIP_v(n) = IP_v[Cl^-(H_2O)_n] - IP_v[Cl^-(H_2O)_{n-1}]$, respectively.

The values for $IP_v$, $dIP_v$, and $DIP_v$ obtained from Koopman's theorem from MP2 calculations are shown in Table 4. As the vertical ionization potentials for one isomers are close to those for the other isomers, stable isomers cannot be identified by use of the vertical ionization potentials, although the calculated vertical ionization potentials for the isomers are close to the observed experimental values.

We have also considered the energy band gap or the ionization potential at the situation of the CTTS system ($E_{CTTS}$).[54] An empirical estimate of this energy is obtained by

$$E_{CTTS} = E[Cl^-(H_2O)_n] - E[Cl] - E[(H_2O)^-_{n-1}]$$

This energy is also listed in Table 4. Figure 10 shows the linear relationship of IP with $E_{CTTS}$. A similar trend has been found for $F^-(H_2O)_n$.[23]

Table 4 shows that the charge transfer from $Cl^-$ to $(H_2O)_n$ in $Cl^-(H_2O)_n$ increases with cluster size. A similar trend has been found for $F^-(H_2O)_n$.[23] The charge transfer in $Cl^-(H_2O)_n$ is slightly smaller than that in $F^-(H_2O)_n$.

Table 5 shows the shift of the OH harmonic frequencies for $Cl^-(H_2O)_n$. These results are useful for the identification of isomers using vibrational spectroscopy.

Fully optimized structural parameters are available free from the author.

## IV. Conclusions

From this work we draw the following conclusions. (1) The structures of various $Cl^-(H_2O)_n$ isomers differ considerably from those of the corresponding $F^-(H_2O)_n$ isomers for $n = 2$ and 4−6, and especially so for $n = 6$. (2) The relative stability of the $Cl^-(H_2O)_n$ isomers is markedly different from that of the corresponding $F^-(H_2O)_n$ isomers at 0 and 298 K. For $Cl^-(H_2O)_n$, the lowest energy structures for $n = 1-6$ are predicted to be (1′), (cpl2), (3′), (9′), (cpl5), and (cpl6), respectively at 0 K, and the most stable isomers of the isomers for $n = 1-6$ are predicted to be (1′), (2′), (3′,4′,5′), (10′,12′,-14′), (19′), and (27′), respectively at 298 K. For $F^-(H_2O)_n$, the lowest energy structures for $n = 1-6$ are predicted to be (1), (2), (3), (6), (17), and (22, 24), respectively at 0 K, and the most stable isomers of the isomers for $n = 1-6$ are predicted to be (1), (2), (3), (14), (18), and (24), respectively at 298 K. (3) The relative stability of the $Cl^-(H_2O)_n$ isomers at 298 K is very different from that at 0 K owing to the entropy effect. (4) The calculated vertical ionization potentials for the isomers are in close agreement with experimental values. However, since the vertical ionization potentials for one isomers are close to those for the other isomers, stable isomers cannot be identified by means of their vertical ionization potentials. (5) Our results for the $E_{CTTS}$ and vibrational spectral characteristics of these clusters will be useful in future experimental investigations.

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