

Photodetachment spectra of $\text{Cl}^-(\text{H}_2\text{O})_n$ clusters. Predictions and comparisons

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Abstract

Using molecular dynamics computer simulations we calculated the photodetachment spectra of $\text{Cl}^-(\text{H}_2\text{O})_n$ ($n = 2, 3, \dots, 15$) clusters. The dependence of the spectra on the variations in the temperature of the clusters and the potential parameters used to describe the interaction of the post-ejected ion with the water was investigated. We also studied the dependence of the spectra on the type of the potential used in the simulations: pair-wise versus many-body. The calculated data are compared to the experimental data for $n \leq 7$ and to the predicted data for $8 \leq n \leq 15$ since the experimental data are not available for clusters in this size range.

1. Introduction

The location of a simple anion such as F^- , Cl^- , Br^- or I^- in small and medium sized water clusters is an issue of considerable recent interest both in theory and experiment. Molecular dynamics computer simulations performed on $\text{F}^-(\text{H}_2\text{O})_n$ ($n = 1, 2, \dots, 15$) clusters predict that the ion's location is dependent on the temperature of the cluster [1]. While at low temperatures the ion is located on the surface of the cluster, at temperatures above 100 K the ion moves inside the cluster and gets solvated. For the $\text{Cl}^-(\text{H}_2\text{O})_n$ clusters the simulation results depend on the type of the potential used. Thus, the simulations predict that the chloride ion is solvated inside the clusters [2] with $n > 10$ when the potential model used in the simulations is of a pair-wise type, for example the OPLS model [3,4]. The Cl^- ion is located on the surface of the water cluster when polarizations of the water molecule and the ion are explicitly introduced into the potential model, like it

is done in the POL1 (also known as SPCE/POL) model [5]. The same conclusion that the location of the Cl^- ion in a cluster depends on the potential model used in the simulations was recently reached by Stuart and Berne who performed simulations on $\text{Cl}^-(\text{H}_2\text{O})_n$ clusters [6] using both pair-wise and non-pair-wise potentials. In the simulations with non-pair-wise potentials Stuart and Berne used the fluctuating charge model for water [7] and the Drude oscillator model to describe the polarizable nature of the ion (DI/FQ model). From their simulations with the DI/FQ model Stuart and Berne concluded that the Cl^- ion is on the surface of even a relatively large cluster containing 255 water molecules [6]. For Br^- ion both pair-wise and polarizable models predict that the ion is located on the surface of the cluster, although the polarizable model predicts a lower coordination number for the ion [8]. Finally, in the case of I^- ion both non-polarizable and polarizable models again agree that the ion is located on the surface of the water cluster [9]. Only for the case of

Cl^- ion the simulations are reported for the larger sized water clusters ($n = 255$), while for other ions the simulations are reported for small sized clusters with $n < 20$.

One would like to be able to resolve the question related to the location of the chloride ion in water clusters using the information obtained from experiment. Two sets of experimental data are available and both of them are related to the energetics of the $\text{Cl}^-(\text{H}_2\text{O})_n$ clusters. One set gives the enthalpies of formation of these clusters [10]. Unfortunately, the data on formation enthalpies, which provide us with the most direct information about the energetics of the clusters, are available for small sized clusters only, i.e. for clusters with n ranging from 1 to 7. Although the data for enthalpies of cluster formation obtained from the simulations using the POL1 and DI/FQ models showed a better agreement with experiment compared to the data from the calculations using OPLS potentials, uncertainty in experiment does not allow us to make a definite conclusion about the merits of each potential model.

The other set of data gives the electrostatic stabilization energy, or the vertical excitation energy for photodetachment of the electron from the chloride ion [11]. To get these data it is postulated that the peaks of the measured photoelectron spectra represent the average vertical binding energies of the electrons in the clusters. The difference between the vertical binding energy of a cluster and the electron affinity of the bare ion is defined as $E_{\text{stab}}(n)$. With respect to photodetachment data on water clusters with chloride there are two problems related to comparison of the data from experiment and simulations. The first problem is that the data are again available for the clusters with n up to seven water molecules. The second problem, more general in character, and applying to clusters with any anion, is related to the fact that the data in experiment are obtained from the clusters at temperatures that are estimated to be in the region 70–100 K, while the simulations were performed in the region 200–275 K. Moreover, the polarizability and Lennard-Jones parameters for post-ejected chloride should be treated in such a way that they are closer to the values for neutral species than for the ion. In the first calculations of photodetachment spectra of $\text{Cl}^-(\text{H}_2\text{O})_n$ the post-ejected chloride was assigned the same parameters as the

pre-ejected ion [12], since it is difficult to know the exact values of polarizability and Lennard-Jones parameters for the post-ejected ion. The temperature of the cluster was taken to be above 200 K in order to effectively explore the configuration space available to the cluster. In our subsequent work on the photodetachment spectra from $\text{Br}^-(\text{H}_2\text{O})_n$ ($n = 1, 2, \dots, 15$) clusters [8] the value of the polarization for the post-ejected bromide was the same as for bromine atom and the Lennard-Jones parameters were determined in such a way that the calculated maxima for the spectra with two and three water molecules were close to the ones from experiment. The temperature of the cluster with Br^- still remained above 200 K in our simulations. A simple procedure was devised recently to sample configurational space and perform simulations for clusters at temperatures around 100 K [13]. This procedure was used to calculate the photoelectron spectra of Cl^- , Br^- and I^- in acetonitrile clusters [13]. In these simulations the values of polarizabilities for the post-ejected ions were taken to be equal to atomic polarizabilities and Lennard-Jones parameters were modified to obtain good agreement with experiment for the smallest sized clusters ($n = 2$ and 3). In the present Letter we return to the issue of the comparison of the photoelectron spectra obtained from experiment and simulations on the $\text{Cl}^-(\text{H}_2\text{O})_n$ ($n = 2, 3, \dots, 15$) clusters and study the dependence of these spectra on the temperature and on the values of the potential parameters used to treat the post-ejected ion.

2. Prediction for the stabilization energies of $\text{Cl}^-(\text{H}_2\text{O})_n$ ($n = 8, 9, \dots, 15$) clusters

As we have already mentioned, the first problem that appears when one compares the experimental data with the simulation results for the photodetachment spectra of chloride in water clusters is due to the fact that experimental data are available only for clusters with $n \leq 7$. To circumvent this problem we devised a procedure that extrapolates the data for clusters that contain more than seven water molecules. The procedure is based on the idea of similarity of stabilization energies for the $\text{Cl}^-(\text{H}_2\text{O})_n$, $\text{Br}^-(\text{H}_2\text{O})_n$ and $\text{I}^-(\text{H}_2\text{O})_n$ clusters when $n = 1, 2, \dots, 15$ [12]. We observed that the

experimental data for $\text{Br}^-(\text{H}_2\text{O})_n$ and $\text{I}^-(\text{H}_2\text{O})_n$ clusters with $n = 1, 2, \dots, 15$ can be superimposed if properly scaled. That means that for both cluster systems the stabilization energy E_{stab} , which depends on the size of the cluster n and the nature of the ion μ , can be multiplied by a scaling factor C_μ to produce a universal function $f(n)$ independent of the nature of the ion in the cluster, i.e.

$$f(n) = C_\mu E_{\text{stab}}(\mu; n). \quad (1)$$

We also observed that the data for photodetachment spectra on $\text{Cl}^-(\text{H}_2\text{O})_n$ clusters with $n = 1, 2, \dots, 7$, if scaled, can be superimposed with the curve given by Eq. (1). While experiment shows that Eq. (1) is correct for chloride/water clusters with up to seven water molecules we assume that it is also correct for clusters with up to 15 water molecules. Therefore Eq. (1) can be used to predict the photodetachment spectra for $\text{Cl}^-(\text{H}_2\text{O})_n$ clusters with $n = 8, 9, \dots, 15$. To find these values we first of all assume that $C_{\text{Cl}} = 1$ and therefore we get

$$f(n) = E_{\text{stab}}(\text{Cl}; n). \quad (2)$$

For bromide from Eq. (1) one has

$$\sum_{n=1}^7 f(n) = C_{\text{Br}} \sum_{n=1}^7 E_{\text{stab}}(\text{Br}; n). \quad (3)$$

Finally, from Eqs. (2) and (3)

$$C_{\text{Br}} = \frac{\sum_{n=1}^7 E_{\text{stab}}(\text{Cl}; n)}{\sum_{n=1}^7 E_{\text{stab}}(\text{Br}; n)}. \quad (4)$$

The same procedure is applied to the data on clusters with iodide. This results in the following values for scaling factors: $C_{\text{Br}} = 1.21$ and $C_{\text{I}} = 1.52$. Using these two factors we get scaled stabilization energies for clusters with iodide and bromide. The predicted stabilization energy of clusters $\text{Cl}^-(\text{H}_2\text{O})_n$ with n between 8 and 15 is taken to be the average between the scaled stabilization energies of the same size clusters with bromide and iodide, i.e.

$$E_{\text{stab}}(\text{Cl}; n) = \frac{C_{\text{Br}} E_{\text{stab}}(\text{Br}; n) + C_{\text{I}} E_{\text{stab}}(\text{I}; n)}{2}, \quad (5)$$

Table 1

Experimental and predicted electrostatic stabilization energies (in eV) of $\text{Cl}^-(\text{H}_2\text{O})_n$ clusters. Predicted values were based on scaling of experimental data for Br^- and I^- with respect to those for $\text{Cl}^-(\text{H}_2\text{O})_n$ ($n = 1 \dots 7$)

n	Br^-		I^-		Cl^-	
	(Exp.)	Scaled	(Exp.)	Scaled	Exp.	Prediction
1	(0.57)	0.69	(0.45)	0.68	0.76	(0.69)
2	(1.08)	1.31	(0.86)	1.31	1.36	(1.31)
3	(1.58)	1.92	(1.23)	1.87	1.89	(1.90)
4	(1.91)	2.32	(1.53)	2.33	2.31	(2.32)
5	(2.17)	2.64	(1.71)	2.60	2.60	(2.62)
6	(2.45)	2.98	(2.05)	3.12	2.97	(3.05)
7	(2.71)	3.29	(2.14)	3.25	3.27	(3.27)
8	(2.83)	3.44	(2.22)	3.38	–	3.41
9	(2.87)	3.49	(2.34)	3.56	–	3.52
10	(2.96)	3.60	(2.40)	3.65	–	3.62
11	(2.99)	3.64	(2.43)	3.70	–	3.67
12	(3.14)	3.82	(2.49)	3.79	–	3.80
13	(3.17)	3.85	(2.57)	3.91	–	3.88
14	(3.32)	4.04	(2.58)	3.92	–	3.98
15	(3.33)	4.05	(2.63)	4.00	–	4.02

where $n = 8, 9, \dots, 15$. The values of experimentally measured $E_{\text{stab}}(\mu; n)$, scaled values of $E_{\text{stab}}(\mu; n)$ obtained from Eq. (1) and predicted values of $E_{\text{stab}}(\text{Cl}; n)$ obtained from Eq. (5) are given in Table 1.

3. Calculation of stabilization energies

The electrostatic stabilization energies can be calculated from molecular dynamics simulations. This is done by calculating the difference in energies of the cluster with the post-ejected halide and the cluster with the ion prior to ejection. In this calculation the nuclear configurations remain frozen while the fast degrees of freedom (induced dipoles) are allowed to relax. The average of the energy difference over the equilibrated trajectory represents the stabilization energy. To study the effect of temperature and potential parameters on the stabilization energy we performed simulations at ‘high’ temperature (i.e. above 200 K), at ‘low’ temperature (i.e. 100 K), and calculated stabilization energies using different values of the Lennard-Jones parameter σ and polarizability α for the post-ejected ion when the POL1 model was used. We also studied the effect of tem-

perature and the parameter σ on the stabilization energy calculated from the simulation using the OPLS potential. Results from six sets of calculations are reported here: three sets of calculations performed with the POL1 model (sets 1, 2 and 3) and three sets performed with the OPLS model (sets 4, 5 and 6). Every set contains calculations for clusters $\text{Cl}^-(\text{H}_2\text{O})_n$ where $n = 2, 3, \dots, 15$. As we observed it previously, the results from the calculations on clusters with $n = 1$ may depend on the initial conditions and that is why we do not report them here.

The energy of the cluster in the simulations under the POL1 model is:

$$U_{\text{tot}} = U_{\text{el}} + U_{\text{LJ}} + U_{\text{pol}} + U_{3\text{-body}}, \quad (6)$$

where U_{el} is the electrostatic energy, U_{LJ} is the Lennard-Jones energy, U_{pol} is the polarization energy and $U_{3\text{-body}}$ is the water–ion–water correction energy. The functional forms of these energies are well known and are given in our previous papers [1,2,12]. The changes in parameters that distinguish between the sets of simulations under the POL1 potential are related to the terms that describe the Lennard-Jones post-ejected ion–water interaction:

$$U_{\text{LJ}} = 4\varepsilon_{\text{IO}} \left[\left(\frac{\sigma_{\text{IO}}}{r_{\text{IO}}} \right)^{12} - \left(\frac{\sigma_{\text{IO}}}{r_{\text{IO}}} \right)^6 \right] \quad (7)$$

and the polarization energy of the post-ejected ion:

$$U_{\text{pol}}(\text{I}) = -\frac{1}{2}\alpha_1 \mathbf{E}_1 \cdot \mathbf{E}_1^0. \quad (8)$$

In Eq. (7) σ_{IO} is the Lennard-Jones σ parameter for the post-ejected ion–water oxygen interaction which is obtained using the sum rule:

$$\sigma_{\text{IO}} = \frac{\sigma_{\text{II}} + \sigma_{\text{OO}}}{2}. \quad (9)$$

It is the parameter σ_{II} that we change in the calculations of the stabilization energies. In Eq. (8) α_1 is the polarizability and \mathbf{E}_1 and \mathbf{E}_1^0 are respectively the total electric field and the electric field due to permanent charges at the ion site. The polarizability α_1 from Eq. (8) is also changed to reflect the ejection of the electron. For the OPLS model only the Coulomb energy and the Lennard-Jones energy terms contribute and therefore we change only the parameter σ_{II} to reflect the change due to the ejection of the electron. A more detailed description of the Hamiltonian for the cluster and the methodology used in the

simulations are given in our previous papers [1,2,12]. For simulations with the POL1 potential the first set (set 1) was done in the same way as in our previous simulations, i.e. the values of the Lennard-Jones parameter σ_{II} and the polarizability for the post-ejected ion remained the same as for the Cl^- ion ($\sigma_{\text{II}} = 4.32 \text{ \AA}$ and $\alpha_1 = 3.25 \text{ \AA}^3$) [12]. Also the temperature of the clusters was ‘high’; more specifically for clusters with 2 to 4 water molecules it was 275 K, for clusters with 5 to 9 water molecules it was 250 K and for clusters with 10 to 15 waters it was 225 K. For each cluster size we performed after 50 ps equilibration a molecular dynamics run of 1 ns duration. The time step was 1 fs and every 100th configuration was saved, providing us with 10000 configurations, which were used for calculations of the stabilization energies. To see the effect of temperature, we selected equally spaced 100 (out of 10000) configuration points from the ‘high’ temperature trajectory and dropped the temperature of these points to 100 K. Each point served as a starting point for a trajectory at the ‘low’ temperature of 100 K. The total runtime of each trajectory was divided into two periods: equilibration and production. We report here results with 5 ps equilibration and 5 ps production run. We tested different periods of equilibration and production, including lengthier ones of 50 ps. No substantial difference in the results was found. During the 5 ps production run, configurations were recorded at every 50 fs giving us 100 configurations per each 100 starting configurations. The stabilization energy for each cluster was therefore computed from an average over these $100 \times 100 = 10000$ points in the configuration space. We observed that lowering the temperature and retaining the potential parameters results in increased values of the stabilization energies. The reduction of the σ parameter for the post-ejected ion decreased the values of the stabilization energies. We report here the values of the stabilization energies for two sets of calculations both of which were performed at 100 K and in both of the sets we assigned the same value of polarizability $\alpha_1 = 2.30 \text{ \AA}^3$ to the post-ejected ion. This value corresponds to the polarizability of the neutral Cl atom. Sets 2 and 3 differed in the value of the σ_{II} parameter. In the second set we used $\sigma_{\text{II}} = 3.70 \text{ \AA}$, as prescribed by Markovich et al. [13], while in the third set we used $\sigma_{\text{II}} = 4.00 \text{ \AA}$. The results are given

Table 2

Electrostatic stabilization energies (in eV) for $\text{Cl}^-(\text{H}_2\text{O})_n$ calculated from the POL1 model

	Exp. and prediction	Set 1		Set 2		Set 3	
		(unscaled)	scaled	(unscaled)	scaled	(unscaled)	scaled
$\sigma_{\text{Cl}-\text{Cl}}$		4.32 Å		3.70 Å		4.00 Å	
α		3.25 Å		2.30 Å ³		2.30 Å ³	
Temperature		'high'		'low'		'low'	
n		(unscaled)	scaled	(unscaled)	scaled	(unscaled)	scaled
1	0.76	–	–	–	–	–	–
2	1.36	(1.34)	1.34	(1.24)	1.29	(1.32)	1.30
3	1.89	(1.89)	1.88	(1.79)	1.86	(1.90)	1.88
4	2.31	(2.32)	2.31	(2.27)	2.36	(2.39)	2.36
5	2.60	(2.71)	2.70	(2.59)	2.69	(2.73)	2.70
6	2.97	(2.99)	2.98	(2.87)	2.98	(3.01)	2.97
7	3.27	(3.22)	3.21	(3.09)	3.21	(3.23)	3.19
8	3.41	(3.44)	3.43	(3.29)	3.42	(3.44)	3.40
9	3.52	(3.58)	3.57	(3.39)	3.52	(3.54)	3.50
10	3.62	(3.74)	3.73	(3.48)	3.62	(3.63)	3.59
11	3.67	(3.83)	3.82	(3.59)	3.73	(3.75)	3.70
12	3.80	(3.88)	3.87	(3.63)	3.77	(3.78)	3.73
13	3.88	(3.92)	3.91	(3.71)	3.86	(3.87)	3.82
14	3.98	(4.02)	4.01	(3.78)	3.93	(3.94)	3.89
15	4.02	(4.06)	4.05	(3.80)	3.95	(3.96)	3.91

in Table 2 and are denoted as 'unscaled'. Similarly, three sets (sets 4, 5 and 6) of calculations were performed using the OPLS model. In set 4, the value

of the σ_{II} parameter for the post-ejected ion was the same as for the pre-ejected ion. The temperatures for the clusters in this set was 'high'. The calculation

Table 3

Electrostatic stabilization energies (in eV) for $\text{Cl}^-(\text{H}_2\text{O})_n$ calculated from the OPLS model

	Exp. and prediction	Set 4		Set 5		Set 6	
		(unscaled)	scaled	(unscaled)	scaled	(unscaled)	scaled
$\sigma_{\text{Cl}-\text{Cl}}$		4.31 Å		3.69 Å		3.98 Å	
Temperature		'high'		'low'		'low'	
n		(unscaled)	scaled	(unscaled)	scaled	(unscaled)	scaled
1	0.76	–	–	–	–	–	–
2	1.36	(1.21)	1.17	(1.13)	1.17	(1.18)	1.18
3	1.89	(1.78)	1.73	(1.65)	1.70	(1.72)	1.71
4	2.31	(2.30)	2.23	(2.17)	2.24	(2.25)	2.24
5	2.60	(2.78)	2.70	(2.60)	2.69	(2.69)	2.68
6	2.97	(3.21)	3.11	(3.03)	3.13	(3.14)	3.13
7	3.27	(3.57)	3.46	(3.36)	3.47	(3.47)	3.46
8	3.41	(3.86)	3.74	(3.67)	3.79	(3.79)	3.78
9	3.52	(4.13)	4.00	(3.95)	4.08	(4.10)	4.09
10	3.62	(4.37)	4.24	(4.19)	4.33	(4.32)	4.31
11	3.67	(4.60)	4.46	(4.41)	4.56	(4.55)	4.53
12	3.80	(4.76)	4.62	(4.55)	4.70	(4.69)	4.67
13	3.88	(4.91)	4.76	(4.78)	4.94	(4.92)	4.90
14	3.98	(5.11)	4.96	(4.88)	5.04	(5.03)	5.01
15	4.02	(5.18)	5.02	(5.02)	5.19	(5.17)	5.15

sets 5 and 6 were performed at 100 K and with the reduced value of the parameter σ_{II} . The reduction was taken to be in the same proportion as in the case of the POL1 model. The results from the calculations with the OPLS model are given in Table 3 and are also denoted as 'unscaled'. As we can see from Tables 2 and 3 the stabilization energies do not change substantially with the change in temperature and with the change of the Lennard-Jones parameter (and polarizability, in case of the POL1 model) of the post-ejected ion. As a matter of fact we found that by reducing the temperature to 100 K and the Lennard-Jones parameter σ_{II} by $\approx 10\%$ we retain practically the same stabilization energy as calculated from the simulations with temperatures above 200 K and with unchanged polarization and Lennard-Jones parameters. This is seen from the comparison of sets 1 and 3 in case of the POL1 model and sets 4 and 6 in case of the OPLS model. The close agreement between the calculated stabilization energies in these sets occurs because the decrease in temperature increases the stabilization energy and the reduction in Lennard-Jones parameter decreases the stabilization energy, therefore the two factors compensate each other.

As we can see the calculated stabilization energies using the POL1 model show a good agreement with the experimental data for clusters with up to seven water molecules and with the predicted data for clusters that contain 8 to 15 water molecules. The energies do not change much when the temperature of the clusters is lowered and when the potential parameters for post-ejected ion are changed. For the simulations with the OPLS model we observed that by reducing the Lennard-Jones parameter we get results closer to the predicted data for clusters with more than seven water molecules, but at the same time we get further away from the experimental data for clusters with 1 to 3 water molecules. It seems that in this case, the experimental data together with the predicted data are described by one type of curve, while the calculated data, if scaled, belong to another type of curve. This idea can be easily checked. Let us say that the stabilization energies obtained from the i th calculation set can be scaled to some curve $g(n)$ which is independent of the set, i.e. we can write that

$$g(n) = \tilde{C}_i E_{\text{stab}}(i; n). \quad (10)$$

If the function $g(n)$ can be scaled to $f(n)$, the same function that was defined by Eq. (2), we have that

$$f(n) = C_0 g(n). \quad (11)$$

From the last two equations one gets

$$f(n) = C_0 \tilde{C}_i E_{\text{stab}}(i; n) = C_i E_{\text{stab}}(i; n). \quad (12)$$

To find the coefficients C_i we sum the last equation for clusters with $n = 2-7$ to get:

$$C_i = \frac{\sum_{n=2}^7 f(n)}{\sum_{n=2}^7 E_{\text{stab}}(i; n)}. \quad (13)$$

In Eq. (13) $f(n)$ are the experimental data for stabilization energies in clusters $\text{Cl}^-(\text{H}_2\text{O})_n$ with $n = 2, 3, \dots, 7$ (see Eq. (2)). The coefficients C_i from Eq. (13) were calculated for all six sets of cluster calculations and the calculated stabilization energies were scaled using these coefficients. The results, which are denoted as 'scaled', are presented together with the 'unscaled' data in Tables 2 and 3. To get a quick grasp on the data we have also presented them in a graphical way. The unscaled data calculated using three sets under the POL1 model together with the data from experiment and predictions are presented in Fig. 1a. The scaled data from the POL1 sets, experimental data and predicted data are presented in Fig. 1b. Fig. 2a and b present the same type of data calculated using the OPLS model. Finally in Fig. 3 we present the experimental, predicted and best fit to scaled data from the calculations using POL1 and OPLS models. As we can see from Fig. 3 the agreement between the curve from the POL1 model and the experimental data and predictions is quite remarkable. At the same time there is an obvious disagreement between the experimental data together with predictions and the scaled curve obtained from the calculations using the OPLS model.

4. Conclusions

Recently it was pointed out [6] that to compare the computed stabilization energies for $\text{Cl}^-(\text{H}_2\text{O})_n$ clusters with the measured ones, the temperature of

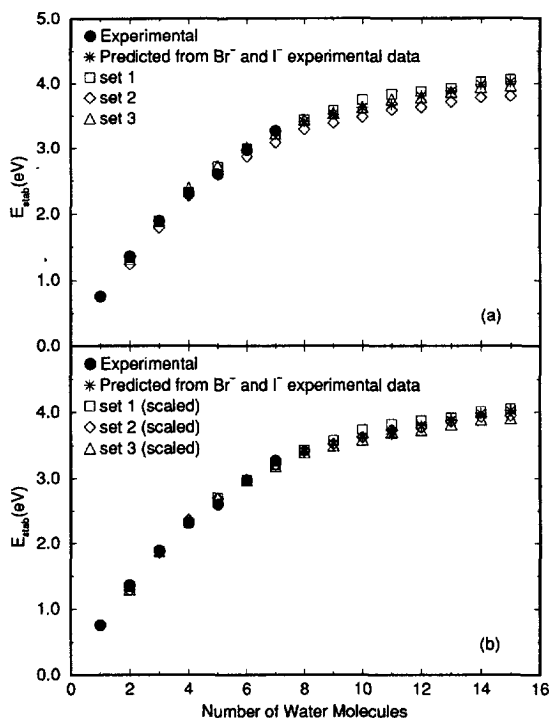


Fig. 1. (a) Electrostatic stabilization energies calculated using the POL1 model. Squares, diamonds and triangles denote E_{stab} obtained from simulations using the POL1 model with parameter sets 1, 2 and 3, respectively. Circles and stars represent experimental and predicted data for Cl^- , respectively. (b) Same sets of data as in (a), only with scaling for calculated E_{stab} .

the clusters in the simulations must be close to the experimental one, i.e. around 100 K. Also, the potential parameters describing the interaction of post-ejected ion with water should be different from the ones describing the interaction of the pre-ejected ion with the water. We reported here calculations that take the changes in temperature and potential parameters into account. Our results show that for calculations on the $Cl^-(H_2O)_n$ clusters with $n = 2, 3, \dots, 15$ the results do not change dramatically. Moreover, when the results are scaled in a simple fashion, we see that they are independent of temperature or the potential parameters and that they belong to the same curve. We observed that simulations under different potential models produce different curves. We also observed that the curve that is obtained by a best fit to the scaled data from the simulations where the potential includes explicit polarization (POL1), is in a very good agreement with the data from the

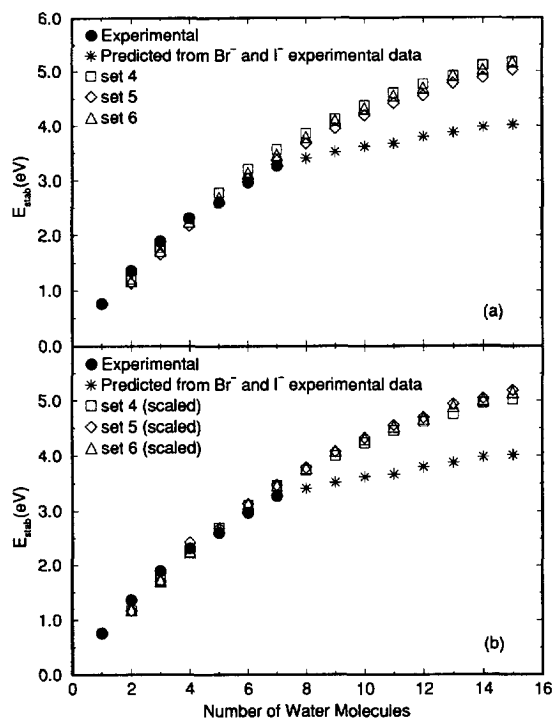


Fig. 2. (a) Electrostatic stabilization energies calculated using the OPLS model. Squares, diamonds and triangles denote E_{stab} obtained with parameter sets 4, 5 and 6, respectively. (b) Same sets of data as in (a), only with scaling for calculated E_{stab} .

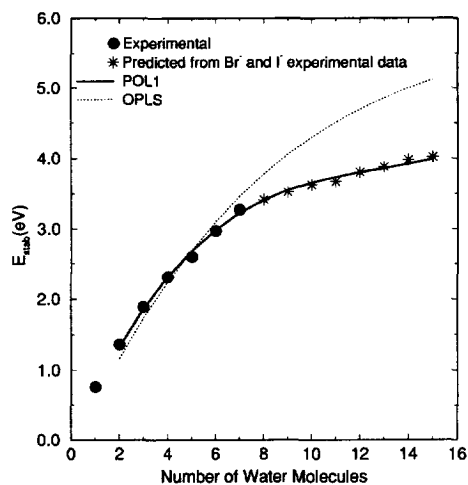


Fig. 3. Comparison between the calculated, the experimental (circles) and the predicted (stars) stabilization energies. Solid and dotted lines represent the best fitted curves for scaled E_{stab} calculated from the simulations with POL1 and OPLS models, respectively.

experiment and with the predicted data, while the curve obtained from the simulations with the pairwise potential is different from the experimental/prediction curve.

One should not forget that the data for the stabilization energies in the clusters with more than seven water molecules are our predictions. If they are correct (the very good agreement between the calculations with POL1 potential and the predictions indicates that this may be the case), then the comparison given in Fig. 3 illustrates why the inclusion of the explicit polarization into the computational scheme is really needed to correctly describe the photodetachment experiment for the Cl^- ion in aqueous clusters and the location of the ion in these clusters.

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