Surface solvation of halogen anions in water clusters:
An ab initio molecular dynamics study of the Cl⁻(H₂O)₆ complex

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ABSTRACT

The structure and dynamics of Cl(H₂O)₆ has been studied by *ab initio* molecular dynamics using the Car-Parrinello approach, and compared to results of *ab initio* quantum chemical calculations, molecular dynamics based on both polarizable and non-polarizable empirical potentials, and vibrational spectroscopy. The electronic structure methodology (density functional theory with the gradient-corrected BLYP exchange-correlation functional) used in the Car-Parrinello dynamics has been shown to give good agreement with MP2 results for the structures and energetics of Cl(H₂O)ₙ, n = 1–4, clusters. The configurational sampling during the 5 ps *ab initio* MD simulation at 250 K was sufficient to demonstrate that the chloride anion preferred a location on the surface of the cluster, which was significantly extended compared to the minimum energy geometry. The structure of the cluster predicted by the polarizable force field simulation is in agreement with the *ab initio* simulation, while the non-polarizable force field calculation was in qualitative disagreement, predicting an interior location for the anion. The time evolution of the electronic structure during the *ab initio* simulation was analyzed in terms of maximally localized orbitals (Wannier functions). Calculation of the dipole moments from the centers of the Wannier orbitals revealed that the chloride anion is significantly polarized, and that the extent of water polarization depends on location in the cluster, thus underscoring the importance of electronic polarization in halogen ion solvation. The infrared absorption spectrum was computed from the dipole-dipole correlation function, including both nuclear and electronic contributions. Aside from a systematic red shift by 3% to 5% in the frequencies, the computed spectrum was in quantitative agreement with vibrational predissociation data on Cl(H₂O)₅. Our analysis suggests that accounting for anharmonicity and couplings between modes is more important than the fine tuning of the electronic structure method for the quantitative prediction of hydrogen bond dynamics in aqueous clusters at elevated temperatures.
I. INTRODUCTION

The phenomenon of ion solvation in water clusters has received considerable attention in recent years for several reasons. First, the size of clusters can be gradually increased to the point where they exhibit many properties of the bulk while still containing a relatively small number of particles. The limited number of degrees of freedom in clusters opens up the possibility for high resolution experiments and accurate theoretical calculations. The recent development of new spectroscopic techniques for charged clusters has renewed interest in the fundamental aspects of the structure and dynamics of the ion-water hydrogen bond.\textsuperscript{1-9} Moreover, because of their large surface to interior ratio, clusters are useful models for investigating ion solvation at interfaces of aqueous solutions, which is of relevance to atmospheric chemistry. As a prominent example, highly concentrated sea salt aerosols have been recently identified as a potential global source of halogens in the marine boundary layer.\textsuperscript{10-12}

The most common species used in the study of aqueous ionic solvation are the halogen anions and alkali cations. Bulk ionic solutions are trivially prepared by dissolving the appropriate salt in liquid water. The preparation of the corresponding clusters by supersonic jet expansion into the vacuum is much more difficult due to the very low vapor pressure of most alkali halides.\textsuperscript{13} On the theoretical side, for the most common salt, sodium chloride, \textit{ab initio} calculations on clusters including a single ion pair and one to ten water molecules have been performed,\textsuperscript{14-16} primarily with the goal of establishing the onset of ionic solvation, \textit{i.e.} creation of a solvent separated ion pair. In contrast to previous studies,\textsuperscript{15,17} the most recent work shows that NaCl solvation occurs already in the water hexamer,\textsuperscript{16} however, conclusive experimental verification of this result is still lacking.

Halogen ion solvation in clusters can be directly accomplished by supersonic jet expansion, and size selection can be performed by mass spectrometry. Size selected halogen ion-water complexes were first studied with high pressure mass spectrometry\textsuperscript{18,19} and
photoelectron spectroscopy. More recently, higher resolution techniques such as infrared and ZEKE spectroscopies have been applied to the study of the structure and dynamics of halogen anion-water clusters and their neutral counterparts. Halogen-water clusters, in most cases containing a chloride anion, have been also studied theoretically either by using electronic structure methods, or molecular dynamics (MD) simulations. A remarkable result of both theory and experiment is that the halogen anions behave very differently from alkali cations. While the small non-polarizable alkali cations dissolve very well in water clusters, with complete solvation occurring already for six water molecules, the large and polarizable halogen anions remain on the surface and, even in relatively large clusters, the anion solvation is far from complete.

Quantitative theoretical description of halogen ion solvation in water clusters is demanding both on the quality of the interaction potential and on the sampling of the accessible phase space. It has been shown that, for example, including a many-body polarization term in an empirical force field notably moves the anion from the interior towards the surface of the cluster. Advanced ab initio methods provide, at least for small clusters, a sufficiently accurate interaction model. However, since quantum chemical methods directly provide results relevant to 0 K, sampling of the phase space of these non-rigid clusters with many local minima and low-lying barriers is likely to be insufficient. The advent of the Car-Parrinello ab initio molecular dynamics approach permits phase space sampling of non-rigid systems with non-empirical potentials. With this technique it is presently feasible to simulate clusters with tens of heavy atoms for several picoseconds. Recently, a Car-Parrinello simulation was successfully applied to the study of microsolvation and chemical reactivity in sodium and water clusters.

Here, we report a Car-Parrinello molecular dynamics (CPMD) simulation, with electronic structure computed from density functional theory including a gradient-corrected exchange-correlation functional, of a chloride anion in a water hexamer. One of our goals is to quantitatively describe the structure of this intermediate size complex, with a focus on the surface solvation of the Cl⁻ species. In addition, a localized orbital approach is used to describe
the polarization of the anion and the water molecules, and the vibrational spectrum is computed and compared to available experimental data. The CPMD simulation is also compared to standard MD with non-polarizable and polarizable potentials. The density functional employed in the CPMD simulations is validated by comparison to accurate ab initio calculations for minimal structures of Cl(H_2O)_n (n = 1–4) complexes.

II. METHODS

The ab initio MD trajectory was generated using the CPMD program\textsuperscript{38} starting with a configuration from a non-polarizable force field based simulation (described below) of Cl (H_2O)_6. The equations of motion for the electrons and ions were integrated using the method of Car and Parrinello,\textsuperscript{39} with a fictitious electron mass of 800 a.u., and a time step of 0.121 fs. The electronic structure was computed within the Kohn-Sham formulation of density functional theory,\textsuperscript{40} with the gradient corrected BLYP exchange-correlation functional,\textsuperscript{41,42} which has been shown to provide an accurate description of many properties of aqueous systems.\textsuperscript{43-45} Only the valence electrons were treated explicitly, and the valence-core interactions were described by norm-conserving pseudopotentials of the Troullier-Martins form.\textsuperscript{46} The Kohn-Sham orbitals were expanded in a plane-wave basis set up to an energy cutoff of 70 Rydbergs. The clusters were placed in a cubic box of length 13.2 Å, and cluster boundary conditions were applied using the method of Martyna and Tuckerman.\textsuperscript{47} A continuous trajectory of 6 ps was obtained in the microcanonical ensemble, with the last 5 ps used for the computation of average properties and time correlation functions. The average ionic temperature was 250 K. The ab initio MD simulation required approximately 35 hours per ps using 16 CPUs and 580 MBytes of memory on a Cray T3E computer.

Optimized structures of Cl(H_2O)_n, n = 1–4, were obtained by energy minimization using the same electronic structure description as in the ab initio MD simulation. The optimization was stopped when the root-mean-squared gradient was less than 10^{-3}.
In our analysis of the \textit{ab initio} MD trajectory we have employed a recent development in the description of electronic structure in a periodic system using a plane wave basis that involves the transformation of the Kohn-Sham orbitals into maximally localized Wannier functions\textsuperscript{48}, as implemented in the CPMD program\textsuperscript{49}. Thus, the total charge distribution in a system can be partitioned into individual molecular contributions (e.g. bonding pairs and lone pairs). The coordinates of the centers of these localized orbitals, the Wannier function centers (WFCs), can then be used in electrostatic calculations, for example, to describe polarization in terms of fluctuations of the dipole moments\textsuperscript{45}.

For comparison with the \textit{ab initio} simulation, force field based simulations of the Cl\textsuperscript{−} (H\textsubscript{2}O)\textsubscript{n} (n = 1–6) clusters were performed with both polarizable and non-polarizable potentials at 250 K. We employed the polarizable chloride and SPCE/POL model of Caldwell et al.\textsuperscript{50} and the non-polarizable SPC/E water model\textsuperscript{51} with the chloride ion from the CHARMM 22 force field\textsuperscript{52}. The simulation with the polarizable potential was carried out for 350 ps with the \textit{AMBER6} program\textsuperscript{53} and that with the non-polarizable potential for 1,200 ps with the \textit{PINY_MD} program\textsuperscript{54}. All of the non-bonded interactions were included in the force field calculations.

### III. RESULTS AND DISCUSSION

#### A. Minimum energy geometries and relative energies of Cl\textsuperscript{−} (H\textsubscript{2}O)\textsubscript{n} (n = 1–4) clusters

To give an indication of the performance of the density functional methods employed in this study, we compare relative energies and geometrical parameters of minimum energy configurations of the Cl\textsuperscript{−} (H\textsubscript{2}O)\textsubscript{n} (n = 1–4) complexes (Fig. 1) to the corresponding MP2 results\textsuperscript{22} in Table I. Overall, it is evident that the DFT and MP2 results for the structures of the complexes agree very well. The water O–H bond lengths are systematically slightly longer in the DFT results, with a maximum increase relative to the MP2 results of about 0.02 Å, and the DFT and MP2 predictions of the H–O–H angles are essentially identical. Likewise, the
intermolecular separations are generally overestimated in the DFT results but, for the most part, the deviations are only about 0.01 Å, the exceptions being Cl–O distances in Cl(H₂O)₂ and Cl(H₂O)₄, and the O–O distance in Cl(H₂O)₄, which are about 0.03 Å and 0.05 Å too long, respectively. The DFT values of the intermolecular angles are within 1° of the corresponding MP2 results, except for the Cl–H₂O–O in Cl(H₂O)₂, Cl(H₂O)₃, and Cl(H₂O)₄, which show a maximum deviation of roughly 3°. The energy changes associated with adding a water molecule to form the clusters (incremental association energies, ΔEₙ) computed using DFT are also in reasonable agreement with the MP2 results. The magnitudes of the DFT results are generally smaller, with deviations relative to the MP2 values ranging from 0.1 kcal/mol in Cl(H₂O) to 1.4 kcal/mol in Cl(H₂O)₄.

B. Vertical photodetachment energies

The quality of the density functional electronic structure method used in our simulation may be further calibrated by comparing measured and computed vertical photodetachment energies for Cl(H₂O)₆. Assuming that the ejection of the electron occurs sufficiently fast that the structure of the cluster does not rearrange, these energies are equal to the energy difference between the neutral and ionic cluster in the geometry of the anionic cluster. Photodetachment energies have been measured by photoelectron spectroscopy of Cl(H₂O)ₙ, n = 1–7, by Markovich et al. We have computed the vertical electron binding energy as an average over five configurations at 1 ps intervals during the ab initio MD simulation, obtaining 5.15 eV, which is significantly smaller than the experimental value, 6.58 eV. Evidently, the electron is too loosely bound in our simulation.

There are two possible explanations for the discrepancy. One is that average temperature of our simulation, 250 K, is higher than that of the experiment, which has been estimated to be approximately 75 K. At higher temperature we expect a looser cluster in which the chloride ion is less tightly bound by the water molecules, and the electron is therefore
easier to remove. To test this hypothesis we quenched a configuration from our 250 K simulation to 100 K and ran an additional 2 ps dynamics. The quenching resulted in a constriction of the cluster in which the conformational fluctuations were much smaller. The vertical photodetachment energy computed as an average over four configurations from the 100 K run was 5.27 eV, which is only 2% greater than the value obtained at 250 K where the conformational sampling was much more extensive. Thus, it appears that the electron binding energy is not very sensitive to the cluster structure, and differences in the structures sampled in the simulation and the experiment do not appear to be solely responsible for the discrepancy in the electron binding energies. Another possibility is a deficiency in the density functional approach employed. We have computed the vertical detachment energy at the MP2/6-311G** level using Gaussian98 for the minimum energy (0 K) configuration (Fig. 1) found recently by Gora et al., obtaining 5.98 eV. Gora et al. obtained 6.45 eV at the MP2 level with the polarized GTO/CGTO basis set. For comparison the HF/6-311G** and plane wave/pseudopotential BLYP results for the same configuration are 5.27 eV and 5.25 eV, respectively. The MP2 results are the closest to the experimental value, but all of the electronic structure methods considered predict that the electron is underbound in the Cl⁻(H₂O)₆ cluster. The greater underestimation of the binding energy by our DFT calculations could be related to the fact that DFT gives a positive energy of the highest occupied Kohn-Sham (pseudo)orbital for atomic anions. However, we expect that this problem of DFT for atomic anions should be much less serious for anion-water clusters, where the anion is stabilized by the polarization field.

C. Structure and fluctuations of the Cl⁻(H₂O)₆ cluster

The distance between the chloride anion and the cluster center-of-mass has been employed in previous studies as a measure of the extent of solvation of the anion. Obviously, if the anion is completely solvated, this distance is close to zero. We have plotted this quantity as a function of time during the ab initio MD simulation in Fig. 2a, along with its
average values from the non-polarizable and polarizable force field-based MD simulations. The distance rapidly increases by about 1 Å in less than 1 ps from its initial value that is characteristic of the interior, solvated location of the anion predicted by the non-polarizable force field. For the remainder of the simulation, the distance appears to oscillate in the vicinity of the value predicted by the polarizable force field, which implies a surface location of the anion in the cluster. The evolution from the interior to surface locations is clearly evident in the snapshots from the \textit{ab initio} simulation shown in Fig. 3. It is clear from Fig. 3, and also from previous force field based simulations,\textsuperscript{26,31} that at temperature of 250 K the cluster is significantly extended compared to the compact, "4+2" minimum energy geometry (Fig. 1) found recently by Gora et al.\textsuperscript{25} In summary, the present \textit{ab initio} simulation and all previous quantum chemical calculations and MD simulations using polarizable force fields consistently predict a surface location for the chloride anion in water clusters. The surface preference of large, polarizable anions can be qualitatively rationalized as follows:\textsuperscript{57,58} anisotropic solvation gives rise to an electric field on the ion that increases the magnitude of the induction energy. This favorable effect outweighs the loss of ion-dipole interactions when the anion is taken from the interior to the surface of a cluster.

Another indicator of the extent of chloride solvation, which we have used to discuss the potential reactivity of chloride in sea salt aerosols that appear to be important in atmospheric chemistry,\textsuperscript{11} is the chloride solvent accessible surface area. The time evolution of the chloride area accessible to a water-sized probe during the CPMD simulation, computed using a standard technique from structural biology\textsuperscript{59} (using a probe radius of 1.7 Å, and the van der Waals radii of the Cl and O atoms from the non-polarizable force field), is plotted in Fig. 2b, along with the average values from the force field-based simulations. According to the accessible surface areas, the chloride anion is significantly exposed in all of the simulations. The average fractional exposure relative to the bare ion (using 217 Å\textsuperscript{2} as the accessible area of the bare ion) is 0.28 and 0.38 in the non-polarizable and polarizable force field calculations, respectively. After an initial rise during the first 0.5 ps of the CPMD simulation, the chloride accessible area fluctuates
throughout the range of values defined by the averages from the force field-based simulations, and eventually ends up at the value obtained from the polarizable force field calculation.

To provide a more detailed illustration of the fluctuations of the cluster structure during the \textit{ab initio} simulation, we have plotted in Fig. 4 the time evolution of the distance between the chloride ion and the oxygen atoms of each of the six water molecules. It is evident that three water molecules (labeled in Fig. 4 and subsequently as waters 1, 2, and 6) define the first solvation shell, remaining tightly bound to the chloride ion, for the duration of the simulation. Two of the water molecules (3 and 4) are rapidly ejected (within 1 ps) to the second solvation shell from the initial configuration, in which the chloride is completely solvated, and remain there for the remainder of the simulation. One of the water molecules begins a transition from the first solvation shell to the exterior of the cluster after 3.5 ps, and then fluctuates between the third and second solvation shells between 4 and 5 ps.

The average structure of the cluster may be described in terms of radial distribution functions, $g(r)$. We have plotted the Cl-O and Cl-H $g(r)$ from the \textit{ab initio} and force field simulations in Fig. 5. The Cl-O $g(r)$ all display sharp peaks corresponding to the first solvation shell, and small, broad humps corresponding the second solvation shell. Explicit inclusion of electronic polarization in the force field shifts population from the first to the second solvation shell, and moves the first solvation shell closer to the ion. Similar effects have been noted previously in simulations of Cl$(\text{H}_2\text{O})_6$ and Cl$(\text{H}_2\text{O})_{14}$\textsuperscript{26,31} These "polarization effects" appear to be further enhanced in the \textit{ab initio} simulation compared to the polarizable force field. The water molecules in the first solvation shell are typically arranged with one O–H bond pointing toward the ion and one away, as opposed to a symmetrical arrangement with both O–H bonds pointing toward the ion. Thus, the first solvation shell displays two peaks in the Cl-H $g(r)$, at approximately 2.3 \AA\ and 3.5 \AA. The second solvation shell shows up as a shoulder on the second peak in the Cl-H $g(r)$. The modifications of the Cl-H $g(r)$ upon moving from the non-polarizable to the polarizable force field to the \textit{ab initio} simulation are similar to those noted for the Cl-O $g(r)$. It should be noted that some of the differences between the \textit{ab initio}
and force field results could be an artifact of inadequate sampling in the *ab initio* simulation. Although the CPMD method permits the sampling of finite temperature fluctuations of the cluster, and we have seen that the cluster exhibits appreciable structural fluctuations at 250 K on the 5 ps time scale of the *ab initio* simulation, it is clear that the *ab initio* simulation samples only a small fraction of the available phase space in comparison to the force field-based simulations.

D. Localized orbital analysis of electronic polarization

The electronic structure of the cluster in the *ab initio* simulation is conveniently discussed in terms of the Wannier function centers. In Fig. 6 we show a snapshot of the cluster including the WFCs. Four WFCs, each corresponding to an electron pair, are associated with each water molecule in a roughly tetrahedral arrangement. The centers corresponding to the bonding pairs are approximately 0.5 Å from the oxygen, and the centers corresponding to the lone pairs are approximately 0.3 Å from the oxygen. The eight valence electrons of the chloride ion are also arranged in a roughly tetrahedral arrangement expected for sp³ hybrid orbitals, with each center on average 0.48 Å from the Cl nucleus. The non-centrosymmetric environment of the chloride ion distorts the electronic structure away from perfect tetrahedral symmetry, producing an appreciable dipole moment.

We have used the positions of the nuclei and WFCs to compute the time evolution of the dipole moments of the ion and water molecules during the *ab initio* simulation. Histograms of the dipole moments are plotted in Fig. 7. The chloride ion samples a broad distribution of dipole moments as the structure of the cluster fluctuates, ranging from near zero to 1.7 D, with an average of roughly 0.8 D. This modest average dipole moment is another manifestation of the asymmetric solvation of the anion, which resides primarily on the surface of the cluster. The water dipole distribution is bimodal, and, not surprisingly, the values of the individual water dipole moments are correlated with location in the cluster. The two water molecules (1 and 6)
that simultaneously maintain hydrogen bonds with the ion and at least one other water molecules have average dipole moments of approximately 2.7 D, which is slightly less than the bulk water value of 2.95 D and significantly greater than the water dimer value of 2.15 D.\textsuperscript{45} Water molecules on the edge of the cluster, participating in one hydrogen bond, either with the chloride ion (water 2) or other water molecules (4 and 5), have significantly smaller average dipole moments of about 2.2 D, close to the water dimer value. Water 3 moved between locations in which it was involved in either one or two hydrogen bonds with the ion and/or neighboring water molecules, and its dipole distribution accordingly exhibits an asymmetric dipole moment distribution with a peak around 2.2 D, skewed toward higher values.
E. Vibrational spectra

We have calculated the infrared absorption spectrum, $\alpha(\omega)\eta(\omega)$, of the cluster from the Fourier transform of the time correlation function, $\langle M(t) \cdot M(0) \rangle$, of the total (ionic plus electronic) dipole moment of the system, $M(t)$, according to equation (1):\(^{60}\)

$$\alpha(\omega)\eta(\omega) = \frac{4\pi\omega \tanh(\beta h\omega / 2)}{3hcV} \int_{-\infty}^{\infty} \langle M(t) \cdot M(0) \rangle e^{-i\omega t} dt,$$

(1)

where $V$ is the volume, $\beta = 1/k_B T$, $T$ is the temperature, and $c$ is the speed of light. The electronic contribution to the dipole moment was computed in the CPMD program using a Berry phase scheme,\(^{60-62}\) and the spectrum was obtained from the time series of the dipole moment using the maximum entropy method.\(^{63}\) The validity of the semiclassical quantum correction factor, $\tanh(\beta h\omega / 2)$, has been discussed by Silvestrelli and Parrinello.\(^{60}\) In the present paper, since we are primarily concerned with the positions of the absorption peaks and not their intensities, we will assume that more sophisticated quantum corrections are not necessary. The infrared absorption spectrum computed from our \textit{ab initio} MD simulation of Cl–(H$_2$O)$_6$ is plotted in Fig. 8. It is qualitatively similar to the spectrum computed for liquid water,\(^{60}\) with a series of bands due to water translational/librational modes between 100 cm$^{-1}$ and 600 cm$^{-1}$, the water bend at 1550 cm$^{-1}$, and OH stretch between 2800 cm$^{-1}$ and 3400 cm$^{-1}$.

Experimental data on the OH stretch in chloride-water clusters are available for comparison.\(^{3-5,7}\) For a fair comparison, we must correct our spectrum to account for the effect of the inertia of the fictitious electron dynamics on the high frequency vibrations. To this end, we have carried out a series of \textit{ab initio} MD simulations of H$_2$ at low temperature to maintain harmonic vibrations. The fictitious electron mass, $\mu$, was varied, and the harmonic vibrational frequency obtained from the power spectrum of the stretching coordinate was plotted as a function of $\mu$. As expected, the plot was linear with an intercept at the harmonic vibrational...
frequency computed for H$_2$. From this analysis we deduced a frequency scaling factor of 1.075 for use with $\mu = 800$ a.u., the fictitious electron mass used in our simulation of Cl(H$_2$O)$_6$.

The OH stretching region of the infrared spectrum, plotted versus the scaled frequency in the inset of Fig. 8, contains four distinguishable features: a weak peak at 3580 cm$^{-1}$, a strong, sharp peak at 3380 cm$^{-1}$, and a strong, broad peak at 3200 cm$^{-1}$, with a shoulder at 3120 cm$^{-1}$. The broad features of our spectrum may be contrasted with experimental data on Cl$^-$ (H$_2$O)$_n$, $n = 1$–3, measured by argon predissociation spectroscopy, which display relatively sharp lines. The similarity of the argon predissociation spectra and harmonic analysis at the global minima from ab initio calculations on these small chloride-water clusters suggests that the experimental data were measured at very low temperatures, where only the minimum energy configuration is populated. At higher temperatures, the spectrum is expected to be simpler, with broader lines, due to the disruption of weak water-water hydrogen bonds and inhomogeneous broadening via thermal fluctuations, as recently observed in a MD simulation study of Cl$^-$ (H$_2$O)$_2$ using a polarizable empirical potential.$^{24}$ The OH stretch region of our Cl(H$_2$O)$_6$ spectrum looks qualitatively very similar to that of Cl(H$_2$O)$_5$ measured by vibrational predissociation spectroscopy at a high cluster temperature where, evidently, multiple conformations were sampled.$^7$ This is not surprising because both Cl(H$_2$O)$_5$ and Cl(H$_2$O)$_6$ contain more than one solvation shell and are thermally disordered at high cluster temperatures. Indeed, the Cl(H$_2$O)$_5$ spectrum also displays four broad bands in the OH stretching region, at 3233 cm$^{-1}$, 3441 cm$^{-1}$, 3548 cm$^{-1}$, and 3696 cm$^{-1}$. The bands at 3441 cm$^{-1}$, 3548 cm$^{-1}$ and 3696 cm$^{-1}$ were sensibly assigned to water-bound, ion-bound, and free OH stretches, respectively, and the band at 3233 cm$^{-1}$ was tentatively assigned to a ring OH stretch in cyclic water structures containing at least four waters. If we assume that there is a one-to-one correspondence between the four features noted above in our computed Cl(H$_2$O)$_6$ spectrum and the measured Cl(H$_2$O)$_5$ spectrum, then we conclude that the frequencies in our computed spectrum are systematically underestimated, by roughly 100 cm$^{-1}$ to 200 cm$^{-1}$.
Based on the very recent theoretical analysis of the vibrational spectrum of Cl\((\text{H}_2\text{O})\) by Wright and Gerber,\(^6\) one source of error in our calculation is likely the BLYP exchange-correlation functional used in the DFT electronic structure calculation. Wright and Gerber found that the BLYP harmonic frequencies computed with the medium-sized "aug-cc-pVDZ" basis set for the minimum energy geometry of Cl\((\text{H}_2\text{O})\) were fortuitously in good agreement with experimental data. However, when anharmonicities and couplings between modes were taken into account, the BLYP OH stretch frequencies were underestimated by more than 200 cm\(^{-1}\); for example, the computed\(^6\) and measured\(^3\) free OH stretch frequencies were 3483 cm\(^{-1}\) and 3690 cm\(^{-1}\), respectively. We find a significantly smaller discrepancy with the free OH stretching frequency measured for Cl\((\text{H}_2\text{O})_6\) (3696 cm\(^{-1}\))\(^7\) in our BLYP based MD simulation of Cl\((\text{H}_2\text{O})_6\) (3580 cm\(^{-1}\)). Since anharmonicities and coupling between fundamentals are naturally included in our \textit{ab initio} MD simulation, and the plane wave basis is more complete than Gaussian basis sets, the larger discrepancy of the Wright and Gerber calculation with experiment could possibly be attributed to the restricted basis set used. Indeed, Wright and Gerber found a systematic increase in frequencies computed for an isolated water molecule when they used the larger "aug-cc-pVTZ" basis set. It appears that the effects associated with anharmonicities, couplings, and thermal fluctuations at ambient temperatures are more significant than the errors due to inaccuracies of the BLYP functional. Overall, the agreement with the experimental spectrum that we obtain with the BLYP functional is satisfactory, and this suggests that the hydrogen bond dynamics are faithfully reproduced by the simulation.

\textbf{IV. SUMMARY}

We have performed an \textit{ab initio} MD simulation of Cl\((\text{H}_2\text{O})_6\) at 250 K. The electronic structure method (density functional theory with the BLYP gradient-corrected exchange-correlation functional) used to compute the forces has been validated by a favorable comparison of the structures and energies with MP2 results for the minimum energy geometries
of Cl\((\text{H}_2\text{O})_n\), \(n = 1\text{--}4\). The \textit{ab initio} simulation predicts that the chloride anion is located on the surface of the cluster, in agreement with simulations based on polarizable empirical force fields, and in contrast to non-polarizable force fields, which predict an interior location for the anion. The electronic structure of the cluster was analyzed in terms of localized orbitals (maximally localized Wannier functions). This analysis revealed that the chloride anion is significantly polarized (with an average dipole moment of 0.8 D), and that the dipole moments of the water molecules depend strongly on their location in the cluster, ranging from the value in the water dimer at the extremities of the cluster, to almost the bulk water value in the interior of the cluster. The infrared spectrum of the cluster was computed from the dipole-dipole autocorrelation function, taking into account both the nuclear and electronic fluctuations, and the computed spectrum was compared to experimental data on Cl\((\text{H}_2\text{O})_5\) in the OH stretch region. The simulation consistently underestimated the stretching frequencies by 3\% to 5\%, reproducing correctly, nevertheless, the number and relative positions of all features in the experimental spectrum. Comparison with previous quantum chemical calculations suggests that the deficiencies in the BLYP functional with regard to the hydrogen bond dynamics are smaller than the effects of including anharmonicity and coupling between vibrational modes.
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TABLE I. Geometrical parameters and incremental association energies for $\Gamma$(H$_2$O)$_n$ ($n = 1$–4) clusters.\(^\dagger\)

<table>
<thead>
<tr>
<th>Quantity(^\ddagger)</th>
<th>$\Gamma$(H$_2$O)$_1$ minimum ($C_s$)</th>
<th>$\Gamma$(H$_2$O)$_2$ cyclic ($C_1$)</th>
<th>$\Gamma$(H$_2$O)$_3$ pyramidal ($C_3$)</th>
<th>$\Gamma$(H$_2$O)$_4$ pyramidal ($C_4$)</th>
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<tr>
<td>O–H$_b$ (Å)</td>
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<td>0.993</td>
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<td>–</td>
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<td>166.5</td>
</tr>
<tr>
<td>O–Cl–O (°)</td>
<td>–</td>
<td>–</td>
<td>56.9</td>
<td>56.7</td>
</tr>
<tr>
<td>$\Delta E_n$ (kcal/mol)(^§)</td>
<td>–13.8</td>
<td>–13.7</td>
<td>–13.7</td>
<td>–13.2</td>
</tr>
</tbody>
</table>

\(^\dagger\) The MP2 results were obtained previously by Xantheas\(^\ddagger\) using the augmented correlation-consistent polarized double zeta basis set. The DFT results were obtained in the present study; details are given in the Methods section.

\(^\ddagger\) Subscripts $f$, $b$, and $bw$ are used to denote H atoms that are free, bonded to chloride, and bonded to water, respectively.\(^\ddagger\)

\(^§\) Incremental association energies are defined as, $\Delta E_n = E_n - E_{n-1} - E_w$, where $E_n$ is the energy of a cluster with $n$ water molecules, and $E_w$ is the energy of an isolated water molecule. The MP2 results have been corrected for basis set superposition error.\(^\ddagger\)
FIGURE CAPTIONS

FIG. 1. Optimized geometries of Cl(H$_2$O)$_n$ ($n = 1–4$) clusters. The chloride ion is colored black, the water oxygen atoms gray, and the hydrogen atoms white.

FIG. 2. Snapshots of configurations sampled during the *ab initio* MD simulation. The chloride ion is colored black, the water oxygen atoms gray, and the hydrogen atoms white.

FIG. 3. Time evolution during the *ab initio* simulation of (a) the distance between the chloride anion and the cluster center-of-mass; (b) the chloride accessible surface area. For reference, the accessible area of a bare chloride ion is 217 Å$^2$.

FIG. 4. Time evolution of the distances between the water oxygen atoms and the chloride anion during the *ab initio* simulation.

FIG. 5. Radial distribution functions, $g(r)$, from the *ab initio* simulation and force field based simulations with polarizable and non-polarizable force fields: (a) Cl–water O; (b) Cl–water H.

FIG. 6. Snapshot from the *ab initio* MD simulation including the centers of the maximally localized Wannier orbitals of the valence electrons. The chloride ion is colored dark gray, the water oxygen atoms light gray, the hydrogen atoms white, and the Wannier function centers black. The numbering is the same as in Fig. 4.

FIG. 7. Histograms of the dipole moments of the chloride ion and individual water molecules from the *ab initio* simulation. The numbering is the same as in Figs. 4 and 6.
FIG. 8. Infrared absorption spectrum computed by the maximum entropy method from the time evolution of the total dipole moment of the cluster during the \textit{ab initio} simulation. Inset: OH stretching region with frequencies corrected for the fictitious electron inertia as described in the text.
REFERENCES


