Electronic Excitation of Cl^- in Liquid Water and at the Surface of a Cluster: A Sequential Born−Oppenheimer Molecular Dynamics/Quantum Mechanics Approach[†]

Nuno Galamba,[‡] Ricardo A. Mata,[‡] and Benedito J. Costa Cabral*[,‡,§]

Grupo de Física Matemática da Universidade de Lisboa, Av. Professor Gama Pinto 2, 1649-003 Lisboa, Portugal, and Departamento de Química e Bioquímica, Faculdade de Ciências, Universidade de Lisboa, 1749-016 Lisboa, Portugal

Received: May 19, 2009; Revised Manuscript Received: August 11, 2009

A sequential molecular dynamics/quantum mechanics approach is applied to investigate the electronic excitation of Cl^- in liquid water and in a water cluster. Time-dependent density functional theory (TDDFT) and equation-of-motion coupled-cluster with single and double excitations (EOM-CCSD) are used to calculate the excitation energies from Born−Oppenheimer molecular dynamics configurations. The selected configurations include a quantum system with the Cl^- anion and a number of explicit water molecules (n_w) as well as an embedding background defined by fractional point charges on the remaining water molecules. Our results indicate that for both the liquid and the cluster environments the excited electron is delocalized on the hydrogen atoms of the first hydration shell and in a nearby cavity. Convergence of the charge-transfer-to-solvent (CTTS) energy with the number of water molecules is observed for a quantum system embedded in the polarizing charge background for $n_w \geq 3$. Furthermore, we find that the CTTS energy of Cl^- in both solution and cluster environments is very similar. The predicted CTTS energy threshold for the ionic solution (~6.6 ± 0.3 eV) is in good agreement with experiment (6.8 and 7.1 eV).

1. Introduction

Electronic properties of ionic solutions are of great relevance for understanding energetics and dynamics of chemical reactions. Specifically, the photochemistry of halide anions in solution has merited the attention of some review works.[1−4] It is well known that electron photodetachment from anionic species in solution is a dynamic process driven by the interactions with the solvent. The excited state is stabilized by the solvent molecules, and there is no analog for halide ions in the gas phase. Electronic excitations of anionic species in solution may lead to the delocalization of the electronic density over the solvent and to the definition of a charge-transfer-to-solvent (CTTS) process, which is characterized by a specific energy (CTTS energy). A CTTS process can therefore be interpreted as a solvent-assisted photoinduced electron-transfer reaction from the ionic species to the nearby solvent molecules. The phenomenology of excitation and photodetachment[3] in the liquid phase involve several other fundamental aspects beyond the energetical one, including the time-evolution of the ejected electron population and geminal recombination.[2] Several aspects about the very nature of the CTTS precursor state are still the object of debate. These are the specific structural, dynamic, and electronic features of the solvent contributing to the excitation process and the electronic density delocalization upon excitation. The first involves the discussion of the importance of the solvent long-range electrostatic field for stabilizing the excited state versus the role played by the first hydration shell alone, probed in cluster studies. The second deals with either the possible electron transfer to the solvent molecules in the anionic hydration shell or alternatively the delocalization to a cavity in the solvent.

Several experimental[4−12] and theoretical[13−20] works were dedicated to investigating the photochemistry of anionic species in solution. Moreover, the development of techniques for generating aggregates of a given size fostered the study of CTTS energetics and dynamics in clusters.[21−27] Several theoretical works were also dedicated to investigate CTTS in clusters.[28−32] These studies are of relevance to investigate the dependence of the excitation energies on the cluster size[28,31,32] or on the position of the anionic species in the cluster (interior or surface).[31] It is also expected that studies on clusters may contribute to a better understanding of CTTS in solution. However, in contrast with the situation in small clusters, the excitation energies in solution should be dependent on long-range polarization effects because of the electrostatic field of the solvent molecules beyond the first coordination shell. These polarization effects should also be relevant for predicting CTTS in large clusters where an anionic species can be at the cluster surface, as in the case of Cl^- in water.[42−46] The hydration of alkali halides at the liquid−vapor interface has received much attention recently with chemical reaction dynamics[33−35] and MD[36,37] studies as well as different surface-specific experimental techniques[38−41] showing that large anions are hydrated preferentially at the surface whereas small cations are fully hydrated in the bulk part of the liquid. Theoretical results on the excitation spectra of iodide in the liquid and for a planar liquid−vapor interface environment have been presented by Bradford and Jungwirth,[30] exploring therefore the importance of surface solvation of large halide ions on the CTTS energy.

The present work intends to address three distinct problems. The first concerns the possibility of providing accurate theoretical CTTS energies by using a relatively small quantum system. The second focuses on the relationship of the CTTS energetics

---

[†] Part of the "Vincenzo Aquilanti Festschrift".

* Corresponding author. E-mail: ben@cii.fc.ul.pt.

[‡] Grupo de Física Matemática da Universidade de Lisboa.

[§] Faculdade de Ciências, Universidade de Lisboa

10.1021/jp904687k

with the polarizing medium created by the surrounding solvent molecules. Finally, we discuss charge transfer effects with an emphasis on the role played by the water molecules to delocalize the excited electron. To carry out this task, we are reporting a sequential molecular dynamics/quantum mechanics study on the electronic excitations of Cl^- in water. Emphasis is placed on the comparison between results for a solution with one Cl^- in 64 water molecules and for an anionic cluster with 32 water molecules. The quantum mechanical calculations of the electronic properties are based on time-dependent density functional (TDDFT)[47] and equation-of-motion coupled-cluster with single and double excitation (EOM-CCSD)[48] theories. The configurations selected for the a posteriori quantum mechanical calculations were generated by Born−Oppenheimer molecular dynamics.

2. Computational Details

The Born−Oppenheimer molecular dynamics (BOMD) for a solution of 1 Cl^- anion in 64 water molecules under periodic boundary conditions was carried out with the hybrid Gaussian and plane-wave GPW method, as implemented in the QUICKSTEP program.[49] Goedecker, Teter, and Hutter norm-conserving pseudopotentials[50] were used to represent core electrons, and only valence electrons were explicitly included in the quantum mechanical DFT calculations for generating the dynamics. In these calculations, Kohn−Sham orbitals were expanded into atom-centered DZVP Gaussian-type orbital functions, whereas the electron density is represented with an auxiliary plane-wave basis-set. The wave function optimization was carried out with the OT scheme.[51] A charge density cutoff of 250 Ry was used for the auxiliary basis set, and the self-consistent-field energy threshold for calculating the electronic density was 10^{-8} Ha. The MD was carried out without any specific counterion; therefore, a uniform background charge was used instead to ensure the electroneutrality of the system. BOMD was performed with the Perdew−Burke−Ernzerhof (PBE) exchange-correlation functional.[52] The dynamics was carried out in the microcanonical ensemble for a system with a density of 1 $g \cdot cm^{-3}$ and a target temperature $T = 298.15$ K. The time step was 0.5 fs. The starting configuration was generated by classical molecular dynamics. A total of 65 000 steps were carried out, and the temperature was scaled each 20 steps during the first 35 000 steps. The last 30 000 steps (15 ps) were then used for the production phase and the average temperature was 308 ± 14 K.

The BOMD for a Cl^- anion in a cluster with 32 water molecules was also carried out in the microcanonical ensemble. The dynamics was generated by using an MD program that has been recently applied for investigating the hydrogen bond network of a water cluster.[53] The MD program was coupled to the Gaussian 03 package.[54] The electronic energy and forces were calculated with the PBE exchange-correlation functional and a 6-31+G(d,p) basis set. The all-electron BOMD was carried out with a convergence criterion of 10^{-8} Ha for the energy. The equations of motion were integrated with a Verlet "leap-frog" algorithm with a time step of 0.9 fs. The starting configuration for the cluster BOMD was defined as follows. The experimental gas-phase geometry was attributed to each water molecule ($r_{O-H} = 0.957$ Å, $\theta(H-O-H) = 104.5°$). The molecules were then displayed on the surface of two concentric spheres, 2.91 Å apart, around the chloride anion. The first sphere surface accommodated 6 molecules, whereas 26 molecules were spread at the surface of the second. The molecules were then randomly rotated between 0 and 2π, and the cluster was equilibrated for 4.7 ps, followed by a production phase of 12.2 ps. The average temperature during the production phase was 331 ± 23 K.

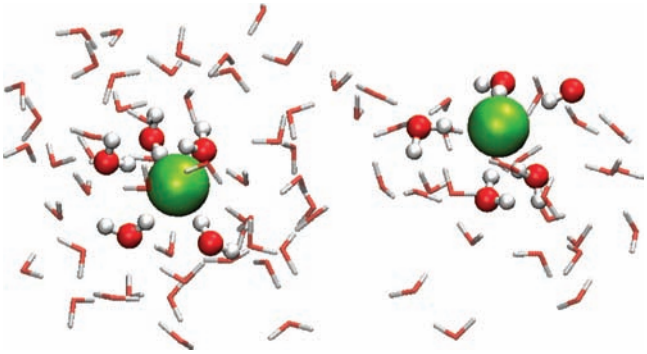

Figure 1. Snapshot from Born−Oppenheimer molecular dynamics illustrating a quantum system with the Cl^- anion (vdW) and the closest five water molecules (ball-and-sticks) embedded in the charge distribution of the remaining ones (transparent sticks). Ionic solution (left panel); $[Cl(H_2O)_{32}]^-$ cluster (right panel).

For performing sequential calculations of the electronic properties, 50 configurations from the BOMD simulations were selected. For each configuration, we defined a quantum system with the Cl^- anion and a given number of explicit water molecules ($n_w = 1$ to 6) in close interaction with the anionic species. The quantum systems are embedded in the Coulombic field of n_{emb} surrounding water molecules that are represented by fractional atomic charges. A quantum system including the Cl^- anion and five water molecules embedded in the charge distribution of the remaining water molecules is illustrated in Figure 1 for both the ionic solution (left panel) and the $[Cl(H_2O)_{32}]^-$ cluster (right panel). The point charges define the electrostatic embedding of the quantum system. Previous studies on liquid water indicated that electronic properties are strongly dependent on the correct treatment of the charge background but are only weakly dependent on the specific choice of the background.[55,56] In the present case, atomic charges corresponding to the SPC/E model[57] for water were chosen. We have verified that changes in the CTTS energy computed through TDDFT are on the order of +0.1 eV for different values of n_w when changing the charges on the oxygen atoms from values of −0.8 to −0.9 au, which encompass the SPC/E charges. To discuss the importance of the electrostatic embedding, we are also reporting some results for nonembedded quantum systems ($n_{emb} = 0$). Further results of the excitation energy for the chloride in the embedded charge distribution with $n_w = 0$ were also obtained. This calculation will allow us to examine to what extent the real CTTS process can be mapped onto that of an isolated chloride anion in an electric field, neglecting all other anion−water interactions.

Excitation energies from the ground (S_0) to singlet excited (S_1) states were calculated with time-dependent density functional theory (TDDFT)[47] and equation-of-motion coupled-cluster with single and double excitations (EOM-CCSD).[48] TDDFT calculations were carried out with the BHandHLYP exchange-correlation functional, which is based on Hartree−Fock and Becke88[58] functional for exchange and the Lee−Yang−Parr (LYP) functional for correlation.[59] The limitations of TDDFT for predicting excitation energies associated with charge transfer (CT) have been recently dicussed (ref 72 and refs therein), and it is generally accepted that the high percentage (50%) of the exchange contribution included in this functional should contribute to a better performance of the BHandHLYP model. A Dunning's aug-cc-pVDZ basis set[60] was used in all sequential

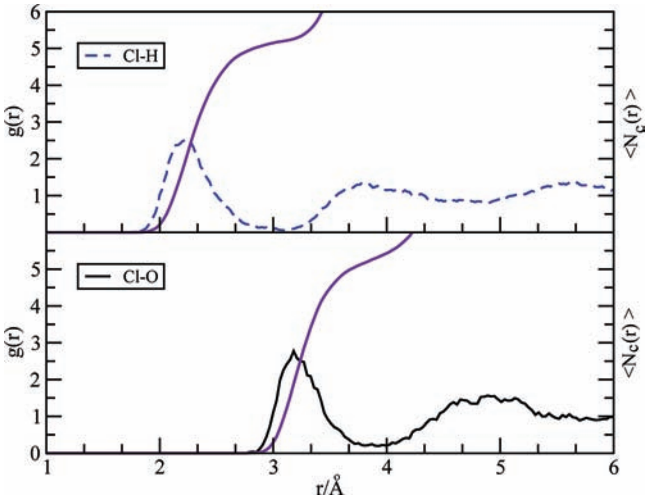

Figure 2. Cl−O and Cl−H RDFs for a solution of 1 Cl anion in 64 water molecules from Born−Oppenheimer molecular dynamics and the corresponding average coordination numbers.

quantum mechanical calculations. Test calculations with larger basis sets show that the CTTS excitation energies are well converged with this basis set. (These results are later discussed in the text.) The sequential quantum mechanical calculations were carried out with the Gaussian 03 program[54] (TDDFT) and with the MOLPRO 2008.1 package (EOM-CCSD).[61]

3. Results and Discussion

3.1. Structure of the Ionic Solution and Cl^-−Water Cluster from Born−Oppenheimer Molecular Dynamics. Several theoretical studies on the structure of the Cl^- hydration shell have been reported.[62−66] Here our main interest is to select a representative set of configurations for a posteriori analysis of electronic properties. The Cl−O and Cl−H radial distribution functions (RDFs) for the solution are reported in Figure 2. The Cl−O RDF shows a first peak of 2.77 height at 3.18 Å. Integration of this RDF up to the first minimum (0.19 at 3.9 Å) leads to a coordination number of 5.4. This value is below the experimental value (~6),[67] although it is similar to other theoretical predictions.[65] The Cl−H RDF shows a first peak of 2.50 height at 2.22 Å, and integration of this RDF up to the first minimum (0.06 at 3.1 Å) leads to a coordination number of 5.2. These predictions are in reasonable agreement with neutron diffraction results for the structure of the chloride ion solvated in deuterated water reported by Yamagami et al.[75] Their results are 2.29 Å and 5.8 ± 0.5 for the position of the first peak and coordination number, respectively. It should be observed that the PBE functional leads to an overstructured description of liquid water. (See refs 68−70 and references therein.) One serious limitation of the PBE functional concerns the prediction of dynamic properties such as the diffusion coefficient of liquid water that is significantly underestimated in comparison to experiment.[70] However, for the purposes of the present work, this should not be a problem. Moreover, our predictions for the structure of the first hydration shell are in reasonable agreement with experimental information.

The time evolution of the distance [$d_{cm}(Cl^-)$] of the chloride anion to the center of mass of the water molecules (i.e., excluding the chloride) in the cluster in the equilibration and production stages of the MD simulation is depicted in Figure 3 (inset panel). As can be seen, [$d_{cm}(Cl^-)$] continuously increases during the equilibration period and then fluctuates at ~5 Å, close to the surface of the cluster. The chloride is hydrated in the 90−10% density region of the cluster commonly used to define the interfacial region of liquid drops, as determined from the density profile (not shown here). This result is in agreement with previous classical molecular dynamics simulations of anionic clusters[42−46] using polarizable intermolecular potentials for water as well as with the more recent findings concerning the surface hydration of large polarizable ions on the aqueous planar liquid−vapor interface.[36,37]

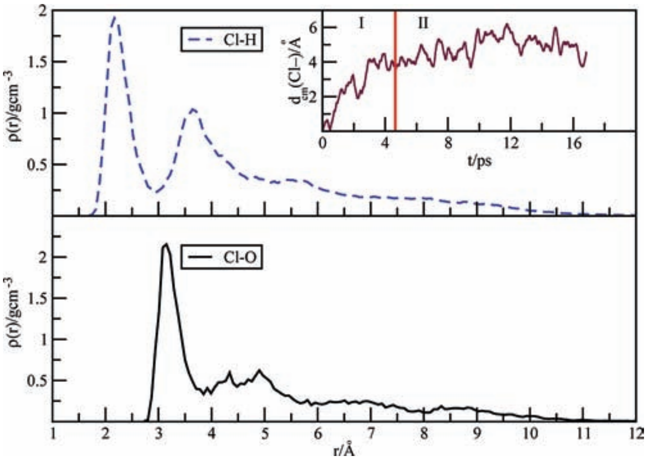

Figure 3. Non-normalized pair correlation functions [$\rho(r)$] for Cl−O and Cl−H in a Cl^-−water cluster with 32 water molecules. The inset shows the time evolution of the Cl^- distance to the cluster center-of-mass [$d_{cm}(Cl^-)$]. The red line separates the two phases (I) equilibration (4.7 ps) and (II) production (12.2 ps).

The non-normalized pair correlation functions $\rho(r)$ (in grams per cubic centimeter) describing the Cl−O and the Cl−H local structures in the cluster are further shown in Figure 3. These functions were computed the same way as density profiles in clusters or liquid drops only substituting the center of mass of the system by the anion position. The Cl−O function depicts a first maximum at ~3.10 Å and a minimum at 3.85 Å ($r_{\min}$). The second hydration shell is highly asymmetric because the Cl^- is hydrated near the surface, which explains the poorly defined second maximum. The coordination number corresponding to the first peak of the Cl−O pair correlation function was found to be ~5.0. The Cl−H pair correlation function is also displayed in Figure 3 and exhibits two well-defined coordination layers with maxima at 2.15 and 3.65 Å, respectively. The first minimum appears at 2.90 Å, and the coordination number was estimated to be 4.7. The coordination numbers of the pair correlation functions for the cluster were calculated from $\sum_r^{r_{\min}} N(r \pm \delta r)$, where N is the average number of O and H atoms, respectively, for the pair correlation functions in a layer centered at r with thickness δr. Comparison of the pair correlation functions for both the chloride solution and the anionic cluster shows that the first peak of the Cl−O and Cl−H in the cluster are slightly contracted (<0.1 Å). The average coordination numbers of the first hydration layer of the Cl−O and Cl−H pair correlation functions are smaller (~0.5) for the cluster, as expected.

3.2. Excitation Energies of the Ionic Solution and Cl^-−Water Cluster. Before presenting results for the excitation energies in the ionic solution and cluster, it is important to discuss how adequate the description of the polarizing field using fractional point charges for liquid water is. A relevant issue concerns the dependence of the results on the number of polarizing charges. Figure 4 shows the dependence of the average excitation energies on the number of point charges for a quantum system including the Cl^- anion and one water

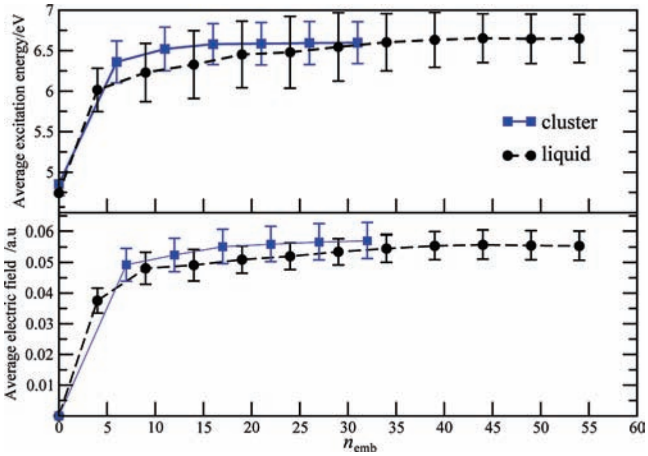

Figure 4. Dependence of the average excitation energy (eV) on the number of embedding point charge waters (n_{emb}) for a quantum system including the Cl^- anion and one water molecule (top). Dependence of the average electrostatic field (a.u.) on the number of embedding point charge waters (bottom). Ionic solution (black circles); cluster (blue squares).

molecule. We are reporting results for configurations corresponding to the ionic solution and also for the $[Cl(H_2O)_{32}]^-$ cluster. As it may be seen, excitation energies are very dependent on the number of point charges representing the polarizing field. However, our results indicate that a correct description of polarization effects, leading to converged excitation energies, is attained by including embedding charges of a rather small number of water molecules. No significant dependence is observed for $n_{emb} > 40$. For the cluster, the results indicate that converged excitation energies are attained for $n_{emb} \approx 20$.

The faster convergence in the case of the cluster is due to the fact that the anion is found at its surface. Consequently, if we assume that the influence of the embedding charges on the excitation energies is negligible beyond a given distance from the anion, it is expected that the number of point charge waters needed for convergence of the CTTS energy in the cluster should be approximately half of the number needed in solution. Moreover, the CTTS convergence can be related to the electric field at the anion position. This has been calculated by replacing all water molecules by fractional point charges. The dependence of the electric field on the number of embedding charges is represented in the bottom panel of Figure 4 and follows the same trend of the excitation energies.

Bradforth and Jungwirth,[30] in their study of iodide in water, have pointed out the importance of including long-range electrostatic effects for describing the stability of CTTS states. This refers to the binding energy of the excited electron, which is given by the vertical detachment energy. Because this quantity is calculated by computing the energy difference between the neutral system and the charged excited state, a long-range dependence on the electrostatic field is expected. The charged system will be preferentially stabilized with a close to $1/r$ dependence. However, in this work, we are concerned with the energy difference between the anion S_0 and S_1 states. The difference between the two will be mainly found in the spatial distribution of an electron, which will be somewhat "smeared" in the first solvation shell. The difference between the two states is therefore closely related to a dipole, and the radial dependence on the electrostatic field is much smaller. This is in agreement with the present results, which indicate that the excitation energies are converged by including the polarization field beyond the second hydration shell.

TABLE 1: Dependence of the Average $S_0 \rightarrow S_1$ Vertical Excitation Energy (electronvolts) in $Cl^-{-}(H_2O)_{n_w}$ Aggregates with the Number of Water Molecules in the Quantum System (n_w)[a,b]

n_w	ionic solution	BHandHLYP	EOM-CCSD
0		7.52 ± 0.15	7.53 ± 0.14
1		6.65 ± 0.30 [4.74 ± 0.17]	6.77 ± 0.22
2		6.52 ± 0.30 [5.08 ± 0.16]	6.68 ± 0.24
3		6.45 ± 0.30 [5.43 ± 0.18]	6.63 ± 0.26
4		6.43 ± 0.30 [5.68 ± 0.18]	6.62 ± 0.25
5		6.37 ± 0.30 [5.87 ± 0.18]	6.59 ± 0.27
6		6.36 ± 0.32 [6.05 ± 0.25]	
n_w	cluster	BHandHLYP	EOM-CCSD
0		7.51 ± 0.19	
1		6.60 ± 0.26	6.69 ± 0.23
2		6.56 ± 0.25	6.68 ± 0.24
3		6.52 ± 0.24	6.62 ± 0.22
4		6.50 ± 0.24	6.62 ± 0.21
5		6.48 ± 0.24	6.62 ± 0.22
6		6.49 ± 0.24	
exptl			6.76[c]; 7.1[d]

[a] Results for non-embedded systems are shown in brackets. [b] Averages were calculated over 50 configurations. [c] From Blandamer and Fox.[1] [d] From Loeff et al.[6] and Fox et al.[5]

Vertical excitation energies based on TDDFT and EOM-CCSD calculations are reported in Table 1 for both the ionic solution and Cl^-−water cluster. Results for nonembedded quantum systems are shown in brackets. In keeping with previous studies for gas-phase-optimized clusters,[28,32] excitation energies of nonembedded aggregates are blue-shifted with increasing n_w. By including the electrostatic environment of the surrounding waters (embedded results), the dependence of the $S_0 \rightarrow S_1$ excitation energies with n_w is significantly reduced. This fact indicates that the solvent effects, even in the first shell, are mainly of electrostatic nature. The only difference is a slight red shift, particularly upon going from one to three water molecules.

The reasons behind the shift are unclear. By increasing the number of water molecules treated quantum mechanically, the following effects have to be taken into account: improved description of the electrostatics (which could also involve charge-transfer), inclusion of Pauli repulsion as well as correlation, excitonic coupling, and an increase in the AO basis space. The first three effects cannot be individually accessed. The latter, however, can be inspected by increasing the basis set. We have performed calculations for the 50 bulk configurations, including in the quantum system only the chloride and the closest water molecule ($n_w = 1$). The basis sets used were the aug-cc-pVXZ and d-aug-cc-pVXZ (X = D,T,Q).[76] In the d-aug-cc-pVQZ, the extra diffuse basis exponents for Cl were the same as those in the triple-ζ basis, whereas the extra g function set was given an exponent of 0.15. The results for $n_w = 1$ with the aug-cc-pVXZ basis set are 6.77 ± 0.22 (X = 2), 6.77 (X = 3), and 6.79 eV (X = 4). These average values are quite similar and only change by as much as 0.02 eV. The results for $n_w = 1$ with the d-aug-cc-pVXZ basis set are 6.37 (X = 2), 6.41 (X = 3), and 6.44 eV (X = 4). In this case, a small blue shift (0.07 eV) of the average value for the first excitation energy is observed when we move from X = 2 to 4. The comparison between the results with the aug-cc-pVXZ and d-aug-cc-pVXZ for $n_w = 1$ indicates that the average excitation energies are red shifted by ~0.4 eV from the singly to the double augmented basis sets. For $n_w = 2$, we will discuss results based on calculations performed with the aug-cc-pVDZ and the d-aug-cc-pVQZ basis sets. In this case, the average excitation energy is red shifted by ~0.26 eV, changing from 6.68 (aug-cc-pVDZ) to 6.42 eV (d-aug-cc-pVQZ). The comparison between the results for $n_w = 1$ and 2 shows the following trends. First, there is a ~0.09 eV red shift when we compare the average excitation energies calculated with the aug-cc-pVDZ basis sets. Moreover, comparison between the results with the d-aug-cc-pVQZ basis set shows a significantly smaller red shift (0.02 eV). Therefore, it appears that the shift is in fact strongly linked to the available AO space. However, this effect is mainly due to the more diffuse basis functions of the set, which allow some electronic density to localize close to the surrounding point charges. We find that despite the apparent weight of the basis-set effects, it is physically sounder to also increase the number of water molecules in the quantum system. In this way, one avoids artifacts due to the use of embedding charges (which are mainly justifiable in cases where the electronic density is not significantly overlapping). The presently observed trend (for embedded aggregates, the average excitation energy is red shifted with an increasing number of water molecules) is apparently in agreement with data based on calculations using a few snapshots[30] for $I^-(H_2O)_{7-9}$ clusters embedded in a charge background. This trend is however opposite to what is observed for nonembedded $I^-(H_2O)_{2,6}$ clusters (blue shift of the excitation energies with an increasing number of water molecules). [30] Both trends are in keeping with the present findings. (See Table 1, where we present results for embedded and nonembedded aggregates.)

The possibility of convergence to bulk values of the CTTS energies of $[X(H_2O)_{n_w}]^-$ (X = Cl,I) clusters with an increasing number of water molecules has been discussed by several authors.[21,28,25] The dependence of the CTTS energies on the cluster size in X^-−water clusters allows us to discuss the importance of taking explicitly into account hydrogen bond and CT effects. However, it remains unclear how the convergence of the CTTS energy would be attained and how many water molecules should be involved for considering that the CTTS state in clusters is equivalent to what is observed in the bulk phase. Another apparently opposite perspective was pointed out by Bradforth and Jungwirth for predicting CTTS in a I^-−water solution.[30] The authors argued that the CTTS wave function is not highly extended and that an estimate of the CTTS energy can be made by correctly describing the long-range polarization field of the bulk phase. Therefore, the explicit consideration of water molecules in the quantum system would be less important than an adequate treatment of long-range polarization effects.

We have also included values for $n_w = 0$ in Table 1. A large difference is observed between this value and the one for $n_w = 1$. However, for $n_w = 0$, a strong basis-set dependence of the results should be expected because the aug-cc-pVDZ basis set is not adequate for describing the electronic delocalization of the isolated anion in the charge background. It was verified that the excitation energies significantly decrease with increasing basis sets. Nevertheless, we would like to stress that most of the basis set effect is removed by including a single water molecule in the quantum system, as previously discussed.

To obtain a more complete description of the $S_0 \rightarrow S_1$ excitation, we carried out natural population analysis (NPA)[77] calculations on all configurations under study. We computed the nonrelaxed CCSD and EOM-CCSD density matrices for ground and excited states, respectively, which were then used as input for the NPA program in MOLPRO. The results show that the chloride anion, initially with a charge of ~−0.9 au, loses its excess charge in the S_1 state. Close inspection of the 100 configurations (cluster and liquid) for a quantum system with $n_w = 5$ shows that about half of the transferred charge is assigned to the hydrogens of one to two solvent molecules. However, these observations alone give no conclusive evidence of whether the charge is located on the waters, in solvent cavities, or even in a diffuse distribution centered around the excited anion. This analysis is biased toward the atoms that provide the AO basis space to describe the excited electron and should be taken with caution.

For a more reliable analysis, we stored the S_0 and S_1 states' density matrices and computed the difference between the two as $\mathbf{D}_{\text{diff}} = \mathbf{D}_{S_1} - \mathbf{D}_{S_0}$. The resulting density was then used to visualize the charge migration. In Figure 5, two representative configurations are depicted, one for the cluster (bottom) and the other for the solution (top). The leftmost panels show the NPA charge difference between the two states. Only values above a 0.05 au threshold are displayed. As mentioned above, NPA analysis seems to indicate a significant charge migration from the chloride to some of the solvent hydrogens. The right panels show the density difference as isodensity surfaces using two different values. (See caption of Figure 5.) At higher density values, one only observes charge migration on the chloride and solvent molecules. Upon lowering the density, a diffuse surface becomes visible close to the hydrogens, which NPA indicated, but centered on a solvent cavity. In the case of the cluster, the electron density follows the same pattern with an increase close to the surface but still inside the cluster. Crossing the two informations (NPA and isodensity surfaces), the overall picture is rather close to the one given in the case of iodide by Bradforth and Jungwirth.[30] Our conclusions are that a significant part of the electron density is transferred to a cavity, but there is also significant charge reorganization in the solvent molecules, which underlines the importance of their explicit quantum treatment. We also observed that CT is almost converged for $n_w \geq 3$, which supports the observation of a constant CTTS energy value for this number of quantum water molecules.

Comparison between BHandHLYP and EOM-CCSD excitation energies reported in Table 1 shows that their differences increase with the cluster size. For the ionic solution, TDDFT and EOM-CCSD results are pratically coincident when $n_w = 0$. Then, the differences between the two methods increase from 0.12 ($n_w = 1$) to 0.22 eV ($n_w = 5$). These differences are possibly related to CT effects, which increase with n_w, and it is known that TDDFT presents some limitations for an accurate prediction of excitations involving CT. Differences between TDDFT and EOM-CCSD results for the Cl^-−water cluster are in the 0.09 to 0.14 eV range. CTTS energies from both TDDFT and EOM-CCSD methods show a similar behavior with n_w, and our results strongly indicate that for embedded clusters the average CTTS energy is converged for $n_w \geq 3$. Our best estimate for the CTTS energy of the ionic solution (EOM-CCSD) is 6.59 ± 0.27 eV and relies on the calculation with $n_w = 5$ embedded in the polarizing field of the remaining water molecules. The EOM-CCSD results for the cluster are ~6.62 eV for $n_w = 3$ to 5. The behavior of the excitation energies with the number of water molecules in the quantum system (n_w) is also illustrated in Figure 6.

Another relevant issue concerns the comparison between the CTTS values for the solution and Cl^-−water cluster. Although experimental CTTS energies for several ionic species in solution are known,[1,18] we are not aware of experimental results for ionic species at a cluster or liquid surface. However, a theoretical prediction for I^- at the air−water interface was reported by Bradforth and Jungwirth.[30] Their CIS result indicates that for the I^-−water system the CTTS energy at the air−water interface

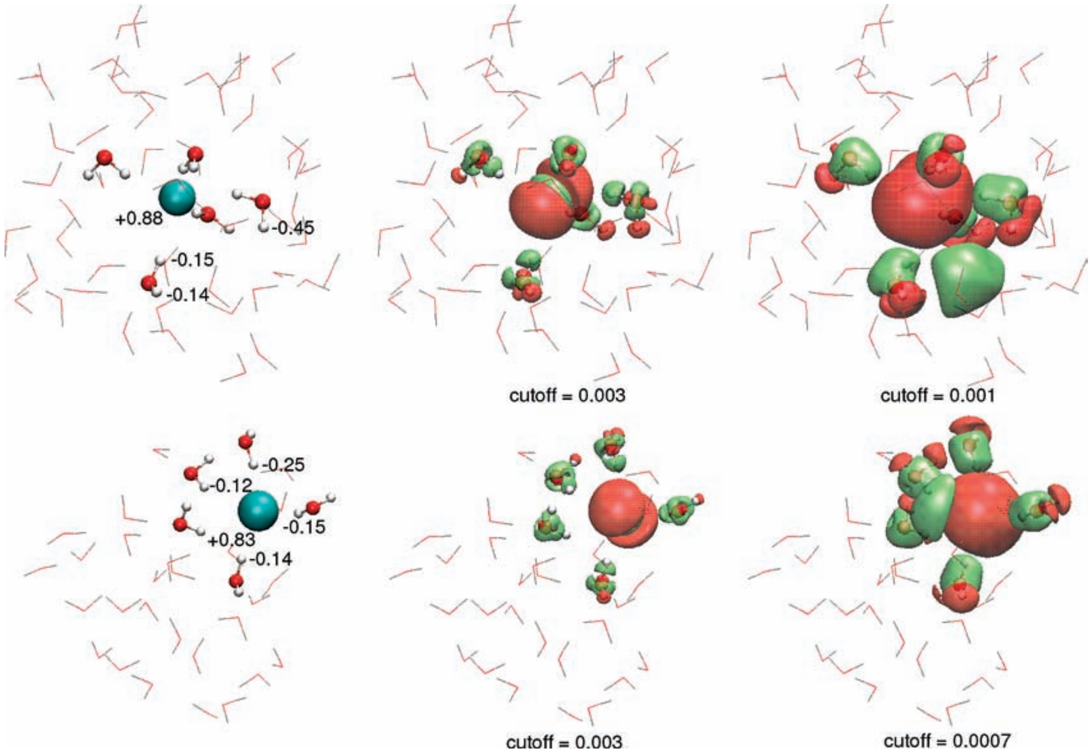

Figure 5. Sample configurations for a Cl^- solution (top panels) and water cluster (bottom panels) with $n_w = 5$. The leftmost panels show the NPA charge difference between the S_0 and S_1 states (only values above 0.05 au). The other panels show isodensity surfaces (cutoffs ($Å^{-3}$) are given in the Figure) with negative density regions shown in dark red and positive density regions in bright yellow. All values refer to EOM-CCSD/aug-cc-pVDZ densities.

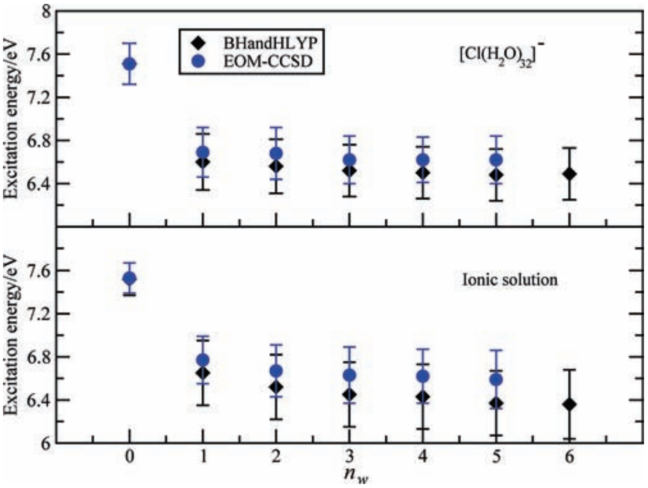

Figure 6. Behavior of the $S_0 \rightarrow S_1$ vertical excitation energies for embedded $[Cl(H_2O)_{n_w}]^-$ aggregates with the number of water molecules in the quantum system (n_w). Top: Cl^-−water cluster; bottom: ionic solution.

was ~0.15 eV smaller than the prediction in solution.[30] For Cl^-−water, our best estimates for the CTTS energies in the ionic solution and Cl^-−water cluster (6.6 ± 0.3 eV) are pratically the same. They are also close to experimental results for the ionic solution (6.76 and 7.1 eV).

4. Conclusions

Results for the excitation energies associated with CTTS in a Cl^-−water solution and for a Cl^-−water cluster are reported. The excitation energies were calculated by using configurations generated by BOMD using the PBE functional. The structure of the hydration shell in solution was found to be in reasonable agreement with experimental data (~6), although a smaller coordination number (~5.4) is predicted. BOMD results for a Cl^-−water cluster show that the anionic species at equilibrium is near the surface, which is in agreement with previous studies, portraying a slightly smaller coordination number (~5) than that found in solution. We have investigated the dependence of the excitation energies on the presence of the polarizing electrostatic background and concluded that a relatively small number of point charges is enough for a correct prediction of the $S_0 \rightarrow S_1$ excitation in condensed phase. By including a polarizing background, a weak dependence of the excitation energies on n_w is observed, and the present results suggest that a reliable prediction of the CTTS energies in Cl^-−water solutions can be made with three to five explicit water molecules.

The analysis of the electronic density differences between the ground and excited states provided further information on the nature of the excitation process. It was found that the excited electron delocalizes over a small number of water molecules in the first hydration shell and in a cavity close to the hydrogen atoms where the largest NPA CT was observed. Comparison between TDDFT and ab initio results for the excitation energies shows that BHandHLYP predictions are ~0.3 eV below the EOM-CCSD results. Our best estimates for the average CTTS energy in the ionic solution (~6.6 eV) are in very good agreement with experimental data (6.76 and 7.10 eV). We are also predicting the average CTTS excitation energy for a Cl^-−water cluster where the anion is at the cluster surface. This is found to be coincident with the value predicted for the ionic solution.

Acknowledgment. This work was partially supported by Fundaçao para a Ciência e a Tecnologia (FCT), Portugal (grant no. PTDC/QUI/68226/2006). R.A.M gratefully acknowledges the FCT (Portugal) (grant no. SFRH/BPD/38447/2007).

References and Notes

(1) Blandamer, M. J.; Fox, M. F. *Chem. Rev.* **1970**, *70*, 59.

(2) Dessent, C.; Kim, J.; Johnson, M. A. *Acc. Chem. Res.* **1998**, *31*, 527.

(3) Chen, X.; Bradforth, E. *Annu. Rev. Phys. Chem.* **2008**, *59*, 203.

(4) Winter, B. *Nucl. Instrum. Methods Phys. Res., Sect. A* **2009**, *601*, 139.

(5) Fox, M. F.; Barker, B. E.; Hayon, E. *J. Chem. Soc., Faraday Trans. I* **1978**, *74*, 1776.

(6) Loeff, I.; Treinin, A.; Linschitz, H. *J. Phys. Chem.* **1992**, *96*, 5264.

(7) Markovich, G.; Pollack, S.; Giniger, R.; Chesnovsky, O. *J. Chem. Phys.* **1994**, *101*, 9344.

(8) Gauduel, Y.; Gelabert, H.; Ashokkumar, M. *Chem. Phys.* **1995**, *197*, 167.

(9) Kloepfer, J. A.; Vilchiz, V. H.; Lenchenkov, V. A.; Bradforth, S. E. *Chem. Phys. Lett.* **1995**, *298*, 120.

(10) Sauer, M. C.; Crowell, R. A.; Shkrob, I. A. *J. Phys. Chem. A* **2004**, *108*, 5490.

(11) Winter, B.; Weber, R.; Hertel, I. V.; Faubel, M.; Jungwirth, P.; Brown, E. C.; Bradforth, S. E. *J. Am. Chem. Soc.* **2005**, *127*, 7203.

(12) Winter, B.; Aziz, E. F.; Ottosson, N.; Faubel, M.; Kosugi, N.; Hertel, I. V. *J. Am. Chem. Soc.* **2008**, *130*, 7130.

(13) Jortner, J.; Ottolenghi, M.; Stein, G. *J. Phys. Chem.* **1961**, *65*, 1232.

(14) Jortner, J.; Ottolenghi, M.; Stein, G. *J. Phys. Chem.* **1961**, *66*, 2029.

(15) Sheu, W.-S.; Rossky, P. J. *J. Am. Chem. Soc.* **1993**, *115*, 7729.

(16) Sheu, W.-S.; Rossky, P. J. *Chem. Phys. Lett.* **1993**, *202*, 186.

(17) Borgis, D.; Staib, A. *Chem. Phys. Lett.* **1994**, *230*, 405.

(18) Takahashi, N.; Sakai, K.; Tanida, H.; Watanabe, I. *Chem. Phys. Lett.* **1995**, *246*, 183.

(19) Staib, A.; Borgis, D. *J. Chem. Phys.* **1996**, *103*, 2642.

(20) Staib, A.; Borgis, D. *J. Chem. Phys.* **1996**, *104*, 9027.

(21) Serxner, D.; Dessent, C. E. H.; Johnson, M. A. *J. Chem. Phys.* **1996**, *105*, 7231.

(22) Becker, I.; Markovich, G.; Chesnovsky, O. *Phys. Rev. Lett.* **1997**, *79*, 3391.

(23) Lerh, L.; Zanni, M. T.; Frischkorn, C.; Weinkauf, R.; Neumark, D. M. *Science* **1999**, *284*, 635.

(24) Lee, H. M.; Kim, D.; Kim, K. S. *J. Chem. Phys.* **2002**, *116*, 5509.

(25) Robertson, W. H.; Johnson, M. A. *Annu. Rev. Phys. Chem.* **2003**, *54*, 173.

(26) Kammrath, A.; Verlet, J. R. R.; Bragg, A. E.; Griffin, G. B.; Neumark, D. M. *J. Phys. Chem. A* **2005**, *109*, 11475.

(27) Ehrler, O. T.; Griffin, G. B.; Young, R. M.; Neumark, D. M. *J. Phys. Chem. B* **2009**, *113*, 4031.

(28) Majumdar, D.; Kim, J.; Kim, K. S. *J. Chem. Phys.* **2000**, *112*, 101.

(29) Kim, J.; Lee, H. M.; Suh, S. B.; Majumdar, D.; Kim, K. S. *J. Chem. Phys.* **2000**, *113*, 5259.

(30) Bradforth, S. E.; Jungwirth, P. *J. Phys. Chem. A* **2002**, *106*, 1286.

(31) Sheu, W.-S.; Liu, Y.-T. *Chem. Phys. Lett.* **2003**, *374*, 620.

(32) Godinho, S. S. M. C.; Couto, P. C.; Cabral, B. J. C. *Chem. Phys. Lett.* **2006**, *419*, 340.

(33) Knipping, E. M.; Lakin, M. J.; Foster, K. L.; Jungwirth, P.; Tobias, D. J.; Gerber, R. B.; Dabdub, D.; Finlayson-Pitts, B. J. *Science* **2000**, *288*, 301.

(34) Hu, J. H.; Shi, Q.; Davidovits, P.; Worsnop, D. R.; Zahniser, M. S.; Kolb, C. E. *J. Phys. Chem.* **1995**, *99*, 8768.

(35) Laskin, A.; Gaspar, D. J.; Wang, W. H.; Hunt, S. W.; Cowin, J. P.; Colson, S. D.; Finlayson-Pitts, B. J. *Science* **2003**, *301*, 340.

(36) Jungwirth, P.; Tobias, D. J. *J. Phys. Chem. B* **2001**, *105*, 10468.

(37) Dang, L. X. *J. Phys. Chem. B* **2002**, *106*, 10388.

(38) Weber, R.; Winter, B.; Schmidt, P. M.; Widdra, W.; Hertel, I. V.; Dittmar, M.; Faubel, M. *J. Phys. Chem. B* **2004**, *108*, 4729.

(39) Petersen, P. B.; Saykally, R. J. *J. Phys. Chem. B* **2006**, *110*, 14060.

(40) Liu, D.; Ma, G.; Levering, L. M.; Allen, H. C. *J. Phys. Chem. B* **2004**, *108*, 2252.

(41) Ghosal, S.; Brown, M. A.; Bluhm, H.; Krisch, M. J.; Salmeron, M.; Jungwirth, P.; Hemminger, J. C. *J. Phys. Chem. A* **2008**, *112*, 12378.

(42) Perera, L.; Berkowitz, M. L. *J. Chem. Phys.* **1991**, *95*, 1954.

(43) Perera, L.; Berkowitz, M. L. *J. Chem. Phys.* **1992**, *96*, 8288.

(44) Perera, L.; Berkowitz, M. L. *J. Chem. Phys.* **1993**, *99*, 4236.

(45) Perera, L.; Berkowitz, M. L. *J. Chem. Phys.* **1994**, *100*, 3085.

(46) Stuart, S. J.; Berne, B. J. *J. Phys. Chem.* **1996**, *100*, 11934.

(47) Marques, M. A. L.; Gross, E. K. U. Chapter 4. In *A Primer in Density Functional Theory*; Fiolhais, C.; Nogueira, M.; Marques, M., Ed.; Springer: Berlin.

(48) Stanton, J. F.; Bartlett, R. J. *J. Chem. Phys.* **1993**, *98*, 7029.

(49) VandeVondele, J.; Krack, M.; Mohamed, F.; Parrinello, M.; Chassaing, T.; Hutter, J. *Comput. Phys. Commun.* **2005**, *167*, 103.

(50) Goedecker, S; Teter, M; Hutter, J. *Phys. Rev. B* **1996**, *54*, 1703.

(51) VandeVondele, J.; Hutter, J. *J. Chem. Phys.* **2003**, *118*, 4365.

(52) Perdew, J. P.; Burke, K; Ernzerhof, M. *Phys. Rev. Lett.* **1996**, *77*, 3865.

(53) Galamba, N.; Cabral, B. J. C. *J. Am. Chem. Soc.* **2008**, *130*, 17955.

(54) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03*, revision C.02; Gaussian, Inc.: Wallingford, CT, 2004.

(55) Brancato, G.; Rega, N.; Barone, V. *Phys. Rev. Lett.* **2008**, *100*, 107401.

(56) Mata, R. A.; Cabral, B. J. C.; Millot, C.; Coutinho, K.; Canuto, S. *J. Chem. Phys.* **2009**, *130*, 014505.

(57) Berendsen, H. J. C.; Grigera, J. R.; Straatsma, T. P. *J. Phys. Chem.* **1987**, *91*, 6269.

(58) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098.

(59) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.

(60) Woon, D. E.; Dunning, T. H., Jr. *J. Chem. Phys.* **1993**, *98*, 1358.

(61) Werner, H.-J.; Knowles, P. J.; Lindh, R.; Manby, F. R.; Schültz, M.; Celani, P.; Korona, T.; Mitrushenkov, A.; Rauhut, G.; Adler, T. B.; Amos, R. D.; Bernhardsson, A.; Berning, A.; Cooper, D. L.; Deegan, M. J. O.; Dobbyn, A. J.; Eckert, F.; Goll, E.; Hampel, C.; Hetzer, G.; Hrenar, T.; Knizia, G.; Köppl, C.; Liu, Y.; Lloyd, A. W.; Mata, R. A.; May, A. J.; McNicholas, S. J.; Meyer, W.; Mura, M. E.; Nicklass, A.; Palmieri, P.; Pflüger, K.; Pitzer, R.; Reiher, M.; Schumann, U.; Stoll, H.; Stone, A. J.; Tarroni, R.; Thorsteinsson, T.; Wang, M.; Wolf, A.; *MOLPRO*, version 2008.1, a package of ab initio programs. http://www.molpro.net.

(62) Bounds, D. G. *Mol. Phys.* **1985**, *54*, 1335.

(63) Sprik, M.; Klein, M. L.; Watanabe, K. *J. Phys. Chem.* **1990**, *94*, 6483.

(64) Koneshan, S.; Rasaiah, J. C.; Lynden-Bell, R. M.; Lee, S. H. *J. Phys. Chem. B* **1998**, *102*, 4193.

(65) Heuft, J. M.; Meijer, E. J. *J. Chem. Phys.* **2003**, *119*, 11788.

(66) Tongraar, A.; Rode, B. M. *Phys. Chem. Chem. Phys.* **2003**, *5*, 357.

(67) Bergstroem, P. A.; Lindgren, J.; Kristiansson, O. *J. Phys. Chem.* **1991**, *95*, 8575.

(68) Grossfield, A.; Ren, P. Y.; Ponder, J. *J. Am. Chem. Soc.* **2003**, *125*, 15671–15682.

(69) Asthagiri, D.; Pratt, L. R.; Kress, J. D. *Phys. Rev. E* **2003**, *68*, 041505.

(70) Sit, P.H.-L.; Marzari, N. *J. Chem. Phys.* **2005**, *122*, 204510.

(71) Guidon, M.; Schiffmann, F.; Hutter, J.; VandeVondele, J. *J. Chem. Phys.* **2008**, *128*, 214104.

(72) Krekeler, C.; Hess, B.; Delle Site, L. *J. Chem. Phys.* **2006**, *125*, 054305.

(73) Magyar, R. J.; Tretiak, S. *J. Chem. Theory Comput.* **2007**, *3*, 976.

(74) Kemp, D. D.; Gordon, M. S. *J. Phys. Chem. A* **2005**, *109*, 7688.

(75) Yamagami, M.; Wakita, H.; Yamaguchi, T. *J. Chem. Phys.* **1995**, *103*, 8174.

(76) Woon, D. E.; Dunning, T. H., Jr. *J. Chem. Phys.* **1994**, *100*, 2975.

(77) Reed, A. E.; Weinstock, R. B.; Weinhold, F. *J. Chem. Phys.* **1985**, *83*, 735.

JP904687K