Molecular Dynamics Simulations of a Silver Atom in Water: Evidence for a Dipolar Excitonic State

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The properties of a silver atom in bulk water were studied for the first time by molecular dynamics simulations using two complementary mixed quantum-classical approaches. The first one consists of treating by quantum mechanics one electron only, which interacts with a classical silver cation and solvent through one-electron pseudopotentials. The second one is Car-Parrinello molecular dynamics that treats all the valence electrons quantum-mechanically. Very good agreement is obtained between these two methods, and the calculated absorption spectrum of the solvated silver atom agrees very well with experimental data. Both simulations reveal that the silver atom is in the critical region for the appearance of a dipolar excitonic state and exhibits a dipole moment of ~ 2 D with large fluctuations of ± 1 D. The structure of the solvation shell is also analyzed.

Understanding elementary chemical events in terms of basic physical properties is a subject of considerable interest today. Among those, the electron transfer process has been widely studied, due to the importance of redox reactions in everyday physical chemistry and biophysics. Even in the simplest case of metal atoms in polar solvents, the optical and electrical properties of the solvated atom, which strongly depends on the metal-solvent system, are not fully understood. In some cases, such as sodium in water, the ionization is complete and leads to two well separated solvated species, i.e., the electron and the ion. In contrast, the reduction of silver cations in a radiolysis experiment or when solvated silver halide is exposed to light leads to the formation of silver atoms, followed by a multistep coalescence into charged metallic clusters [1]. The role of the solvent is of critical importance, as illustrated by the dependence on the polarity of the solvent of the optical properties of solvated metal atoms [2]. The solvent indeed mediates effective interactions between the ion and the electron. These interactions depend on both solvent and ion, or atom properties. The precise nature of the effective electron-ion interactions can be usefully addressed by mixed quantum-classical simulations. We present here a complement to earlier research focusing on alkali metals in solution [3]. The silver atom in water is studied for the first time, using two different simulation methods.

Quantum classical molecular dynamics.—We performed a mixed quantum-classical molecular dynamics (QCMD) of an excess electron plus a silver cation in bulk water. Only the excess electron was treated quantum mechanically, using the Born-Oppenheimer approximation. In addition to the Hellmann-Feynman forces acting on each classical degree of freedom due to the excess charge are those arising from the empirical models for the solvent and the cation. Water/water interactions were described by the SPC model [4], while for the excess electron/water interaction we used a pseudopotential developed by Turi and Borgis [5]. Details on the method can be found in Ref. [6]. The Ag^+/water molecule interactions were modeled by a point charge on silver $q_{Ag^+} = +1e$ and a 6–12 Lennard Jones (LJ) term, where $\epsilon_{Ag^+/O} = 0.40$ kJ/mol and $\sigma_{Ag^+/O} = 2.78$ Å. These values were calibrated using classical molecular dynamics simulations of Ag^+ in 300 SPC water molecules to reproduce experimental structural and thermodynamical properties. Using these parameters, we obtained the maximum of silver oxygen radial distribution function (RDF) at 2.36 Å and a coordination number of 5.5 water molecules, while the experimental values are 2.35 Å and 4.5, respectively [7]. The calculated hydration enthalpy was about 120 kcal/mol, while the experimental value is around 127 kcal/mol. The discrepancy found for the coordination number is inherent to our choice to limit ourselves to a very simple LJ two-body potential for the Ag^+/water interaction [8,9]. It has been shown, for example, that the inclusion of dipolar and quadrupolar polarizability of Ag^+ greatly enhances the description of silver chloride [10]. A repulsive semilocal pseudopotential was also added to the Coulomb attraction in the electron Hamiltonian to describe the electron/Ag^+ interaction. The coefficients were evaluated in vacuum to reproduce the experimental electron/silver properties [11].

The periodic simulation box used in the QCMD contains 300 SPC water molecules, one Ag^+ cation, and an excess electron. A short simulation with 800 SPC was

also carried out in order to test the influence of the box dimension on the results with no significant differences; hence, the small box was used. The simulation was run for 30 ps in the canonical ensemble at 298 K using a Nosé-Hoover thermostat, with the density fixed to 1.000 g/cm^3. A Gear predictor-corrector algorithm was employed with a time step of 0.5 fs, using Ewald summation for electrostatic interactions. Finally, the basis set for the electron was a $7 \times 7 \times 7$ cubic grid of spherical Gaussian functions of about 7.9 Å length. For technical details on the resolution of the Schrödinger equation for the electron, see Nicolas *et al.* [6].

To calculate the total electron absorption spectrum we used the cumulant expansion and the vibration-rotation decorrelation hypothesis [12]:

$$I(E) = E(1 - e^{-\beta E}) \sum_{n=1}^{M} \langle |\mu_{0n}| \rangle_0 \exp\left[-\frac{(E - \langle E_{0n} \rangle_0)^2}{\langle \delta E_{0n}^2 \rangle} \right],$$
(1)

where $E_{0n} \equiv E_{0n}(\vec{S})$ is the solvent-dependent energy gap between the ground and the nth excited state, whereas $\mu_{0n} \equiv \mu_{0n}(\vec{S})$ is the corresponding transition dipole matrix. $\langle \ldots \rangle_0$ indicates an average over the solvent configurations with an electron equilibrated in its ground state. It represents an excellent approximation to the absorption spectrum in the "slow modulation" (or "inhomogeneous broadening") limit and has been previously tested for an excess electron in water [13]. The three components of the total absorption spectrum (Fig. 1) were directly computed by averaging the instantaneous excitation spectrum over the adiabatic motion of the ions.

Car-Parrinello molecular dynamics.—An *ab initio* molecular dynamics was also performed on the same system using the CPMD program [14]. The plane wave pseudopotential implementation of the Kohn-Sham method used in this code has been validated in numerous previous studies of aqueous systems. We used the Becke-Lee-Yang-Parr functional [15,16] with local spin density, as this combination of generalized gradient approximations to exchange and correlation has been shown to give good results for the structure and dynamics of water [17,18]. The specification of the various parameters of the simulation was standard and essentially identical to settings used in Ref. [19] for the simulation of one Ag$^+$ cation in water. In this previous work it was shown that Car-Parrinello molecular dynamics leads to correct structural parameters of Ag$^+$ in water compared to x-ray scattering experiments [7]. The unit cell was 9.860 Å and consisted of one silver atom immersed in 32 water molecules with full periodic boundary conditions. H atoms were replaced by deuterium atoms to allow for a better separation of atomic dynamics and fictitious electronic dynamics time scales. The one-electron orbitals were expanded in a plane wave basis up to an energy cutoff of 70 Ry. For technical details of the norm conserving pseudopotentials we refer to Ref. [19]. The starting configuration was an equilibrated configuration of Ag$^+$ in 32 water molecules, to which an electron was added. The *ab initio* trajectory was then equilibrated to an average temperature of 300 K for about 1 ps, and data were collected over a total of 3 ps. During the last 800 fs of this trajectory, we have computed every 1 fs the maximally localized Wannier orbitals [20,21]. The following analysis uses the Wannier orbital and the corresponding Wannier center of the 5s electron of silver.

Results.—The maximum of the absorption band in the UV-vis region obtained from QCMD is around 347 nm in good agreement with recent experimental data reporting a maximum around 355 nm [1]. Also, the general behavior of the calculated spectrum seems to reproduce quite well the experimental data (see Fig. 1). Preliminary calculations [11] reproduce the slight redshift of the wavelength maxima with increasing temperature observed experimentally [1], ensuring the validity of the pseudopotential in a wide range of thermodynamical conditions (from ambient to supercritical conditions). The absorption spectrum can be decomposed into three components. These three bands correspond to the transitions from the s ground state to three p nondegenerate excited states: projecting these states onto the spherical harmonics the largest coefficients are around 0.9, denoting an s character for the ground state and a p character for the first three excited states.

The identity of the silver atom was found to be preserved in both simulations, while a spontaneous dipole appears on the silver atom with an average electron-silver distance $\zeta = \langle r \rangle = 0.44$ and 0.53 Å in the CPMD and QCMD simulations, respectively. Although noticeably nonzero, these values are well within the electron radius
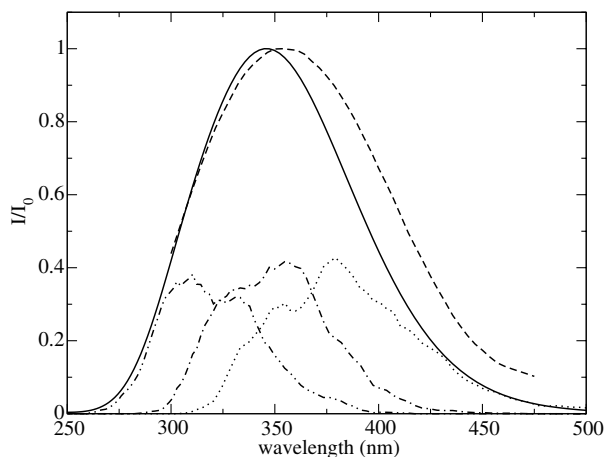

FIG. 1. Absorption spectrum: calculated (solid line); experimental (dashed line). The three components are separately shown (dotted, dash-dotted, and dash-dotted–dotted lines) corresponding to s-p transitions.

estimated from the width of the maximally localized Wannier orbital of the $5s$ electron in the CPMD simulation, 2.00 Å, or from the width of the electron wave function in QCMD, 1.98 Å, with very good agreement between both simulations. This is illustrated in Fig. 2, which displays a snapshot of the silver atom and its close surrounding extracted from the QCMD simulation.

The standard deviations of the electron-silver distance were $\sigma_r = 0.14$ Å and $\sigma_r = 0.21$ Å, respectively. It was further checked in the QCMD simulation that the average of each component of the electron-silver vector taken separately is around zero, as it should be. This suggests that the values we found for the electron-silver distance are statistically meaningful.

Because the $5s$ electron and the Ag^+ cation are not superimposed, we have studied the solvation structure of silver from both the silver/water RDF and the electron/water RDF (see Fig. 3). The most striking feature of the silver/water RDF is that the oxygen peak is significantly shifted to shorter distances than the hydrogen peak, indicating a net positive charge at the silver position. The CPMD curves are more structured than the QCMD ones, presumably due to finite size effects in the CPMD simulation and/or to the different underlying Ag^+/water interaction. On the other hand, the oxygen and hydrogen peaks of the electron/water RDF's are found at the same distance, similarly to the solvation shell of a hydrophobic species. A tail in the electron/hydrogen RDF is found, however, below $r = 2.7$ Å, which contains approximately one hydrogen atom pointing towards the electron. Note that the water/electron distance is larger than that of a solvated electron in water as found in recent simulations with the same QCMD method as presented here: this strengthens the view that we are observing a solvated atom.
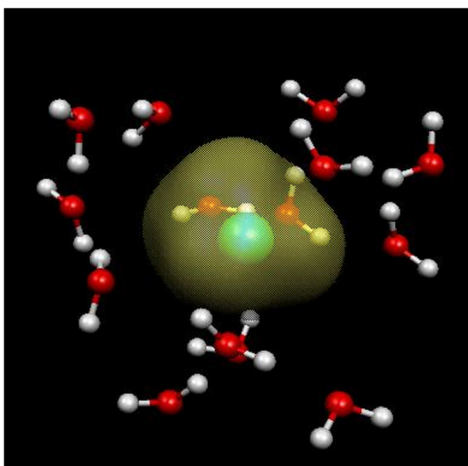
This silver atom bears an average dipole moment $\langle \mu \rangle = e\zeta = 1.9$ D (CPMD)–2.4 D (QCMD) in water. It corresponds to a dipolar atom or dipolar excitonic state (ES) which can arise spontaneously from the dipole/reaction field interaction when a polarizable atom is placed in a polarizable medium [22]. Such ES has been earlier reported as a metastable state of lithium in ammonia [3]. In a mean-field approach Logan determined the average dipole moment on the polarizable atom [22]:

$$\left(\frac{\langle \mu \rangle}{M} \right)^2 = \frac{[\alpha_0 g(\rho)]^2 - 1}{\alpha_0 g(\rho)}, \tag{2}$$

where α_0 is the atom polarizability and $M = \langle S|\hat{\mu}_\gamma|P_\gamma \rangle$; $\gamma = x, y, z$ is the transition dipole from the S ground state of the atom in vacuum and the first P excited states (for a closed-shell atom). We have $\alpha_0 = 7.9$ Å^3 and $M = 4.8$ D for silver. $g(\rho)$ is the reaction field factor characterizing the polarizable surrounding. From continuum dielectric theory [23], $g = (8\pi/3)\rho[\epsilon - 1]/[2\epsilon + 1]$. Note that in this mean-field approach a critical density ρ_c is present; hence, for $\rho \leq \rho_c$ no ES is present, while it arises for $\rho > \rho_c$. In our case $\rho = 1.000$ g/cm^3, $\epsilon = 78.3$, and the resulting $\alpha_0 g(\rho) = 1.09 > 1$ corresponds to the presence of an ES with a net atomic dipole $\langle \mu \rangle = 1.96$ D and a small stabilization free energy of the order of 1 kJ/mol. The system is much closer to criticality than

FIG. 2 (color online). Instantaneous configuration from QCMD calculation. The Ag^+ cation (the central sphere) is localized inside the electronic cloud representing the excess electron.
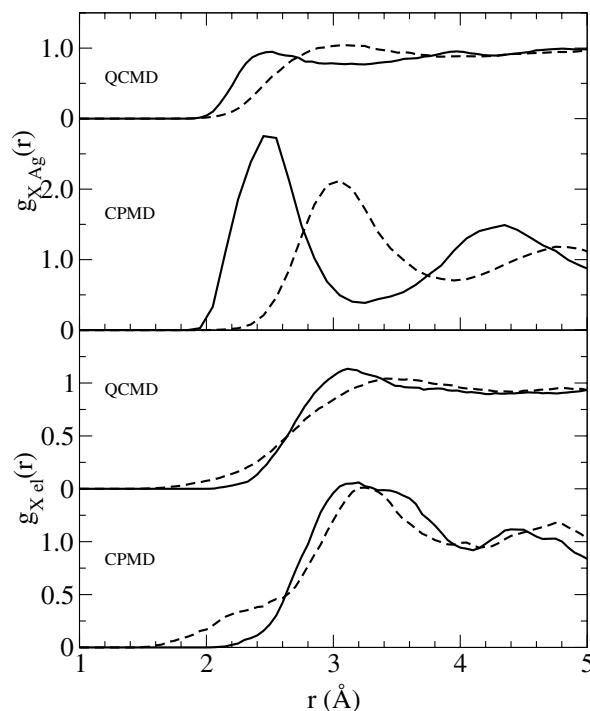

FIG. 3. Ag^+/water (top panel) and electron/water (bottom panel) radial distribution function calculated during QCMD (upper curves) and CPMD (lower curves) simulations. In each case the solid line refers to oxygen atoms and the dashed line to hydrogen atoms.
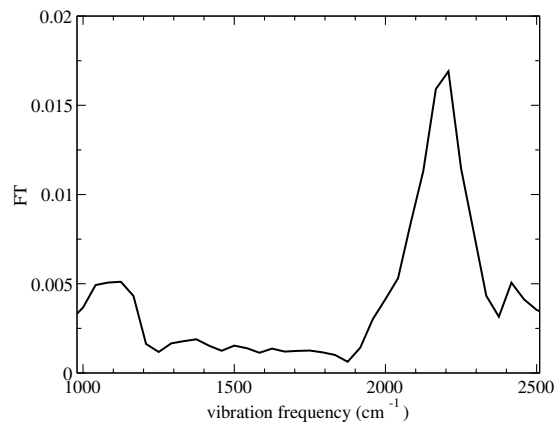
FIG. 4. Infrared spectrum calculated by Fourier transformation of the electron-Ag^+ distance in CPMD.

in the case of a lithium atom in ammonia: interpreting the Li ionization study of Sprik *et al.* [3], Logan has found a $\alpha_0 g(\rho)$ of 2.1 [22].

Winn and Logan reported that the well defined transition found in mean-field theory becomes a sharp but continuous transition when fluctuations are included [24]. At this sharp turning point, one can expect the fluctuations of the electric field generated by the solvent on the polarizable atom to be quite large. These fluctuations are found to be $\sqrt{\langle \mathcal{E}^2 \rangle} = 14$ MV/m in the QCMD simulation, indeed much larger than the value in absence of silver polarizability which can be inferred from the fluctuation-dissipation theorem: $\sqrt{\langle \mathcal{E}^2 \rangle_0} = kTg(\rho) = 5.75$ MV/m. The silver dipole follows adiabatically the electric field applied by the solvent; this leads to the large standard deviations found for the silver/electron distance. The power spectrum of the silver dipole dynamics, related to the infrared spectrum of aqueous silver, should also reflect the characteristic dynamics of the solvent. Indeed, as shown in Fig. 4, it clearly exhibits two peaks corresponding to the stretching (around 2200 cm^{-1}) and the bending (around 1100 cm^{-1}) motions of heavy water.

Conclusions.—We provide numerical evidence that at ambient conditions a silver atom solvated in water is in the critical region for the appearance of an excitonic state: it has an average dipole of about 2 D induced by the solvent electric field, with large fluctuations of ± 1 D. The identity of the atom is preserved, however, as confirmed by experimental evidence. These findings increase our insights into the physics of polarization processes in the polar metal/polar solvent systems. They will certainly help in the better understanding of the chemistry of solvated silver atoms and clusters in aqueous solutions, a problem of major interest in chemical physics.

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