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1996 J. Phys.: Condens. Matter 8 9389

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Ultrafast spectroscopy of the aqueous chloride ion studied by quantum molecular dynamics simulations

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Received 30 July 1996

Abstract. The dynamics of the photodetachment of an electron from a chloride ion in water induced by excitation of the lowest charge-transfer-to-solvent state is explored by using quantum molecular dynamics simulations. The ejected electron is described in terms of floating Gaussian orbitals, and solvent electronic polarization effects are accounted for in a fully self-consistent way. The simulation results point to a two-step photodissociation mechanism: the formation of a metastable electron–atom pair on a subpicosecond time-scale followed on a picosecond time-scale by the competition between two different reaction channels, (i) a diffusive barrier-impeded dissociation of the pair, yielding a solvated halogen atom and a free electron, and (ii) a non-radiative quantum recombination, eventually leading to the chloride ion in its ground state. The computed transient absorption spectra are compatible with the experimental data either at early times during the formation of the electron–atom pair or at longer times when dissociation–recombination occurs.

1. Introduction

The dynamics of the photodetachment of electrons from aqueous chloride ions has been studied recently by means of ultrafast time-resolved spectroscopy [1]. In spite of the simplicity of the ionic solute, the excitation of the so-called charge-transfer-to-solvent (CTTS) states, which are no property of the isolated ions but are induced by the geometrical confinement by the surroundings [2, 3], may induce a wealth of elementary reaction channels: direct ejection of the excited electron into a solvent cavity away from the parent core, geminate recombination, association with a solvated positive counterion, formation of a transient electron–atom pair. Mixed quantum–classical molecular dynamics (MD) simulations represent a powerful tool for elucidating the mechanism of these photoinduced reactions on a molecular level [4, 5].

We have recently introduced a quantum MD variant to simulate the dynamics of a solvated excess charge [6–9], which differs from related approaches with respect to two key points. First, the one-electron solute wavefunction is represented as a superposition of s-, p- and d-component shells which are in turn built up of Gaussian basis functions. Unlike the commonly employed plane-wave expansion [4], the Gaussian basis set is local; its intrinsic limitation is to be restricted to the description of confined rather than extended (band-like) states. Also, it must be allowed to float as an entity through the solvent to cover the regions of non-vanishing solute electronic density. These limitations and technical complications are compensated by the substantial reduction in computational cost which permits one to incorporate another essential physical feature in the theoretical model: the solvent electronic

polarization. The excess charge participates in the self-induction of the solvent which, in the case of water for example, is responsible for the significantly augmented dipole moment in the bulk compared to the gas phase. From a dynamical point of view, the solvent electronic polarization has to be treated as an explicit degree of freedom separate from the orientational polarization [10]. An adequate procedure has been proposed in references [6, 7] to determine the solvent electronic polarization in a self-consistent fashion and simultaneously with the electronic excess charge distribution during a quantum MD simulation.

We have exploited the quantum MD approach described above to investigate the photodetachment dynamics of an electron from an aqueous chloride ion in the lowest CTTS channel [8, 9]. In the light of the simulation results, a two-step photodissociation mechanism was proposed: the formation of a metastable electron–atom pair on a subpicosecond time-scale followed at longer times by the competition between two different reaction channels: a diffusive, barrier-impeded dissociation of the pair, yielding a solvated halogen atom and a free electron, and a non-radiative quantum recombination, eventually leading to the Cl^- ion in its ground state.

In this paper, we focus on the spectral characteristics of the photodetachment process either on the subpicosecond/picosecond time-scale during the formation of the electron–atom pair or at longer times when dissociation–recombination occurs. In the former case, the transient absorption can be computed directly by using the statistical formulation of non-linear spectroscopy. At longer times, the absorption signal at around 1.7 eV, i.e. at frequencies pertinent to the fully hydrated electron, can be inferred from a spectral population kinetic model.

2. Quantum molecular dynamics simulation

2.1. The model and method

The key features of our mixed quantum–classical MD approach for simulating the ground- and excited-state dynamics of solvated excess charges in water, as well as the details of the molecular model used for describing electron detachment from a chloride ion in water, are discussed in references [6–9].

Briefly, the model system contained 255 rigid water molecules and a chloride ion as a solute. For the solvent we chose the polarizable TIP4P water model of Sprik and Klein in which the induced dipole is described in terms of distributed induced charges [11]. The solute Cl^- is treated by an effective one-electron approach and represented by a chlorine core plus an excess electron. The electron–chlorine interaction is described by the gas-phase pseudopotential of Ganas *et al* [12]. The chlorine–solvent interaction consists of the usual LJ term and a polarizability term. Further, the excess electron is coupled to the solvent via repulsive, electrostatic and polarization interactions. We have adopted a so-called primitive model, in which repulsion contributions are accounted for by smoothly damping the Coulomb interactions at short distances [13].

Through the electron–solvent and electron–atom pseudopotentials the quantum excess charge distribution is coupled to the solvent and the chlorine core. In this case the electronic wavefunction depends on the position of all nuclei in the system. If the single-electron wavefunction is represented by a set of basis functions, the expansion coefficients depend on the heavy-particle configuration. It was shown that a localized basis set represented in terms of floating spherical Gaussian orbitals (FSGO) is well suited for mixed quantum–classical MD simulations of solvated excess charges. The idea of the FSGO approach is to distribute N spherical Gaussians in space in order to mimic orbitals of different symmetries.

Since the FSGO basis is local, its origin must be chosen to ensure a proper representation of the solute electronic wavefunction. For studying dynamics of photodetachment of the electron from the atomic core, it is necessary to split the basis into two parts: one stays constantly on the parent atom and describes the core orbitals; the other has a mobile origin adiabatically following the position expectation value of the excess electron. This scheme provides sufficient basis-set flexibility to describe the complex charge repartitioning involved in the electron photodetachment process [7–9].

We have employed the adiabatic quantum–classical MD simulation technique in combination with a self-consistent electronic polarization optimization. At a fixed configuration of nuclei the polarization charges on all water molecules and on the chlorine and the coefficients of the excess electronic wavefunction are optimized simultaneously in an iteration loop. For the computation of radiative or non-radiative transition properties, the self-consistent optimization has to be performed independently for the selected occupied electronic state and for all other (lower or upper) accessible states [14]. This is computationally much more demanding than a simpler variant, where all solute states would have the same solvent electronic polarization energy as that of the occupied initial state, i.e. transitions between the Born–Oppenheimer levels are described within the Franck–Condon approximation for both the orientational and electronic polarization of the solvent. In a recent work we have shown that computing the stationary absorption spectrum of the hydrated electron with the full optimization for each state shifts the band maximum by 0.3 eV with respect to the Franck–Condon calculation presented in reference [6], thus yielding an excellent agreement between the theoretical and experimental spectra, with a peak position at exactly 1.7 eV [14].

2.2. Photodetachment trajectories

Within the one-electron model, the ground electronic state of Cl^- is described by the chlorine core plus the excess electron residing in a 3p orbital. From an extensive ground-state trajectory we have computed the excess electron density of accessible states; the numerical results are displayed in figure 1. The lowest CTTS excited state appears well detached from the higher states, with a mean excitation energy from the 3p states of 6.7 eV (solvent electronic polarization optimization included), quite close to the experimental estimate of 6.8 eV. This non-degenerate isolated state is referred to as the ‘4s’ state.

The excited-state dynamics of aqueous chloride induced by a promotion of an electron to the 4s CTTS state has been studied with the MD approach described in the preceding section. The system has been equilibrated to the chloride ground state and a set of initial configurations were selected. For each configuration, the electronic solute state was instantaneously switched from the 3p to the 4s state, the time was set to zero and the non-equilibrium adiabatic dynamics on the excited-state surface was monitored for typically 2 ps.

For a given non-equilibrium initial configuration, the energetics of the photodetachment process can be discussed by means of a characteristic trajectory shown in figure 2. There the energy levels of aqueous chloride as a function of time are displayed. At the beginning the energy spectrum is that of ground-state Cl^- in water. The 4s state slightly below -2 eV, which now determines the time evolution, is marked with a thick line. Its energy rapidly drops down to -3 eV and fluctuates around this value. The states below the 4s level belong to the parent core and their rise in energy reveals the reorganization of the surrounding water molecules now favouring the solvation of the electron instead of the chlorine atom. Out of the manifold of states at higher energies the three lowest levels become detached

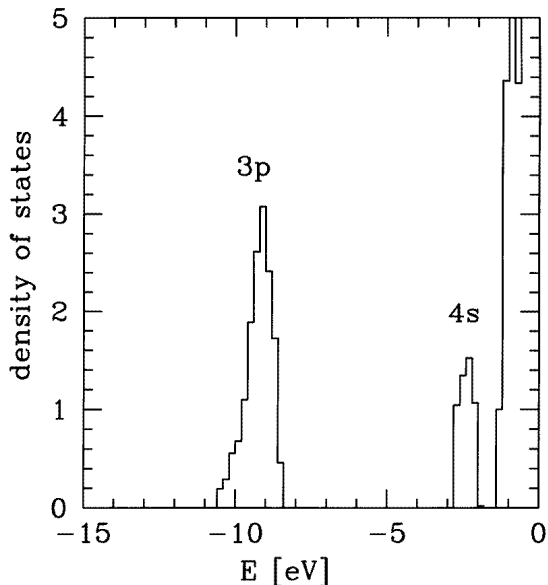


Figure 1. The density of states for a chloride anion in water computed from an adiabatic MD trajectory in the 3p ground state.

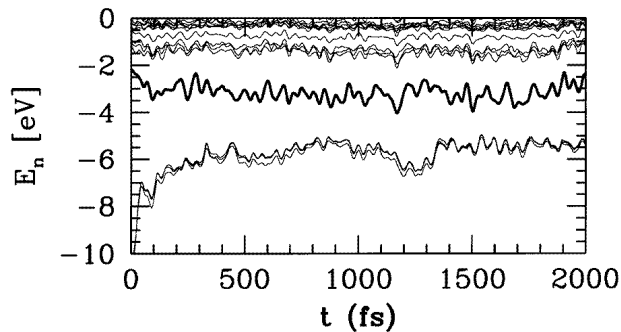


Figure 2. Energy levels of aqueous chloride as a function of time, after the excitation of the 4s CTTS state at $t = 0$. The adiabatic MD simulation has been carried out in the 4s state marked with a thick line. The levels below the thick line represent 3p chlorine core states; those above are higher CTTS states.

from the others and after 1 ps they resemble the p states of the hydrated electron.

On the same time-scale, it was observed by monitoring the electron–atom distance that the electron escapes quickly from the core, then reaches progressively an electron–chlorine separation of about 6 Å and fluctuates around that distance. None of the observed trajectories has led to a direct, complete detachment with electron–core separations beyond 8 Å. In our preceding work, we were able to show that that an electron and a chlorine atom at roughly 6 Å form a metastable entity characterized by a free-energy minimum. The system can linger around that minimum for several tens of picoseconds before dissociating. The dissociation of the pair competes with a non-adiabatic transition mechanism yielding the Cl^- ion [8, 9].

3. Transient spectroscopy

3.1. The subpicosecond/picosecond regime

The transient absorption characterizing the formation of the electron–atom pair can be discussed by inspecting the time-dependent energy pattern in figure 2. At early instants after the preparation of the system in the 4s CTTS, a first absorption band appears at around 1 eV, corresponding to a 4s \rightarrow 4p transition in the initial cage of the chloride ion. Further, this cage breaks down and the electron separates from the atomic core. During the separation, the s \rightarrow p energy gap increases smoothly from \sim 1 eV to \sim 1.7 eV. The latter value corresponds to the relaxed electron–atom pair, which was shown to absorb at roughly the same frequency as a fully hydrated electron [9]. The main spectroscopic feature which emerges from the simulations in the 1–2 eV spectral region is therefore a *solvent-driven spectral shift mechanism*.

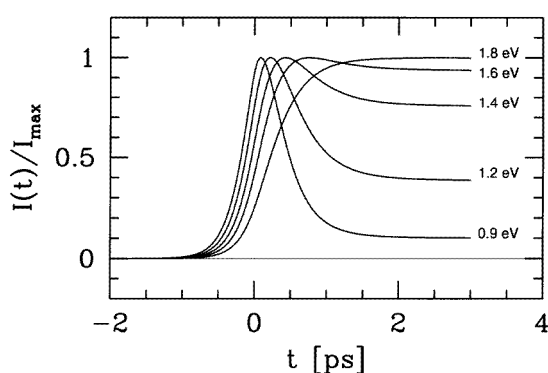


Figure 3. The normalized transient absorption at different probing frequencies obtained from the simulation results.

The transient spectra corresponding to the above mechanism can be quantified by applying the well-developed formalism of non-linear spectroscopy [15–18]. The theoretical absorption spectra computed from the simulation data in the framework of a one-photon excitation scenario [19] are displayed in figure 3 for different probing frequencies from the infrared (0.9 eV) to the blue, close to the maximum of absorption of the hydrated electron (\sim 1.8 eV). These curves should be compared with those of Gauduel *et al* at the same frequencies in reference [1]. Although we do not quite reproduce the asymptotic decays, the overall good agreement between theoretical and experimental results is striking. At 1.8 eV, we observe the progressive rise of the absorption signal of the hydrated electron, with a saturation at roughly 1 ps. This corresponds in our simulation to the adiabatic detachment of the electron and formation of the electron–atom pair. In the 1 eV region, we detect the presence of a short-lived ‘infrared electron’, which in our case is a 4s electron still captured in the water cage of the initial chloride ion. This cage breaks very quickly due to the amount of kinetic energy put in the system and the 4s electron is expelled from the core, yielding the decay of the infrared signal. Finally at intermediate energies, we find that the signal reaches a maximum and then decays to a plateau. The theoretical predictions for the form of the different transient absorption curves as well as the value of the plateau for each curve are in good agreement with the experimental evidence.

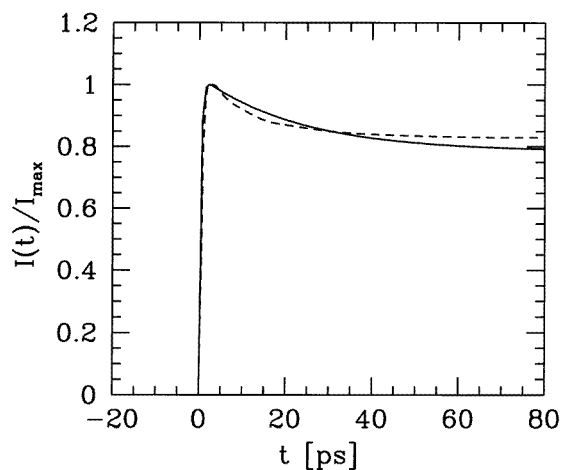
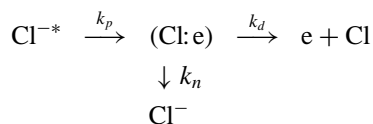


Figure 4. Normalized time-dependent number densities obtained from the kinetic model described in the text (solid line) compared to the experimental probe absorption signal at 1.8 eV of reference [1] (dashed line).

3.2. The subnanosecond regime

As discussed in section 2.2, the photoexcitation of the lowest CTTS state in aqueous chloride induces three processes: the formation of a hydrated electron–chlorine pair at short times followed by adiabatic dissociation or non-adiabatic recombination at longer times. We have constructed a simple kinetic model to elucidate the interplay of the three channels:



The CTTS excited aqueous chloride Cl^{-*} is converted into the hydrated pair $(\text{Cl}:\text{e})$ at a rate k_p which can be inferred directly from the simulations ($k_p^{-1} = 0.4$ ps). The dissociation rate k_d has been determined in reference [8] by calculating the adiabatic free-energy surface of the dissociative $4s$ channel ($k_d^{-1} \sim 30$ ps). The non-adiabatic recombination rate k_n could be estimated by using a time-dependent version of the Golden Rule formula ($k_n^{-1} \sim 100$ ps); in this calculation, the solvent electronic polarization was shown to play a very crucial role. Assuming that both the electron–chlorine pair and the hydrated electron give rise to the probe absorption signal at 1.8–2 eV, a time-dependent signal can be constructed from the number density $N(t)$ of these species which can be determined from the kinetic scheme described above. By dividing $N(t)$ by its maximum value one obtains a function which provides a good approximation to the normalized time-dependent absorption signal for any frequency characteristic of the hydrated electron, e.g., around the maximum at 1.7 eV. In figure 4, we have compared the theoretical function to the experimental time-dependent normalized absorption at probe energy 1.8 eV [1]. We find that the theoretical curve reproduces the rise, the first decay and the asymptotic long-time behaviour of the experimental signal which indicates that the three rate constants k_p, k_d, k_n computed with quantum MD simulations have reasonable orders of magnitude.

It should be noted that the direct comparison between theory and experiment presented in this section as well as in the preceding one assumes implicitly that the adiabatic

photodetachment from the 4s state (possibly after some ultrafast relaxation of higher CTTS states) is the dominant channel. This mechanism is plausible even for the two-photon excitation scenario and is in conformity with the non-adiabatic photodetachment simulations of Sheu and Rossky concerning iodide [5]. It should be kept in mind also that the experiments are performed at finite salt concentration whereas our mechanism assumes an infinite dilution of chloride. Still, the overall correspondence is quite satisfactory, especially with regard to the simplicity of the kinetic model proposed above which describes the CTTS photodynamics as a sequence of rate processes with an equilibrated electron-atom pair as an intermediate species. A unified spectral theory covering the whole time and frequency domain is currently under study.

Acknowledgments

This work was performed with the support of the Groupement de Recherche 'Acte Chimique Elementaire en Phase Liquide' of the CNRS and of the scientific committee of the Institut du Développement et des Ressources en Informatique Scientifique (IDRIS).

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