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Polarization-Bound Quasi-Continuum States Are Responsible for the “Blue Tail” in the Optical Absorption Spectrum of the Aqueous Electron

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Abstract: The electronic absorption spectrum of the aqueous electron in bulk water has been simulated using long-range-corrected time-dependent density functional theory as well as mixed quantum/classical molecular dynamics based on a one-electron model in which electron−water polarization is treated self-consistently. Both methodologies suggest that the high-energy Lorentzian tail that is observed experimentally arises mostly from delocalized *bound-state* excitations of the electron rather than bound-to-continuum excitations, as is usually assumed. Excited states in the blue tail are bound only by polarization of the solvent electron density. These findings have potentially important ramifications for understanding electron localization in polar condensed media as well as biological radiation damage arising from dissociative electron attachment.

The notion of a “solvated electron” was introduced more than a century ago to explain the electrical conductance and optical spectra of solutions of alkali metals.[1] Because of the relatively short lifetime of this species in water, however, direct observation of the aqueous electron, e^-(aq), was not made until 1962,[2] but since that time it has been recognized that e^-(aq) is one of the primary radicals formed upon radiolysis of aqueous systems.[3] Nevertheless, important questions persist concerning the structure and dynamics of this diffuse, polarizable, and fundamentally quantum-mechanical solute, especially with regard to its excited electronic states.

Solvated electrons can be generated not only by ionizing radiation but also by UV irradiation of liquid water at energies just above the band edge of water’s UV spectrum;[4] the details of this low-energy ionization mechanism remain a matter of debate.[5] Moreover, the “prehydrated” (or “wet”) electron, a short-lived (<1 ps) nonequilibrium precursor to the fully solvated electron whose existence has been inferred from ultrafast spectroscopy, has only recently been definitively assigned as an excited state of e^-(aq).[6] The time scale for internal conversion to the ground state remains controversial, however, with experimental and theoretical estimates ranging from 50 to 1000 fs.[7] Dissociative electron attachment of the prehydrated species by nucleic acids has recently been implicated[8] as a mechanism for DNA damage by low-energy electrons,[9] suggesting that reductive chemistry might play a prominent role in biological radiation damage, alongside the more familiar oxidative damage mechanisms involving OH radicals. In contrast to the prehydrated electron, however, ground-state e^-(aq) appears to be relatively ineffective in inducing DNA strand breaks.[10]

Given the importance of excited states of e^-(aq) in radiation chemistry and in view of the fact that the optical absorption spectrum of e^-(aq) is the primary means of detecting and characterizing this species in bulk water, it is significant that no theoretical model or calculation to date has provided a qualitatively satisfactory description of this spectrum. The spectrum (shown in Figure 1) exhibits a Gaussian line shape at the red edge with a peak absorption intensity at 1.72 eV (720 nm).[11] Previous simulations do reproduce the overall shape of this Gaussian feature, albeit with a small blue shift, and the prevailing view (based upon simulations using one-electron pseudopotential models) is that this feature arises from three s → p excitations of an electron in a cavity.[12,13] In contrast, the high-energy side of the spectrum exhibits a Lorentzian line shape (the “blue tail”)[11] that is absent in all previous simulations of the e^-(aq) absorption spectrum, including ab initio calculations.[14]

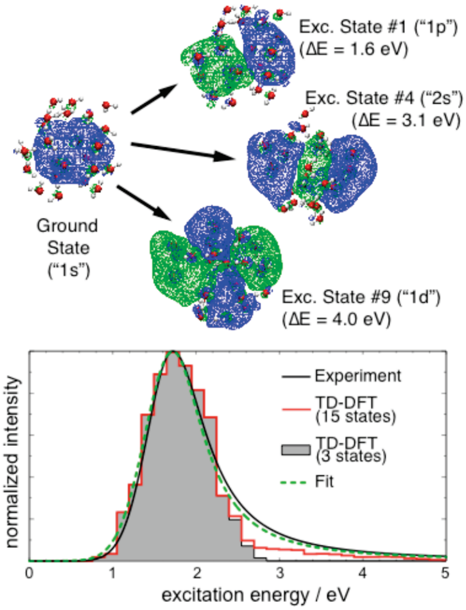

Figure 1. Comparison of the experimental absorption spectrum of e^-(aq) (using line-shape parameters from ref 11) with results obtained from TD-DFT calculations and a fit of the 15-state TD-DFT data to the line-shape function used in ref 11. Also shown are examples of the NTOs associated various excited states (only QM water molecules are shown, and these plots represent 90% isoprobability contours).

We have simulated the electronic absorption spectrum of e^-(aq) in bulk water using both one-electron and many-electron quantum-mechanical (QM) models. The one-electron model is one recently developed by us[15] that incorporates many-body electron−water polarization in a self-consistent way. The many-electron model is time-dependent density functional theory (TD-DFT) using a long-range-corrected functional that affords accurate electron binding energies in $(H_2O)_n^-$ clusters[16] and is free of spurious low-energy charge-transfer excited states that often plague condensed-phase TD-DFT calculations.[17] These are two very different theoretical paradigms, yet both give the same result: a spectrum that, for the first time, reproduces the qualitative features of the experimental spectrum on both the red side *and* the blue side. Our simulations reproduce the peak position quantitatively and, more importantly, afford significant oscillator strength in the blue tail. The calculations

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indicate that these higher-energy states (beyond the p manifold) extend deep into the interstices between water molecules and are bound only by the overall polarization of numerous water molecules with which they interact.

The TD-DFT simulation of the $e^-(aq)$ absorption spectrum was performed by sampling over snapshots extracted from a simulation of $e^-(aq)$ in bulk water obtained using a one-electron model that has been used in many recent $e^-(aq)$ simulations.[13] Roughly two solvation shells (~28 water molecules) were described using DFT, whereas the remaining bulk solvent was represented by molecular mechanics (MM) point charges. The basis set (6-31+G*) is atom-centered, yet the orbitals shown in Figure 1 make clear that this basis is diffuse enough to describe an electron inhabiting the voids between water molecules.

As shown in Figure 1, the TD-DFT simulation exactly reproduces the location of the peak absorption intensity, without adjustable parameters, and also reproduces the width of the Gaussian portion of the spectrum. As in the one-electron models, this feature arises from three s → p excitations. This is true despite small contributions to the e^- wave function from the frontier orbitals of the water molecules. These small contributions appear to be necessary to explain certain quantitative features of $e^-(aq)$ spectroscopy[18] but do not qualitatively alter the cavity picture of $e^-(aq)$. Well into the blue tail, each excited state is still well-described by a single particle−hole pair of natural transition orbitals[19] (NTOs) and can still be categorized in terms of a "spherical box" model.[20] Examples of some NTOs are depicted in Figure 1.

Notably, when only the lowest three excited states are included in the TD-DFT calculation, the spectrum obtained is strictly Gaussian. When additional excited states are considered, however, we observe a long tail at higher excitation energies. (In all, 15 excited states were included in these calculations; tests indicated that the next five states support <1% of the total oscillator strength.) The combined oscillator strength of the three s → p excitations is extremely sensitive to the size of the QM region in these calculations; somewhat smaller QM regions afford similar excitation energies, but in such calculations, the p states carry essentially all of the oscillator strength. Thus, relaxation of the solvent electron density upon excitation of the cavity-bound electron facilitates intensity borrowing by the higher-energy states, which is manifested as the blue tail seen in Figure 1.

Since the higher-lying excited states penetrate beyond the QM region employed here, it will be extremely difficult to reproduce the blue tail *quantitatively* using QM/MM calculations of this sort. To complement this approach, we turned to our polarizable one-electron model, where simulations in bulk water can be performed using periodic boundary conditions.

Our model, which is described in detail in ref 15, employs an electron−water pseudopotential in conjunction with a polarizable water model and thereby includes many-body electron−water polarization. This model reproduces numerous ab initio benchmarks in $(H_2O)_n^-$ clusters ($n = 2-33$) and provides a vertical electron binding energy (VEBE) for bulk $e^-(aq)$ that is in far better agreement with experiment than previous (nonpolarizable) models, as a result of a large (~1.4 eV) dipole relaxation energy upon vertical electron detachment.

We calculated the absorption spectrum from this model in several different ways, and the results are shown in Figure 2. In principle, one should calculate the dipole relaxation energy by converging the H_2O dipoles self-consistently with the excited-state e^- wave functions, but this proved to be difficult because the relaxation energy is large compared to the energy-level splittings. Complete neglect of dipole relaxation (by freezing the H_2O dipole moments at their ground-state values) afforded the "unrelaxed" spectrum in Figure 2a, which is qualitatively incorrect but quite similar to results obtained using the most recent nonpolarizable one-electron model.[13] This spectrum consists of a low-energy Gaussian part arising from the s → p excitations along with a higher-energy feature (>3 eV) consisting of bound → continuum excitations. In between these features is a conspicuous intensity gap that is not seen experimentally.

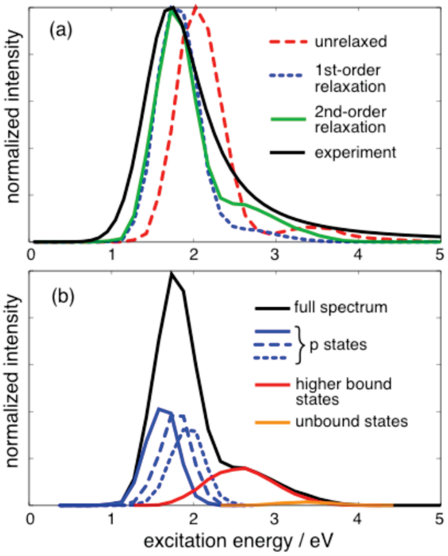

Figure 2. (a) Absorption spectra for $e^-(aq)$ computed from a polarizable one-electron model using various approximations for the dipole relaxation energy. (b) Spectrum computed using second-order relaxation and its decomposition into contributions from various excited states.

To go beyond this crude approximation, and thereby include the polarization response of the solvent upon excitation of the e^- wave function, we estimated the dipole relaxation energy using perturbation theory. We took the perturbation to be

$$\hat{W} = \hat{H}[\{\mu_{ex}\}] - \hat{H}[\{\mu_{gs}\}]$$

where $\hat{H}[\{\mu_{gs}\}]$ represents the one-electron Hamiltonian determined using dipoles $\{\mu_{gs}\}$ converged self-consistently with the ground-state wave function, whereas the dipoles $\{\mu_{ex}\}$ are converged to the excited-state eigenfunctions of $\hat{H}[\{\mu_{gs}\}]$. We did not allow the ground state to mix with the perturbed wave functions, so all of the latter are orthogonal to the ground state, even if they are not quite orthogonal to one another because of the state-specific nature of the perturbation.

The first-order correction for $\hat{W}$ brings the peak absorption intensity into nearly perfect agreement with experiment, as shown in Figure 2a. However, the line shape changed only slightly, because first-order perturbation theory alters the line shape only via the excited-state energies, E_n, that appear in the expression for the oscillator strength $f_{0\to n}$:

$$f_{0\to n} = \frac{2m_e}{3\hbar^2}(E_n - E_0)|\langle\psi_0|\hat{\mu}|\psi_n\rangle|^2$$

Second-order perturbation theory is required in order to obtain a correction to the transition dipoles, and this correction results in a qualitative change in the distribution of oscillator strengths, leading to significant intensity in the blue tail and far better agreement with the experimental line shape. To the best of our knowledge, no other model affords a blue tail with significant oscillator strength.

According to this model, polarization of the water molecules has the effect of binding >20 excited states that were unbound in

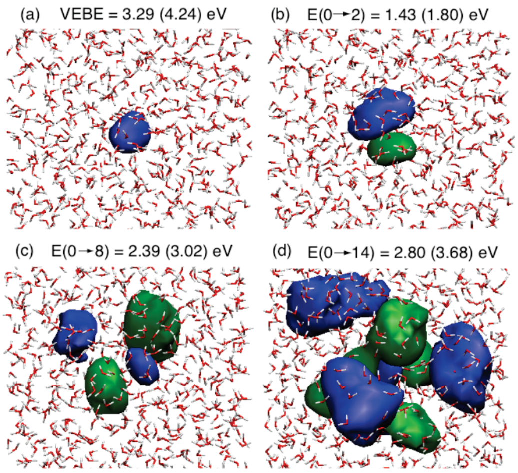

Figure 3. Typical examples of (a) the ground-state wavefunction and (b−d) excited-state wave functions obtained from the one-electron model. The VEBE and excitation energies are shown as well, with unrelaxed values given in parentheses. These isosurfaces encapsulate 90% of the total probability density.

the absence of relaxation, and these states comprise the blue tail seen in Figure 2b. These higher-energy bound-state wave functions are quite diffuse, with radii of gyration >10 Å in some cases (as compared with 4.0−4.5 Å for the p states), and thus, the excited-state electron penetrates well beyond the cavity occupied by the ground-state electron. Examples of these wave functions are depicted in Figure 3.

In the one-electron simulations, the p-state manifold extends no higher than ∼2.5 eV, whereas unbound excitations appear at 3.0−3.5 eV. In the narrow window in between, the excited states must evolve from compact, hydrogenic wave functions (as in Figure 3b) into completely delocalized plane waves. Whereas the blue tail has previously been discussed exclusively in terms of bound → continuum excitations,[12,21] our results suggest that the gap between the p states and the continuum is bridged by “quasi-continuum” states (as in Figure 3d) that are (vertically) bound but only via polarization of numerous water molecules that interact with these highly delocalized electronic wave functions.

In summary, we have calculated the absorption spectrum of e$^-$(aq) using two completely different methodologies: (1) a many-electron method in which the water molecules possess explicit molecular orbitals that may contribute to the e$^-$ wave function and (2) a one-electron model where this is not possible but where the H_2O molecules possess inducible dipoles that respond to excitation of the e$^-$ wave function. Qualitatively, both calculations support the same physical picture: the “blue tail” in the electronic absorption of e$^-$(aq) arises from *bound-state* excitations into delocalized excited states that are stabilized by polarization of water molecules beyond the first solvation shell. Solvent polarization facilitates intensity borrowing from the p states, and while this effect is small, the substantial number of these polarization-bound quasi-continuum states affords significant intensity in the blue tail.

It is interesting to speculate whether the disjoint nature of the e$^-$ lobes in higher excited states (e.g., Figure 3d) could facilitate excited-state electron “hopping” and thereby explain excited-state e$^-$(aq) migration[21] without invoking conduction-band states, as is usually done. Such a hopping process might play a role in dissociative electron attachment of the prehydrated electron by biomolecules and thus warrants further investigation.

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Supporting Information Available: Additional computational details and complete ref 3 (as SI ref 1). This material is available free of charge via the Internet at http://pubs.acs.org.

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