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Charge-Transfer-to-Solvent Spectra of an Aqueous Halide Revisited via Computer Simulation

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Abstract: The charge-transfer-to-solvent (CTTS) spectrum of an aqueous halide ion is examined via a fully molecular, quantum molecular dynamics, approach applied to a model of iodide. The properties of the solute ground and excited electronic states are analyzed with respect to their energies and approximate symmetries. The CTTS spectra are found to have a complex structure with several unresolved subbands, with an overall line shape resulting from the separate response of each subband to the field exerted by the solvent surrounding the ionic cavity. We find that each of the first few electronic states are under significant influence of the field created by the atomic halogen atom as well as both the attractive and repulsive forces due to the solvent. Hence, earlier models neglecting any of these influences do not fully describe the electronic energetics or the angular distributions characterizing the excited states. Implications for the states accessed via multiphoton excitation are noted.

I. Introduction

While there are no bound excited states for many negative ions, such as halide ions, in the gas phase, it was found over 60 years ago that such ions can have stable excited states in solutions of polar solvents, as indicated by strong, broad absorption spectra in the UV region.[1] This type of spectrum, requiring for its existence the presence of the solvent supported excited states, is known as a charge-transfer-to-solvent (CTTS) spectrum. It is also found experimentally that solvated electrons can be created following such a UV absorption, apparently a result of ionization from such an excited state, although the quantum yield depends strongly on both the solute species and the exciting wavelength.[1,2] Due to the fundamental role played by the solvent in supporting these electronic bound states, the spectra can provide information about the local solvent structure around the ion. For a general review, readers are referred to ref 1.

The purpose of the present paper is to address the excited state electronic structure underlying the CTTS spectra of halide ions in water, with specific focus on the particular, but representative, case of aqueous iodide. We focus here on the characterization of the excited states in terms of both energetic and spatial distributions. The specific effects of electronic interaction with both solvent and atomic parent cores on these aspects are of special interest. In order to put the following discussion in perspective, we first very briefly describe the experimental and theoretical histories of these CTTS spectra. We then turn to the details of the present work.

The experimental absorption spectrum of a solvated iodide ion shows an otherwise featureless well-resolved doublet at the lowest energies for which absorption occurs. The energy of the absorption maximum for the lower of these two bands, $E_{\max}$, reflects the energy difference between the ground state and the first excited state of the aqueous ion and shows high solvent sensitivity. $E_{\max}$ varies from 4.5 to 6 eV with solvent, and mildly red-shifts (of the order of 10^{-3} eV/per deg K) with increasing temperature. Most experimental studies have focussed on these lowest absorption bands, since higher absorption bands are located in the far-UV region where solvent absorption presents experimental difficulties. By considering solvent spectra explicitly, Fox and Hayon[3] were able to observe the spectra of the higher energy region. A lognormal fitting technique was used in an attempt to resolve the observed spectra. Although the determination was ambiguous due to strong band overlap, their results suggested that each peak could be resolved into several subbands, with each displaying distinct variation with solvent polarity. This analysis suggests the existence of a complex spectral structure.

Existing theoretical models for CTTS spectra are also more than 30 years old, and are therefore necessarily relatively crude. They were built on the basis of the redistribution of an electron over the adjacent solvent molecules upon photoexcitation of the ion. Several mean field theoretical models, most notably the so-called diffuse model[1,4,5] and the confined model[1,6,7] were proposed to aid in understanding the factors affecting CTTS absorption bands. Several thermodynamic cycles were adopted to calculate band maxima. However, a key step involved in the implementation of these models is the introduction of a very simple quantum mechanical model for the excited electron.

The confined model was introduced on phenomenological grounds and emphasizes the short-ranged repulsive interactions (due to the Pauli exclusion principle) between the excited electron and the solvent surroundings. The excited electron is described by states of the particle-in-a-sphere model, although it was recognized[7] that such a description could only be relevant to the outer part of the electronic distribution. Similarity of the spectra measured in solution to those obtained in ionic crystals provided support for the use of the model for interpretation of the data.[7] The diffuse model[4,5] is based on a continuum description of the polarization of the solvent media by the ionic charge of the ion and emphasizes the long-ranged interaction of the electron with the solvent reaction field. The resulting excited electronic states are thus bound and hydrogenic.

In both approaches, for simplicity, the excited states were presumed to be supported solely by the solvent field, while the ground state was taken to be supported by the field of the parent atomic core. The cavity radii[1,4,6,7] play a critically important role in these models, and the dependence of $E_{\max}$ on environmental factors, such as temperature and solvent, is mainly accounted for by the dependence of these size parameters on such factors. However, since the radii cannot be determined a priori, these

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early models cannot be considered first principles in nature. The ability to address spectral line shape is also necessarily limited in these earlier models. In both models, only a single excited state is associated with the lowest energy absorbtion band, so that contributions of spectral subbands to the observed spectra are excluded. Further, the contribution of inhomogeneous broadening to the absorption band shapes, originating from solvent fluctuations, are beyond the reach of these early efforts.

Although it is not the focus of the present report, it is also clear that such theories are not readily extendable to the description of the dynamical aspects associated with the ionic excited states. A more sophisticated theory is also required for such generalizations.

In this paper, we discuss the equilibrium steady state CTTS spectra from a completely microscopic point of view using the methods of quantum mechanical molecular simulation. In particular, we focus on an understanding of the nature of the electronic states of a solvated ion and their variation with solvent environment, along with an analysis of the conseqeunces for the CTTS band shape. At the same time, we examine the validity of the simplifying assumptions made in the early models outlined above. We focus our model development and discussion on the system of aqueous iodide, although the results are fully expected to generalize to related solutes.[1]

In the next section, we describe our model and the calculational methods used to sample the configurations needed to analyze the aqueous halide electronic states and the low-lying bands of the CTTS spectra. To avoid the complexities of the many-electron problem, we introduce a simplified one-electron modified Heine–Abarenkov (or Shaw)[8] pseudopotential to model the interaction between an electron and a halogen atom. In section III, the electronic structure and its response to the solvent environment are discussed, forming the foundation for understanding the CTTS spectrum. The features of the calculated spectrum are presented in section IV, along with a discussion of the significance of these results, and a comparison with experimental results where possible. In the last section, the conclusions are given.

II. Model and Methods

A semiclassical molecular dynamics simulation method is adopted for calculating the electronic properties and the absorption spectra of a halide ion. There are basically three components in the system setup and calculation, namely, the prescription of the assembly of an appropriate molecular system, specification of the intermolecular, or interparticle, interaction, and the mechanism for sampling over the appropriate system configurations. The description of each element follows.

The simulated system includes 500 rigid SPC water molecules[9] and one halide ion in a cubic cell of side length 24.66 Å under periodic boundary conditions. The halide ion is modeled by one electron and one halogen atom. While the electron is described quantum mechanically, the water molecules and one halogen atom are described classically in the sense that Newtonian dynamics are applicable to these particles.

The interactions between the elements in the system have several components. Several years ago, Schnitker and Rossky[10] developed a pseudopotential to describe the interaction between water molecules and an electron, and we adopt this for the interaction of the solute electron and the solvent. Other similar forms of an electron–water pseudopotential have also been proposed.[11,12] The pseudopotential used here consists of three parts: electrostatic terms between the electron and the solvent, represented through the atomic partial charges of the SPC water molecules, a molecular polarization term, providing for the induced interaction of the electron on the solvent, represented via a semiempirical expression taken from electron–molecule scattering calculations, and finally a set of repulsive terms which reflect the electron–molecule wave function orthogonality constraints that would arise in a full quantum mechanical description of the solution electronic structure. It is the last term which puts the interaction into the class of pseudopotentials. A complete description of this pseudopotential can be found in the literature.[10]

The halide was modeled via a simple pseudopotential which is a modification of the Heine–Abarenkov (HA) or Shaw[8] form used for neutral atoms. An HA pseudopotential has been applied to the problem of the aqueous ferrous–ferric electron-transfer process.[13] It is a one-electron model with the electron interacting with the residual charge distribution of the halogen atom in the following form:

$$V_{1\text{–}e^-}(r) = \begin{cases} V_{\mathrm{HA}}(R) & r < R \\ V_{\mathrm{HA}}(r) & r \geq R \end{cases} \tag{1}$$

where R is the single adjustable parameter, to be fixed below.

This form is not arbitrary. In pseudopotential theory,[14] the constraint of orthogonality between valence orbitals and core orbitals is replaced by an additional potential V_p in the interaction. The cancellation theorem[14] states that, to a good approximation, there is considerable cancellation between the typically positive potential V_p and the negative net electrostatic interaction of valence electrons with the core electrons and nucleus at short range. This is the physical basis for assuming a constant potential in the inner region $r < R$.

$V_{\mathrm{HA}}(r)$ is the pseudopotential for the interaction between the halogen core and the electron in the outer range beyond R. Its explicit form is taken as

$$V_{\mathrm{HA}}(r) = -7e^2 \exp(-\mu r)\left[\frac{1}{r} + \frac{\mu}{10}\sum_{k=1}^{8} \frac{9-k}{(k+1)!}(\mu r)^k\right] \tag{2}$$

where e is the charge of an electron. This potential arises from the incomplete shielding of the nuclear charge by the core electrons and the seven other valence electrons. Only the wave functions of the seven valence electrons are considered explicitly in the derivation, and these wave functions are each described by a single Slater wave function with an exponent $\zeta = \mu/2$. The value of μ accounts for the screening of the nucleus by the core electrons.

In the present work, we minimize the number of adjustable parameters of the potential and do not attempt to optimize the quantitative agreement of the calculated results with experiment. Hence, taking iodide as the halide, we use for the parameter μ a textbook value $2.9/a_0$ au[15] (a_0 is the Bohr radius). The potential for the valence electron in eq 2 is then simply obtained by summing electrostatic interactions from two sources: the effective charge of the core (the nucleus and the core electrons) and the integrated charge density of the seven valence electrons determined by the Slater wave functions. Note that for simplicity an isotropic field has been assumed in this modified HA pseudopotential.

With the explicit potential given in eqs 1 and 2, R is the only adjustable parameter in V_{HA}, and it is determined by a fit to the gas-phase electron affinity of the iodine atom (3.063 eV).[15] We find R to be equal to 1.447 Å. This value is physically reasonable in comparison to the standard iodide ionic radius of 2.16 Å.[16]

The interaction between water molecules and the iodine atom is taken to be of the Lennard–Jones (LJ) 6–12 type. The LJ ϵ and σ parameters are obtained by the relation of the polarization α_i of a compound with the dispersion energy ΔE_{dis}[15]

$$\Delta E_{\mathrm{dis}} = \frac{3}{4}\frac{E_{\mathrm{1P,i}}}{R_{\mathrm{ii}}{}^6}\alpha_{\mathrm{i}} = 4\epsilon_{\mathrm{ii}}\frac{\sigma_{\mathrm{ii}}{}^6}{R_{\mathrm{ii}}{}^6} \tag{3}$$

and by the combination rules[17]

$$\sigma_{\mathrm{ij}} = {}^1/_2[\sigma_{\mathrm{ii}} + \sigma_{\mathrm{jj}}] \tag{4a}$$

$$\epsilon_{\mathrm{ij}} = [\epsilon_{\mathrm{ii}}\epsilon_{\mathrm{jj}}]^{1/2} \tag{4b}$$

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from the LJ parameters for the model water–water interaction and for water–iodide interaction.[18] Here $E_{IP,i}$ and R_{ii} are the ionization energy of compound i and the interparticle distance, respectively. The polarizability of an iodine is 6.31 Å^3, while that of an iodide is 11.0 Å^3, which is extrapolated from the data of iodine in its various oxidized states.[19] With this route, we obtain σ_{IW} = 3.5803 Å and ϵ_{IW} = 1.09673 KJ/mol, which is referred to hereafter as Model 1. Note that only the interaction between the solvent oxygen center and the iodine is considered explicitly for each water–iodine pair LJ interaction.

As noted above, in the present work, we do not attempt to explore the parameter space of the model interactions used here. However, to establish the effects of this solvent–ion interaction on the electronic structure and CTTS spectra, another set of LJ parameters will also be considered. The set of values σ_{IW} = 3.995 Å and ϵ_{IW} = 1.850 constitute Model 2. Note that the repulsive force for Model 1 starts at a smaller distance than that of Model 2, although the attractive well for Model 1 is somewhat shallower. This fact will be seen below to have a consequence for the overall appearance of the calculated spectra, although not on the physics of the electronic states. For convenience, we have concentrated on the results of Model 1 in the work presented below. It will be indicated explicitly when the results of Model 2 are addressed.

The initial configuration of water molecules for quantum molecular dynamics is taken from a configuration equilibrated with standard classical molecular dynamics at a temperature of 298 K for a standard charged LJ model of the iodide ion.[18] The interaction between the iodide ion and water molecules in this model is taken as $\sigma_{I\text{-}W}$ = 4.41 Å and $\epsilon_{I\text{-}W}$ = 0.2282355 kJ/mol.[18] After equilibration, the classical ion was replaced by the one-electron model for the ion. The electron wave function is represented on a grid of 32^3 points (grid spacing 0.7706 Å).

We note that in the present model we do not consider many-body polarization effects in the interactions[11,20] but rather retain a standard effective pair potential model. In studies of the hydrated electron, quantitative effects on spectra are apparently seen,[11] but no differences in the underlying physical description are observed. Considering the extra computational complexity of polarizable models and the very simple form assumed for the anion electronic structure, such an enhancement in the model does not appear justified for the present study. Further, in the present work, all potentials are calculated by using a spherical truncation distance of 8 Å. Hence, the full long-ranged solvent polarization that is included by the continuum treatment of the diffuse model[4,5] is not included here (nor would it be by any available treatment of a finite solution sample). Nevertheless, in corresponding simulation studies of solvated electrons in water[21] and in ammonia,[22] spectra computed by using comparable truncation procedures are qualitatively consistent with experiment.

For a given solvent and iodine atom configuration, providing a specified potential for the electron, the electronic states of the model ion can be determined. The Hamiltonian for the electron was diagonalized via a block Lanczos procedure to accurately obtain the eigenenergies and the corresponding wave functions for the lowest 15 states. The detailed algorithm has been published recently, and interested readers are referred to the literature.[23]

To discuss the algorithm for generating our sample, it is convenient to first describe one element of the electronic state analysis. The nature of the electronic states will be usefully characterized in terms of spherical harmonics, since the potential, in the absence of solvent, is spherically symmetric. Correspondingly, deviations from pure angular momentum states are solvent-induced effects. A particularly convenient algorithm has been used for projection of the wave functions onto spherical harmonics with respect to the electronic center of mass. The detailed description of this method will be described in another publication. In outline form, a delta function and its Fourier expansion are introduced to avoid the complication of the transformation of the wavefunctions between Cartesian coordinates, used in the remainder of the calculation, and spherical coordinates. A total of 16 spherical harmonics (s, p, d, and f) are used in the present analysis.

We now turn to the quantum mechanical molecular dynamics sampling procedure. Here we are interested in equilibrium, so that we need to sample the system for the physical electronic ground state of the ion. Thus, the occupied electronic state for the one-electron model must be a p-like state. The HA model pseudopotential yields as bound states a 1s and three 2p states, where we use for convenience a hydrogenic nomenclature for the valence electron, due to the suppression of the remaining iodide electrons. No higher energy bound states are supported by the model potential, as required. The s and p states would accommodate the explicit valence electron and the remaining 7 valence electrons. Nevertheless, we consider explicitly only one valence electron; the remaining valence electrons are already treated implicitly by the HA pseudopotential presented above. For the present purpose of sampling equilibrium solvent configurations, we simply assign the lowest 2p-like state to be that initially occupied by the single explicit electron. We will refer to this state as the physical ground state (GS) in the MD simulation. Correspondingly, the 1s and the other two 2p states will be omitted from further consideration.

The dynamics of the electronic system is then described adiabatically, in the sense that the occupied state at each time is always chosen to be that which evolves continuously from that occupied at earlier time. Practically, the occupied state is chosen for each step as that with maximum overlap with the occupied state of the previous step. A time step of 2 fs was used. The details of the MD simulation are essentially similar to those described by Webster et al.[23] Given a solvent configuration and an iodine position, the block Lanczos algorithm is applied to obtain the lowest few electronic eigenstates and the corresponding wave functions. The new electronic state is then determined by identifying the state which has the maximum wave function overlap with the occupied state at the immediately previous time step. A new solvent configuration and a new iodine atomic position are then obtained by solving the Newtonian equations of motion for each atom, taking account of both the forces from the rest of the classical particles and the quantum force from the electron. The latter term is evaluated via the Hellmann–Feynman theorem. The process is repeated until the desired dynamical length is generated.

In order to reach equilibrium conditions, the system was initially run for 10.5 ps without collecting data. For about 2.9 ps of this period, water velocities were re-initialized according to the Maxwell distribution at 298.15 K. After turning off the velocity reinitialization, it was found that the kinetic energies, potential energies, and total energies of the electron and of the system were fairly stable, while the observed temperature of the classical particles, 317 ± 7 K, was slightly higher than the target temperature. The temperature within each shell of 4.5, 6.0, and 8.0 Å from the center of mass of the electron was verified to be equal within statistical error. Considering that the CTTS spectra are experimentally known to be rather insensitive to the temperature,[1] as noted above, the temperature consistency is completely adequate for the present purposes. The solution configurations for ensemble averaging were collected from running the MD simulation for another 4.8 ps, which requires about 15 Cray Y-MP cpu hours. Two hundred equally spaced configurations were retained from this run for the purpose of analysis.

As we have emphasized, no attempt has been made here to optimize the ion–electron and ion–solvent model parameters. The required multiple simulations of the type just described is a subject for future investigations. However, we note here some of the basic features of the simulated solution structure that support the utility of the halide model. From the simulations carried out for the classical model,[18] one finds the energy of solution from the gas phase to be 68 kcal/mol, in good agreement with the experimental value for the heat of solution[24] of 64 kcal/mol. The first peak in the ion–solvent oxygen pair correlation function occurs at about 3.6 Å. The comparison to the results for Model 1 indicates that the net effective ion–solvent potential corresponds to a halide ion that is somewhat smaller than iodide. The calculated energy of solution is found to be about 80 kcal/mol, closer to the experimental result for bromide[24] of 78 kcal/mol. The radial distribution of solvent around the ion for Model 1 also suggests an ion closer to bromide, peaking at about 3.4 Å, or 0.2 Å shorter than expected for iodide, in accord with the difference in ionic radii between iodide and bromide.[16] Further results for the primary model, Model 1, consistent with the view that the model corresponds to an ion somewhat smaller than the iodide ion will be noted below. For Model 2, with a somewhat expanded atomic core, we find that the solvent distribution peaks at about 3.9 Å, or about 0.3 Å beyond that expected for iodide. Considering that the behavior of iodide and bromide in the present context

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Table I. Characteristics of Ionic Electronic States (Model 1)

states	total probability resolved (%, $l = 0$–3)	most probable symmetry (%)	radius of gyration (Å)	total probability within $r \leq 2$ Å
2p(GS)	~96	~90 (p)	1.56–1.62	0.83–0.85
2s/3d	~90	~45–80 (d) ~20–55 (s)	2.05–2.15 (d) 2.3–2.5 (s)	0.5–0.6
3p	~60–80	~40–65 (p)	4.0–4.6	0.05–0.15

is basically equivalent,[1] the noted quantitative deficiency does not compromise the usefulness of the present model for the purposes of this study. The results obtained from further study of excited states[25] have allowed rationalization of transient spectroscopic experiments on iodide,[26] providing additional, if *a posteriori*, support for the approach as well.

III. Equilibrium Electronic Structure

Before discussing the spectrum, it is important to understand the equilibrium electronic structure. The energetically lowest 15 one-electron eigenstates were calculated from each of the instantaneous water configurations and considered in the analysis. Certain qualitative results are summarized in Table I, which we will discuss below.

While there are no bound excited states in the gas phase, we typically find nine bound excited states observed in aqueous solution in the calculation for either Model 1 or 2. We emphasize that these additional states necessarily correspond only to the low-lying one-electron excitations of the ion, due to the one-electron nature of our model. The spectra at higher energy[1,3] suggest that well-defined localized excited states may also exist corresponding to many electron excitations and excitations of lower energy electrons in the iodine atom. As indicated earlier, we also cannot rule out the possibility that the very longest ranged polarization forces could support localized hydrogenic states[4,5] at higher energy.

The excited states identified here are supported by attractive potentials from both the parent core and the solvent molecules, as we will expand on in later discussion. Since the overall potential is of underlying spherical symmetry, it is appropriate to discuss the nature of the electronic eigenstates in terms of spherical harmonics, as stated previously. Further, it is both convenient and completely adequate[27] to describe these states based only on the character of the one-electron eigenstate of the single electron which lies outside the ^{2}P iodine core, as will be discussed in more detail in the context of the electronic absorption spectra. Hence, in the discussion below, we denote the iodide electronic states via a description of only the characteristics of the single electron explicitly involved in the excitations considered here.

Based on the nomenclature introduced in section II, we find that the lowest ten bound states, in order of increasing eigenenergy, are the 2p-like ground state (GS), six 2s/3d-like states of mixed symmetry, and three predominantly 3p-like states. The 3d/2s states have a significant amount of both 3d and 2s character. As expected, it is found that the degeneracy of the p and the d states is lifted by the instantaneous, asymmetric, solvent field.[28]

Due to radial fluctuations and the local field anisotropy created by the water molecules, the eigenstates can be very heavily mixed in character. Characteristic properties of the wave functions are reported in Table I. Due to the broad distribution with solvent configuration of each quantity generated, the table reports representative values for each quantity. To see how well the nature of the states is characterized by the total of 16 spherical harmonics used, we report the range of the total probability resolved by such symmetry analysis in the second column of the table. The total will be larger if the potential the electron experiences is closer to spherical symmetry. From the second column of the table, it is evident that the total resolved decreases with increasing electronic energy, and that this, in turn, is correlated with an increase in the electronic radius of gyration (column 4 of the table). This indicates that the potential is increasingly anisotropic with increasing distance from the iodine, a result of the increasing role of the electron–solvent interaction. Nevertheless, even the highest energy states examined are dominated by low angular momenta; the excited p-type states are well characterized by $l = 1$.

An alternative view of the influence of the anisotropic field on each state is provided by the value of the probability associated with the most probable symmetry of each one-electron state. This is given in the third column of Table I. The lowest energy states have the most well-defined symmetry, since they reside mainly in the field of the iodine atom and are less influenced by the anisotropic field of the water molecules. In contrast, the 2s/3d-like states are characterized by a combination of s and d symmetry. A significant amount of s character (>20%) is usually distributed unevenly among three out of six possible states. Occasionally, unusually high s character (>50%) is found in just one of the highest energy states, with correspondingly little s character in the other five states. The specific character of each state is just a reflection of solvent environment experienced by these states. This point will be elaborated on more in the later discussion of Model 2.

The next three higher excited states are found to be higher iodide excited states of 3p-like character. Eigenstates corresponding to the ground state of an excess electron in a solvent void are found to occur in a comparable energy range, typically just above these p states. Occasionally, these can have an energy lower than these 3p-like states, and then the two sets interleave.

Since the one-electron ground state of iodide is p-like, the electronic excited states which will contribute strongly to the transition dipole moment matrix describing the CTTS spectra are those with the right (i.e., s or d) symmetry, with, additionally, a center of mass location corresponding to the iodine nucleus. Therefore, the contribution from these three p-like states to the CTTS spectra should be small. However, we note that the transition to these states is not forbidden, since they do have small components of s and d character. On the other hand, the 3p-like states should be the major contributors in a two-photon absorption experiment.[26]

As discussed above, different electronic states experience different degrees of solvent anisotropy. Therefore, the set of electronic states of a halide may be useful as a spectroscopic probe of the anisotropic fluctuations at varying distance from the ion. To examine the sensitivity of the electronic states to their solvent environment and to provide further basis for an understanding of the influence of solvent environment on the CTTS spectra, discussed below, a corresponding simulation has been done with Model 2.

The wave functions obtained with Model 2 are found to have a somewhat larger radial extent than the corresponding wave functions in Model 1. The reason is easily understood. The LJ repulsive force between a water molecule and an iodine in Model 2 starts at a larger distance (about 0.4 Å greater) than that of Model 1. Consequently, the adjacent solvent molecules are held farther from the ion. As noted earlier, the solvent distribution is characteristic of an ion about 0.3 Å larger in radius than iodide. This expanded solvent cavity reduces the strength of the repulsive field experienced by the electron, as well as weakening the attractive solvent field. A red-shift of the one-electron energies and an increase in radius of each state results. Although the character of the electronic excited states, described above, is unchanged, within the 2s/3d group, we find that for Model 2 the

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lower rather than higher states are found to possess the greater s character. The origin of this fact lies in the observation that the states of higher s character have larger radii of gyration (column 4 of Table I). Therefore, an s-like state is more exposed to the solvent influence than are the d-like states. This effect will be considered further as part of the interpretation of the calculated spectra.

A comparison of the present description of the electronic structure with that predicted by the early diffuse[1,4,5] and confined[1,6,7] models is in order. It is not our goal to criticize these much older models, but rather to establish the validity of the simplifying assumptions of these models and the future usefulness of such approaches.

In the present calculations for Model 1, the average radius of gyration for the GS is about 1.6 Å in aqueous solution, which is contracted from that of the gas-phase ion, 1.74 Å. (Note that these root-mean-square values should not be confused with ionic radii.) This contraction is attributed to the compression by the organized water attracted around the iodide. Based on the discussion of solvation at the end of section II, we concluded that the Model 1 ion was more similar in size to bromide than iodide in solution; hence, these electronic dimensions are evidently somewhat smaller (~0.2 Å) than those characterizing iodide. Nevertheless, the confined model and the diffuse model assume only a small perturbation to the ground state and neglect any contraction from solvent compression.[1,5]

As noted in the introduction, both the diffuse model and the confined model neglect any contribution of the parent atomic core potential to the electronic excited states, in addition to emphasizing different aspects of the solvent field. This is a more significant issue. As a simple but adequate basis for judging the expected effects of the halogen atom on the wave functions of the electron, it is useful to examine the total excited state electronic probability within an effective interaction range between the electron and the halogen atom. A physical value would be about the size of the halide. Here, we take the effective interaction range to be that value of the distance corresponding to a potential energy equal to 25% of the most negative value of the electron–halogen interaction potential. The precise definition of this cutoff point will not affect our conclusions. This distance turns out to be about 2 Å, consistent with physical expectations.

The value of the integrated probability inside this distance for each energy region is shown in column 5 of Table I. The first six excited states (2s/3d), which are expected to dominate the lowest energy portion of the absorption spectrum, have quite large contributions within this range (~55%). The next group of excited states (3p) also have significant probability in this region. These observations are consistent with the observation that these states, in fact, are fairly good angular momentum eigenstates. We note that the lowest energy (s/d) band of states does remain confined within the solvation shell of the ground state, in accord with the view of the confined model, while the p-type band mainfests significant solvent penetration. However, the strong interaction with the atomic halogen potential in both cases indicates that the neglect of the electron–atom interaction after photoexcitation in either the confined or diffuse models is not a good approximation.

We are led to conclude that the interactions relvant for these states cannot be described successfully with any of the extreme simplifications considered in earlier work.[1,4-7] As a consequence of the fact that these states interact strongly with the non-Coulombic field of the atomic core and with both the attractive and repulsive contributions of the solvent, one finds that the electronic structure discussed above, and, correspondingly, the absorption spectrum discussed further in the next section, does not correspond well to that derived from the earlier efforts, although features of both appear. While the atomic potential strongly influences the states identified, even for hydrogenic angular momentum states the degeneracy among them would necessarily be lifted and such states would be strongly mixed by the short-ranged solvent field. Correspondingly, for the particle-in-a-sphere states, strong perturbations of the d and s states (which that model correctly predicts are the lowest lying excited states above the first p level) would result from the core and solvent attractive terms and from the deviation from spherical symmetry.

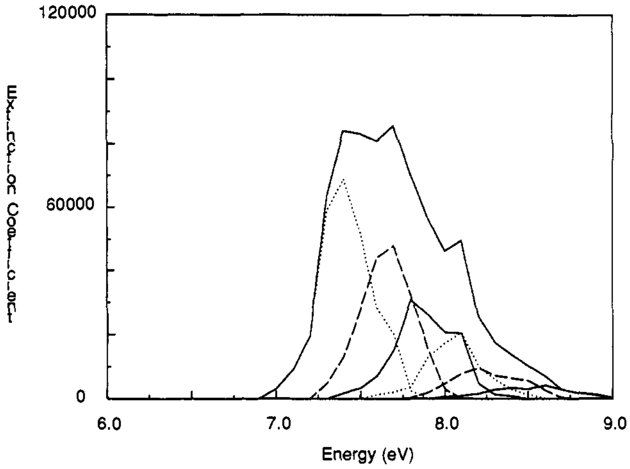

Figure 1. Ground state absorption spectrum of an aqueous iodide calculated via simulations based on Model 1 (see text). The solid line denotes the envelope corresponding to the full spectrum. Also shown are the subbands associated with the transitions to the six 2s/3d states.

IV. CTTS Spectra

With this background on the electronic structure, we are in a position to discuss the absorption spectrum of an aqueous halide. In this section, we consider our simulated spectra. In particular, motivated in part by the available analysis of experimental data,[1,3] we address whether a complex substructure underlies CTTS spectra. Further, if it does, how might each subband respond to solvent variation, and what will be the influence of such a response on the line shape?

The absorption spectra here are evaluated directly from calculated transition dipole moment matrix elements in the Frank–Condon approximation. For each nuclear configuration, we accumulate the contribution of transition dipole matrix elements between the GS and 36 higher excited states. After considering the 200 nuclear configurations in our sample, 7200 transition lines were included in the spectral calculation. The final oscillator strength is calculated considering the existence of six equivalent p electrons in an iodide ion.[5]

The calculated spectrum from Model 1 is considered first and is shown in Figure 1. In general accord with experimental expectations, we observe a strong and broad one-photon absorption in the UV region. The calculated absorption peak is located around 7.6 eV with an asymmetrical tail to the high-energy side. Also detailed in the figure is the contribution of those six excited states with 2s/3d symmetry; these account for 97.5% of the absorption intensity. The contribution from the 30 higher states to the one-electron absorption spectrum is thus negligible. These results agree with the expected transition from a p-like ground state to s/d-like excited states via the dipole interaction. This complex spectrum is in contrast to simple spectra anticipated based on earlier models.[1]

Each subband is inhomogeneously broadened by the time varying local solvent field each state experiences. It is observed that the subband line shape is broader for states with more s character, since, as noted above, an s-like state tends to have a larger radius of gyration (by about 10%; see Table I). The full line width for Model 1 is about 0.8 eV (fwhm), somewhat larger than the experimentally observed value for iodide of about 0.6

eV. However, of most importance, this width is not accounted for by inhomogeneous broadening alone; each component is individually broadened by only roughly half this value, with the remainder of the width due to the multiple underlying states. This behavior is in close correspondence to that observed for the solvated electron.[21] That this observation is not sensitive to the ionic model is demonstrated by the results derived for Model 2, discussed below.

Since the influence of spin is not included in the calculation, the spectrum has only one peak, instead of the two observed in experiment. Thus, some manipulations need to be done before the comparison of the calculated spectrum with the experimental one can be made. The physical source for the two peaks in the spectrum is explained by ***j,l*** coupling, which was applied to the interpretation of the spectra of heavy metals and inert gases successfully long ago.[29] For the present purposes, we give only a brief, and somewhat simplified,[30] account of the coupling here. After photoexcitation, the configuration of an iodide consists of a hole in the iodine core and one electron in an outer shell. In this case, the magnetic interactions between spin and orbital angular momentum are weak for the outer electron and strong in the core (compared with the electrostatic interactions). The total angular momentum of the core yields the $^2P_{1/2}$ and $^2P_{3/2}$ states. The energy difference between these two states accounts well for the spacing between the two well-separated peaks in the experimental spectra.[1] The resultant $\boldsymbol{j}$ of the electronic core is then coupled with the $\boldsymbol{l}$ of the electron to form a final angular momentum $\boldsymbol{k} = \boldsymbol{j} + \boldsymbol{l}$, which, along with the selection rule discussed below, accounts for the fine structure within each absorption band. A selection rule for $\boldsymbol{J}$ is valid, namely,

$$\Delta \boldsymbol{J} = 0, \pm 1; \ \Delta \boldsymbol{J} \text{ not } 0 \text{ for } \boldsymbol{J} = 0$$

$$\Delta m_J = 0, \pm 1 \tag{5}$$

Since the statistical weight $2\boldsymbol{J} + 1$ is the same in either core state, each band has equal intensity, which was pointed out by Jortner et al.[31] This accounts for the near equality of the intensities of the two bands in the CTTS spectrum for an iodide ion in an aqueous solution.[1,3,31] The apparent larger extinction coefficient of the higher energy band for the ion in other solvents[3] may be attributed to the overlap of this absorption with others, such as those originating from core or many-electron excitations. As already noted, such other transitions are beyond the scope of the model used here.

With this background, we can locate the experimental peak position of the CTTS spectra that would be found if there were no spin–orbit coupling. From the atomic configuration of the parent core and the theorem of the center of gravity of a term for spin–orbit interaction,[30] one finds that, with respect to the absorption peak with spin–orbit coupling absent, the ratio of the peak position of the higher energy band to that of the lower energy band will be about 1:2. Experimentally,[3] the two peaks for iodide are located at 44 170 and 51 105 cm^{-1}, respectively. Therefore, in the absence of spin–orbit coupling, the spectrum should peak at about 6.05 eV.

For Model 1, we find a calculated peak position of about 7.6 eV. A significant positive deviation of the peak position from experiment that is found here is seen also in calculated spectra of solvated electrons in water[21,22] and in ammonia.[32] This difference is expected to be a reflection of the simplifications in the interaction potentials necessitated by the realities of computational resources. Nevertheless, in the case of solvated electrons, all models considered have produced the same physical description of the electronic states. In the present case, plausible molecular models lead to a spectrum in qualitative agreement with experiment (see also below). Hence, in this case as well, we believe the essence of the physics is captured in our models.

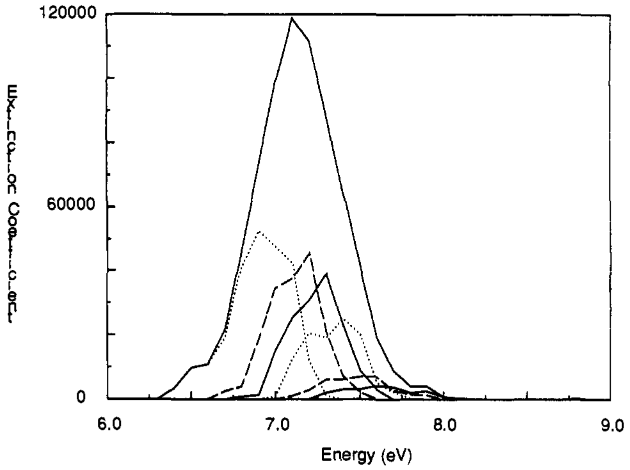

Figure 2. Ground state absorption spectrum of an aqueous iodide calculated via simulations based on Model 2 (see text); otherwise, as in Figure 1.

Further elucidation of the role of the solvent field in the spectral results and insight into the response of spectra to solvent variation can be developed on the basis of the results for an alternative model. In Figure 2, we show the spectra obtained for Model 2. Since the water molecules adjacent to the ion are now further away from the iodine, the absorption maximum is red-shifted by about 0.5 eV, a direction that would be expected on the basis of earlier discussion. The agreement with the experimental value is considerably improved, although there is still a substantial positive deviation. The absorption band again consists mainly of the six absorption subbands from 2s/3d states, although the absorption spectrum now assumes a fairly symmetrical shape with a line width of about 0.6 eV, in close agreement with experiment.[1]

A closer look at the absorption to 2s/3d excited states shows that although the line shapes for the two models are similar to each other, the energy gap between any pair of adjacent peaks for the GS-2s/3d transitions in Model 2 is smaller than that of Model 1. This indicates that the relative influence of the solvent potential is a major reason for the degree of asymmetry in the line shape. In addition, a longer high-energy tail is observed in Model 1, arising from the mainly s-like character of the highest states in the 2s/3d region. There is no such tail in Model 2 where we have already noted that the greater s character is shifted to the lower energy region of this band. In terms of spectral line shape, Model 2 appears more realistic, although we emphasize that the physical description of the states that would be obtained for either of the two models is essentially the same.

From the spectra generated from these two models, we conclude that the principal, lowest lying, excitation in the CTTS spectrum is complex, resulting mainly from the states of mixed s and d symmetry. Moreover, the different sensitivity of the calculated subbands to variation in solvent influence can lead to both spectral shifts and line shape variation, with a less symmetrical line shape in the case of stronger solvent perturbation. This is in accord with conclusions drawn from experimental spectral analysis of iodide in different solvents,[3] although our results suggest that the decomposition of spectral contributions in such earlier work is not physically correct in detail. From the consideration of our two spectra obtained above, we conclude that the experimental observation of a nearly symmetrical CTTS line shape for iodide in water is accidental and that the behavior in other solvents[3] is

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(31) Jortner, J.; Raz, B.; Stein, G. *Trans. Faraday Soc.* **1960**, *56*, 1273.

(32) Sprik, M.; Impey, R. W.; Klein, M. L. *J. Chem. Phys.* **1987**, *83*, 5802.

(33) Motakabbir, K. A.; Schnitker, J.; Rossky, P. J. *J. Chem. Phys.* **1989**, *90*, 6916.

a reflection of the more clear manifestation of the substructure in nonaqueous solvents.

Finally, we note that the experimental result[3] for the total oscillator strength is about 1.1. In comparison, the total oscillator strength calculated from Model 1 is about twice as high, 2.56. For the simplified one-electron model with one strongly allowed band, we would expect to get nearly the maximum physically allowed absorption strength, 2.0. Our value exceeds this due to the contribution of emission to the unphysical 1s state lying below the ground state, with oscillator strength about 0.65. Considering the simplicity of the model Hamiltonian, we consider the magnitude of the calculated result satisfactory.

V. Conclusion

We have presented the results of a fully molecular description of the electronic states and the CTTS spectrum of an aqueous halide ion, comparable to iodide or bromide. The method of adiabatic quantum molecular dynamics was used to sample the equilibrium solution configurations, from which the electronic states of the aqueous ion were analyzed and the absorption spectrum calculated.

For the model used, we identify nine low-lying bound excited states that are absent in the gas phase, associated with one-electron excitations of the ion. These are comprised of the ^2P iodine core coupled to, first, a group of six excited one-electron states of predominantly mixed s and d symmetry and, second, a group of three excited one-electron states of predominantly p symmetry. The first group can account for the lowest energy intense one-photon UV absorption of the ion in solution, with that substructure experimentally unresolved.

The role of the parent atomic core in determining these states was examined and determined to be a crucial aspect. The s/d states are found to remain primarily within the first solvation layer of the ground state ion, while the states of the higher energy band manifest significant solvent penetration. Hence, we conclude that much simpler descriptions which do not simultaneously account for interaction with the atomic core and with both the attractive and repulsive components of the solvent field do not provide a sufficient basis for interpretation of the experimental observations.

The calculated electronic states of the aqueous halide were found to have distinct sensitivities to the solvent environment, with comparable contributions to the line shape due to inhomogeneous broadening of the individual states and to the energetic splitting within each band, in parallel with earlier results for the hydrated electron.[21] The solvent sensitivity was found to be sensibly correlated with the electronic radius of gyration. One result is that the spectral line shape associated with the envelope of the subband contributions is expected to vary with solvent, as might be inferred from earlier spectral analysis.[3]

Experimental verification of the results on subband structure may be obtainable, in principle, via photophysical holeburning experiments. Further, due to subband overlap, such experiments would be most likely to resolve the effect on the red side of the peak. However, by analogy to simulated results for the hydrated electron,[33] one would anticipate that a time resolution of at least 100 fs would be necessary to observe this clearly, and such an experiment requires such measurements be carried out in the UV.

Although we have focused in this study on the electronic structure and CTTS spectra of aqueous iodide, we expect that these principles are applicable to other ions and other solvents, as they do not originate in features of the system that are unique to iodide or even to halides.[1]

This study has provided us with the tools for the investigation of the, more complicated, dynamical problem of photodetachment. Ultrafast transient spectroscopic results for the specific system studied here have been reported by Long et al.[26] These results manifest a stepwise process, suggesting some complexity in the electronic dynamics. On the basis of the present results, one can already surmise that for the multiphoton photoexcitation in the cited experiments, the most probable initial state should be one lying above the CTTS (2s/3d) band. Results devoted to analysis of the excitation and detachment dynamics in this system will be presented elsewhere.[25]

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