In view of the theoretical prediction for configuration A, the three levels identified are ascribed to T_{2u} , E_u , and T_{1u} in order of increasing energy. The location of the fourth level, A_{2u} , can not be determined from this experiment since the existence of a weakly emitting sublevel above the strongly emitting sublevel hardly affects the lifetime.

We are thus able to locate the three lowest triplet sublevels. The splitting between the lowest two levels is due to the secondorder spin-orbit coupling. The energy gap between the second and the third levels exactly corresponds to the atomic spin-orbit coupling parameter, ζ_d . We thus conclude that ζ_d in the cluster is $\sim 610 \text{ cm}^{-1}$.

Once the levels are assigned as above, the temperature dependence of the spectral distribution discussed in the Introduction may well be understood. The final energy level scheme shown in Figure 5 predicts that the 300 K spectrum shifts from the 4.2 K spectrum by \sim 700 cm⁻¹ in the 0–0 band. If the emission from the lowest sublevel is induced only vibronically, shift is expected to be a little larger in agreement with the observation.

Concluding Remarks

As far as we are aware, this is the first attempt to theoretically interpret the phosphorescence properties of the Mo cluster in terms of the spin-orbit split triplet sublevels. The present theoretical model is based on the basic assumption that the electron-repulsion energy is much greater than the spin-orbit coupling. We believe that this assumption is rather reasonable as long as we focus attention on lower sublevels. However, if we are interested in much higher energy levels, violation of this assumption would become crucial and the theory should have to be improved a lot. As an example, it is tempting to analyze the nature of the strongly emitting level which was proposed to exist $\sim 3000 \text{ cm}^{-1}$ above the lowest energy level by Zietlow et al.9 However, such an analysis is certainly out of the scope of the present model.

Finally, our main conclusions are summarized: (1) The space part of the lowest triplet state is ${}^{3}T_{1u}$ that is originated from the excitation of an electron from the $t_{2g}(\xi\eta)$ occupied orbital to the $t_{1u}(\theta)$ vacant orbital. (2) The spin sublevels associated with the lowest triplet states are T_{2u} , E_u , T_{1u} , and A_{1u} in order of increasing energy. (3) The third sublevel T_{1u} is the most emitting, and the temperature dependence of the population of this level largely accounts for the observed temperature dependence of the phosphorescence lifetime as well as the spectral distribution. (4) The spin-orbit coupling parameter for the molybdenum d orbital is determined to be $\sim 610 \text{ cm}^{-1}$.

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Behavior of the Hydrated Electron at Different Temperatures: Structure and Absorption Spectrum

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The properties of a solvated electron have been investigated at 300 and 373 K by use of path integral Monte Carlo methods with a refined pseudopotential, both with and without many-body polarization terms. The solvated electron at both temperatures is shown to reside in a solvent cavity. The water molecules surrounding the electron point one of their hydrogen bonds in toward the electron. The localization of the electron is enhanced by the many-body polarization term over pair polarization. The inhomogeneous optical absorption spectrum of the electron is calculated by solving the Schrödinger equation, using a fast Fourier transform technique in imaginary time, for a distribution of water configurations generated by the path integral Monte Carlo. The eigenfunctions and eigenvalues are used to calculate the optical spectrum. This is the first path integral Monte Carlo study that has correctly determined the position of the absorption maximum at 300 K. Unfortunately the simulated absorption maximum does not exhibit the observed red shift with temperature. In addition the simulated spectra do not exhibit the large high-energy wing that is observed experimentally.

1. Introduction

The various spectroscopic, 1-6 kinetic, 7-11 and thermodynamic12-15 properties of the solvated electron have been intensively studied.¹⁻¹⁵

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Investigations of the hydrated electron in different solvent states have been performed: electrons in ice and ice solutions,¹⁶ in liquid water at room temperature, 17,18 and in various electron detachment processes in organic molecules.¹⁹⁻²¹

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The process of localizing or solvating an injected electron in aqueous media seems to follow the path^{9,10}

$$e_{qf} \rightarrow e_{loc} \rightarrow e_{eq}$$
 (1.1)

where e_{qf}^{-} denotes a quasi-free extended state; e_{loc}^{-} denotes a localized, not necessarily equilibrated, state; and e_{eq}^{-} denotes a localized equilibrated state. The first step is fast with a decay time of less than 10⁻¹² s,¹¹ whereas the second step apparently involves restructuring of the surrounding liquid and takes a few picoseconds at room temperature. The time dependence of the electron absorption spectra in various solvents has been widely documented.^{4-6,11} There has been much speculation on the nature of the first state, $e_{qf}^{-3-6,22}$ One notion is that the electron forms a geminate ion pair with a hydrogen atom in the fluid and stays localized for some period of time after which it either combines with an atom or forms a localized equilibrated system by rearranging the solvent. Another possibility is that the electron is trapped in shallow potential minima in the fluid and can freely hop between these minima on a short time scale before it localizes as an e_{eq} with a concomitant rearrangement of the solvent. The existence of these local traps can partly explain the relaxation kinetics of a pulse radiolysis generated electron in aqueous solutions

It has been proposed¹⁹⁻²¹ that a cluster of four water molecules with an electron delocalized over the entire cluster may be the preferred geometry of these shallow traps. In contrast Haberland²³⁻²⁶ has found in molecular beam experiments that tetramers with attached electrons are relatively unstable. Another interesting idea is that these local traps are preexisting holes in the fluid.²⁷ Especially in liquid water these local holes, once formed, would be able to exist for quite some time due to the persistence of the hydrogen-bonded network around them.

Our study is concerned with the equilibrium structure of the solvated electron, e_{eq} . The final state of the localization process can be studied and described in detail by using equilibrium path integral techniques. In fact the equilibrium behavior of excess electrons in water has recently been the subject of several theoretical studies by Jonah et al.,²⁸ Sprik et al.,²⁹ Rossky et al.,^{27,30-32} and Wallqvist et al.,³³ in which the quantum nature of the electron is treated by using discrete path integral methods. These calculations are based on a pseudopotential for the electron-water interaction combined with path integral Monte Carlo techniques to sample the electron configurations. Our calculation is the first one to take into account many-body effects in the polarization of the electron-water interaction. As shown below this is important to correctly reproduce the electron absorption band maximum. For details of the models, the simulation techniques used, etc., the reader is referred to the original articles.

The shape of the equilibrium solvated electron absorption spectrum is well-known to be a structureless asymmetric band with a blue tail. It has been measured in different solvents and at different temperatures and pressures.^{17,18} As the optical absorption spectrum is strictly a dynamic quantity it is not readily calculated

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in the normal Monte Carlo procedure; it is however possible to determine imaginary time correlation functions for a quantum particle using equilibrium techniques.³⁴ Presently there is no numerically accurate method to analytically continue these correlation functions to real time. Instead we solve the Schrödinger equation for the excess electron in the Born-Oppenheimer approximation for many solvent configurations generated by PIMC.^{35,36} Using fast Fourier transforms³⁷ this task is readily achieveable on supercomputers for a few hundred configurations with a moderate CPU cost.

2. Methodology

2.1. Path Integral Monte Carlo. The Hamiltonian for a system of N water molecules interacting with one excess electron can be written as

$$H = \frac{\mathbf{p}^2}{2m} + \sum_{i=1}^{N} \sum_{\alpha=1}^{3} \frac{\mathbf{P}^2_{i(\alpha)}}{2M_{\alpha}} + \sum_{i$$

where \mathbf{R}_i denotes the collection of the coordinates of the *i*th water molecule, \mathbf{r} is the position of the excess electron, \mathbf{p} is the momentum conjugate to r, m is the electron mass, $\mathbf{P}_{i(\alpha)}$ is the momentum of the α th species of the *i*th water molecule, and M_{α} is the corresponding mass where $M_1 = M_{\text{oxygen}}$ and $M_{2,3} = M_{\text{hydrogen}}$. The potential of interaction, $V(\mathbf{R}_i, \mathbf{R}_j)$, between two water molecules with coordinates \mathbf{R}_i and \mathbf{R}_j is taken to be a central force potential (CF2); i.e., it is taken to be the sum of the potentials between atoms.³⁸⁻⁴⁰ The internal vibrations of the water molecule are modeled by a set of Morse potentials.⁴¹⁻⁴³ The pseudopotential, $U(\mathbf{r},\mathbf{R}_i)$, describing the interaction between the electron and the water molecule is described in the next section. In the simulations the water molecules are treated classically. This is reasonable because the thermal de Broglie wavelength of even the proton at the temperatures of interest here, namely T = 300, 373 K, is much smaller than that of the electron. The internal vibrations of the water molecule are expected to have negligible effect on the structural properties of the hydrated electron. The canonical partition function for the system may be written as

$$Q = \operatorname{Tr} \left(e^{-\beta H/P} \right)^{P} \tag{2.3}$$

If P is very large Q, for the mixed quantum-classical system, can be approximated by $Q \sim Q_P$ where

$$Q_{P} = \left(\frac{mP}{2\pi\hbar^{2}\beta}\right)^{3P/2} \left(\frac{M_{\text{oxygen}}P}{2\pi\hbar^{2}\beta}\right)^{3N/2} \left(\frac{M_{\text{hydrogen}}P}{2\pi\hbar^{2}\beta}\right)^{3N} \times \int e^{-\beta S_{\text{eff}}} \prod_{i=1}^{N} \prod_{j=1}^{P} \mathrm{d}\mathbf{R}_{i} \,\mathrm{d}\mathbf{r}^{(j)}$$
(2.4)

where the Euclidian action is

$$S_{\rm eff} = V_{\rm e^--W} + V_{\rm W-W}$$
 (2.5)

$$V_{e^{-}-W} = \sum_{j=1}^{P} \left[\frac{mP}{2\hbar^{2}\beta^{2}} (\mathbf{r}^{(j)} - \mathbf{r}^{(j+1)})^{2} + \frac{1}{P} \sum_{i=1}^{N} U(\mathbf{r}^{(j)}, \mathbf{R}_{i}) \right]$$
(2.6)

and

$$V_{W-W} = \sum_{i < j} V(\mathbf{R}_i, \mathbf{R}_j)$$
(2.7)

The set $\{\mathbf{r}^{(t)}\}$ denotes the electron coordinates for different Euclidian time points. The explicit derivation of the action for the problem is presented in detail elsewhere.⁴⁴ Thus in the discretized path

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integral formulation the system consisting of an electron interacting with N classical water molecules is isomorphic to N + P classical particles moving in an effective potential field given by eq 2.5. This formulation becomes exact only in the limit that P goes to infinity. In practice a sufficiently large value of P is chosen such that averages over the distribution change negligibly on a further increase of P.

The scheme outlined above is suitable for calculation using Monte Carlo techniques. Some care has to be taken to avoid inefficient diffusion through phase space of the large isomorphic electron polymer chain. Single particle moves employed in the ordinary Metropolis Monte Carlo scheme is inefficient for P greater than a few hundred. Instead we employ an algorithm devised by Pollock and Ceperley⁴⁵ that is able to make large multiparticle moves with an appreciable acceptance probability. This "staging" technique⁴⁵⁻⁴⁸ and others⁴⁹⁻⁵² have proven to be crucial in sampling the fluctuation of the electron polymer chain. In our experience the Pollock-Ceperley algorithm gives the most rapid convergence.

2.2. Electron-Water Pseudopotential. The electron-water potential used was developed earlier³³ and is only briefly described here. The form chosen for the potential consists of three parts. A static potential term describes the electrostatic interaction between the electron and the localized charges on the water molecule. If **r** represents the coordinates of the electron and \mathbf{R}_0^i , $\mathbf{R}_{H,i}$, $\mathbf{R}_{H,i}$ are the coordinates of the *i*th water molecule, \mathbf{R}_{i} , the interaction can be written

$$U^{\rm S}(\mathbf{r}, \mathbf{R}_i) = \frac{2Z_e e}{|\mathbf{r} - \mathbf{R}_{\rm O}^{\,i}|} - \frac{Z_e e}{|\mathbf{r} - \mathbf{R}_{\rm H_1}^{\,i}|} - \frac{Z_e e}{|\mathbf{r} - \mathbf{R}_{\rm H_2}^{\,i}|} \qquad (2.8)$$

where Z_e is the charge of the central force model given as 0.329 83e.

The repulsion due to the orthogonality of the wave function of the excess electron to the wave function of the inner core electrons water molecule is given by three different terms centered on each nuclei of the water molecule. The hydrogen repulsion is written as

$$U_{\rm H}^{R}(\mathbf{r}, \mathbf{R}_{\rm H}^{i}) = 0.185 e^{-|\mathbf{r}-\mathbf{R}_{\rm H}^{i}|/a_{0}} + Z_{e} e^{\frac{e^{-|\mathbf{r}-\mathbf{R}_{\rm H}^{i}|/a_{0}}{|\mathbf{r}-\mathbf{R}_{\rm H}^{i}|}}$$
(2.9)

where a_0 is the Bohr radius and we used atomic units. For the oxygen repulsion we employ an exponential form

$$U_{\rm O}^{R}(\mathbf{r}, \mathbf{R}_{\rm O}^{i}) = V_{0} e^{-|\mathbf{r}-\mathbf{R}_{\rm O}^{i}|/r_{\rm OH}^{\rm eq}}$$
(2.10)

where $V_0 = 0.046793$ hartree and r_{OH}^{eq} is the equilibrium oxygen-hydrogen bond length of the water molecule.

The last term we consider is a self-consistent polarization⁵³ term including the electron-induced dipole interactions. Here the electron creates a self-consistent induced dipolar field with which it interacts. For simplicity we assume that the many-body polarization effect can be approximated by a static spherical molecular polarizability tensor. It is difficult to ascertain what new features might arise from a frequency-dependent polarizability including quantum dispersion.⁵⁴ The need for including manybody effects in treating the excess electron in liquid water has been shown to be important for obtaining the properties of the electron-water system.33

The excess electron induces a dipole moment at the oxygen atom on all the water molecules. The additional dipole moment induced on the oxygen atom of the *i*th water molecule by the *t*th electron bead of the isomorphic electron polymer chain and all the induced dipoles on the other water molecules (except the *i*th water molecule) is given by electrostatics as

$$\boldsymbol{\mu}_{i0}^{(t)} = \alpha_0 \mathbf{G}_i^{(t)} \tag{2.11}$$

where α_0 is the oxygen spherical polarizability of 1.444 Å³ and $\mathbf{G}_{i}^{(t)}$ is the external electric field due to the *t*th excess electron and all other induced dipole moments. The vector field, $G_i^{(t)}$, is explicitly given by

$$\mathbf{G}_{l}^{(t)} = \frac{e\mathbf{r}_{l0}^{(t)} S_{1}(|\mathbf{r}_{l0}^{(t)}|)}{|\mathbf{r}_{l0}^{(t)}|^{3}} - \sum_{\substack{k=1\\k\neq i}}^{N} \frac{\mathbf{T}_{lk}^{(t)} \cdot \mathbf{\mu}_{k0}^{(t)} S_{1}(|\mathbf{r}_{lk}^{(t)}|)}{|\mathbf{r}_{kl}^{(t)}|^{3}}$$
(2.12)

where $\mathbf{r}_{i0}^{(t)} \equiv \mathbf{r}^{(t)} - \mathbf{R}_0^{i}$ and the second term in the above equation is the induced dipole-induced dipole interaction between the *i*th and kth water molecule and $T_{ik}^{(i)}$ is given by

$$\mathbf{T}_{ik}^{(t)} = 1 - \frac{3\mathbf{r}_{ik}\mathbf{r}_{ik}}{|\mathbf{r}_{ik}|^2}$$
(2.13)

where $|\mathbf{r}_{ik}|$ is the distance between the oxygen atoms of the *i*th and kth water molecule. The function $S_1(r)$, in eq 2.12 is an appropriate switching function which partially accounts for the diffuse nature of the charge distribution around the oxygen atom. For a given value of $\{\mathbf{r}^{(t)}\}\$ and the coordinates of all the water molecules $\{\mathbf{R}\}$ the set of linear equations 2.11 and 2.12 can be solved for $\mu_{i0}^{(i)}$ (i = 1, 2, ..., N). Having obtained $\mu_{i0}^{(i)}$, the polarization potential is given by

$$\Phi_{\text{pol}}(\{\mathbf{r}^{(t)}\},\{\mathbf{R}\}) = -\frac{e}{2P} \sum_{t=1/-1}^{P} \sum_{j=1/-1}^{N} \frac{\mu_{(0}^{(t)} \cdot \mathbf{r}_{(0)}^{(t)} S(|\mathbf{r}_{(0)}^{(t)}|)}{|\mathbf{r}_{(0)}^{(t)}|^3}$$
(2.14)

In our simulation we choose $S_1(r)$ to be the switching function defined in Stillinger and David's work.⁵⁵ The effect of $S_1(r)$ was found to be negligible. The $\Phi_{pol}({\mathbf{r}^{(t)}}, {\mathbf{R}})$ is turned off at close distances by another switching function S(r)

$$S(r) = (1 - e^{-r/r_c})^6$$
(2.15)

In the Monte Carlo simulation one has to calculate $\Phi_{pol}({\mathbf{r}^{(t)}},{\mathbf{R}})$ by solving eq 2.11 and 2.12 for every Monte Carlo step. It is appropriate to include only those water molecules which are within a cutoff distance of the *t*th electron bead in the algorithm. We choose this cutoff distance R_c to be about 5.5 Å so that after each step only a third of the water molecules were included in the calculation of $\Phi_{\text{pol}}(\{\mathbf{r}^{(t)}\}, \{\mathbf{R}\})$. At distances larger than R_c a radial two-body term for the polarization potential is used

$$U^{\mathsf{P}}(\mathbf{r},\mathbf{R}_{i}) = -\frac{\alpha_{\mathsf{O}}}{2|\mathbf{r}-\mathbf{R}_{\mathsf{O}}^{i}|^{4}}S(|\mathbf{r}-\mathbf{R}_{\mathsf{O}}^{i}|) \qquad (2.16)$$

The matrix equation, for the induced dipole moments, was solved by using an iterative scheme.

It is important to note that including a many-body polarization term leads to a more repulsive interaction between the electron and the water molecules of the cavity than the two-body pseudopotential.33

Other electron-water pseudopotentials have been introduced 28,29,31,56 and used in extensive path integral simulations, but many-body polarization effects have been ignored. Moreover, the potential due to Schnitker and Rossky³¹ predicts³⁵ a band maximum in the excess electron absorption spectrum that is on the average 0.5 eV blue-shifted of the experimental band maximum.

2.3. Calculation of Absorption Spectrum. The solvent configurations generated by the path integral Monte Carlo calcula-

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tions outlined above are distorted from configurations of the pure fluid due to the presence of the electron. These configurations thus sample the equilibrium fluctuations of the solvent cavity around the electron. Using the Born-Oppenheimer approximation, together with the Fermi golden rule, we can calculate the inhomogeneously broadened absorption spectrum of the solvated electron by evaluating the energies and dipole matrix elements of the electron in each of the frozen solvent configurations sampled during our Monte Carlo runs. The broadening of the spectrum is thus assumed to result from the equilibrium fluctuations in the size and shape of the solvent cavity. The electronic wave function is assumed to respond instantly to these fluctuations in the solvent potential. According to the Fermi golden rule expression, the absorption spectrum can be written as a sum over the transitions between all eigenstates of the system. We demonstrate below that the behavior of the electron-water system exhibits ground-state dominance so we can simplify the Fermi golden rule expression for the absorption spectrum and only consider transitions from the ground state to the higher excited states.

A variety of techniques could be used to obtain the eigenvalues and eigenfunctions of an electron in the complicated potential provided by a configuration of solvent molecules. Recently Sprik and Klein⁵⁷ have employed an optimized Gaussian basis set approach to study hydrated electronic energy levels and wave functions. In our work we have essentially used the method of Schnitker et al.³⁵ Our implementation of this method is described in ref 58. The method relies on an imaginary time version of the fast Fourier transform technique developed by Feit, Fleck, and Steiger.37

In this approach we make a short time approximation and write the propagator, $\exp(-\Delta \tau H/\hbar)$, as the product of a potential part, $\exp[-\Delta \tau V(\mathbf{r},\mathbf{R})/\hbar]$, and a kinetic part, $\exp[-\hbar \Delta \tau \nabla^2/2m]$ where $\Delta \tau = i\tau t$. (This is correct to order $\Delta \tau^2$ and for sufficiently small $\Delta \tau$ gives results in agreement with the factorization of the full propagator into three terms.) The initial wave function is established on a three-dimensional grid in position space. First, the wave function is partially propagated by simply multiplying it by the potential part of the propagator. Next we Fourier transform the resulting wave function to give us a partially propagated solution in momentum space. In this representation the kinetic propagator becomes a simple Gaussian matrix $\exp[-\hbar\Delta\tau \mathbf{p}^2/2m]$. After multiplying the partially propagated solution by this matrix we obtain the wave function in momentum space advanced by one time increment, $\Delta \tau$. Inverse Fourier transforming gives the propagated wave function in position space. By repeating this cycle many times the wave function can be advanced to any time, τ . The propagation is only accurate if $\Delta \tau$ is sufficiently small.

Any arbitrary initial wave function can be written as a superposition of the eigenfunctions of the problem. The imaginary time evolution of the nth eigenstate is a simple exponential decay whose rate is determined by the eigenvalue; i.e., the contribution of the *n*th eigenstate to the superposition at time τ will be proportional to $\exp[-E_n\tau/\hbar]$. Thus at long times the lowest energy eigenstate present in the superposition will have exponentially larger amplitude than all the other eigenstates. The long time decay of the wave function amplitude thus gives an estimate of the lowest energy eigenvalue contained in the propagating solution and the spatial distribution of the long time solution gives the corresponding eigenfunction. Excited-state information can be obtained by "filtering" the contributions of the lower energy eigenstates from the propagating solution. This is achieved by holding the propagating solution orthogonal to the previously determined lower lying eigenstates. Details of the techniques we have used here are presented in the work of Coker and Berne.58

2.4. Simulation Details. Simulations were performed at two different state points of water. A system of 216 water molecules was employed. A room temperature simulation was carried out at 300 K and at a density of 1.00 g/cm³ and one at 373 K at a

3554.

of finding a water molecule hydrogen bonded to fewer waters is increased. Thus the structural change induced in the neat liquid at a higher temperature is due to a reduction of the hydrogen-bond ordering. Similarly there is a 10% reduction in the oxygen-oxygen pair correlation function at 373 K. A feature of the central force water model, common with many other models, is a tendency to overemphazise the structure of liquid water. In particular the height of the first oxygen peak at 300 K is 35% larger than the experimental X-ray data.⁶⁰ At 373 K the central force water model overestimates the first peak by 50%. This artificial enhancement of the structure can be understood in terms of the electrostatics of the water model. As the central force water model has a charge distribution appropriate for the monomer it is important that a liquid simulation properly take into account the electrostatic properties of water. Preliminary calculations of the

value of the dielectric constant for central force water predicts a low dielectric constant, a common trait of many model potentials.^{61,62} A low dielectric constant causes the charges in the

density of 0.96 g/cm³. Each simulation employed the self-consistent polarization potential and generated the equivalent of 48 000 primitive passes of which 1200 configurations were saved for later analysis. Each run took approximately 40 CPU hours on a CRAY 2 or XMP 48. In order to overcome the problems of slow convergence in the sampling of the electron pseudoparticle chain the Ceperley-Pollock "staging method"45 was used and 40 pseudoparticles were moved at a time. As pointed out in Coker et al.⁴⁸ and Wallqvist et al.,33 the method used by Pollock and Ceperley45 is best suited for our problem and has been adapted here. The detailed structural and energetic properties of the room temperature system has been described earlier by us³³ for our pseudopotential and for other pseudopotentials.²⁸⁻³²

The electron was simulated by using a P of 900; the convergence of the results with P was discussed in detail previously.³³ The higher temperature simulations were also carried out with a Pof 900.

For the calculation of the optical absorption spectra we used a discretization grid of $(16)^3$ points and a FFT box size of 70% of the box length with an initial time step of 1 au followed by a second time step of 0.125 au to assure convergence. The eigenvalues were calculated with a tolerance of 1 ppm; the residual error arising from space discretization, choice of time step, convergence, etc. can be estimated to be about 1%. The calculation of the spectra using fast Fourier transforms⁵⁹ took approximately 12 CPU hours on the XMP 48 for the analysis of 200 configuration of each state point.

3. Results and Discussion

3.1. Structural Properties. At elevated temperatures the hydrogen-bond network of neat liquid water becomes more disordered. The structure of the environment local to a water molecule is conveniently described by a pair correlation function between two atoms

The strong local ordering of neighboring water molecules is due

to the hydrogen bonds developed in the liquid. In Figure 1 the

pair correlation function $g_{OH}(r)$ is shown. The first peak corre-

sponding to the hydrogen bond between two neighboring waters

is reduced 15% at 373 K from the room temperature value. The

probability of finding a water molecule hydrogen bonded to a given

number of water molecules is also shown in the bottom of Figure

1. A water pair is considered to be hydrogen bonded if the

potential energy of that pair is less than -4.0 kcal/mol. At high

temperatures the probability of finding four hydrogen bonds is

reduced versus room temperature, and similarly the probability

$$g_{AB}(r) = \frac{1}{4\pi\rho_{AB}} \left\langle \sum_{i}^{N} \sum_{j}^{N} \delta(r + |\mathbf{r}_{A_{i}} - \mathbf{r}_{B_{j}}|) \right\rangle \qquad (3.17)$$

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Behavior of the Hydrated Electron



Figure 1. The pair correlation function $g_{OH}(r)$ for the two different temperatures studied. The first peak in the distribution function corresponds to the closest OH distance between two neighboring water molecules. The reduction of this hydrogen bond is seen to be about 15% when going from room temperature to T = 373 K. Also shown is the probability of finding a water molecule hydrogen bonded to *n* other water molecules at the different temperatures studied. A hydrogen bond is defined as a pair of water molecules having a total potential energy of -4.0 kcal/mol or less. At higher temperature the probability of finding many hydrogen-bonded water goes down.

system to be insufficiently screened, resulting in a stronger interaction and thus a more structured liquid.

There are two classes of model potentials now being used to simulate water. The central force potential (CF2) due to Stillinger and co-workers^{38,39,40} used in our work belongs to the first class where the charges assigned to the oxygen and hydrogen atoms are such that a water molecule has the dipole moment of 1.85 D, the value measured for gas-phase water molecules. In the second class, e.g., Berendsen's⁶³ central force model (SPC), the charges assigned to the three moieties are such that the water dipole moment is 2.2 D, the values corresponding to liquid water. (In addition the difference between these two models is that in the Stillinger model the average HOH bond angle is 104° whereas in Berendsen's model it is fixed at 109°.) Neither approach is the best solution in problems where interfaces are important because the electrostatic character of interfacial water should lie somewhere in between an isolated monomer and that of a monomer immersed in the fluid. For a proper treatment of the electrostatics of a water interface the polarization forces among the water molecules need to be treated in an explicit many-body potential form, analogous to the electron-water polarization described above. Thus the cavity induced by the electron in the central force models of liquid water may not be wholly appropriately described by either type of water model.

The interaction energy of the water system, shown in Table I, is reduced at 373 K due to the increased thermal motion of the water molecules with a concomitant reduction of hydrogen bonding and loss of binding energy between molecules. The internal vibrations of the water molecules are more excited, which results in a higher internal energy of the water molecule.

It is now well established that water molecules form a cavity around the electron in room temperature liquid water.²⁸⁻³³ The hydrogens of the water molecules lining the cavity show a prop-

TABLE I: Energies for the Water-Electron System^a

•		
T = 300 K	T = 373 K	
-10.05 (0.23)	-9.22 (0.23)	
+1.28(0.07)	+1.47(0.08)	
-63 (18)	-77 (15)	
+20 (8)	+19(8)	
	T = 300 K -10.05 (0.23) +1.28 (0.07) -63 (18) +20 (8)	T = 300 K $T = 373 K$ $-10.05 (0.23)$ $-9.22 (0.23)$ $+1.28 (0.07)$ $+1.47 (0.08)$ $-63 (18)$ $-77 (15)$ $+20 (8)$ $+19 (8)$

^aEnergy terms for various quantities of the electron-water system. Water energies given in kcal/mol of water and electron energies in kcal/mol of electron. The standard deviation is given in parentheses. The kinetic energy was calculated by using the virial estimator.^{67,68}



Figure 2. The electron center of mass (barycenter) oxygen pair correlation functions, g_{e^-om0} , for both temperatures. The electron cavity is clearly seen as the excluded region from 0 to ~ 2 Å. The ordering of the surrounding oxygen atoms is weak compared to a classical ion like F⁻. The temperature effect is seen in the pushing out of the first peak of the distribution, though the hard-core repulsive region is quite similar.

ensity to point toward the electron; thus the electron can be categorized as being hydrogen bonded as opposed to being dipolar bound. The waters in the shell around the electron correspondingly lose a water-water hydrogen bond. The shape of the cavity is roughly spherical with a region of electron-water overlap extending into the first water shell. This implies that the structure of the cavity is rather diffuse and not well ordered as is found around a classical anion. These characteristics of the electron water system have been described in more detailed by us elsewhere³³ and by other workers.²⁸⁻³²

To further describe the water structure around the electron, an electron center of mass (barycenter) is defined as the averaged position of the pseudoparticles comprising the electron chain polymer. Figure 2 shows the electron center of mass oxygen pair correlation functions, $g_{e_{com}O}$, for both temperatures. Two important features are worth noting: the hard-core repulsive region of the innermost waters, r = 2.0-2.8 Å, has changed very little with temperature, but the actual first peak of the distribution has been shifted outward. The repulsive part of the cavity persists at the higher temperatures because of the enhanced structure of the central force model. The number of water molecules in spherical shells centered on the electron barycenter can be determined from the running coordinating number

$$n_{\rm H_2O}(r_1, r_2) = 4\pi\rho \int_{r_1}^{r_2} s^2 g_{\rm e^-_{com} - O}(s) \, ds \qquad (3.18)$$

For the shell extending from r = 2.8 to r = 3.8 Å it is found that there are 6 waters at 300 K and 5 at 373 K, and for the shell between r = 3.8 and r = 4.8 Å there are 8 waters at 300 K and 10 waters at 373 K. The potential energy of interaction between the electron and the water, shown in Table I, is more attractive at higher temperatures. There are two contributions to this effect: (a) The electron can tunnel into the first shell of water molecules, r = 2.8 to r = 3.8 Å, at both temperatures. The short-range

⁽⁶³⁾ Berendsen, H. J. C.; Postma, J. P. M.; Van Gunsteren, W. F.; Hermans, J. In Intermolecular Forces; Pullman, B., Ed.; Reidel: Dordrecht, 1981.



Figure 3. The electron pseudoparticle oxygen pair correlation functions $g_{e_{read}O}$, at the different temperatures studied. The main difference is that the distribution peaks earlier at 373 K than at 300 K in the region r = 3.8-4.8 Å. Thus the electron is correlated more strongly in this region at 373 K. There is a hard-core repulsion close to the oxygen atoms preventing the electron from overlapping with the implicit charge distribution on the oxygen atom. There is no shell structure around each electron pseudoparticle.

interaction between the oxygen and the electron is repulsive. There are fewer oxygens in the first shell at 373 K. Therefore the potential energy at 373 K is lower than at 300 K. (b) The presence of two more water molecules with H atoms pointing toward the electron in the second shell, r = 3.8 to r = 4.8 Å, at 373 K, leads to a larger Coloumb attraction thereby lowering the energy. One can conjecture as to why there are fewer water molecules in the first shell at higher temperatures. This might be due to the fact that at higher temperatures the hydrogen bonds between the waters in the first shell and the electron are weaker, allowing these waters to share more hydrogen bonds with each other. This would lead to a more open network with a concomitant reduction of the water density in the first shell. Similarly the hydrogen-bonded network in bulk water gets weaker as the temperature is increased, thereby allowing the electron to perturb the bulk water structure more. In effect it is easier for the electron to orient the OH bonds favorably at higher temperatures and thus increase the solvation energy. As the region closest to the electron, the hard-core repulsive region, is not markedly changed at the higher temperature most of the reordering effect takes place further out in the fluid. This is consistent with the two extra excess coordinated water molecules in the region r = 3.8-4.8 Å at 373 K. The change in water density from 1.00 to 0.96 g/cm^3 , although small, leads to weaker hydrogen bonding and consequently stabilizes the electron solvation even further.

Looking at the true electronic oxygen pair correlation functions, i.e., between each pseudoparticle and the oxygen atoms, g_{e^-peadO} , in Figure 3 we see that it peaks earlier at 373 K than at 300 K. There is an exclusion region close to the oxygen atoms. The graph also shows the expected lessening of tunneling effects; i.e., the electron cannot tunnel as far into the surrounding waters at 373 K as it can at 300 K. The lack of structure in the distribution functions is a reflection of taking the average over all the pseudoparticles. It is due to quantum dispersion. Because there is less tunneling into the oxygen atoms at 373 K g_{e^-beadO} exhibits a more well-defined peak at higher temperatures.

As mentioned earlier the electron-water interaction energy becomes more attractive at higher temperatures, see Table I. This is a reflection of the more favorable orientations of the waters and the reduction in tunneling at 373 K, i.e., the increased solvation of the electron at the higher temperature. Another way of looking at the energetics of the electron in the cavity is to look at the effective potential in the attractive region. Defining a potential of mean force as

$$V_{\rm eff}(r) = -(1/\beta) \ln g_{\rm e^-_{com}O}(r)$$
 (3.19)

the effective potential is plotted in Figure 4 for the two different



Figure 4. Potential of mean force at T = 300 and 373 K. The lower temperature curve has an attractive minimum corresponding to the first peak in the g_{e^-comO} distribution. The well depth is about -0.15kT with a corresponding σ of 2.9 Å. The high-temperature minimum is broader and pushed further out but still of the same depth, again in accord with the g_{e^-comO} distribution. The repulsive region is quite similar in both cases.



Figure 5. Fluctuations of $R^2(\beta\hbar/2)$ as a function of the simulation length for the temperatures investigated. There are no long-time correlations evident in this graph or from a study of the autocorrelation of this series. The Gaussian nature of the fluctuations is displayed in the frequency diagram to the right. The values are normally distributed at a 5% level of significance. The value of the standard deviation is 1.8 Å² at 300 K and 1.9 Å² at 373 K.

temperatures. The system at room temperature has a well depth of about -0.15kT with a corresponding σ of 2.9 Å. The high-temperature system has its well shifted outward by about half an angström and is of approximately the same depth.

A useful quantity to examine is the Euclidian time correlation function between two electron pseudoparticles at different complex time points, i.e. positions along the electron pseudoparticle chain,⁶⁴ defined as

$$R^{2}(t-t') = |\vec{\mathbf{r}}(t) - \vec{\mathbf{r}}(t')|^{2}$$
(3.20)

where $\vec{r}(t)$ is the position of an electron bead along the path, $0 \le t \le \beta\hbar$. In the quantum-classical isomorphism, the electron is represented by a polymer chain and the value at $R^2(\beta\hbar/2)$ is the mean square distance between two beads on opposite sides of the chain. In Figure 5 simulation records of $R^2(\beta\hbar/2)$ are exhibited showing the fluctuations during a long simulation. The fluctuations were found to be Gaussian with a mean of 10.9 Å² and standard deviation of 1.8 Å² at 300 K and a mean of 10.84 Å² and standard deviation of 1.9 Å² at 373 K. Thus the size of the electron chain polymer has not changed significantly with the increase of temperature. It is important to note that trial simulations of similar length, not using a staging algorithm, exhibit far fewer fluctuations and thus sample a much smaller number of independent configurations with correspondingly much larger error in the solvation properties. This could be a problem in either

⁽⁶⁴⁾ Nichols III, A. L.; Chandler, D.; Singh, Y.; Richardson, D. J. Chem. Phys. 1984, 81, 5109.



Figure 6. The equilibrium-averaged function $R^2(\tau)$. The function is independent of τ as $\tau \rightarrow \beta \hbar/2$ and is an indication of ground-state behavior. The physical extent of the electron polymer chain is given by the value of $R^2(\beta\hbar/2)$. The function is almost identical at both temperatures when using the many-body polarization potential due to the similarity of the hard-core repulsive region of the water cavity in both cases. The increased localization due to the many-body effects are seen in the decrease of the plateau value at 300 K when comparing the potentials. Note that the x ordinate is plotted with the value of β fixed at T = 300 K.

molecular dynamics or nonstaging Monte Carlo simulations where great care must be taken to ensure that enough sampling has been generated. This was originally pointed out by Sprik et al.⁵⁰ in connection with their simulation of an electron in fluid He.

The ensemble-averaged function $R^2(\tau)$ for the two different temperatures T = 300 and 373 K investigated is shown in Figure 6. The graph also includes $R^2(\tau)$ calculated using the two-body potential (eq 2.16).³³ The spatial correlation of two electron beads at short τ is dominated by the strong harmonic nearest neighbors interaction. At large τ the correlation between two beads is lost. Then the characteristic distance between the beads gives the rms diameter of the isomorphic electron polymer. The overall structure of the isomorphic electron polymer chain is not significantly different at the two temperatures of water, except for slightly larger fluctuations in size at the elevated temperature.

The effect of using the many-body polarization terms in the electron-water potential causes the electron to become more localized. At 300 K the value of $R^2(\beta\hbar/2)$ taken from a simulation using the two-body polarization potential (eq 2.16)³³ was 12.66 Å² compared to 10.95 Å² for the many-body potential (eq 2.14). The interactions between the electron and the surrounding waters has become more repulsive. This screening effect arises from the electron-induced dipole in a water in turn inducing an antiparallel dipole in a nearest-neighbor shell water molecule which repulses the electron. The net result is to move the hard-core electron-water repulsive region to larger distances. The electron is thereby more strongly repelled from the oxygens and must move in a smaller free volume.

The thermal de Broglie wavelength $\lambda_T = (\hbar/m_ekT)^{1/2}$ is 17.2 Å at 300 K and 15.4 Å at 373 K. Thus the electron behaves more classically at higher temperatures and the delocalization due to kinetic energy decreases with temperature. This is consistent with the decreased tunneling of the electrons into the surrounding waters lining the cavity seen in Figure 3. On the other hand the water structure becomes more compliant as temperature increases, though not as much as one would expect from experiment because the central force model overestimates the ordering of liquid water. The net result is that the electron size changes very little with temperature.

The quantum nature of the electron solute stands in sharp contrast with the behavior of a classical anion. For a classical solute the increased thermal fluctuations would enlarge the accessible free volume of the ion, decrease the correlation with the surrounding waters and lower the interaction energy.



Figure 7. Typical wave functions of the first four states of the electron in a frozen matrix of water molecules. The plots show the isosurfaces, $|\Psi_i| = 0.010$, of the normalized wave functions. The ground-state wave function does not have any nodes, is clearly spherical, and can thus be characterized as a S state. The next three excited states all show typical P-state behavior with two lobes of opposite sign and a nodal plane between them. These states are all well confined within the simulation box.

3.2. Absorption Spectrum. The absorption spectrum of the hydrated electron has been determined experimentally. At 300 K the band shape is asymmetric with a maximum at 1.72 eV, a width of about 0.8 eV, and a high-frequency tail. There have been extensive speculations on the nature of the transitions and the asymmetric band shape.^{7,8,12-15,17,65}

From the behavior of $R^2(\tau)$ we see that the correlation function rises sharply to a plateau value which is constant as $\tau \rightarrow \beta \hbar/2$, see Figure 6. This can be understood in terms of the energy levels in the system if one rewrites eq 3.20 in terms of the electronic eigenfunctions $\Psi_n(r) \equiv |n\rangle$ and eigenenergies ϵ_n . If $Q_{\rm ele} = \sum_n e^{-\beta \epsilon_n}$ is the partition function of the excess electron using bracket notation we can write^{32,64,66}

$$R^{2}(\tau) = \frac{2}{Q_{\text{ele}}} \left[\sum_{m} \langle m|r^{2}|m\rangle e^{-\beta\epsilon_{m}} - \sum_{m,n} |\langle m|r|n\rangle|^{2} e^{-\beta\epsilon_{m}} e^{-(r/\hbar)(\epsilon_{n}-\epsilon_{m})} \right]$$
(3.21)

Let n = 0 and n = 1 denote the ground state and the first excited state. If $\epsilon_1 - \epsilon_0 \gg kT$ only, the ground-state m = 0 will contribute to the sum and, for sufficiently large τ , $R^2(\tau)$ will become independent of τ , as noted by Nichols et al.⁶⁴ Thus the system is ground state dominated at both temperatures. In principle this formulation could yield dipole transition matrix elements enabling one to reconstruct a spectrum if one could evaluate eq 3.20 sufficiently accurately for each electron-water configuration. There are two problems associated with this approach: first, the method will not be able to differentiate between closely lying energy levels due to the problem of fitting multiple exponentials, and second, in order to ensure convergence the path integral in each water configurations requires prohibitively long simulations. The split operator technique described above is superior in these respects. As a consistency check we used the energy levels and dipole matrix elements calculated from the solution of the Schrödinger equation with the FFT method to reconstruct $R^2(\tau)$ using eq 3.21. The agreement is excellent for all state points.

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⁽⁶⁷⁾ Herman, M. F.; Berne, B. J. J. Chem. Phys. 1982, 78, 4103.



Figure 8. Wave functions of higher excited states of the hydrated electron for a sample configuration. The plots show the isosurfaces, $|\Psi_i| = 0.010$, of the normalized wave functions. Ψ_4 have three lobes, two negative outer ones separated by a smaller positive ones, with two nodal surfaces. This d character is also seen very clearly in Ψ_5 which has four lobes of alternating sign with two intersecting nodal planes. This is very reminiscent of a $d_{x^2-y^2}$ orbital. Higher excited states do not have quite such easily distinguishable features and are more complicated to interpret.

The ground-state eigenfunction calculated for each electronwater configuration looks like a typical S state. Typical eigenfunctions of the first four states, Ψ_0 through Ψ_3 are shown in Figure 7. Clearly the ground state is roughly symmetrical and well confined within the simulation box. It is without any nodes. As the cavity is not perfectly spherical the next P state is split into three components, P_x , P_y , P_z . As they each have one node we designate these as P states. These states are separated on the average by 0.2 eV. Their transition dipole matrix elements are roughly similar, contributing equally to the spectrum, forming a P band in the spectrum.

Higher excited-state wave functions are plotted in Figure 8. The higher excited states are more complex with more nodes, but, for example, Ψ_4 and Ψ_5 have some characteristic d-type orbital behavior. Ψ_1 has two nodal planes separating three lobes with alternating signs - + -, and Ψ_5 has two intersecting nodal planes separating four lobes of alternating sign. This is suggestive of a $d_{x^2-y^2}$ -type orbital. Higher excited states do not have quite such easily distinguishable features and are more complicated to interpret. The higher excited states tend to become more influenced by the finite box, and the highest excited wave function calculated, Ψ_{10} , extends over a large portion of the simulation box. The higher excited-state dipole matrix elements are typically on the order of 100 times smaller than the contribution of the average $1S \rightarrow 2P$ transition.

The density of states is presented in Figures 9 and 10. The three peaks in the distribution correspond to the ground state at ~ -1.5 eV, the three P states all fall under the second peak at $\sim +0.2$ eV, and finally the higher states form a third peak beginning at $\sim +1.5$ eV. The density of states falls off at high energy because we can only determine a limited number of high-energy states in our calculation. It is still an open question if this is the beginning of the continuum band. The zero of energy refers to the electron infinitely separated from the water sample, making it difficult to uniquely associate the energy of a higher excited state with a bound or unbound state. Examination of the wave



Figure 9. Density of states at T = 300 K with and without including the polarization part of the potential self-consistently. The energy scale zero refers to the electron infinitely separated from the liquid and does not necessarily indicate whether a state is bound or not. The energy distribution of the ground state is shifted in a nonconstant fashion. The falloff of the higher excited states band after 1.5 eV is due to the limited amount of higher excited states included in the calculation.



Figure 10. Density of states at T = 300 K and T = 373 K using the self-consistent polarization potential. The most notable difference between the two temperatures is the nearly constant shift of the density of states with higher temperature. The ground-state and P-state distributions are shifted 1.0 eV to lower energies. The higher excited states slightly less so. The shape of the bands are still very similar. The energy zero is with respect to an electron separated from the sample and the falloff of the higher excited states distribution is due to the limited number of states included.

functions indicates that the S and P states are well localized whereas some of the higher states extend over a large area of the simulation box and are thus affected by the finite size of the sample.

The effect of including many-body polarization terms is to shift the density of states to higher energies as seen in Figure 9. The change is roughly ($\sim 0.2 \text{ eV}$) for the ground-state distribution whereas it is larger ($\sim 0.4 \text{ eV}$) for the P states. The higher excited states are also shifted slightly but given their uncertainty in terms of finite size problems this may not be significant. To understand these shifts it is convenient to think of the electron-water system in terms of an effective one-dimensional potential defining the states of the system. The many-body polarization terms lead to a more strongly repulsive potential and thus to stronger localization of the electron. Thus the effective potential has become narrower, pushing the electronic states toward higher energies.

In Figure 10 the change of temperature to 373 K shifts the entire distribution to lower energies. The band due to the P states is better separated from the higher excited states. Again the higher



Figure 11. Calculated absorption spectra using two different potentials at T = 300 K compared to the experimental value.¹⁷ The graphs are plotted with equal area. The effect of the self-consistent polarization is to shift the band maximum to higher energies and slightly broaden the spectra. Comparisons with the experimental spectrum show a poorly developed high-energy tail though the half-width is in good agreement.

excited states roughly falls in the same place indicating a finite size effect. Note that the energy shift of the states is constant ($\sim 1.0 \text{ eV}$).

It is worth noting that a continuum dielectric description predicts a different result. Consider an electron trapped in a cavity in a continuum dielectric with dielectric constant ϵ . Clearly a smaller ϵ leads to a smaller attractive energy of the electron. Since the dielectric constant of water is $\epsilon \simeq 80$ at 300 K and $\epsilon \simeq 50$ at 373 K we would expect the density of box states to be shifted to higher energies as temperature increases. This is opposite to what is obtained here. Given the above it is more realistic to adopt a dielectric model which assigns different dielectric constants to different solvent shells around the electron.

The picture that emerges is that of an electron trapped in a soft repulsive spherical box which is roughly of the same size at 300 and 373 K. The electronic states are determined by the box. However, because the electron interacts more attractively with the waters outside the box at 373 K than at 300 K, the energy eigenstates at 373 K are red-shifted from those at 300 K. The spacing between energy levels are however determined by the repulsive box radius and are thus the same at the two temperatures.

The absorption spectrum was calculated by using the method in section 2.3. Figure 11 shows the absorption spectrum at T =300 K for pair and many-body polarization. The absorption maximum for the pair polarization is lower in energy than the experimental spectrum, but the self-consistent polarization potential blue shifts the maximum $\sim +0.2$ eV to coincide with the experimental absorption maximum. The width of the calculated spectra at half the maximum height is 0.64 and 0.80 eV for the two-body and the many-body potential, respectively. Compared to the experimental value 0.84 eV^{17} the calculated spectra based on pair polarization is too narrow but agrees well with experiment for the many-body polarization potential. The splitting in the simulated spectrum reveals the fine structure of the P bands. Averaging more than 200 water configurations should smooth these peaks. The dominant contribution of oscillator strength in the first peak arises from the $1S \rightarrow 2P$ transition. The shift in spectrum arising from the many-body polarization term is consistent with the density of states distribution showing a nonconstant shift of the energy levels corresponding to the P states. In terms of an effective potential defining the states of a system the increased repulsion has made the potential narrower, shifting the energy levels further apart to higher energies. The calculated spectra all show a very weak tail, corresponding to small dipole matrix elements in the ground to higher state excitation. This tail is much smaller than observed experimentally.

It is clear that the spectrum generated by using many-body polarization terms included in a self-consistent manner slightly



Figure 12. Calculated absorption spectra at two different temperatures using the self-consistent polarization potential compared to experiment.¹⁷ The lower graphs showing the experimental values clearly show the shift to lower energies with higher temperatures. The calculated spectra maintain roughly the same shape. There is no appreciably larger highenergy tail for the higher temperature calculation. The graphs are plotted with equal area.

shifts the spectrum to the blue—toward the experimental spectrum¹⁷—compared to the pure two-body potential. However, it does not give enough oscillator strength for the more highly excited states and thus does not produce the experimentally observed high-frequency tail, nor does it produce enough low-energy transitions.

The Kuhn-Thomas sum rule $\sum_{n=1}^{9} 2/3(E_n - E_0) |\langle \Psi_0 | \mathbf{r}_e | \Psi_n \rangle|^2$ averaged over all the configurations yields 0.9 or greater indicating that the calculations are including the bulk of the oscillator strength for all the systems investigated here.

It is of considerable interest to compare this calculation with a similar calculation of Schnitker and Rossky^{31,32,35} employing a similar procedure but with different potential models for the interactions. These studies are based Berendsen's SPC (simple point charges) water model⁶³ with larger charges (fitted to a liquidlike dipole moment) than the central force model^{38,39,40} (fitted to a monomer dipole moment) used by us. They also treat the polarization potential as pairwise additive as opposed to the many-body polarization terms used in our model. The increase of charges results in both stronger attraction near the hydrogens and stronger repulsion at the site of the lone electron pair on the oxygen.

The absorption spectrum reported by Schnitker et al.³⁵ exhibits an absorption maximum at 2.25 eV compared to the experimentally¹⁷ observed maximum at 1.72 eV and our results at 1.72 eV. Despite this very large discrepancy with experiment, their spectral line shape exhibits a high-frequency tail similar in shape but smaller in intensity than found experimentally.

The many-body polarization effect can now be interpreted in terms of the electrostatics of the interfacial waters. A pairwise electron-water polarization using the monomer charge distribution (CF2) would underestimate the repulsive forces defining the cavity. Likewise a pair polarization utilizing the liquid charge distribution (SPC) would overestimate the repulsive charge. A many-body polarization term using a monomer charge distribution (CF2) will induce an appropriate set of dipoles on the surrounding waters and correct the result of pair polarization repulsion accordingly. In effect the many-body polarization used here has compensated for the lack of a self-consistent electrostatic treatment of the water interaction. In this context is very important to note that the CF2 model gives a sepctral peak at $\simeq 1.4$ eV when only pair polarization is included and at $\simeq 1.7$ eV with many-body polarization. Thus even the pair polarization model used here is superior to the model of Schnitker et al.³⁵ from this perspective.

The temperature dependence of the absorption spectrum is shown in Figure 12. There is hardly any temperature dependence of our simulated band maximum. Again the broad high-energy tail of the high-temperature spectrum is missing in the simulated spectrum. The simulated band shape and width at half peak height are roughly the same at both temperatures. This is consistent with the constant shift in the distribution of the density of states with temperature. The repulsive hard-core region of the cavity has not changed with temperature, making the shape of the effective potential very similar at the two different temperatures and thus the spectra. As the temperature dependence of the central force water model predicts too much structure, it would be great interest to employ a more realistic temperature-dependent water-water potential. It is probably for this reason that the simulated spectrum is insensitive to the temperature. Unfortunately, work using other potential models has been carried out only at 300 K.

The agreement of the many-body polarization potential prediction of the electron absorption spectrum maximum is very encouraging. The lack of oscillator strength at higher transition energies could be due to a number of sources. Vibrational coupling to the surrounding water molecules has been neglected to a first approximation. The spherical shape of the electron could be an artifact of the too strongly arranged water cavity. A more asymmetric cavity could excite higher modes, bringing down the high-energy states, and couple them more strongly to the ground state.

4. Conclusions

We have shown that the structure of a hydrated electron at the temperatures investigated is roughly spherical, is ground state dominated, and resides in a definite cavity in the solvent.³³ The electron orders the fluid but does not have a well-defined coordination shell as does a classical anion like F^- . The change in cavity structure with temperature is consistent with the increased thermal motion of the solvent molecules. The loss of solvent structure at higher temperatures allows the electron to find an energetically more stable environment. At the same time the magnitude of the change is not enough to change the hard-core repulsive region defined by the innermost layer of water molecules in the electron-water cavity.

The calculation of absorption spectra from simulations allows one to make comparison in detail with experimental data. The simulations do not include the inhomogeneous broadening due to the vibrating and rotating water molecules lining the electron water cavity. At room temperature the spectrum calculated including many-body polarization terms is in better agreement with experiment than the pair polarization model. This is due to the increased localization of the electron caused by the change in hard-core repulsion in the self-consistent polarization treatment. Even though we seem to include almost all of the oscillator strength the high-energy tail of the spectrum is not reproduced. The largest contributions to the calculated spectra come from the bound to bound S to P transitions. The dipole matrix elements corresponding to the transition from the ground state to states higher than the three P states are far too small to give agreement with the high-energy wing of the experimental band. Very recently Coker and Berne have made a detailed study of the electronic states of an excess electron in He as a function of density. They have explored the energy threshold separating localized and delocalized states and show that the boundary conditions in finite systems strongly affect the delocalized states as expected.

The calculated high-temperature spectrum is similar to the low-temperature spectrum in contrast to the experimental spectra which show a large shift to lower energies with higher temperature. This is consistent with the lack of destruction of the hard-core repulsive region of the water cavity. This is a reflection of the temperature dependence of the central force water model. This model consistently overestimates the structure of liquid; real water loses its structure over a much smaller temperature range than does central force water. Again the high-frequency wing of the high-temperature spectra is poorly reproduced. The largest change in going to a higher temperature is the shift of the density of states,but since the difference is almost constant this is not reflected in the spectrum.

Given the two facts that our model does not reproduce the temperature dependence and underestimates the intensity of the blue tail is clear that attention should be directed to a better model of the excess electron in liquid water. The discrepancies might be due to inaccuracies in the electron-water pseudopotential or the water-water potential. The main point is to seek agreement with the only experimentally observable property, i.e., the absorption spectrum. It is also important to investigate the influence on the absorption spectrum of finite size effects as well as vibronic coupling to the surrounding water. In spite of this, this work represents a major effort in understanding the electron-water system.

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