Absorption Spectrum of the Solvated Electron. 1. Theory

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Optical absorption band-shape theory of the solvated electron in condensed media is presented. The solvated electron motion occurs in the Born–Oppenheimer energy potential well and is coupled to the intramolecular vibrational modes of the solvent. Both the energy potential well and the anharmonic coupling are randomly modulated. The time evolution of the anharmonic coupling constant is governed by the resonance energy exchange between the vibrational mode and the bath. The fluctuations of the energy potential arising from the direct coupling to the bath obey the stochastic Liouville equation.

1. Introduction

The properties of the solvated electron have been studied by a variety of experimental and theoretical methods such as ab initio molecular orbital calculations, computer modelling, and theoretical models.

One of the most important and frequently investigated physical properties of solvated electrons in liquids and glasses is the optical absorption spectrum, which probes the short time dynamics of the solvated electron. Optical absorption spectra are exceptionally broad, structureless and with an asymmetric high-energy tail. Different theoretical and quantum simulations of the optical spectrum try to explain such characteristic features. The optical absorption maximum position as a function of temperature, polarity, and pressure are relatively well understood in the framework of the semiclassical models.

Most of the existing theories are notably unsuccessful in treating the optical absorption band shape. However, neglecting the time dependence of the coupling strength (the operator $\hat{A}$, which creates the "dressed" electron, does not depend on time) and the fluctuations of the potential well makes the model unable to introduce in a natural way inhomogeneous band broadening. Generally, one can expect that three factors contribute to the solvated electron band shape: coupling to the vibrational degrees of freedom, inhomogeneous broadening due to molecular motions of the solvent molecules forming the trap, and nonlocalized transitions due to electron tunneling. It would be valuable to produce a unified model that takes into account all these factors. The present approach is based on the linear response theory formalism. Strong coupling limit theory with the canonical transformation for the diagonalization of the vibrational Hamiltonian has been used for the description of coupling between the solvated electron and intramolecular vibrational coordinates of the solvent molecules. The anharmonic coupling constant is regarded as a stochastic variable undergoing intramolecular resonant energy exchange with the bath (translational, rotational) motions and the low-frequency intermolecular solvent modes. The time evolution of the anharmonic coupling constant is treated by aid of the reduced density operator formalism with the Liouville equation solved by the method of Louissell and Walker.

direct coupling of the bath is assumed to be weak and is treated by perturbation theory using cumulant expansion and the Markov–Gauss approximation for the stochastic processes governing motions of the solvent.

2. Model

2.1. General Description. We consider the one-electron (solvated electron) approximation. This approximation involves not explicitly treating all of the electrons belonging to the $N$ solvent molecules in order to deal with a one-electron Schrödinger equation.

In the present approach, we shall study the solvated electron spectrum in liquid or frozen matrices assuming that the electron motion occurs in a single- or double-well potential (if tunneling exists) created by the solvent molecules. This motion is accompanied by the anharmonic coupling to the intramolecular vibrational modes of the solvent. Both the potential well and the strength of the coupling to the vibrational degrees of freedom are randomly modulated with time. The origin of the fluctuations is molecular motions of the medium in which the electron is dissolved. This coupling regarded as a stochastic process allows one to calculate the absorption band for the trapped electron in terms of a superposition of Franck–Condon lines.

2.2. Band Profile Theory. 2.2.1. Hamiltonian. In the linear response scheme, the absorption band shape $T(\omega)$ for a solvated electron can be expressed as the Fourier transform of the correlation function $^{42}$ of the electronic dipole moment operator $M$

$$I(\omega) = (2\pi)^{-1} \omega \left[ 1 - \exp(-\hbar \omega / kT) \right] \int dt \, \exp\left(iM(t) M(0)\right)$$  \hspace{1cm} (1)

To calculate $I(\omega)$ we have to know the time evolution of the dipole moment operator $M(t)$ appearing in eq 1. The symbol ( ) means averaging over electronic and vibrational degrees of freedom and bath. Thus, let us first discuss the Hamiltonian governing the time dependence of $M(t)$.

We consider here a solvated electron in the presence of a large number of photons, which make the system jump between two electronic states. The electron moves in a double-well potential (Figure 1). The absorption and emission of photons is considered instantaneous with respect to tunneling. In this case, the initial (ground) and final (first excited) electronic states may be split by tunnelling through the barrier. This would lead to an appearance of additional bands, whose origins would be displaced from the others by the frequencies of tunneling in the ground and excited states. If the solvated electron is trapped in a single potential well, we observe only one transition. Assuming that the solvated electron is coupled to the intramolecular vibrational modes of the solvent molecule, one can write the Hamiltonian of the system in the form

$$H(r,q) = h(r,q) + P^2/2M$$  \hspace{1cm} (2)

and

$$h(r,q) = P^2/2m + U(r,q)$$  \hspace{1cm} (3)

where $m$ is the electron mass, $M$ is the reduced mass of the vibrational oscillator, $r$ denotes the coordinate of the solvated electron, and $q$ is the vibrational normal coordinate of the mode coupled to the electron. We assume that only one vibrational mode is modified in the electronic transition. In fact, the electron motion can also be coupled to all of the other normal modes of the solvent. Such couplings, as long as they are linear, introduce no essential complication into the Hamiltonian. Using the Born–Oppenheimer approximation, we can write the eigenfunctions $\Psi(r,q)$ of the Hamiltonian $H$ as a simple product

$$\Psi(r,q) = \phi(r)\chi(q)$$  \hspace{1cm} (4)

where $\phi(r)$ is the electron eigenfunction of $h(r,q)$ and $\chi(q)$ is the vibrational eigenfunction. The potential energy operator $U(r,q)$ consists of two contributions

$$U(r,q) = V(r,q) + U(q)$$  \hspace{1cm} (5)

where $V(r,q)$ is the potential energy of the solvated electron (Figure 1) and $U(q)$ is the vibrational potential energy operator of the $q$ mode.

Assuming that the $q$ mode is harmonic, one can write the total Hamiltonian (eq 2 and 3) in the form

$$H_m(r,q) = E_m(q) + P^2/2M + \gamma q^2$$  \hspace{1cm} (6)

The basis for the solvated electron is defined as the tunneling stationary basis for the Hamiltonian (eq 3)

$$h(r,q) = \sum_m E_m|m\rangle \langle m|$$  \hspace{1cm} (7)

where $E_m$ are the electron eigenenergies in the double well of the electron in its ground and first excited states at fixed (equilibrium) vibrational displacements.

Using the creation–annihilation operators $a, a^\dagger$ (with $[a,a^\dagger] = 1$) for the vibrational mode $q$

$$P = ((\hbar \omega_0)/2)^{1/2}(a^\dagger - a)$$

$$q = (\hbar/2M\omega_0)^{1/2}(a^\dagger + a)$$  \hspace{1cm} (8)

we obtain for the ground and first excited states of the solvated electron

$$H_0 = \hbar \omega_0\left[a^\dagger a + \frac{1}{2} - \frac{1}{2} \omega_0(a^\dagger + a)\right] + E_0(q)$$

$$H_1 = \hbar \omega_0\left[a^\dagger a + \frac{1}{2} - \omega_0(a^\dagger + a)\right] + \hbar \omega_0^2 + E_0(q)$$  \hspace{1cm} (9)

where $E_0(q)$ is the value of $E_0(q)$ for the equilibrium displacement $q$ and $\omega_0$ the dimensionless anharmonic coupling constant, reflects the strength of the coupling between the electron and the $q$ mode

$$\omega_0 = a^{1/2}\left(\frac{\partial E_0}{\partial q}\right) \left(\frac{\hbar}{2M\omega_0}\right)^{-1/2} 2 \frac{\hbar}{\omega_0^2}$$  \hspace{1cm} (10)

Here, the index $m$ at $\omega_0^2$ goes over all the electronic transitions from the ground to the first excited electronic state.
The anharmonic coupling between the electron and vibrational motions can be treated in a general method, called the "strong-coupling theory". In this method, the coupling term is treated in an exact, nonperturbative way, on which a canonical transformation is performed as is common in polaron theory. The transformed Hamiltonian describes the dynamic effects of vibrational motion on the electron as it moves between its Born-Oppenheimer eigenstates. The usual jargon is that the "bare" electron is "dressed" in a cloud of solvent vibrations.

Performing the transformation on $H_0$ and $H^\dagger$

$$ H_0 = A(1/2\alpha_0)H_0A(1/2\alpha_0) $$
$$ H^\dagger = A(1/2\alpha_0)H^\dagger A(1/2\alpha_0) $$

with the operator

$$ A(1/2\alpha_0) = \exp[1/2\alpha_0(\sigma^+ - \sigma^-)] $$

and changing the origin of the energy level, we obtain

$$ H_0 = \hbar \omega_0 a^a - \alpha_0 a^a a - \omega_0 \alpha_0^2 \hbar \omega_0 + \hbar \omega_0^0 $$

The vibrational basis corresponding to this Hamiltonian (eq 13) is denoted as $|\alpha\rangle$. It is convenient to pass to a new representation, in which the Hamiltonian governing the $q$ mode is diagonal for the solvated electron in its first excited state. Using the transformation, which is in this case the displacement operator of the normal coordinates $a^q$ and $a$

$$ A(\alpha_0) = \exp[\alpha_0(a^q - a)] $$

we can write finally

$$ H^\dagger = \hbar \omega_0 a^q a - \alpha_0 a^q a - \omega_0 \alpha_0^2 \hbar \omega_0 + \hbar \omega_0^0 $$

with the vibrational basis $|\alpha\rangle$.

2.2.2. Dipole Correlation Function Calculation. As can we see from eq 1, in order to calculate the absorption band shape, we have to know the time evolution of the dipole correlation function (M(t) M(0)). The dipole correlation function can be expressed as

$$ G(t) = \text{Tr}(\rho^{\text{ib}}(0) \rho^{\text{ib}}(t) M^*(t) M(0)) $$

where, following the adiabatic approximation, we may write the total density operator of the system $\rho(t)$ at $t = 0$ as a product of the solvated electron and vibrational density operators

$$ \rho(0) = \rho^{\text{el}}(0) \rho^{\text{vb}}(0) $$

The index 0 at $\rho^{\text{vb}}(0)$ denotes, that the solvated electron is in its ground state. The symbol $\langle \cdot \rangle$ means averaging over the bath. First, we average over electronic degrees of freedom. Using a representation of the eigenstates of the electron in the adiabatic basis (eq 7), we may write

$$ G(t) = \text{Tr}(\rho^{\text{vb}}(0) \sum_{mn} \rho^{\text{el}}(0) M_{mn}(t) M^*_{mn}(0)) $$

where the sum over $m$, $n$, and $n'$ is restricted to 0, 0', 1, and 1' states (Figure 1). The density operator $\rho^{\text{el}}(0)$ governing the electronic motion corresponds to an equilibrium

$$ \rho^{\text{el}} = \exp(-E_{\text{el}}/kT)/(\text{Tr} \rho^{\text{el}}) $$
$$ \rho^{\text{vb}} = \exp(-E_{\text{vb}}/kT)/(\text{Tr} \rho^{\text{vb}}) $$

In the strong coupling limit theory, the dipole moment for the solvated electron becomes

$$ M_{nm}(t) = A(\alpha_0) r_{nm}(t) $$
$$ M^*_{nm}(t) = A^*(\alpha_0) r_{nm}(t) $$

where $m$ and $n$ are restricted to $n = 0$, 0', and $m = 1$, 1', whereas $A(\alpha_0)$ and $A^*(\alpha_0)$ represent the displacement operators at $t = 0$ (eq 14) and at time $t$, respectively.

The time evolution of $r_{nm}(t)$ is governed by the Heisenberg equation

$$ -i\hbar \frac{\partial r_{nm}}{\partial t} = [H,r_{nm}] $$

where Hamiltonian $H$ is given by (15). Because $H$ is acting only on the subspace corresponding to the first excited state, the equation is simplified to the form (let us take for example the $r$ matrix element for the electronic transition $0^+ \rightarrow 1^-$)

$$ -i\hbar \frac{\partial r_{1+1^-}}{\partial t} = (\hbar \omega_{1+1^-} - 2\alpha_0^2 \hbar \omega_0) r_{1+1^-} $$

In the same way, we can express the time evolution of the other elements $r_{mn}$. Thus, the dipole correlation function (eq 18) may be written as

$$ G(t) = \text{Tr}(\rho^{\text{vb}}(0) \rho^{\text{vb}}(t) M^*(t) M(0)) + \sum_{n,n'} \rho^{\text{el}}(0) M^*_{mn}(t) M_{n'n'}(0) $$

where $\omega_1$ is the tunneling frequency in the electronic ground state and

$$ \epsilon = \exp(-E_{\text{vb}}/kT)/(\text{Tr} \rho^{\text{vb}}) $$

2.2.3. Time Evolution of the Displacement Operator $A(t)$. Now, we shall perform the averaging over the vibrational states of mode $q$, which is coupled to the solvated electron. The density operator $\rho^{\text{vb}}(0)$ governing the vibrational mode corresponds to Boltzman equilibrium when the solvated electron is in its ground state

$$ \rho^{\text{vb}}(0) = \epsilon_1 \exp(-\hbar \omega_0 a^q/kT) $$

where the trace $\text{Tr} \rho^{\text{vb}}$ is equal to $\epsilon_1^{-1}$

$$ \epsilon_1 = 1 - \exp(-\hbar \omega_0 a^q/kT) $$

If we take a representation of the displacement operator $A$ in terms of the basis of the Hamiltonian (eq 13) of the $q$ mode

$$ A = \sum_{n\alpha} \rho_{n\alpha} \langle \alpha | \beta \rangle $$

we obtain from (23)

$$ G(t) = \langle \alpha | A(t) | \alpha \rangle \times \langle \gamma | A(0) | \gamma \rangle \times e^{i \omega_{q0} t} $$

$$ \exp(-i(\omega_{q0} t - 2\alpha_0^2 \omega_0) t) $$

$$ \exp(-i(\omega_{q0} t - 2\alpha_0^2 \omega_0) t) $$

The matrix elements appearing in (28) are Franck-Condon factors. According to Koide, we have for $\gamma \geq \alpha$

$$ \langle \gamma | A(0) | \alpha \rangle \times \exp(-\gamma \alpha/2) $$

$$ \exp(-\gamma \alpha/2) $$

In order to find the time-dependent matrix elements $\langle \alpha | A(t) | \gamma \rangle$, we must know the time evolution of the total density operator $\rho(t)$. Let us assume that the vibrational mode $q$ is relaxing to a bath (i.e., the vibrational modes other than the $q$ mode coupled with the solvated electron, reorientational, or translational degrees of freedom), when the solvated electron has jumped abruptly to its first excited state. Thus, the total density operator $\rho(t)$ may be written as

$$ \rho(t) = \rho^{\text{vb}}(0) \rho^{\text{el}}(t) $$


frequency mode relaxing to a bath. By use of their method, it can be shown that \( A(t) \) is expressed as

\[
A(t) = \exp[a^*(t)a - a(t)a]
\]

where

\[
a(t) = a_0 \exp[-i\omega_0 t] \exp(-\Gamma t/2)
\]

Here \( \Gamma \) is the damping parameter given by

\[
\Gamma = 2\pi \sum_j |K_j|^2 (\omega_j - \omega_0)
\]

When there is no coupling to the bath (the coupling constants \( K_j = 0 \)), the expression for \( a(t) \) takes the form

\[
a(t) = a_0 \exp(-i\omega_0 t)
\]

Using (31), we calculate \( \langle \bar{a} | A'(t) | \bar{a} \rangle \)

\[
\langle \bar{a} | A'(t) | \bar{a} \rangle = \exp(-a^2(t)/2) (a(t))^2 \times \sum_{j=1}^\infty (-1)^j \langle \bar{a} | a(t) | \bar{a} \rangle
\]

Substituting (35) and (29) into (28), we obtain

\[
G(t) = \langle e^{i\epsilon} \sum_{\alpha=\pm} \text{sign}(\gamma) \sum_{\alpha=\pm} \sum_{\alpha=\pm} \sum_{\alpha=\pm} A_{\alpha\beta}(t) \text{H}_{\alpha\beta} C_{\alpha\beta}(t) F_{\alpha\beta} \rangle
\]

with

\[
A_{\alpha\beta}(t) = \frac{1}{\rho} \exp\left(-\frac{\epsilon^2}{2}\right) \gamma^0 \gamma^+ (\gamma^+ \gamma)_{a+b+c}
\]

\[
B_{\alpha\beta} = f_m \exp\left(-\frac{\epsilon^2}{2}\right) \left(\omega_0 - 2\omega_0^2 \omega_0 + (\gamma - \alpha \omega_0) t\right)
\]

\[
F_{\alpha\beta} = \exp\left(-\frac{(\gamma - \alpha) + 2p + 2j}{2}\right) \Gamma / 2
\]

\[
C_{\alpha\beta} = \alpha_0 \exp[(\gamma + \alpha + \epsilon_0) + \epsilon_0]
\]

where

\[
f_1 = r_0^2 \epsilon_0^2 \quad f_2 = r_0^2 \epsilon_0^2 \quad f_3 = r_0^2 \epsilon_0^2 \exp(-\hbar \epsilon_k / kT)
\]

\[
f_4 = r_0^2 \epsilon_0^2 \exp(-\hbar \epsilon_k / kT) \quad \omega_0 = \epsilon_0 \quad \omega_0^2 = \omega_0^2 \quad \epsilon_0 = \exp(-\hbar \epsilon_k / kT)
\]

As we can see from eqs 36–40, the optical band of the solvated electron potentially may consist of four lines shifted by the tunneling frequencies of the ground and/or first excited states. Each electron transition band consists of many vibrational lines peaked at \( \omega_0^2 - 2\omega_0^2 \omega_0 + (\gamma - \alpha \omega_0) t \) and differing by their half-width

\[
\Gamma_{\alpha\beta} = [(\gamma - \alpha) + 2p + 2j] \Gamma
\]

Each vibrational line consists of a number of Lorentzians differing by their intensities, which depend on products of the form \( A_{\alpha\beta}(t) \cdot s_\gamma \cdot C_{\alpha\beta}(t) \).

### 2.2.4. Tunneling in the Presence of Fluctuations

So far, we have taken into account the influence of molecular motions in the neighborhood of the trapped electron, which enter indirectly through the coupling of the electron with the vibrational mode \( q \) relaxing to the bath. However, the solvent acts also directly through creation of a fluctuating electric field, which perturbs the energy levels of the ground and excited states of the electrons tunneling from one trap formed by a solvent to another. This concept has been used in many statistical models.\(^{4,25,53-57}\) There is, however, another factor, that may be much more important, resulting in fluctuations with time of the electron potential well. During an electronic transition, the positions and the velocities of all atomic nuclei forming the trap remain constant (Franck–Condon principle), but the electronic charge distribution is altered. Because of the change in the electronic structure, the transition occurs between the energy surfaces characterized by different equilibrium geometries. Generally, the difference between the energy surfaces is much more complicated than only linear displace with the \( q \) mode as we have assumed in the Hamiltonian (eq 9). Additionally, the electron is coupled not only to the \( q \) mode but to all of the other vibrational modes of the solvent molecule, which modify the potential well. Thus, the electronic transition between the ground and first excited Born–Oppenheimer potentials can be regarded as a transition in the same potential fluctuating with time. The influence of these factors on the band shape of the solvated electron is formally included in our model by averaging over molecular motions in eq 36. In this section, we will concentrate on the averaging of the dipole correlation function \( G(t) \) in expression 36. Using the static double well (Figure 1), that is, a double well in the case of Born–Oppenheimer electron–nucleus separation and working in the basis given by (7), one can write the following Hamiltonian for the isolated system

\[
\tilde{H}_0 = \begin{pmatrix}
E_{0^+} & 0 \\
0 & E_{0^-}
\end{pmatrix}
\]

where \( E_{0^+} \) and \( E_{0^-} \) are the energies of the \( 0^+ \) and \( 0^- \) levels when the electron is in its ground state. Let us simulate the effect of the environment by assuming that the matrix elements of the Hamiltonian undergo fluctuations

\[
\tilde{H}_H = \begin{pmatrix}
E_{0^+} + \rho_{0^+}(t) & \theta(t) \\
\theta(t) & E_{0^-} + \rho_{0^-}(t)
\end{pmatrix}
\]

We can write the same expression for the electron in its first excited state.

In order to calculate the time evolution of the energy matrix elements, one has to solve a Liouville equation with stochastic matrix elements. We have used the method proposed recently by Lami and Villani\(^{47}\) with

\[
\frac{\partial \rho}{\partial t} = A \rho
\]

with

\[
\rho = \begin{pmatrix}
\rho_{0^+}(t) & \theta(t) \\
\theta(t) & \rho_{0^-}(t)
\end{pmatrix}
\]

and the stochastic vector

\[
\tilde{r}(t) = \begin{pmatrix}
\tilde{r}_{0^+}(t) \\
\tilde{r}_{0^-}(t)
\end{pmatrix}
\]

The matrix \( A \) for the Hamiltonian (eq 43) is given by the expression

\[
A = \begin{pmatrix}
0 & 0 & -\theta(t) & \theta(t) \\
0 & 0 & \theta(t) & -\theta(t) \\
-i \hbar & -\theta(t) & (E_{0^+} + \theta(t)) - (E_{0^-} + \theta(t)) & 0 \\
0 & -\theta(t) & (E_{0^+} + \theta(t)) - (E_{0^-} + \theta(t)) & 0
\end{pmatrix}
\]

If the stochastic vector \( \tilde{r}(t) \) is a Markov process then, it has been shown\(^{48}\) that the joint process \( (\rho, \tilde{r}) \) is also Markovian and its probability density \( p(\rho, \tilde{r}, t) \) (i.e., the probability density that at time \( t \) the density matrix will be that specified by the vector \( \rho \) for the realization of \( \tilde{r} \) indicated by \( \tilde{r} \)) satisfies the equation

\[
\frac{\partial p(\rho, \tilde{r}, t)}{\partial t} = -\sum_{\rho', \tilde{r}'} A_{\rho \rho'} \frac{\partial}{\partial \rho'} p(\rho, \tilde{r}, t) + \tilde{W}(\rho, \tilde{r}, t)
\]


\(^{48}\) van Kampen, N. G. Stochastic Processes in Physics and Chemistry; North Holland: Amsterdam, 1981.
where $\hat{W}$ is the operator that appears in the master equation for the transition probability density of $\mathbf{r}$, i.e.

$$\Pi(\dot{\mathbf{r}}, \mathbf{F}_0, 0) = \hat{W} \Pi(\mathbf{r}, \mathbf{F}_0, 0)$$

(49)

Let us return to the special situation considered in our model. The frequency values of electronic transitions $\omega_m^m$ appearing in (38) fluctuate with time according to the fluctuations of the energy levels governed by the Hamiltonian (eq 43). Thus, one may write

$$\omega_m^m(t) = \langle \omega_m^m \rangle + \Delta \omega_m^m(t)$$

(50)

where

$$\Delta \omega_m^m(t) = \langle \omega_m^m \rangle - \langle \omega_m^m \rangle$$

Returning to (36), we perform the averaging over the environment (term $B_m^m$ in eq 38)

$$\langle B_m^m \rangle = f_m \exp[-i(2\alpha_2 \omega_0 + (\gamma - \alpha) \omega_0)] \langle \exp[-i\omega_m^m(t)] \rangle$$

(51)

It is convenient to express the electronic transitions $\omega_m^m$ in the following way

$$\omega_m^m(t) = \langle \omega_m \rangle + \Delta \omega_m(t) + \Delta \omega_m^m(t)$$

(52)

where

$$\langle \omega_m \rangle = 0 \quad \Delta \omega_m(t) = 0$$

$$\langle \omega_m^m \rangle = -\langle \omega_m \rangle \quad \Delta \omega_m(t) = -\Delta \omega_m(t)$$

$$\langle \omega_m^m \rangle = -\langle \omega_m \rangle \quad \Delta \omega_m(t) = -\Delta \omega_m(t)$$

$$\Delta \omega_m^m(t) = -\langle \omega_m^m \rangle + \langle \omega_m \rangle$$

(53)

where $\omega_m$ and $\omega_m^m$ are the tunneling frequencies of the ground and first excited electronic states.

The average of the exponential may be expressed as the exponential of an average (central limit theorem, cumulant expansion).

Substituting (52) into (51), the average $\langle B_m^m \rangle$ will take the form

$$\langle B_m^m \rangle = f_m \exp[-i(2\alpha_2 \omega_0 + (\gamma - \alpha) \omega_0)] \langle \exp[-i\omega_m^m(t)] \rangle -$$

$$\int_0^t dt_1 \int_0^t dt_2 \langle \Delta \omega_m(t_1) \Delta \omega_m(t_2) \rangle$$

(54)

Two different processes govern the time dependence of the correlation functions $\langle \Delta \omega_m(t_1) \Delta \omega_m(t_2) \rangle$ and $\langle \Delta \omega_m^m(t_1) \Delta \omega_m^m(t_2) \rangle$. The tunneling correlation functions $\langle \Delta \omega_m(t_1) \Delta \omega_m(t_2) \rangle$ due to the fluctuations of the energy levels of the ground or first excited electron states, whereas in the frequency correlation function $\Delta \omega_m^m(t_1) \Delta \omega_m^m(t_2)$ both electronic states are involved. The fluctuations in this case are due to the change of the potential well, which is generally not the same for the ground and first excited electron states. Because electronic transitions are assumed to be instantaneous with respect to tunneling there are no “cross” correlations $\langle \Delta \omega_m(t_1) \Delta \omega_m(t_2) \rangle$ in (54).

Now, let us concentrate on the tunneling correlation functions. The energy level fluctuations are created by the solvent molecular motions, and we can model this situation by assuming that only the diagonal matrix elements of $\mathbf{h}_0$ and $\mathbf{h}_1$ (eq 43) are stochastic.

According to eq 43, we can write

$$\Delta \omega_m(t) = \omega_m(t) - \langle \omega_m \rangle = h^{-1}[e_\rho(t) - e_\rho(t)]$$

$$\Delta \omega_m^m(t) = \omega_m^m(t) - \langle \omega_m^m \rangle = h^{-1}[e_\rho(t) - e_\rho(t)]$$

(55)

From eq 55, we see that the stochastic vector $\mathbf{r}$ (eq 46) fluctuates among four situations

$$r_1 = \begin{pmatrix} a \\ a \end{pmatrix}, \quad r_2 = \begin{pmatrix} a \\ -a \end{pmatrix}, \quad r_3 = \begin{pmatrix} -a \\ a \end{pmatrix}, \quad r_4 = \begin{pmatrix} -a \\ -a \end{pmatrix}$$

(56)


G_{m}(t) = \exp[-2a^2(\tau_e^2 \exp(-t/\tau_e) - 1) + \tau_e t)] \quad (65)
G_{j}(t) = \exp[-b^2(\tau_g^2 \exp(-t/\tau_g) - 1) + \tau_g t)] \quad (66)

Two limiting situations can then be written down, namely, that the correlation times \( \tau_e \) and \( \tau_g \) decay much slower or much faster than the amplitude coherence, i.e.,

\[
\langle \Delta \omega^2 \rangle_{1/2} / \tau_e \gg 1 \quad (\Delta \omega^2)_{1/2} / \tau_g \gg 1 \quad \text{slow limit}
\]

\[
\langle \Delta \omega^2 \rangle_{1/2}^2 / \tau_e \ll 1 \quad (\Delta \omega^2)_{1/2} / \tau_g \ll 1 \quad \text{fast limit}
\]

In our case, the amplitudes are given by the change \( a \) in tunneling phase angular speed and the change \( b \) in the electronic transition phase angular speed

\[
\langle \Delta \omega^2 \rangle_{1/2} = 2^{1/2} a \quad (\Delta \omega^2)_{1/2} = b \quad (68)
\]

In the slow limit, eqs 65 and 66 simplify to

\[
G^{m}(t) = \exp(-2a^2 t^2/2) \quad G^{j}(t) = \exp(-b^2 t^2/2)
\]

with an associated Gaussian profile.

The equations 69 describe static situations, that is to say, time-independent distributions \( \langle \Delta \omega^2 \rangle_{1/2} \) and \( \langle \Delta \omega^2 \rangle_{1/2} \) of the line shifts around the unperturbed electron transition frequency.

The fast limiting situation predicts Lorentzian band profiles

\[
G_{m}(t) = \exp(-2a^2 \tau_e t) \quad G_{j}(t) = \exp(-b^2 \tau_g t)
\]

with the half widths

\[
\Delta f_{1/2} = 4a^{2} \tau_e \quad \Delta f_{1/2} = 2b^{2} \tau_g
\]

It is of interest to compare, as far as possible, the present theory to the treatments presented in other papers. The present development is more general as opposed to treatments considering only one aspect of the problem, such as vibrational coupling,\(^{13,29}\) tunneling,\(^{28}\) or inhomogeneous broadening due to the statistical variety of trapping sites.\(^{21,25,33,41}\) In the theory of Banarjee and Simons,\(^{38}\) the vibrational coupling is treated as in our treatment with the aid of the canonical transformation in the framework of strong coupling limit theory. However, they neglect the time evolution of operator \( A \), creating the "dressed" electron, which does not allow one to include inhomogeneous broadening effects due to the fluctuations of the anharmonic coupling strength. This effect arises naturally in the course of the present development, where the time evolution of \( A \) is governed by the Liouville equation for the vibrational mode coupled to the bath.

Another important difference between our theory and that of Banarjee and Simons is the procedure of equilibrium averaging over bath. Their bath is restricted to the translational and rotational modes, and they ignore the time dependence in the procedure of averaging, which is justifiable, taking into account different time scales for the electronic transitions compared to the molecular motions. In our model, averaging over the bath includes also fluctuations of the potential well in which the solvated electron is stabilized. Formally, the origin of these fluctuations is due to ignoring the assumptions that were introduced in the strong coupling treatment of the electron-vibrational mode coupling: (i) the vibrational frequencies in the ground and excited states of the cavity (or anion) are the same; (ii) only one vibrational mode is modified in the absorption process; (iii) the equilibrium geometry of the potential well in the excited electronic state is displaced linearly with respect to the normal vibrational coordinate. In this case, the time scale of the fluctuations cannot be ignored and the short time expansion of the cumulants is not justifiable.

In the following paper,\(^{31}\) we will present the numerical calculations concerning the effect of the environment, fluctuations of the potential well, and influence of the vibrational properties of the matrix on the absorption band shapes of the solvated electron from eq 62 obtained in this paper.

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Appendix A

Here we will derive eq 60 for the frequency correlation function \( \langle \Delta \omega^{m}(t_1) \Delta \omega^{m}(t_2) \rangle \). The electronic transition between the potential wells characterized by the different equilibrium geometries can be simulated as a two level problem in the same potential well fluctuating between two values corresponding to the ground and first excited electronic states. Thus, the stochastic vector \( f \) (eq 46) fluctuates between the realizations

\[
\bar{f} = (\theta(t))
\]

where

\[
r_1 = b \quad r_2 = -b
\]

with the probability

\[
W = f_3/2 \begin{pmatrix} 1 & 1 & 1 & 1 \\ 1 & -1 & 1 & -1 \\ 1 & 1 & -1 & -1 \\ 1 & -1 & 1 & -1 \end{pmatrix}
\]

and with the matrix \( A \) (eq 47)

\[
A = -i/\hbar \begin{pmatrix} 0 & 0 & \theta(t) & \theta(t) \\ 0 & 0 & \theta(t) & -\theta(t) \\ -\theta(t) & \theta(t) & 0 & 0 \\ \theta(t) & -\theta(t) & 0 & 0 \end{pmatrix}
\]

Appendix B

Here we will derive eq 58 for the tunneling correlation function \( \langle \Delta \omega^{m}(t_1) \Delta \omega^{m}(t_2) \rangle \). The correlation function can be calculated if we know the initial distribution of the frequencies \( P_{0} \) and the conditional transition probabilities \( \Pi_{j/k} \) at \( t = t_1 - t_2 \), since \( \langle \Delta \omega^{m}(t_1) \Delta \omega^{m}(t_2) \rangle = \langle \Delta \omega^{m}(t) \Delta \omega^{m}(0) \rangle \)

Thus, one may write

\[
\langle \Delta \omega^{m}(t_1) \Delta \omega^{m}(t_2) \rangle = \sum_{j,k} \Pi_{j/k} \langle \Delta \omega^{m}(j) \Delta \omega^{m}(k) \rangle P_{0} \langle \Delta \omega^{m}(k) \rangle \quad (A1)
\]

where \( \Pi_{j/k} \) is governed by the master equation (eq 49) with \( W \) given by (57). \( P_{0} \langle \Delta \omega^{m}(k) \rangle \) is equal to \( 1/4 \) since each of the four realizations of the stochastic vector (eq 56) have the same probability at \( t = 0 \). Solving the master equation by matrix diagonalization

\[
\frac{\partial \Pi_{j/k}}{\partial t} = \sum_{i} W_{i/j} \Pi_{i/k} \quad (A2)
\]

we have

\[
\Pi_{i/k} = \sum_{m} C_{im} [\exp(W_{mm})] C_{mk} \quad (A3)
\]

where

\[
W = \begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & -f & 0 & 0 \\ 0 & -f & 0 & 0 \\ 0 & 0 & 0 & f \end{pmatrix}
\]

and

\[
C = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 & 1 & 1 & 1 \\ 1 & 1 & -1 & -1 \\ 1 & -1 & 1 & -1 \\ 1 & -1 & 1 & -1 \end{pmatrix}
\]

Substituting (A3) into (A1), we obtain

\[
\langle \Delta \omega^{m}(t_1) \Delta \omega^{m}(t_2) \rangle = 2a^2 \exp(-f_3(t_1 - t_2)) \quad (A6)
\]
electron jumps from the ground to first excited state with the probability per unit time $j_0$. Thus, one can write

$$\langle \Delta \omega \rangle(t_1, \Delta \omega \rangle(t_2)) = \sum \Pi(j/k) \Delta \omega \rangle(j) \Delta \omega \langle(k) P_0(\Delta \omega \langle(k))$$

(B4)

where $P_0(\Delta \omega \langle(k))$ is the initial distribution of the angular speed. The initial distribution is taken as

$$P_0(\Delta \omega \langle(k)) = \delta(\Delta \omega \langle(k) - b)$$

(B5)

and

$$\langle \Delta \omega \rangle(t_1, \Delta \omega \rangle(t_2)) = \Pi(2/1) \Delta \omega \rangle(2) + \Pi(1/1) \Delta \omega \rangle(1) \Delta \omega \langle(1)$$

(B6)

where $\Pi(2/1)$ is the conditional probability that at $t = t_1 - t_2$ the electron jumps from the ground state to its first excited state. The conditional probability $\Pi(j/k)$ is governed by (B2). Solving the master equation, we have

$$\Pi(l/k) = \sum_m C_{lm} \{\exp(w_m t)\} C_{mk}$$

(B7)

where

$$w = cWc = \begin{pmatrix} -f_k & 0 \\ 0 & 0 \end{pmatrix}$$

(B8)

and

$$c = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 & -1 \\ -1 & 1 \end{pmatrix}$$

(B9)

Then, substituting (B7) into (B6), we obtain

$$\langle \Delta \omega \rangle \Delta \omega \rangle(t_2)) = b^2 \exp[-f_k(t_1 - t_2)]$$

(B10)

Absorption Spectrum of the Solvated Electron. 2. Numerical Calculations of the Profiles of the Electron in Water and Methanol at 300 K

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The absorption band profiles of the solvated electrons in the spectral range 0.62-2.48 eV were calculated in terms of the theory presented in our previous paper. We considered the influence of the environment, the effect of fluctuations of the energy potential shape, and the band profiles as a function of the coupling strength with intramolecular vibrations of the solvent. The theory gives good agreement with experiment for the electron solvated in water and alcohols at 300 K.

1. Introduction

The absorption spectra of solvated electrons in liquids and glasses are characterized by the position of the band maximum and the characteristic band shape. Experimentally, almost all solvated electron spectra are broad 0.4-1.86 eV and skewed to the high-energy side, displaying little or no vibrational structure. One of the most interesting results of the time-resolved and stationary measurements at low temperatures is the detection of an absorption band of the solvated electron in the near-infrared spectral range for many liquids and glasses. This problem has received much attention in literature.$^1$ The first major theoretical problem is how to explain the exceptional width of the absorption band.

Most of the theoretical models$^2$-11 predict a line shape that is too narrow and symmetric compared to experiment. Some of them$^2$-6 claim successful fits. A second related problem is how to understand the physical reason for the existence of the IR-absorbing electrons ($e^{-IR}$). Any successful theory should be able to explain all of these characteristics of the absorption spectrum. In the previous paper$^9$ we proposed a theoretical model that takes into account the following mechanisms as the dominant broadening factors: anharmonic coupling of the solvated electron to intramolecular vibrational modes of the solvent, inhomogeneous broadening due to the molecular motion, and nonlocalized transitions due to the electron tunneling.

The purpose of the present paper is to examine to what extent the experimental band profiles of solvated electrons in the visible region can be understood in terms of the theory presented in our previous paper$^9$ and which of the above-mentioned mechanisms gives a dominant contribution to the band broadening. In a further paper we will concentrate on the spectrum in the near-infrared region.

2. Numerical Calculations of the Absorption Band Shape

In the framework of the linear response theory the absorption coefficient is expressed as

$$\varepsilon(\omega) = \frac{2\pi\omega}{3\hbar c n V} (1 - \exp(-\beta \hbar \omega)) \int_{-\infty}^{\infty} \langle M^*(t) M(0) \rangle \exp(i\omega t) dt$$

(1)

where $M$ denotes the dipole moment of the sample, $V$ its volume, and $n$ the refractive index. We have calculated$^9$ that the dipole


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