

Vertical Detachment Energy of Hydrated Electron Based on a Modified Form of Solvent Reorganization Energy

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In this work, the constrained equilibrium principle is introduced and applied to the derivations of the nonequilibrium solvation free energy and solvent reorganization energy in the process of removing the hydrated electron. Within the framework of the continuum model, a modified expression of the vertical detachment energy (VDE) of a hydrated electron in water is formulated. Making use of the approximation of spherical cavity and point charge, the variation tendency of VDE accompanying the size increase of the water cluster has been inspected. Discussions comparing the present form of the VDE and the traditional one and the influence of the cavity radius in either the fixed pattern or the varying pattern on the VDE have been made.

Introduction

The hydrated electron has been a subject of dramatic interest since its discovery in 1962.¹ Experimental evidence has shown that not only bulk polar fluids can readily solvate the excess electron,^{1,2} but also the gas-phase clusters of water molecules can carry an extra charge.^{3–5} Theoretical studies^{6–21} and experimental observations^{3,5,22–27} provide much fundamental understanding of and insights into chemical and physical properties of the hydrated electron. These important investigations, referring to electronic processes, generally involve the reaction mechanism of electron binding in polar solutions,²⁸ electronic excitation of solvated ions,²⁹ the energy level of electron hydration, and vertical detachment in bulk solution.⁶ Moreover, the methods extrapolating hydrated electron from sufficiently large clusters to the bulk solvent can be expected to predict the properties of bulk water, such as the electron binding energy (EBE),³ gyration radius of electron,^{7,30} optical absorption spectrum ($h\nu_{ab}$),^{30,31} and vertical detachment energy (VDE).^{3,22,30,32,33}

In recent years, the real bulk value of VDE is still an intriguing topic, because this quantity is inherently difficult to determine by experiment. Theoretical studies^{28,32,34–37} on the problem of electron binding in solutions have been performed by Jortner and co-workers. However, when they attempted to use the popular nonequilibrium solvation theory to explain the vertical EBE (or VDE), they had to adopt 1.588 Å³⁴ as the radius of the single water molecule, which is different from the one, ~1.925 Å, estimated from the water density. Later Landman and other authors^{32,37} reported results on the relation between VDE and $n^{-1/3}$. Factually, researchers like to use the fitting of VDE against $n^{-1/3}$ in analyzing the experimental measurements and in extrapolating the result of water clusters to the bulk water limit, and their theoretical fittings are also based on the traditional nonequilibrium solvation model. In this work we try to establish and apply the modified single sphere model to the VDE calculation of the hydrated electron, which is based on our recently derived reasonable formula for the nonequilibrium solvation free energy.

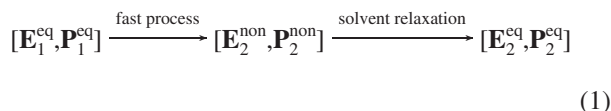
The fundamental interpretation of the solvated electron about its existing form in the condensed phase is still not completely identical at present. Recently, some authors have suggested that “the electron resides in a diffuse orbital localized on a H₃O radical”,³⁸ and in addition the opinion of the hydrated electron locating at the center or the surface of the water cluster is also accepted.²² In the framework of the continuum model, the excess electron is generally treated as a point charge locating at the center in the single sphere model. That is, this additive electron is bound within a dielectric medium by occupying a sphere cavity and trapped in the potential well formed by the polar solvent environment. However, the cavity radius of the hydrated electron (R) is not easy to appropriately account for, because there is no strict and consistent criterion to determine the distributing space of the hydrated electron, which is one of the most important parameters in the solvation models. Fortunately, by analogizing the hydrated electron to real ions, e.g., halide ions, the sphere cavity radius can be easily achieved by the fitting of the thermodynamic parameters.^{39,40} Additionally, the value of R can also be approximately estimated from the moment analysis⁷ of the absorption spectra of the hydrated electron.

In this work, a novel analytical form of VDE for the detachment process of the hydrated electron in the single sphere cavity model with point charge approximation is developed. In the derivation, a modified expression for solvent reorganization energy (λ) is also proposed according to the constrained equilibrium principle of thermodynamics.^{41–43} This paper is arranged as follows. In the section Theory, we introduce the constrained equilibrium manipulation applied to the case of hydrated electron detachment, and the expression of the solvent reorganization energy, which plays a key role in calculating VDE, is derived. Then a novel form for VDE follows. After the theoretical section, we pay attention to the fittings of VDE according to the analytical form in the Results and Discussion. The VDE values by the present model are presented. Comparative discussions on the results by our model and by the traditional one are made in this section. Some conclusions are drawn at the end of the paper.

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Theory

Nonequilibrium Solvation Free Energy of Medium and Solvent Reorganization Energy. In this part, all the expressions are derived in the framework of continuous medium theory, and the solvation free energy in the following part takes only the electrostatic contribution into account. Before and just after light absorption/emission process in the solution, or the vertical detachment of a hydrated electron, the solute–solvent system will experience a change from the equilibrium state $[\mathbf{E}_1^{\text{eq}}, \mathbf{P}_1^{\text{eq}}]$ to the nonequilibrium state $[\mathbf{E}_2^{\text{non}}, \mathbf{P}_2^{\text{non}}]$. After a sufficiently long time, the system arrives at the final equilibrium state through solvent relaxation. This process can be expressed as follows:



Here, \mathbf{P} is the total electric polarization of the solvent and \mathbf{E} is the total electric field. The superscripts “eq” and “non” denote the equilibrium and nonequilibrium polarizations, respectively, and the subscripts “1” and “2” refer to the initial and final solute (free) charge distributions.

For the discussion of a fast physical or chemical process in solution, a crucial aspect is the deduction of the nonequilibrium solvation free energy. Considering the different time scales of solvent response to the solute charge distribution, the solvent polarization \mathbf{P} can be separated into two components: the inertial polarization \mathbf{P}^{in} of low frequencies (orientational and vibrational) and the dynamic polarization \mathbf{P}^{op} of high frequencies (optical or electronic). When the solute undergoes a sudden change from charge distribution 1 to charge distribution 2, the electric field produced by the solute charge in vacuum, \mathbf{E}^{vac} , changes correspondingly. The dynamic polarization is assumed to equilibrate, without time lag, with the solute charge and changes from \mathbf{P}^{op} to \mathbf{P}_2^{op} . However, the inertial polarization of low frequencies cannot catch the fast variation of the solute charge, so it is generally not equilibrated with and is quite independent of the final solute charge distribution. In other words, the inertial polarization will maintain the initial one, i.e., \mathbf{P}_1^{in} , during the fast process. After a long time, the inertial polarization will arrive at the final equilibrium one, \mathbf{P}_2^{in} , through solvent relaxation.

In the past, some researchers performed the reversible electric work integration along the path linking the initial equilibrium state and the mediated nonequilibrium state, to gain the electrostatic free energy change and then the electrostatic free energy of the nonequilibrium state.^{44–46} Please note that we refer here to the “electrostatic free energy” as the total free energy which can be divided into two parts: the self-energy of the solute charge and the solvation free energy due to the solvent polarization. We argue that this approach is inappropriate because it is well-known to us that the reversible work integration for the free energy change can only be done along a thermodynamically reversible path, while the establishment of the nonequilibrium state is obviously not the case. After being conscious of the defect in the traditional theory, we tried to improve the situation. In a series of recent papers,^{47–50} we used the Jackson equation for the electrostatic free energy change, instead of the traditional reversible work method, but we are now aware that the problem remains since the Jackson equation seems to require the electrostatic equilibrium as well.

For the reasonable establishment of the solvation free energy for a nonequilibrium polarization, we explored a new route to

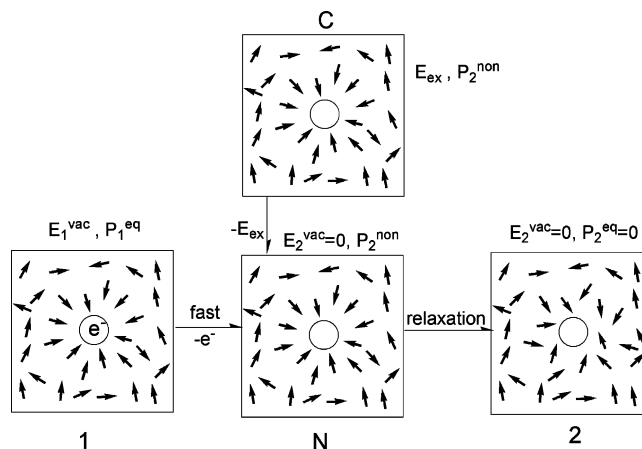


Figure 1. Schematic depiction of the formation of the nonequilibrium polarization.

the final solution of this issue, by invoking the constrained equilibrium principle of classical thermodynamics.^{41–43} As is well-known to us, classical thermodynamics is an extremely important theory for macroscopic properties of systems in equilibrium, but it encounters difficulties for diverse nonequilibrium phenomena, among which the nonequilibrium polarization discussed above is an example. For a nonequilibrium system, thermodynamics often takes the hypothesis of local equilibrium, which divides the whole system into a number of macroscopic subsystems. If the subsystems stand at equilibrium, each of them will obey classical thermodynamics. The concept of local equilibrium makes sense for some cases, but it is difficult to establish a general approach for nonequilibrium situations. Leontovich^{51,52} once introduced a constrained equilibrium approach to treat nonequilibrium states within the framework of classical thermodynamics, but it has not yet been generalized and applied in practice. Only recently we realized that this approach can be recast into a form suitable for deriving the nonequilibrium polarization.

For simplicity we confine ourselves to the vertical detachment of the hydrated electron in the present paper. For the more generalized case of nonequilibrium polarization, readers are referred to the most recent papers by the authors.^{41–43} Electron in water should be one of the simplest solute–solvent systems owing to the point free charge and spherical cavity. In this case the solvent polarization can be schematically depicted by Figure 1. Here state 1 is the equilibrium state of the electron–solvent system, and after a vertical detachment of the hydrated electron, the nonequilibrium state N is formed in the way that the vacuum electric field $\mathbf{E}_1^{\text{vac}}$ by the hydrated electron is removed very quickly, but the inertial polarization \mathbf{P}_1^{in} of the solvent remains the same as the state 1 owing to the retardation of inertial polarization. After a sufficiently long time, the solvent polarization relaxes and the system arrives at the final equilibrium state 2. Please note that state 2 and state N have the same vacuum field ($\mathbf{E}_2^{\text{vac}} = 0$). The electrostatic solvation free energy change from state 2 to state N is defined as the so-called solvent reorganization energy.

We at first recall the essentials of constrained equilibrium.⁴¹

(1) By imposing suitable external conservative (without friction) forces $\{x_k\}$, a nonequilibrium state of an isothermal nonequilibrium system without flow can always be mapped to a constrained equilibrium, meanwhile keeping the internal variables of the state fixed.

(2) The differences in the state functions between the so-constructed constrained equilibrium and any other equilibrium states can be calculated simply by means of classical thermodynamics.

(3) The applied external forces can be removed suddenly without friction from the constrained equilibrium system to recover the true nonequilibrium situation, which will further relax irreversibly to the eventual equilibrium state.

The energy of an equilibrium state is described by a set of external variables $\{a_i\}$ and an internal variable T (temperature). In other words, we have a caloric equation for the equilibrium state, $U = U(a_i, T)$. The thermodynamic fundamental equation is of the familiar form

$$dU = T dS - \sum_i A_i da_i \quad (2)$$

where $\{A_i\}$ denote the internal variables such as the pressure, the chemical potential, the surface tension, and so on, while $\{a_i\}$ stand for the corresponding external variables such as the volume, the number of the molecules, the surface area, and so on. S stands for entropy.

In nonequilibrium state N, the internal variable, $\mathbf{P}_2^{\text{non}}$, deviates from its equilibrium value of $P = 0$ in state 2 (see Figure 1 and note that the hydrated electron has been removed and hence the electric field disappears at state 2). In the construction of the constrained equilibrium state, we superpose a hypothetical external electric field \mathbf{E}_{ex} to state N to exactly reproduce the nonequilibrium polarization. After this manipulation, a constrained polarization equilibrium state $[\mathbf{E}_{\text{ex}}, \mathbf{P}_2^{\text{non}}]$ (hereafter referred as state C, see Figure 1) is formed.

For simplicity, we take the medium as the “system” but both the solute (free) charge and the source of \mathbf{E}_{ex} as the “ambient”. This means that the thermodynamic system is defined to only contain the medium, while the free charges and the constraining field act as the external field. The exclusion of the free charges from the “thermodynamic system” guarantees coherent thermodynamic treatment. However, in previous derivations, the “thermodynamic system” usually includes both the free charges and the medium.^{44–50} Beginning with the constrained equilibrium state C, a fast removal of the constraining force, \mathbf{E}_{ex} , from the system then yields the true nonequilibrium state N. The removal of \mathbf{E}_{ex} should be so fast that the solvent polarization has no time to respond. The energy change of the medium in the fast (adiabatic) process is given as follows:

$$\Delta U_{\text{sol}} = U_{\text{sol}}^{\text{non}} - U_{\text{sol}}^* = -W \quad (3)$$

where U_{sol}^* and $U_{\text{sol}}^{\text{non}}$ denote the energies of the constrained equilibrium state C and the true nonequilibrium state N, respectively. W in eq 3 is the work done by the system during the non-quasistatic removal of the constraining force, and it can be easily expressed as

$$W = \int_V \int_{\mathbf{E}_{\text{ex}}}^0 \mathbf{P}_2^{\text{non}} \cdot d\mathbf{E}_{\text{ex}} dV = - \int_V \mathbf{P}_2^{\text{non}} \cdot \mathbf{E}_{\text{ex}} dV \quad (4)$$

Equation 4 simply indicates the interaction energy change of the polarization and the external field. If one notes that $\mathbf{P}_2^{\text{non}}$ remains invariant during the fast removal of its conjugated variable \mathbf{E}_{ex} , the energy change by eq 4 becomes straightforward. Given the entropy $S_{\text{sol}}^{\text{non}}$ and the internal energy $U_{\text{sol}}^{\text{non}}$ of state N, we can directly define the nonequilibrium solvation free energy according to classical thermodynamics,^{51,52}

$$F_{\text{sol}}^{\text{non}} = U_{\text{sol}}^{\text{non}} - TS_{\text{sol}}^{\text{non}} \quad (5)$$

The solvation free energy of the constrained equilibrium state C is defined in the same way,

$$F_{\text{sol}}^* = U_{\text{sol}}^* - TS_{\text{sol}}^* \quad (6)$$

It is easy to understand that state C and state N have the same temperature T . In particular, the entropies of the two states are the same because of the same configuration of the solvent.^{51,52} Therefore, subtracting eq 6 from eq 5 yields the nonequilibrium solvation free energy

$$F_{\text{sol}}^{\text{non}} = F_{\text{sol}}^* + \int_V \mathbf{P}_2^{\text{non}} \cdot \mathbf{E}_{\text{ex}} dV \quad (7)$$

We see that state N and state C have a solvation free energy difference of $\int_V \mathbf{P}_2^{\text{non}} \cdot \mathbf{E}_{\text{ex}} dV$. This is just the result of the example of nonequilibrium polarization taken by Leontovich in refs 51 and 52 (see the illustrations in p 122 of ref 51 and p 104 of ref 52).

For the more general cases, e.g., $\mathbf{E}_{\text{ex}}^2 \neq 0$, the books by Leontovich^{51,52} and the papers by us^{41–43} can be referred to. Given the formal expression of the nonequilibrium solvation free energy $F_{\text{sol}}^{\text{non}}$, the solvent reorganization energy for the vertical detachment of the hydrated electron can be given as

$$\lambda = F_{\text{sol}}^{\text{non}} - F_{\text{sol},2}^{\text{eq}} \quad (8)$$

where $F_{\text{sol},2}^{\text{eq}}$ is the solvation free energy of the final equilibrium (state 2, see Figure 1). Owing to the electric neutrality of state 2, we have $F_{\text{sol},2}^{\text{eq}} = 0$. In addition, like a real equilibrium state, the solvation free energy of state C is given by⁵³

$$F_{\text{sol}}^* = -\frac{1}{2} \int_V \mathbf{P}^* \cdot \mathbf{E}_{\text{ex}} dV = -\frac{1}{2} \int_V \mathbf{P}_2^{\text{non}} \cdot \mathbf{E}_{\text{ex}} dV \quad (9)$$

Substituting eq 9, eq 7, and $F_{\text{sol},2}^{\text{eq}} = 0$ into eq 8, the solvent reorganization energy is simply expressed as

$$\lambda = F_{\text{sol}}^{\text{non}} = \frac{1}{2} \int_V \mathbf{P}_2^{\text{non}} \cdot \mathbf{E}_{\text{ex}} dV \quad (10)$$

Equation 10 is the central equation for us in evaluating the vertical detachment energy of the hydrated electron, but some deductions by means of electrostatics should be done. The following part is just for the concrete form of λ .

In eq 10, $\mathbf{P}_2^{\text{non}}$ is an intrinsic quantity of the true nonequilibrium state N but \mathbf{E}_{ex} is the external field resulting from distribution of some hypothetical free charges in the “ambient”. \mathbf{E}_{ex} is imposed to match $\mathbf{P}_2^{\text{non}}$. One thing should be clarified, that the polarization induced \mathbf{E}_{ex} includes both inertial and dynamic parts while $\mathbf{P}_2^{\text{non}}$ in the real nonequilibrium is just the inertial part. In the following, we will express $\mathbf{P}_2^{\text{non}}$ with the equilibrium properties and concretize \mathbf{E}_{ex} using the intrinsic quantities of the system.

In the case of an isotropic dielectric of linear behavior, the following relationships hold according to electrostatics and equilibrium response, i.e.

$$\mathbf{P}_i^{\text{eq}} = \chi_s \mathbf{E}_i^{\text{eq}} \quad i = 1, 2 \quad (11)$$

$$\mathbf{P}_i^{\text{op}} = \chi_{\text{op}} \mathbf{E}_i^{\text{op}} \quad i = 1, 2 \quad (12)$$

with

$$\chi_s = (\epsilon_s - 1)/4\pi \quad \text{and} \quad \chi_{\text{op}} = (\epsilon_{\text{op}} - 1)/4\pi \quad (13)$$

where \mathbf{E}_i^{eq} and \mathbf{E}_i^{op} stand for the electric fields under the conditions of full response and dynamic response (only the dynamic polarization of the solvent responds) respectively. ϵ_s and χ_s denote the static dielectric constant and susceptibility, and ϵ_{op} and χ_{op} stand for the optical dielectric constant and susceptibility, respectively. According to the separation of the solvent polarization, the equilibrium and nonequilibrium polarizations can be written as

$$\mathbf{P}_1^{\text{eq}} = \mathbf{P}_1^{\text{in}} + \mathbf{P}_1^{\text{op}} \quad (14)$$

$$\mathbf{P}_2^{\text{non}} = \mathbf{P}_1^{\text{in}} + \mathbf{P}_2^{\text{op}} \quad (15)$$

Unlike eq 11, it is essential to note that $\mathbf{P}_2^{\text{non}} \neq \chi_s \mathbf{E}_2^{\text{non}}$. Here the nonequilibrium field $\mathbf{E}_2^{\text{non}}$ is the total electric field involving both the vacuum field by the solute charge and the field by the nonequilibrium polarization. The nonequilibrium electric field is of the following form:

$$\mathbf{E}_2^{\text{non}} = \mathbf{E}_1^{\text{eq}} + \Delta \mathbf{E}_{\text{op}} \quad (16)$$

with $\Delta \mathbf{E}_{\text{op}} = \mathbf{E}_2^{\text{op}} - \mathbf{E}_1^{\text{op}}$ ($\mathbf{E}_2^{\text{op}} = 0$ in the present case). Note also that both \mathbf{E}_1^{eq} and \mathbf{E}_1^{op} involve the vacuum field $\mathbf{E}_i^{\text{vac}}$ by the solute charge.

On the other hand, the equilibrium response feature remains for the constrained equilibrium state C, i.e.

$$\mathbf{P}^* = \chi_s \mathbf{E}^* \quad (17)$$

where \mathbf{E}^* is the total electric field that comprises the external (vacuum) field \mathbf{E}_{ex} and the polarization field $\mathbf{E}_{\mathbf{P}^*}$ by \mathbf{P}^* . When we recall that $\mathbf{P}^* = \mathbf{P}_2^{\text{non}}$ and notice the following relationship

$$\mathbf{E}_{\mathbf{P}^*} = \mathbf{E}_1^{\text{eq}} - \mathbf{E}_1^{\text{op}} \quad (18)$$

we have

$$\mathbf{P}_2^{\text{non}} = \mathbf{P}_1^{\text{eq}} - \mathbf{P}_1^{\text{op}} = \chi_s (\mathbf{E}_{\text{ex}} + \mathbf{E}_{\mathbf{P}^*}) = \chi_s (\mathbf{E}_{\text{ex}} + \mathbf{E}_1^{\text{eq}} - \mathbf{E}_1^{\text{op}}) \quad (19)$$

Here we have made use of eq 15 and $\mathbf{P}_2^{\text{op}} = 0$ because the final equilibrium state 2 is electrically neutral. A few words are needed for the equality of $\mathbf{P}^* = \mathbf{P}_2^{\text{non}}$. One should note that $\mathbf{P}_2^{\text{non}} = \mathbf{P}_1^{\text{in}}$ is the inertial polarization while \mathbf{P}^* includes both inertial and dynamic polarizations by \mathbf{E}_{ex} . If we recall we are making the thermodynamic discussion, it is unnecessary to distinguish the types of polarization.

Equation 19 can be further changed to

$$\mathbf{E}_{\text{ex}} = \frac{\epsilon_s - \epsilon_{\text{op}}}{\epsilon_s - 1} \mathbf{E}_1^{\text{op}} \quad (20)$$

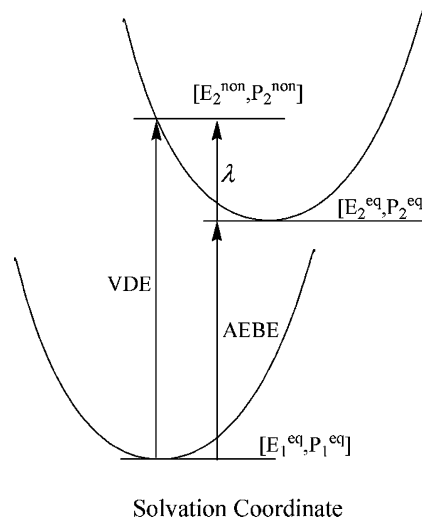


Figure 2. Schematic depiction of VDE.

Substituting eqs 19 and 20 into eq 10 yields

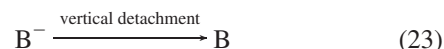
$$\lambda = \frac{1}{2} \frac{\epsilon_s - \epsilon_{\text{op}}}{\epsilon_s - 1} \int_V \mathbf{E}_1^{\text{op}} \cdot (\mathbf{P}_1^{\text{eq}} - \mathbf{P}_1^{\text{op}}) dV \quad (21)$$

Equation 21 can be easily converted to charge–potential form, i.e.^{41–43}

$$\lambda = -\frac{1}{2} \frac{\epsilon_s - \epsilon_{\text{op}}}{\epsilon_s - 1} \oint_S \Phi_1^{\text{op}} (\sigma_1^{\text{eq}} - \sigma_1^{\text{op}}) dS \quad (22)$$

where Φ_1^{op} is the total electric potential due to the hydrated electron in the solvent of ϵ_{op} , while σ_1^{eq} and σ_1^{op} stand for the surface polarization charge densities due to the hydrated electron in medium of ϵ_s and ϵ_{op} , respectively.

Vertical Detachment Energy of Hydrated Electron. A suitable approximation for the present problem is that the point charge is located at the center of a spherical cavity. The process of photoionization of a negatively charged species B is



Taking the excess electron in bulk solvent into account, the VDE of the electron can be expressed as the sum of the adiabatic electron binding energy (AEBE) and the solvent reorganization energy λ (see Figure 2),^{32,34} i.e.

$$\text{VDE} = \text{AEBE} + \lambda \quad (24)$$

Here, AEBE is the difference of the equilibrium solvation free energy between the neutral cluster and the negatively charged one, and the solvent reorganization energy λ is the solvation free energy difference between the nonequilibrium and equilibrium polarizations (see Figure 2 and eq 8).

The localized state of the electron binding with the water clusters is still an intriguing topic. Theoretical research^{8,30,32} and experimental evidence^{3,5,22,23} revealed the existence of both surface and interior states of the hydrated electron. In this work, only the interior state is considered in large and infinite clusters (see Figure 3). Therefore, we assume that the excess electron

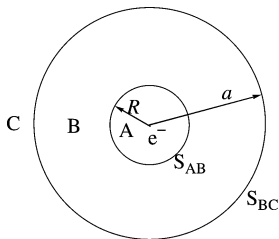


Figure 3. Single-sphere cavity model for the photodetachment of hydrated electron. The excess electron localizes at the center of the cavity. “A”, “B”, and “C” refer to the electron occupied cavity, water cluster region, and outside vacuum region, respectively. R and a represent the cavity radius of hydrated electron and the cluster radius. S_{AB} represents the interface between A and B, and S_{BC} represents the interface between B and C.

locates at the center of a dielectric sphere as a point charge and it occupies a cavity characterized by the averaged effective radius R of the hydrated electron. The water cluster with radius a surrounding the electron forms the intermediate shell, and outside is the vacuum. Applying the spherical symmetry of the electron charge distribution and the uniform dielectric properties of the water cluster, the polarized charge distribution will produce the electrostatic potential at the center of the spherical cavity as

$$\varphi_1^{\text{eq}} = -\frac{1 - \varepsilon_s}{\varepsilon_s} \left(\frac{1}{R} - \frac{1}{a} \right) \quad (25)$$

In the framework of the continuum model, the property of the water cluster shell can be described by the static dielectric constant ε_s and optical dielectric constant ε_{op} . Therefore, AEBE can be expressed as

$$\begin{aligned} \text{AEBE} &= F_{\text{sol},2}^{\text{eq}} - F_{\text{sol},1}^{\text{eq}} \\ &= -\frac{1}{2} \int \rho_1 \varphi_1^{\text{eq}} dV \\ &= -\frac{1}{2} \left(\frac{1}{\varepsilon_s} - 1 \right) \left(\frac{1}{R} - \frac{1}{a} \right) \end{aligned} \quad (26)$$

Here ρ_1 is the solute charge distribution and it is in the present case a unit negative point charge at the center of the cavity. Please note $F_{\text{sol},2}^{\text{eq}} = 0$. As shown in Figure 3, there are two interfaces: S_{AB} and S_{BC} . The first one divides the excess electron and the water molecules in the cluster and the second separates the cluster from the vacuum.

For the solvent reorganization energy, Φ_1^{op} in eq 22 is the isopotential on both surfaces S_{AB} and S_{BC} in the present case. If the following surface integrals are noticed (see the Appendix):

$$\oint_{S_{AB}} (\sigma_1^{\text{eq}} - \sigma_1^{\text{op}}) dS = \frac{1}{\varepsilon_{\text{op}}} - \frac{1}{\varepsilon_s} \quad (27)$$

$$\oint_{S_{BC}} (\sigma_1^{\text{eq}} - \sigma_1^{\text{op}}) dS = \frac{1}{\varepsilon_s} - \frac{1}{\varepsilon_{\text{op}}} \quad (28)$$

equation 22 can be changed to

$$\lambda = -\frac{1}{2} \frac{\varepsilon_s - \varepsilon_{\text{op}}}{\varepsilon_s - 1} \left(\frac{1}{\varepsilon_{\text{op}}} - \frac{1}{\varepsilon_s} \right) (\Phi_{1,S_{AB}}^{\text{op}} - \Phi_{1,S_{BC}}^{\text{op}}) \quad (29)$$

Here, $\Phi_{1,S_{AB}}^{\text{op}}$ and $\Phi_{1,S_{BC}}^{\text{op}}$ are the total electric potentials on the corresponding interfaces due to one electron at the center in the solvent of dielectric constant ε_{op} . They can be easily written as

$$\Phi_{1,S_{AB}}^{\text{op}} = -\frac{1}{a} - \frac{1}{\varepsilon_{\text{op}}} \left(\frac{1}{R} - \frac{1}{a} \right) \quad \text{and} \quad \Phi_{1,S_{BC}}^{\text{op}} = -\frac{1}{a} \quad (30)$$

Therefore eq 29 is changed to the following form:

$$\lambda = \frac{1}{2} \frac{\varepsilon_s - \varepsilon_{\text{op}}}{\varepsilon_{\text{op}}(\varepsilon_s - 1)} \left(\frac{1}{\varepsilon_{\text{op}}} - \frac{1}{\varepsilon_s} \right) \left(\frac{1}{R} - \frac{1}{a} \right) \quad (31)$$

Substituting eqs 26 and 31 into eq 24, VDE for the hydrated electron in the water cluster of radius a is finally expressed as

$$\text{VDE}(a) = \frac{1}{2} \left[\left(1 - \frac{1}{\varepsilon_s} \right) + \frac{(\varepsilon_s - \varepsilon_{\text{op}})^2}{\varepsilon_s \varepsilon_{\text{op}}^2 (\varepsilon_s - 1)} \right] \left(\frac{1}{R} - \frac{1}{a} \right) \quad (32)$$

The above energy expression of VDE can also be applied to the case of infinite bulk solvent. By setting $a = \infty$, $\text{VDE}(\infty)$ can be expressed as

$$\text{VDE}(\infty) = \frac{1}{2} \left[\left(1 - \frac{1}{\varepsilon_s} \right) + \frac{(\varepsilon_s - \varepsilon_{\text{op}})^2}{\varepsilon_s \varepsilon_{\text{op}}^2 (\varepsilon_s - 1)} \right] \frac{1}{R} \quad (33)$$

In this way $\text{VDE}(a)$ is given by

$$\text{VDE}(a) = \text{VDE}(\infty) - \frac{1}{2a} \left[\left(1 - \frac{1}{\varepsilon_s} \right) + \frac{(\varepsilon_s - \varepsilon_{\text{op}})^2}{\varepsilon_s \varepsilon_{\text{op}}^2 (\varepsilon_s - 1)} \right] \quad (34)$$

The cluster radius a can be determined by the water number n in the cluster and the radius a_0 of the water molecule. The cluster volume V can be estimated by $V = nV_0$, with V_0 being the molecular volume of a single H_2O . By approximation, we have $V = (4/3)\pi a^3$ and $V_0 = (4/3)\pi a_0^3$; hence we get $a = a_0 n^{1/3}$. Combining with eq 34, a linear relationship of VDE versus $n^{-1/3}$ can be obtained as

$$\text{VDE}(n) = \text{VDE}(\infty) - A n^{-1/3} \quad (35)$$

with

$$A = \frac{1}{2a_0} \left[\left(1 - \frac{1}{\varepsilon_s} \right) + \frac{(\varepsilon_s - \varepsilon_{\text{op}})^2}{\varepsilon_s \varepsilon_{\text{op}}^2 (\varepsilon_s - 1)} \right] \quad (36)$$

In the past, Marcus first established the formula of solvent reorganization energy as the following form:^{44,45}

$$\lambda' = \frac{1}{2} \int_V \Delta \rho (\Delta \varphi_{\text{op}} - \Delta \varphi_s) dV \quad (37)$$

Here, $\Delta\rho = \rho_2 - \rho_1$ denotes the difference of solute charge density between the final and the initial states, and $\Delta\varphi_{\text{op}}$ and $\Delta\varphi_s$ are the polarization potentials due to $\Delta\rho$ in the medium with dielectric constants ε_s and ε_{op} , respectively. In the case of vertical detachment of hydrated electron, λ' can be expressed as

$$\lambda' = \frac{1}{2} \left(\frac{1}{\varepsilon_{\text{op}}} - \frac{1}{\varepsilon_s} \right) \left(\frac{1}{R} - \frac{1}{a} \right) \quad (38)$$

Substituting eqs 38 and 26 into eq 24, the traditional form for VDE is as follows:

$$\text{VDE}'(a) = \frac{1}{2} \left(1 + \frac{1}{\varepsilon_{\text{op}}} - \frac{2}{\varepsilon_s} \right) \left(\frac{1}{R} - \frac{1}{a} \right) \quad (39)$$

and similarly^{34,54}

$$\text{VDE}'(n) = \text{VDE}'(\infty) - A'n^{-1/3} \quad (40)$$

with

$$\text{VDE}'(\infty) = \frac{1}{2} \left(1 + \frac{1}{\varepsilon_{\text{op}}} - \frac{2}{\varepsilon_s} \right) \frac{1}{R} \quad (41)$$

$$A' = \frac{1}{2a_0} \left(1 + \frac{1}{\varepsilon_{\text{op}}} - \frac{2}{\varepsilon_s} \right) \quad (42)$$

Although our modified VDE expression (eq 32) and the traditional one (eq 39) predict different VDEs, both give the same critical number of waters, $n_{\text{VDE}=0}$, by setting $\text{VDE} = 0$, i.e.

$$n_{\text{VDE}=0} = (R/a_0)^3 \quad (43)$$

$n_{\text{VDE}=0}$ should be regarded as the minimal size of water cluster which can bind an excess electron, and eq 43 tells that this critical number depends solely on the ratio between the cavity radius of hydrated electron and the size of a single water molecule.

Results and Discussion

A modified relationship between VDE of hydrated electron and the size of the water cluster is described by eq 35 by assuming a single sphere cavity and a point charge, which includes two important parameters: the intercept $\text{VDE}(\infty)$ and slope coefficient A . The VDE variation tendency against $n^{-1/3}$ according to eq 35 is shown in Figure 4, together with other theoretically and experimentally fitted lines. The slope of the line, representing the variation tendency of VDE with increasing cluster size, is determined by the cluster properties, such as the mean radius of a single water molecule and optical and static dielectric constants of the solvent. According to the density of the water, the single water molecular radius $a_0 = 1.925 \text{ \AA}$ can be estimated from the single water volume of $V_0 = 29.92 \text{ \AA}^3$. Taking $\varepsilon_s = 78.5$ and $\varepsilon_{\text{op}} = 1.78$, a slope value of $A = 4.83 \text{ eV}$ is given by eq 36 while $A' = 5.75 \text{ eV}$ by eq 42 using the same parameters. The slope value from our derivation is a little smaller

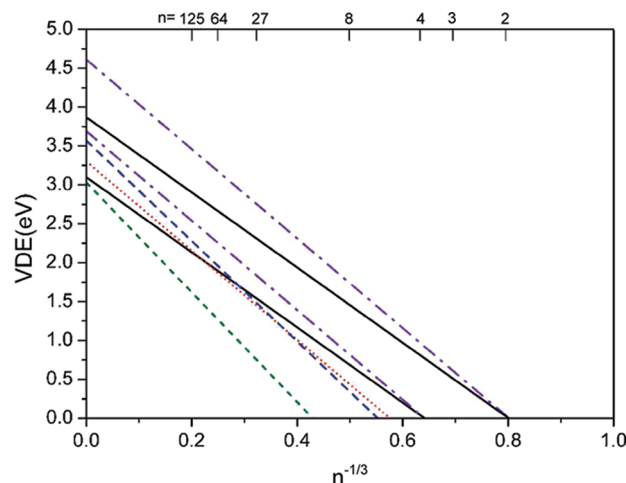


Figure 4. Drawing of VDE against $n^{-1/3}$. Dotted line: fitted and extrapolated from experimental data by Coe.³ Dashed line: fitted and extrapolated from experimental data by Neumark.²² Upper solid line: from eq 35 with $R = 2.4 \text{ \AA}$. Lower solid line: from eq 35 with $R = 3.0 \text{ \AA}$. Upper dashed-dotted line: from eq 40 with $R = 2.4 \text{ \AA}$. Lower dashed-dotted line: from eq 40 with $R = 3.0 \text{ \AA}$. Short dashed line: fitted and extrapolated from simulated values by Rossky.³⁰

than those obtained from experimental fittings by Coe et al. (5.73 eV)³ and Neumark et al. ($\sim 6.46 \text{ eV}$).²²

It can be seen that a key parameter affecting slope A is the radius a_0 . Earlier theoretical work combining QUPID data by Barnett³³ gave a higher slope of 6.80 eV for the vertical electron binding energy by adopting an a_0 of 1.588 \AA . If this value is applied in eq 36, the slope will change to 5.86 eV , which is very close to the experimental value of the slope by Coe.³ However, Newton suggested another value, 1.482 \AA for a_0 ,⁵⁵ which has been used in the semicontinuum calculations. Therefore, it seems that the different values of a_0 were taken according to the purpose of fitting. Here we try to avoid the arbitrary selection of a_0 and prefer to adopt a fixed value of 1.925 \AA for a_0 from the water density.

For the intercept $\text{VDE}(\infty)$, the cavity radius R of hydrated electron is the key factor besides the dielectric properties of the water cluster. It is experimentally challenging to measure the magnitude of the hydrated electron cavity radius in the solvents. The estimation of this value is from $\sim 2.4 \text{ \AA}$ ⁵⁶ to $\sim 3 \text{ \AA}$.⁹ Accordingly, the prediction of $\text{VDE}(\infty)$ would be in the range from 3.10 to 3.87 eV by eq 33 while the range would be from 3.69 to 4.61 eV calculated by eq 41 (see Figure 4). It can be seen that the experimental fittings by Coe and Neumark both fall into the area by us when the number of water molecules in the cluster is larger than ~ 50 , which indicates that the continuum model works well in the cases of large clusters. However, it seems that the traditional relation (eq 41) overestimates the values of VDE for the clusters, compared with the experimental values. Adopting the method of quantum simulation and considering the hydrated electron of the surface state, Turi and Rossky achieved the linear relation of VDE by extrapolating from the small clusters to the bulk solvent (see the short dashed line in Figure 4).³⁰ The fitting in this way achieved a value of 3.03 eV for $\text{VDE}(\infty)$, being lower than experimental ones. By the way, it still remains a puzzle to us to fit VDE versus $n^{-1/3}$ for the surface state with eq 35 or eq 40 since the analytical form of either eq 35 or eq 40 is only valid for the interior state.

Jortner and co-workers successfully predicted the cavity radius of hydrated electron according to the hydration Gibbs free energy ΔG° . By inspecting the transfer process of the singly

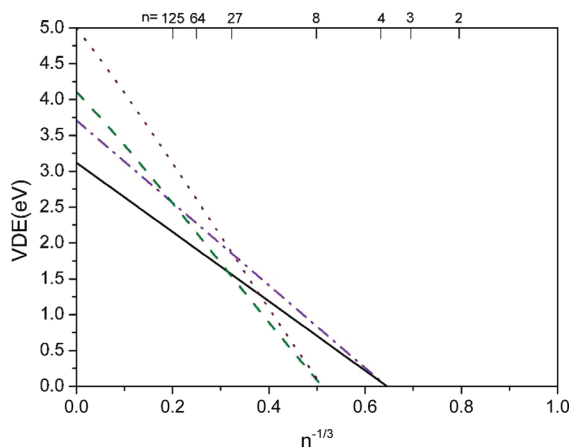


Figure 5. Drawing of VDE against $n^{-1/3}$. Solid line: from eq 35 with $R = 2.98$ Å. Dashed-dotted line: from eq 40 with $R = 2.98$ Å. Dashed curve and dotted curve: from eqs 32 and 39 with a varying R (eq 45), respectively.

charged gaseous anions into water at 25 °C,^{57,58} they proposed a relationship between ΔG° and the ionic radius, i.e.³⁹

$$\Delta G^\circ = 1.58R^2 - 0.568 - 163.89/R + 19.79/R^2 \quad (44)$$

When eq 44 is used for the case of e_g^- (mol/L) + water = e_{aq}^- , an R value of 2.98 Å is obtained according to $\Delta G^\circ = -39.4$ kcal/mol.³⁹ R is in the range 2.4–3.0 Å indeed.^{9,29,56} If we assume a fixed cavity radius $R = 2.98$ Å in the bulk water, we get $VDE(\infty) = 3.12$ eV according to eq 33, but eq 41 gives a value of 3.71 eV for $VDE'(\infty)$. The estimated intercept by us is closer to but slightly lower than the experimental extrapolation of 3.30 eV³ by Coe et al., whereas eq 41 predicts a value of 3.71 eV that is even higher than ~ 3.54 eV²² by Neumark et al.

For the large water clusters where the hydrated electron is surrounded by a large number of water molecules, the cavity radius of the hydrated electron can be considered a fixed value, because further increasing the water molecules is expected not to apply a significant impact on the cavity radius. However, in the case of small clusters, e.g., a few or tens of water molecules, the influence of the cluster size on the cavity radius of hydrated electron cannot be ignored and was pondered over considerably.^{7,33,59,60} The cavity radius determined from electronic absorption spectra was reported by Ayotte and Johnson³³ ($n = 6$ –50) and Coe⁵⁹ ($n = 11$ –50). Inspection showed that the cavity radius of the hydrated electron decreases with increasing cluster size. A recent moment analysis of hydrated electron clusters ($n = 11$ –50) by Coe and Bowen⁶⁰ suggested the relation between cavity radius and the water cluster size (the eq 14 in ref 60) as follows:

$$R = 2.265 + 1.203n^{-1/3} + 3.396n^{-2/3} \quad (45)$$

where R is in angstrom. Equation 45 is a fitted relationship from the clusters of $n = 11$ –50 at the temperature of 210 K, and we substitute it into eqs 32 and 39 and obtain our curve (dashed) with an intercept of 4.11 eV and the traditional one (dotted) with an intercept of 5.0 eV in Figure 5. Compared with the experimental fittings, it is seen that extending eq 45 to the bulk water case will lead to a higher VDE, while a fixed cavity radius (e.g., $R = 2.98$ Å) for the larger cluster cases seems to work better. The overestimation of VDE shows that $R = 2.265$ Å

seems too small for the cavity radius of hydrated electron in bulk water and the fitted eq 45 is unreasonable to describe the bulk condition. When the water molecule number in the cluster decreases from 50 to 11, eq 32 predicts a faster decrease of VDE by using a varying R (eq 45) than that with a fixed $R = 2.98$ Å. Please note we only consider the interior states rather than the surface ones. Meanwhile, comparing with experimental observations, the fitted result seems much better by applying eq 45 than using a fixed cavity. For the moderate cluster case, e.g., $n = 11$ –50, the continuum model can work if we take a varying cavity radius described by eq 45.

For small clusters with less than 12 water molecules, the VDE can be investigated by quantum chemistry. However, we find that the values of VDE strongly depend on the configurations, the computation methods, and the basis sets.¹¹ Sometimes it is difficult to give a qualitative judgment for whether the VDE is positive or negative,¹¹ especially for clusters of two to four molecules. The critical number, $n_{VDE=0}$, of a water cluster is predicted to be roughly from 2 to 4 by eq 43 with R being in the range from 2.4 to 3.0 Å, and it accidentally explains the fact that the negatively charged water dimer can be observed in experiments^{3,5} while the monomer cannot bind an excess electron.¹

In the continuum model, the hydrated electron is under the influence of the whole medium rather than only the surrounding solvent molecules. Solvent molecules are treated in a statistically averaged manner, and the entire medium is represented by continuous dielectric characterized by a static dielectric constant (ϵ_s) and an optical dielectric constant (ϵ_{op}). Thus, although the continuum model is clearly not precise in the small cluster cases, it works in describing the variation tendency of VDE for large clusters. In addition, the linear fitting by using a bulk cavity radius of the hydrated electron gives an approximated upper limit for VDE values, because the cavity takes the minimal size in bulk water.

There are heated discussions about surface and interior states in hydrated electron clusters.^{8,22,30,59} The difference between the two is reflected apparently in experimental observations. At the level of the VDE value, a surface state is lower than an interior one. Furthermore, with increasing cluster size, the variation tendency of VDE for a surface state is also smaller than that for an interior one. Although the slope value of 4.83 eV by eq 36 is smaller than that of the experimental extrapolation of the interior state, it is still higher than the variation tendency of VDE for the surface state.²² In addition, the continuum model can work well for the interior states, but it is extremely difficult to deal with the surface states. The basic starting point of the extrapolation from the bulk to small clusters is the interior state; hence the surface state is not included in our present work.

Conclusion

In this work, the constrained equilibrium principle is introduced and applied to the derivation for the nonequilibrium solvation free energy, because the concerned nonequilibrium state can be mapped to a specified constrained state by adding an external field. By keeping the same entropy and temperature from the constrained equilibrium to the nonequilibrium, the difference of solvation free energies between the nonequilibrium and corresponding constrained equilibrium has been integrated by fast removal of the external field. Based on the modified nonequilibrium solvation free energy, the formula for the modified solvent reorganization energy (eq 21) has been derived.

With the assumption of single sphere cavity and point charge, the expression for VDE for the hydrated electron is derived

based on the modified solvent reorganization energy. A linear relation of VDE against $n^{-1/3}$ is obtained by using a fixed cavity radius of the hydrated electron (R). According to eq 35, two values of R , 3.0 and 2.4 Å, yield two parallel lines with the same slope and different intercepts ($\text{VDE}(\infty)$), 3.10 and 3.87 eV. The experimental extrapolations fall into the range of these two lines for bulk water and the large clusters. For the smaller cluster cases, the performance of the continuum model becomes worse, but it is of some interest that the prediction of $n_{\text{VDE}=0}$ being in the range from 2 to 4 according to eq 43 agrees well with the experimental observation.

A varying R (eq 45) has also been introduced in the expression of VDE versus $n^{-1/3}$, thus both eqs 35 and 40 predict a curve of VDE against $n^{-1/3}$, rather than a straight line. Compared with the experimental extrapolations, it is seen that eq 45 works not too well for the prediction of $\text{VDE}(\infty)$ in the cases of bulk solvent, while a linear form with a fixed cavity radius R seems better in such cases.

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Appendix: Proof of eqs 27 and 28

Please see Figure 3. If we assume that a point charge $Q_1 = -1$ locates at the center of the cavity, according to the Poisson equations and the boundary conditions on each interface, the electric field with a spherical symmetry can be expressed as

$$\begin{aligned} E^A(r) &= -\frac{1}{r^2} \quad (0 < r \leq R) \\ E^B(r) &= -\frac{1}{\epsilon_s r^2} \quad (R < r \leq a) \\ E^C(r) &= -\frac{1}{r^2} \quad (r > a) \end{aligned} \quad (\text{A1})$$

where “A”, “B”, and “C” refer to the regions as defined in Figure 3 and the solvent dielectric property is described by ϵ_s . The surface polarized charge density $\sigma_{S_{AB}}$ on interface S_{AB} satisfies the boundary condition, i.e.

$$E_{n+}(S_{AB}) - E_{n-}(S_{AB}) = 4\pi\sigma_{1,S_{AB}}^{\text{eq}} \quad (\text{A2})$$

$n+$ and $n-$ stand for the surface normal pointing outside and inside, respectively. Substituting eq A1 into eq A2, the expression for $\sigma_{1,S_{AB}}^{\text{eq}}$ can be obtained as

$$\sigma_{1,S_{AB}}^{\text{eq}} = \frac{1}{4\pi R^2} \left(1 - \frac{1}{\epsilon_s} \right) \quad (\text{A3})$$

Similarly, the surface polarized charge density $\sigma_{1,S_{BC}}^{\text{eq}}$ on interface S_{BC} reads

$$\sigma_{1,S_{BC}}^{\text{eq}} = -\frac{1}{4\pi a^2} \left(1 - \frac{1}{\epsilon_s} \right) \quad (\text{A4})$$

If the solute is surrounded by the solvent with the dielectric constant of ϵ_{op} , the above equation can be changed to

$$\sigma_{1,S_{AB}}^{\text{op}} = \frac{1}{4\pi R^2} \left(1 - \frac{1}{\epsilon_{\text{op}}} \right) \quad (\text{A5})$$

According to the above derivation, eq 27 can be obtained. On the interface S_{BC} , a similar equation (eq 28) can be achieved.

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