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Solvation and Ionization near a Dielectric Surface

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Solvation and ionization energies of ions and neutral atomic solutes near planar and spherical (cluster) surfaces were calculated using continuum dielectric theory. For highly polarized solvents, the magnitude of the solvation energy at the surface is similar to that in the bulk, while the reorganization energy and the photodetachment energy of an electron from a negative ion are found to be slightly larger for solutes located at the surface. The cluster size dependence of the solvation and ionization energies is found to be determined only by the properties of the solvent, in good agreement with experimental data, and to be insensitive to the location of the solute in the cluster. Implications for the size dependence of the photodetachment energies from negative ions in water and ammonia clusters are discussed. In particular it is suggested that the observed photodetachment energies from small $(\text{NH}_3)_n^-$ clusters are compatible with the dielectric predictions for electron solvation in solid ammonia.

I. Introduction

Solvation near a dielectric boundary is of considerable theoretical and experimental interest. A solvated ion polarizes the medium about it and stabilizes itself.¹ If the ion is near the surface there is less solvent to polarize and the solvation energy is smaller. In accordance with this picture it is observed experimentally that the ion concentration is lower near the free surface of an electrolyte solution than in the bulk.² To calculate this excess the loss of solvation energy near a surface was first estimated in the dielectric model by Wagner,³ later by Onsager and Samaras,⁴ and by Conway.²

Related problems are the transfer of ions through a free surface or the surface between two immiscible liquids with different dielectric constants and electron transfer near or through such interfaces.^{5,6} The free energies associated with these processes have been studied for specific geometries using both dielectric models and molecular dynamics simulations. These simulations show that the dielectric picture is qualitatively correct with deviations of varying importance from the results of the simulations, depending on the specific system being considered.

Clusters are another system in which the surface plays a prominent role. Studies of solvation of ions in dielectric clusters were pioneered by Kebarle.⁷ However, the methods used in these experiments were limited to relatively small clusters, generally with less than 10 solvent molecules.

Solvation energetics can also be studied by photodetachment of an electron from solvated negative ions or photoionization of solvated neutral atoms. In the first case the work to remove an electron can be considered as the sum of the electron affinity plus additional work against the polarized solvent. In the second case the work is equal to the ionization potential less the energy gained from the fast component of the solvent polarization during the photoionization process. Experiments of both types have been performed on clusters. The solutes have been solvated electrons,⁸ halide ions,⁹ and neutral alkali atoms.^{10,11} The solvents have mainly been ammonia and water. Most of these experiments have been confined to clusters with several tens of solvent molecules, but negatively charged clusters of up to 1100 ammonia molecules have been studied.

These cluster processes have also been studied theoretically, using continuum dielectric models,^{12–14} molecular dynamics simulations,^{15,16} and quantum chemistry calculations.¹⁷ The latter have been confined to small clusters and will not be considered

here. The dielectric models have constrained the solute to be at the center of a spherical cluster^{12,13} or spread symmetrically about the surface (a configuration suggested for solvated electrons).¹⁴ Recent molecular dynamics simulations^{15,16} have brought into focus the issue of surface vs interior solvation in clusters. These simulations, as well as consideration of the balance between the solute–solvent interactions and the solvent reorganization energy, suggest that in some systems solvation takes place on the surface in small clusters, and that at some intermediate (system dependent) cluster size there is a transition from the surface to the interior state.

In this paper we apply continuum dielectric theory to solvation and ionization processes near an interface between two dielectric media. Dielectric theory has been commonly used for the description of solvation and ionization processes in solution.¹⁸ This theory ignores the discrete molecular nature of the solvent, a questionable approximation for molecular scale solutes, where much of the solvation energy is associated with solvent molecules in the immediate vicinity of the solute. This weakness is compounded near liquid–gas and liquid–liquid interfaces, because the continuum theory assumes sharp interfaces while the actual interface width (i.e., the region where the dielectric properties change) is several molecular diameters. In spite of this, dielectric theory has been very useful in developing the qualitative understanding of solvation phenomena in bulk and in clusters. It has also been surprisingly successful in describing some quantitative aspects of solvation processes, see, e.g., ref 18. Continuum dielectric theory thus appears to be useful both as a way to develop qualitative understanding and as a basis for comparison with microscopic theories and computer simulations.

In the context of clusters it may be expected that the validity of dielectric theory will increase with cluster size. In particular we expect that this theory will account correctly for the cluster size dependence of the energetics, e.g., the solvation and ionization energies. The reason for this is that when comparing solvation energies in two clusters of different sizes it is necessary to consider contributions from both short-range and long-range interactions. The bulk of the energy difference is expected to arise from long-range interactions which are described adequately by this model. The structure near the solute is expected to be approximately independent of the cluster size. Indeed, this has been demonstrated recently in calculations of cluster energetics in the mean spherical approximation (MSA) which showed an asymptotic size dependence equal to that predicted by the dielectric theory.¹⁹ Therefore in our application to clusters we emphasize the cluster size dependence, particularly in the limit of large clusters.

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We begin this paper by briefly reviewing the dielectric theory of solvation. Then we discuss its application to solvation near a dielectric interface. Following this we consider its predictions for several problems of theoretical and experimental interest: the free energy of ion solvation and the photodetachment of an electron from a negative ion at a dielectric interface, and the solvation and ionization energies of an ion or an atom at the center and at the surface of a spherical cluster. We conclude this paper by discussing the results and, where relevant, by confronting them with experimental data.

II. Dielectric Theory of Solvation

The dielectric theory of solvation¹ is a classical description of the solvation process. The solvent is described as a dielectric continuum. The solute ions can be modeled in various ways: (i) a charge distribution $\rho(\mathbf{r})$ in a cavity surrounded by the dielectric, (ii) a charged conducting sphere, or (iii) a charge distribution $\rho(\mathbf{r})$ embedded in the dielectric. In a bulk medium the three models are equivalent, but this is not necessarily so in a finite system. For definiteness we model the ion as a charged conducting sphere. The dielectric interface is taken to be a sharp boundary between two dielectric media with static dielectric constants ϵ_1 and ϵ_2 .

Consider first solvation in the bulk of a dielectric medium characterized by a dielectric constant ϵ . The solvation energy is the energy released by the polarization of the medium when the charged solute is transferred into it from the vacuum. The free energy of solvation, ΔG_s , is the difference of the free energies of two equilibrium states, one with the charge outside the dielectric and the other with the charge distribution fully solvated. This difference is found to be¹³

$$\Delta G_s = \frac{1}{2} \int d^3r \rho(\mathbf{r}) \phi(\mathbf{r}) - \frac{1}{2} \int d^3r \rho(\mathbf{r}) \phi_0(\mathbf{r}) \quad (1)$$

where the potentials and charges are related by the Poisson equations:

$$\nabla^2 \phi = -4\pi \rho(\mathbf{r}) / \epsilon \quad (2a)$$

$$\nabla^2 \phi_0 = -4\pi \rho(\mathbf{r}) \quad (2b)$$

The integrals in eq 1 extend over the whole space. $\phi(\mathbf{r})$ is the potential of $\rho(\mathbf{r})$ in the presence of the dielectric medium. It is obtained from eq 2a supplemented by the usual electrostatic boundary conditions. $\phi_0(\mathbf{r})$ is the potential of the same charge distribution in vacuum. When the solute is inside an infinite dielectric medium, only the boundary conditions at infinity, $\phi = 0$ and $\nabla \phi = 0$, are required. When the solute is an electron, an extra term must be added to eqs 1 and 3 to account for the kinetic energy of localization, K .²⁰

$$K = -\frac{\hbar^2}{2m} \int d^3r \Psi^*(\mathbf{r}) \nabla^2 \Psi(\mathbf{r}) \quad (3)$$

where $\Psi(\mathbf{r})$ and $\rho(\mathbf{r})$ are related by

$$\rho(\mathbf{r}) = -e|\Psi(\mathbf{r})|^2 \quad (4)$$

and e is the unit charge.

The Born picture¹ describes the equilibrium solvation of charged species. Platzman and Franck²¹ (and later Marcus,^{22,23} Jortner,²⁰ and others) extended it to describe vertical processes such as electronic excitations and ionization, in which the nuclei do not move during the transition, in the spirit of the Franck-Condon principle. In this picture the excitation is described as a sudden change in the charge distribution

$$\rho_g(\mathbf{r}) \rightarrow \rho_x(\mathbf{r}) \quad (5)$$

where the subscripts g and x denote the ground and excited states, respectively. On the time scale of this transition only the electronic degrees of freedom of the solvent respond. This partial solvent response is described by considering the polarization, $\mathbf{P}(\mathbf{r})$, to be the sum of two contributions:

$$\mathbf{P}(\mathbf{r}) = \mathbf{P}^e(\mathbf{r}) + \mathbf{P}^d(\mathbf{r}) \quad (6)$$

\mathbf{P}^e and \mathbf{P}^d are the electronic and dipolar components of the total polarization. The dipolar part depends on the nuclear coordinates. Only $\mathbf{P}^e(\mathbf{r})$ is assumed to be in equilibrium with the instantaneous charge distribution. It should be noted that this scheme can be applied to any process which involves a sudden change in the charge distribution, and is not specific to optical excitations.

Before the optical transition, the total polarization is in equilibrium with the electric field of the ground-state charge distribution:

$$\mathbf{P}_g = \frac{\epsilon - 1}{4\pi} \mathbf{E}_g \quad (7a)$$

$$\mathbf{P}_g^e = \frac{\epsilon_\infty - 1}{4\pi} \mathbf{E}_g \quad (7b)$$

$$\mathbf{E}_g = -\nabla \phi_g \quad (7c)$$

ϕ_g is the solution of eq 2a with ρ replaced by $\rho_g(\mathbf{r})$. ϵ_∞ is the optical dielectric constant which describes the electronic component of the polarization. Equations 6 and 7 imply that

$$\mathbf{P}_g^d = \frac{\epsilon - \epsilon_\infty}{4\pi} \mathbf{E}_g \quad (8)$$

After the transition the electronic component of the polarization, \mathbf{P}^e , is in equilibrium with the new electric field, while the dipolar component, \mathbf{P}^d , remains initially unchanged. The potential in this final state can be found by solving the Poisson equation:^{13,22}

$$\nabla^2 (\phi_x - \phi_g) = -4\pi (\rho_x - \rho_g) / \epsilon_\infty \quad (9)$$

In this model the transition energy, $W_{g \rightarrow x}$, is obtained to be^{13,20,21}

$$W_{g \rightarrow x} = \Delta K + \frac{1}{2} \int d^3r (\phi_x - \phi_g) (\rho_x - \rho_g) - \frac{1}{2} \int d^3r \rho_x \phi_{x0} + \frac{1}{2} \int d^3r \rho_g \phi_{g0} \quad (10)$$

which is the change in the solvent polarization energy²² plus the net work, ΔK , to change the charge distribution in vacuum. ϕ_{g0} and ϕ_{x0} are defined as ϕ_0 of eq 2b with ρ replaced by ρ_g and ρ_x , respectively. In classical systems ΔK is the difference in the electrostatic energies needed to assemble the charge distributions ρ_g and ρ_x . In general, however, this is a quantum mechanical quantity, given²¹ by the work necessary to perform the analogous transition in vacuum (e.g., for the ionization of a singly charged negative ion in solution ΔK is taken to be the electron affinity of the corresponding neutral in vacuum). For a solvated electron ΔK is taken as the kinetic energy of localization.²⁰

To finish this brief review we consider some results for two types of ionization processes with which we shall be concerned: ionization of a neutral species and electron detachment from a singly-charged negative species.

1. Ionization of a Neutral Species. In this process $\rho_g(\mathbf{r})$ is zero, while $\rho_x(\mathbf{r})$ corresponds to the positive ion. Since only the electronic component of the solvent polarization responds on the time scale of this transition, the process is equivalent to solvation in a medium with only electronic polarization. Therefore the free energy of solvation in this process, ΔG_s^v , is given by eqs 1 and 2 with ϵ replaced by the optical dielectric constant, ϵ_∞ .²³ The ionization energy is then the sum of the ionization potential in

vacuum, ΔK , and the vertical solvation energy:

$$W_{g \rightarrow x} = \Delta G_s^v + \Delta K \quad (11)$$

2. Electron Photodetachment from a Singly Charged Negative Species. In this process the ground-state charge distribution, ρ_g , is that of the negatively charged ion, and ρ_x is zero. The ionization energy is^{20,21}

$$W_{g \rightarrow x} = -\Delta G_s + \Delta K + \chi \quad (12)$$

ΔK for this process is the electron affinity. The ionization energy is seen to be equal to the electron affinity minus the solvation energy plus the reorganization energy, χ . The reorganization energy is the extra work performed because the dipolar component of the solvent polarization does not change during the ionization process. Within the present model it is²³

$$\chi = -\frac{1}{2} \int d^3r \phi_x \rho_g = \Delta G_s^v - \Delta G_s \quad (13)$$

III. Solvation near a Dielectric Surface

In this section we apply the dielectric theory reviewed above to solvation processes near dielectric boundaries and use it to discuss some problems of theoretical and experimental interest. The interface is modeled as a sharp boundary between two dielectric media characterized by the static dielectric constants ϵ_1 and ϵ_2 . In this case the Poisson equations (2 and 9) for the potential have to be written separately in the two media, i.e., $\nabla^2 \phi_i = -4\pi\rho(r)/\epsilon_i$; $i = 1, 2$, and the usual boundary conditions apply at the interface:

$$\phi_1 = \phi_2 \quad (14)$$

$$\epsilon_1 \frac{\partial \phi_1}{\partial x} = \epsilon_2 \frac{\partial \phi_2}{\partial x} \quad (15)$$

where x is the coordinate normal to the surface.

We now apply the theory of section II and the boundary conditions (14 and 15) to several situations:

A. Solvation of an Ion at a Planar Dielectric Interface. When an ion is located in a dielectric medium or near a dielectric interface it polarizes the medium. The change in free energy associated with this process is given, in the dielectric model, by eq 1.

We model the ion as a conducting sphere of radius a and total charge q and the interface as a sharp boundary separating the two solvents, modeled by dielectric continua. Thus $\epsilon(r) = \epsilon_2$ for $x < 0$, and $\epsilon(r) = \epsilon_1$ for $x > 0$. The free energy of solvation can be obtained from eq 1, in the present configuration it is determined by the distance, d , between the sphere center and the surface (see Figure 1).

For a conducting sphere all the charge is at the surface where the potential is constant. Therefore the solvation energy, eq 1, is

$$\Delta G_s = \frac{1}{2} q \phi(a) - \frac{1}{2} q \phi_0(a) \quad (16)$$

ϕ is the potential of the ion in the medium, and ϕ_0 is the potential in the vacuum, i.e., $\phi_0(a) = q/a$.

Consider now $\phi(a)$. If $|d| \gg a$ it is approximated by the image potential²⁴

$$\phi(a) = \frac{q}{\epsilon_1 a} - \frac{q}{2\epsilon_1 d} \frac{\epsilon_2 - \epsilon_1}{\epsilon_2 + \epsilon_1} \quad (d > a) \quad (17a)$$

$$\phi(a) = \frac{q}{\epsilon_2 a} - \frac{q}{2\epsilon_2 d} \frac{\epsilon_2 - \epsilon_1}{\epsilon_2 + \epsilon_1} \quad (d < -a) \quad (17b)$$

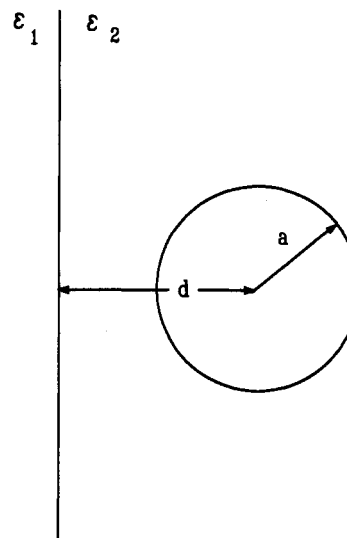


Figure 1. Schematic representation of ion solvation near a dielectric interface.

For $d = 0$ the ion is equally immersed in both dielectrics. Note that the possibility that the interfacial structure is affected by the presence of the ion is disregarded. For this case the potential at the ion is shown in Appendix A to be

$$\phi(a) = \frac{q}{a} \frac{2}{\epsilon_2 + \epsilon_1} \quad (18)$$

We now consider two specific cases: (i) the ion is in the bulk ($d = -\infty$) of medium 1 (ii) the ion is at the surface ($d = 0$). In the first case $\phi(a) = q/(\epsilon_1 a)$ and the solvation energy, eq 16, becomes the well-known Born energy:¹

$$\Delta G_s(d = -\infty) = \left(\frac{1}{\epsilon_1} - 1 \right) \frac{q^2}{2a} \quad (19)$$

In the second case, when the ion is at the surface, the potential is given by eq 18, and the solvation energy is

$$\Delta G_s(d = 0) = - \frac{(\epsilon_1 + \epsilon_2 - 2)}{\epsilon_1 + \epsilon_2} \frac{q^2}{2a} \quad (20)$$

From the ratio:

$$\frac{\Delta G_s(d = 0)}{\Delta G_s(d = -\infty)} = \frac{(\epsilon_1 + \epsilon_2 - 2)}{\epsilon_1 + \epsilon_2} \frac{\epsilon_1}{(\epsilon_1 - 1)} \quad (21)$$

we see that for all values of $\epsilon_1 > \epsilon_2$ the solvation energy at the surface is less than that in the bulk of solvent 1, as would be expected. The relative fraction tends to 1 as $\epsilon_1 \rightarrow \infty$.

It is interesting to note that the exact value of $\phi(a)$ for the case $d = 0$ is the same as would be obtained from the simple interpolation scheme introduced in ref 25 to bridge between the results (17) on both sides of the interface. This interpolation procedure is reviewed in Appendix B. Using this interpolation, we show in Figure 2 the relative energy of solvation of a univalent ion of radius 2 Å (e.g., Br⁻) as a function of the distance from the interface for water ($\epsilon = 80$) and for a solvent with $\epsilon = 3$.

B. Electron Detachment from a Negative Ion Near a Planar Dielectric Surface. Consider a negative ion at the interface between solvents 1 and 2. The photodetachment energy is given in eqs 12 and 13 in terms of the ionization potential of the negative ion in the vacuum (i.e., the electron affinity), ΔK , and of the solvation energies, ΔG_s and ΔG_s^v . ΔG_s was obtained above, and as shown in section II, ΔG_s^v is obtained from similar expressions by replacing ϵ with ϵ_∞ . Thus all the necessary

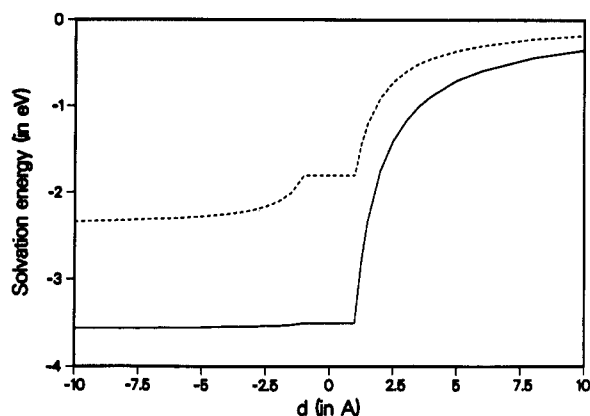


Figure 2. Solvation energy of an ion of radius 2 Å as a function of its distance, d , from a planar surface. The solid line is for a dielectric with $\epsilon = 80$, and the dotted line is for the case $\epsilon = 3$.

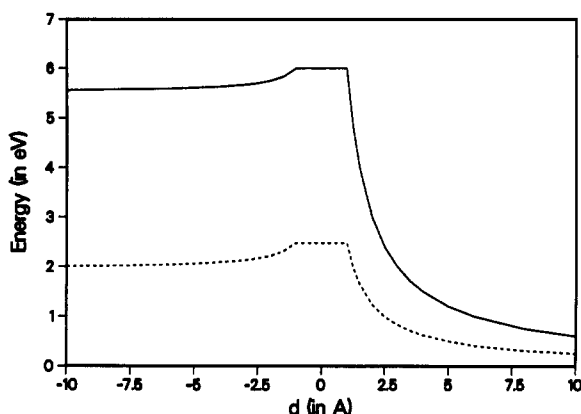


Figure 3. Photodetachment energy of an excess electron from a univalent anion of radius 2 Å (solid line) and solvent reorganization energy for this ion (dotted line) as a function of the distance, d , of the ion from a planar surface, separating water ($\epsilon = 80$, $\epsilon_\infty = 1.8$) and vacuum. The result shown for the photodetachment energy does not contain the ΔK contribution.

quantities are known, and the results are

$$\Delta W_{g \rightarrow x}(d=0) = \Delta K - 2\Delta G_s + \Delta G_s^v = \Delta K + \frac{q^2}{2a} \left(1 + \frac{2}{\epsilon_{1,\infty} + \epsilon_{2,\infty}} - \frac{4}{\epsilon_1 + \epsilon_2} \right) \quad (22a)$$

$$\Delta W_{g \rightarrow x}(d=-\infty) = \Delta K - 2\Delta G_s + \Delta G_s^v = \Delta K + \frac{q^2}{2a} \left(1 + \frac{1}{\epsilon_{1,\infty}} - \frac{2}{\epsilon_1} \right) \quad (22b)$$

For the specific case of the electrolyte vacuum interface ($\epsilon_1 = \epsilon$, $\epsilon_2 = 1$), eq 22a becomes

$$\Delta W_{g \rightarrow x}(d=0) = \Delta K - 2\Delta G_s + \Delta G_s^v = \Delta K + \frac{q^2}{2a} \left(1 + \frac{2}{\epsilon_\infty + 1} - \frac{4}{\epsilon + 1} \right) \quad (23)$$

Result 22b was obtained by Jortner for the vertical detachment energy of a solvated electron²⁰ (in which case ΔK is the kinetic energy of localization). Near the interface, an expression for $\Delta W_{g \rightarrow x}$ for $|d| \gg a$, based on the image approximation, was obtained by Marcus.²⁶ Again, using the procedure of Appendix B to interpolate between the Marcus results on the two sides of the interface yields at $d=0$ a result identical to (22a), supporting the validity of this procedure. Figure 3 shows the results of this interpolation for the photodetachment energy and the reorganization energy, eq 13, as a function of distance from a planar water ($\epsilon = 80$, $\epsilon_\infty = 1.8$) vacuum interface.

From eq 23 it can be seen that for the case $\epsilon = \epsilon_\infty$ (e.g., rare gas solvents) the photodetachment energy at the surface is smaller than that in the bulk. On the other hand, for the case $\epsilon \gg \epsilon_\infty > 1$, typical of polar molecules such as water and ammonia, the photodetachment energy predicted by the dielectric theory is greater at the surface than in the bulk, as can be seen in Figure 3. This behavior can be traced to that of the solvation and reorganization energies. For $\epsilon \gg 1$ almost all of the solvation energy is attained at the surface (see Figure 2 and eq 21). If $\epsilon \gg \epsilon_\infty$ as well, then the reorganization energy attains a maximum value there, which is slightly greater than that in the bulk (see Figure 3). Whether this behavior persists in realistic systems with diffuse interfacial boundaries or is an artifact of our idealized model is an open question.

C. Solvation of an Ion in a Spherical Cluster. The calculation of the solvation energy of an ion in a spherical cluster of radius R , like that for a planar interface, reduces to the problem of finding the potential at the ion surface, $\phi(a)$, as a function of the distance, R_i , between the ion and cluster centers. The distance from the ion center to the cluster surface is $d = R_i - R$. Approximate expressions for $\phi(a)$ are available for $|d| \gg a$:²⁷

$$\phi(a) = \frac{q}{\epsilon a} + q \sum_{n=0}^{\infty} \frac{(\epsilon-1)(n+1)}{\epsilon(\epsilon n + n + 1)} \frac{R_i^{2n}}{R^{2n+1}} \quad (d < -a) \quad (24a)$$

$$\phi(a) = \frac{q}{a} - q \sum_{n=0}^{\infty} \frac{n(\epsilon-1)}{\epsilon n + n + 1} \frac{R^{2n+1}}{R_i^{2n+2}} \quad (d > a) \quad (24b)$$

In Appendix B we present an approximate solution for the case $d=0$, based upon an interpolation procedure similar to that used in the planar case above. The result is:

$$\phi(a) = \frac{q}{a} - q \frac{\epsilon-1}{\epsilon+1} \left(\frac{1}{a} - \frac{1}{R} \right) + \frac{\epsilon-1}{(\epsilon+1)^2} \frac{q}{R} \left(\frac{1}{2} - \ln \left(\frac{a}{R} \right) \right) \quad (25)$$

The solvation energies at the cluster center and at the surface are obtained from eqs 24a and 25, respectively, to be

$$\Delta G_s(R_i=R) = -\frac{q^2}{2} \frac{\epsilon-1}{\epsilon+1} \left(\frac{1}{a} - \frac{1}{R} \right) + \frac{\epsilon-1}{(\epsilon+1)^2} \frac{q^2}{2R} \left(\frac{1}{2} - \ln \left(\frac{a}{R} \right) \right) \quad (26)$$

$$\Delta G_s(R_i=0) = \frac{q^2}{2a} \left(\frac{1}{\epsilon} - 1 \right) + \frac{q^2}{2R} \frac{\epsilon-1}{\epsilon} \quad (27)$$

Equation 27 is identical to results obtained earlier.^{12,25} Note that in the limit $\epsilon \gg 1$, the second term in eq 26 can be disregarded. The two solvation energies become equal in this time limit, but for small values of ϵ they have slightly different size dependences. In particular for large R the solvation energy at the surface depends on the cluster size as $(\ln R)/R$, while in the interior this dependence is proportional to $1/R$. As discussed above, we expect the dielectric model to predict the size dependences correctly.

D. Photodetachment from a Negative Ion in a Spherical Cluster. The photodetachment energy of an electron from a negative ion in a spherical dielectric cluster may be obtained by following the arguments of section III.B and replacing the results for the solvation energy near a planar surface by eqs 26 and 27 for a cluster. This leads to

$$\Delta W_{g \rightarrow x}(R_i=R) = \Delta W_{g \rightarrow x}^b - \frac{q^2}{2R} \left[\left(1 + \frac{2}{\epsilon_\infty + 1} - \frac{4}{\epsilon + 1} \right) - \left(\frac{1}{2} - \ln \left(\frac{a}{R} \right) \right) \left(\frac{\epsilon_\infty - 1}{(\epsilon_\infty + 1)^2} - \frac{2(\epsilon - 1)}{(\epsilon + 1)^2} \right) \right] \quad (28)$$

$$\Delta W_{g \rightarrow x}(R_i=0) = \Delta W_{g \rightarrow x}^b - \frac{q^2}{2R} \left(1 + \frac{1}{\epsilon_\infty} - \frac{2}{\epsilon} \right) \quad (29)$$

where $\Delta W_{g \rightarrow x}^b$ denotes the corresponding energy in the limit $R \rightarrow \infty$ given by eq 22.²⁸ Equation 29 is identical to the earlier results of Barnett *et al.*^{12,13}

E. Ionization of an Atom Solvated in a Spherical Cluster. The ionization energy of an atom was shown in section II to be $\Delta W_{g \rightarrow x} = \Delta K + \Delta G_s^v$, where for this process ΔK is the ionization potential of the atom in vacuum. ΔG_s^v has the form of the solvation energy ΔG_s (eqs 26 and 27) with ϵ replaced by ϵ_∞ . This leads to the following expression for the ionization potential of an atom of radius a at the cluster surface:

$$\Delta W_{g \rightarrow x}(R_i=R) = \Delta K - \frac{q^2}{2} \frac{\epsilon_\infty - 1}{\epsilon_\infty + 1} \left(\frac{1}{a} - \frac{1}{R} \right) + \frac{\epsilon_\infty - 1}{(\epsilon_\infty + 1)^2} \frac{q^2}{2R} \left(\frac{1}{2} - \ln \left(\frac{a}{R} \right) \right) \quad (30)$$

while for an atom at the cluster center, we get

$$\Delta W_{g \rightarrow x}(R_i=0) = \Delta K + \frac{q^2}{2a} \left(\frac{1}{\epsilon_\infty} - 1 \right) + \frac{q^2}{2R} \frac{\epsilon_\infty - 1}{\epsilon_\infty} \quad (31)$$

IV. Discussion and Summary

In this work we have examined the solvation and ionization energies of atoms and ions at planar dielectric interfaces and at the center and surface of spherical dielectric clusters. Results for these quantities were obtained using models based on a continuum dielectric theory with sharp interfaces. The solute was modeled as a conducting sphere of radius a , and the interfacial structure was assumed to be unaffected by its presence. For definiteness we summarize our main results for the dielectric-vacuum interface. For a planar surface we found that:

(a) The solvation energy monotonously increases in magnitude as the ion approaches the dielectric interface from the vacuum, crosses it, and moves into the bulk dielectric (see Figure 2). For solvents with high dielectric constant the bulk of the solvation energy is attained at the surface (see eq 21), e.g., for water the solvation energy at the surface is approximately 98% of the corresponding value in the bulk.

(b) The reorganization energy increases to a maximum at the surface (see Figure 3). This increase is significant only for highly polar solvents, for which it attains a maximum increase of 17% when $\epsilon_\infty = 2.4$. For water the increase above the bulk value is approximately 10%. This peculiar behavior results from the different dependences of the vertical and adiabatic solvation energies on the distance d of the ion from the surface. More specifically, the reorganization energy is given by the difference between these two energies, as seen in eq 13. This equation represents the reduction of the reorganization energy, relative to the value (minus the adiabatic solvation energy) it would have attained for the same ϵ if ϵ_∞ equalled 1 (i.e., no electronic polarization), through the relaxation of the electronic component of the solvent polarization. Near the surface the relaxation of the electronic component is significantly reduced while the overall solvation energy remains almost equal to its bulk value. This causes the reorganization energy to reach a maximum value at the surface.

(c) As a result of the behavior of the reorganization energy, the photodetachment energy of a singly charged negative ion will also attain a maximum at the dielectric/vacuum surface if $\epsilon \gg 1$ (see Figure 3).

It should be kept in mind that these results were obtained in a highly idealized model, and while they can serve as a basis for discussion of more realistic situations, it is not known whether these predictions will be retained by more realistic models. For example the prediction of a modest increase (approximately 10%

TABLE 1: Values of α (Eq 32) Obtained from the Dielectric Theory for Various Processes

process	ion location	α (in eV Å)		
		water ($\epsilon_\infty = 1.8$; $\epsilon = 80$)	solid ammonia ($\epsilon_\infty = 2.1$; $\epsilon = 3.4$)	liquid ammonia ($\epsilon_\infty = 1.8$; $\epsilon = 20$)
solvation	center	7.1	5.1	6.8
	surface	7.0	5.3	6.9
ionization of negative ion	center	-11.0	-6.4	-10.5
	surface	-11.1	-6.7	-10.8
ionization of neutral atom	center	3.2	3.8	3.2
	surface	3.2	3.8	3.2

for water) in the reorganization energy does not seem to be observed in the results of recent simulations.²⁹

For spherical clusters we have derived, within the same model, the cluster size dependence of the solvation and ionization energies of a solvated ion in the cluster and at the surface. We have argued that in spite of its simplicity our model should account correctly for the cluster size dependence of these properties. All the quantities studied were found to depend on the cluster size in the form of the cluster size equation:³⁰

$$E(R) = E^b + \frac{\alpha}{R} \quad (32)$$

For solutes located at the surface α depends on $\ln(R)$, but the experimental size range is generally so small that this term can be taken as constant. The intercept at $R = \infty$ is the energy of the equivalent process in the bulk or near a planar surface, and α characterizes the asymptotic size dependence of the quantity under study in the limit of large clusters.

The behavior represented by eq 32 has been found empirically for many cluster systems and has also been predicted by many theories of cluster energetics.³⁰ Note that for surface solvation the intercept, E^b , represents the relevant energy for a solute restricted to be at the planar surface of an infinite solvent.

The asymptotic dependence on cluster size, α , depends on two factors: (i) the cluster geometry, which we have taken to be spherical and (ii) the dielectric properties of the solvent, which we assume to be those of the bulk. Note that in this theory α is independent of the nature of the solute. The discrete nature of the solvent, the microscopic structure of the solute cavity, and details of the short range solute-solvent interactions all affect the value of E^b , which cannot be determined from dielectric theory alone. However, the value of α should be predicted by this theory for both surface and interior solvation.

It is interesting to see how well the experimental observations in clusters of water and ammonia are accounted for by the predictions of the simple dielectric continuum theory. The results of the dielectric theory are presented in Table 1 for solutes at the center and at the surface of the cluster. In those cases where the term $\ln(a/R)$ appears in the expression for α we set it equal to -1, which is approximately its value in the range of the experimental data. For comparison with cluster experiments we have used bulk values of the dielectric constant: for water clusters we took the values of the dielectric constants to be $\epsilon_\infty = 1.8$ and $\epsilon = 80$, which represent the data for a wide range of temperatures. For ammonia ϵ changes from 25 at the freezing point (-77.7 °C) to approximately 18 in the liquid state at room temperature. For solid ammonia, below the freezing point, $\epsilon = 3.4$.³¹ The magnitude of the optical dielectric constant is approximately 1.8 for liquid ammonia, and we estimate it as 2.1 for solid ammonia.³² Therefore we present two sets of results for ammonia calculated from the dielectric constants corresponding to the liquid phase, $\epsilon = 20$ and $\epsilon_\infty = 1.8$, and to the solid phase, $\epsilon = 3.4$ and $\epsilon_\infty = 2.1$.

From Table 1 it can be seen that the location of the solute has a small effect on the value of α in eq 32. This effect increases for smaller ϵ , but even for $\epsilon = 3.4$ it is less than 5%. Therefore we

TABLE 2: α and E^b Fitted from Experimental Data

cluster	no. of solvent molecules	E^b (eV)	α (eV Å)	ref
$I^-(H_2O)_n$	24–60 ⁹	7.95	−10.5	9
$(H_2O)_n^-$	6–69 ⁸	3.30	−11.1	8
$(NH_3)_n^-$	41–1100	1.25	−5.1	8
$Na(NH_3)_n$	4–20	1.7	4.0	10b
$Cs(NH_3)_n$	2–31	1.4	4.8	11
$Na(H_2O)_n$	4–20	3.17	0.0	10a
$Cs(H_2O)_n$	4–21	3.12	0.0	11

conclude that, according to this model, the location of the solute (or indeed a transition from solvation at surface states to interior states, as in ref 15) cannot be elucidated from the value of α only.

Two types of experiments in clusters can be compared with our results: (i) Photodetachment of an electron from negatively charged clusters, which was discussed in section III.D. (ii) Photoionization of neutral solutes, discussed in section III.E. The experimental data were fitted to the cluster size eq 32 and the results are summarized in Table 2. It should be noted that this comparison between the experimental data for the solvated electron and the dielectric theory involves the assumption that the quantum kinetic energy of localization (ΔK in our notation) does not depend on cluster size for large enough clusters. This assumption is compatible with our previous assertion that the short-range structure about the solute is relatively size-independent, as well as with the simulation and semiclassical results of ref 13.

Comparing the experimental results with the predictions of the dielectric theory we see that the size dependence is indeed almost completely determined by the solvent (e.g., compare $I^-(H_2O)_n$ with $(H_2O)_n^-$). We also see that the sign of the size dependence is correctly predicted by the theory. An attempt to account quantitatively for the observed values of α yields mixed results: For negative solutes in water clusters, $(H_2O)_n^-$ and $I^-(H_2O)_n$, the experimental data fit the predictions of the theory for both surface and interior solvation. The results of photoionization experiments on water clusters containing neutral alkali atoms, for which no size dependence is observed for clusters with more than 4 solvent molecules (i.e., $\alpha = 0$), are especially inexplicable. Two possible reasons for this are: (i) the charge configuration is different from those considered in this work (e.g., the atom is solvated as an alkali ion–electron pair^{10a}) and (ii) this behavior is characteristic only of a small size range and does not reflect the asymptotic size dependence.

For both electrons and alkali atoms solvated in ammonia clusters, the values of α derived from the experimental data are closer to those predicted by the dielectric theory for solid ammonia than to those of liquid ammonia. In the $(NH_3)_n^-$ clusters, the experimental value of α differs from that predicted for solid ammonia by only ca. 15% and from the liquid value by ca 50%. Jortner³⁰ has suggested that the experimental data for the larger ammonia clusters lie on a different straight line than the data for the smaller clusters, with a slope and intercept, $E^b = 1.63$ eV and $\alpha \sim 11.5$ eV Å, corresponding to those predicted for liquid ammonia. This change in slope with cluster size reflects a change in the state of solvation, which could possibly be explained by a solid–liquid transition in the ammonia clusters as they become larger. The smaller clusters may be in a “solid” phase with low ϵ , and the larger clusters are in a “liquid state” with high ϵ . In the $Na(NH_3)_n$ clusters there is a good fit between the experimental and theoretical (solid ammonia) values of α , while for $Cs(NH_3)_n$ there is a discrepancy of ca. 20%.

The values of the intercepts obtained from the fitting of the experimental data to eq 32 should be equal to the ionization energy in the bulk in the same configuration. However, if the solute resides at the surface, then there is no equivalent observable situation in the bulk (where all states are interior states) and E^b may be different from the observed bulk value. The ionization

energy of I^- in the bulk has been measured to be 7.2 eV^{33a} and 7.8 eV^{33b} (these values do not include corrections for dispersion by the solvent) and is in reasonable agreement with the value of E^b given in Table 2.

For the ammoniated electron the bulk vertical detachment energy (VDE) was at first estimated to be 1.8 eV,^{34a} but the data were later reinterpreted to yield an estimate of 1.4 eV.^{34b} Both these bulk values are higher than the extrapolated E^b values. Several interpretations for this discrepancy may be offered:

(i) The electron is solvated in a surface state, in which E^b might be smaller than that in the bulk. The value of α has been shown above to be insensitive to the electron location.

(ii) The ammonia clusters may be solid. The value of E^b for solid ammonia is expected to be lower than that for liquid ammonia, because of the smaller dielectric constant.

(iii) As argued by Jortner,³⁰ there may be a change of the slope in the ΔW vs $1/R$ behavior. The larger clusters lie on a straight line with $E^b = 1.6$ eV³⁰ which corresponds to liquid ammonia. The smaller clusters may be solvated in a different state, e.g., solid ammonia.

To conclude, we have developed the dielectric theory of solvation near surfaces and obtained detailed results for some systems of theoretical and experimental interest. Comparison with experimental data shows that the dielectric theory describes reasonably some, but not all, of the observed trends.

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Appendix A: Potential at the Surface of an Ion Located at a Planar Dielectric Interface

Consider an ion, modeled as a conducting sphere of radius a and charge q , located at the interface of two dielectric media with dielectric constants ϵ_1 and ϵ_2 (This corresponds to Figure 1 with $d = 0$). The potential at the surface can be obtained from the solution of the Laplace equation with appropriate boundary conditions. The general solution of the Laplace equation in this geometry for $r > a$, taking into account the azimuthal symmetry, is

$$\phi_1 = \sum_{n=0}^{\infty} (c_{1n} r^n + b_{1n} r^{-(n+1)}) P_n(\cos \theta) \quad (A1a)$$

$$\phi_2 = \sum_{n=0}^{\infty} (c_{2n} r^n + b_{2n} r^{-(n+1)}) P_n(\cos \theta) \quad (A1b)$$

where r is the distance measured from the ion center, and P_n are the Legendre polynomials. ϕ_1 is the potential in medium 1, for which $\cos \theta > 0$, and ϕ_2 for medium 2 with $\cos \theta < 0$.

The boundary conditions for this problem are

$$\phi_i(r \rightarrow \infty) = 0 \quad (A2a)$$

$$\phi_i(a) = \phi_0 \quad (A2b)$$

where $i = 1$ or 2. The second boundary condition reflects the constant potential, ϕ_0 , at a metal surface. From the first boundary condition we obtain immediately $c_{1n} = 0$ and $c_{2n} = 0$ for all n .

The two solutions, ϕ_1 and ϕ_2 , are related at the $\cos \theta = 0$ surface by the continuity conditions of eqs 14 and 15. Making use of the properties of the Legendre polynomials at $\cos \theta = 0$, we get

$$P_n(0) = 0 \text{ for odd } n; \quad P'_n(0) = 0 \text{ for even } n \quad (\text{A3})$$

and using the continuity equations we obtain the relations between b_{1n} and b_{2n} :

$$b_{1n} = b_{2n} \text{ for even } n; \quad \epsilon_1 b_{1n} = \epsilon_2 b_{2n} \text{ for odd } n \quad (\text{A4})$$

We now apply Gauss's theorem, which relates the flux of the displacement field, \mathbf{D} , through a closed surface A with the charge, Q , enclosed by it

$$\int d\mathbf{A} \cdot \mathbf{D} = 4\pi Q \quad (\text{A5})$$

to a mathematical spherical surface of radius ρ about the center of the ion with $\rho > a$. Note that we employ Gauss's theorem through the interface between two media.³⁵ The displacement normal to this surface is

$$D = -\epsilon_i \frac{\partial \phi_i}{\partial r}(r=\rho) \quad (\text{A6})$$

Explicitly this can be written as

$$4\pi Q = 2\pi \rho^2 \sum_{n=0}^{\infty} (n+1)(\epsilon_1 b_{1n} + (-1)^n \epsilon_2 b_{2n}) \rho^{-(n+2)} \int_0^1 d\cos\theta P_n(\cos\theta) \quad (\text{A7})$$

The identity theorem for power series determines that only the $n = 0$ term on the rhs is nonzero. From A4 $b_{10} = b_{20}$ and we obtain

$$4\pi Q = 2\pi b_{10}(\epsilon_1 + \epsilon_2) \int_0^1 d\cos\theta P_0(\cos\theta) \quad (\text{A8})$$

$P_0(\cos\theta) = 1$, and the integral is unity. b_{10} is obtained from (A8), and using the boundary condition (A2b) at $\cos\theta = 0$, we obtain ϕ_0 :

$$\phi_0 = \frac{Q}{a} \frac{2}{\epsilon_1 + \epsilon_2} \quad (\text{A9})$$

Appendix B: The Surface Interpolation Procedure

Here we review the interpolation procedure introduced in ref 25 for the solvation energy of an ion near a dielectric interface. We consider first a spherical interface and obtain the planar limit as $R \rightarrow \infty$, where R is the sphere radius.

Consider a spherical ion of charge q and radius a , located at a distance R_i from the center of a dielectric sphere of dielectric constant ϵ , where $R_i - R > a$. The potential at the ion is approximately given by the image potential, eq 24b. This approximation becomes exact in the limit $R_i - R \gg a$. When the ion is close to the surface the image potential diverges. In ref 25 an ansatz for the image potential near a dielectric interface was proposed. In this ansatz the classical expression for the image potential is used up to a distance h from the surface, while in the range $+h$ to $-h$ about the surface the potential is taken to be constant. To be consistent with the Born solvation energy, h is determined to be

$$h = \frac{a}{2} \left(1 + \frac{\epsilon - 1}{\epsilon + 1} \frac{a}{4R} \right)^{-1} \quad (\text{B1})$$

where a is the ion radius.

The potential at the surface is, in this approximation, the image potential at a distance h from the surface. In the planar case ($R \rightarrow \infty$) the image potential is²⁴

$$\phi = \frac{q}{a} - \frac{\epsilon - 1}{\epsilon + 1} \frac{q}{2h} \quad (\text{B2})$$

and from (A1) $h = a/2$, so the potential of the ion at the surface is

$$\phi = \frac{q}{a} \frac{2}{\epsilon + 1} \quad (\text{B3})$$

This result of the approximate solution is equal to the exact result (Appendix A), which indicates that this approximation is reasonable.

Near a spherical dielectric cluster the image potential at h is²⁷

$$\phi(a) = \frac{q}{a} - q \sum_{n=0}^{\infty} \frac{n(\epsilon - 1)}{\epsilon n + n + 1} \frac{R^{2n+1}}{(R + h)^{2n+2}} \quad (\text{B4})$$

Using eq A1 for h and the equality

$$\frac{l(\epsilon - 1)}{\epsilon l + l + 1} = \frac{\epsilon - 1}{\epsilon + 1} - \frac{\epsilon - 1}{(\epsilon + 1)^2 (l + (\epsilon + 1)^{-1})} \quad (\text{B5})$$

and introducing the expansion

$$\frac{1}{l + (\epsilon + 1)^{-1}} = \frac{1}{l} - \frac{1}{l^2(\epsilon + 1)} + \frac{1}{l^3(\epsilon + 1)^2} - \dots \quad (\text{B6})$$

we can obtain, after some effort, the potential at the ion:

$$\phi = \frac{q}{a} \frac{\epsilon - 1}{\epsilon + 1} \left(\frac{q}{a} - \frac{q}{R} \right) + \frac{\epsilon - 1}{(\epsilon + 1)^2} \frac{q}{R} \left(\frac{1}{2} - \ln \left(\frac{a}{R} \right) \right) + F(\epsilon, R) + O \left(\frac{1}{R^2} \right) \quad (\text{B7})$$

$F(\epsilon, R)$ is a series originating in the expansion of eq A6

$$F(\epsilon, R) = \frac{(\epsilon - 1)q}{(\epsilon + 1)^3 2R} \left[\frac{\pi^2}{6} - \frac{1.202}{(\epsilon + 1)} + \frac{1.082}{(\epsilon + 1)^2} - \dots \right] \quad (\text{B8})$$

If we approximate the numerator of each of the remaining terms by 1, then their sum is $1/[(\epsilon + 1)^2(\epsilon + 2)]$. However, for all values of ϵ the series F makes a small contribution only to the potential. Therefore in this paper, for reasons of simplicity, we have chosen to disregard it.

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