

Dynamic Solvation

Ionic Vibrations in Non-stationary Solvation Shells

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In this paper we consider the nature of the interaction between the vibrations of the solvent shell and the vibrations of a solvated ion which is trapped inside that shell. The ionic vibrations have been considered elsewhere. The solvation shell vibrations are considered in a continuum representation which is a modification of the hydrodynamic treatment considered several years ago. Two specific vibrational modes of the solvation system are considered. The first is the volume non-conserving breathing mode. This mode is modelled as a density fluctuation. The second mode is a solvation surface mode of oscillation which is volume-conserving. Distortion of the solvation surface arises through the excitation of the surface modes. The coupling between the various modes of oscillation of the solvation shell and the ion are considered. In addition, Born–Oppenheimer levels of separation of the various degrees of freedom are discussed. Finally, the general form of the dynamical interaction between two solvated ions is derived.

1. INTRODUCTION

In two previous papers ^{1, 2} the vibrational spectra of the alkali metal cations dissolved in polar solvents were investigated. In the first paper ¹ the far infrared spectrum of an ion inside a symmetric solvation cage was predicted. In the second paper ² the effects of static distortions of the solvation structure on the far infrared spectrum were examined. In both cases, only the primary, or inner, solvation shell was considered. The analysis in both papers depended upon the assumption that the solvation structure is rigid for a given configuration of the solvent molecules. The ionic vibrations within this rigid structure were then examined in order to predict the location of the far infrared vibrational frequencies for the various ions.

The purpose of this paper is to continue this investigation by examining the relationships which exist in a solvated ionic system in which the solvation structure is free to execute various motions.

Several topics are considered in the following sections. The dynamical features of the solvation surface are presented in a parametric form which is based upon the use of the hydrodynamic model which was introduced previously. ^{3, 4} However, here, in view of the more realistic semicontinuous nature of the solvation system, the giant acoustic vibrational modes discussed earlier ^{3, 4} are replaced by a simpler collective motion, a symmetric density fluctuation. The giant dipole density fluctuation discussed earlier ³ is replaced by the discrete vibration of the ion within the rigid solvation cage. The symmetric density fluctuation, which is handled as a continuum mode, is equivalent to a symmetric stretching, or breathing, mode of the solvation surface.

In addition to the symmetric breathing modes, the density fluctuations, there are also volume-conserving oscillations of the solvation surface. The solvation surface, as defined earlier, ³ is that region about the ion within which the structure of the system differs substantially from the more chaotic, randomly distributed bulk phase

of the solution. The interaction between the surface modes and the density fluctuations is considered. In addition, the interaction between the surface modes and the ionic vibrations within the solvent cage is derived. This particular interaction is very important. It is through this coupling that much of the distortion of the solvation surface occurs when a solvated ion interacts with an external charge.

Finally, the general form of the interaction between two solvated ions is considered. The dependence of the interaction upon surface dynamical parameters is derived. As a result, it is possible to be able to specify the shape of solvation structure about an ion when it interacts with other species.

2. SYMMETRIC DENSITY FLUCTUATIONS

BREATHING MODES OF THE SOLVATION SHELL

The collective symmetric stretch, or breathing, vibration for a solvated ionic or molecular species is locally a volume *non*-conserving motion. The solvated ionic system in a definite thermodynamic equilibrium state occupies a definite volume. Moreover, any deviation from that equilibrium volume experiences a restoring force which depends upon the extent to which the density moves away from the equilibrium density. Thus, the potential energy function for the system can be expressed in the following form :

$$U = \rho_0 \int d^3r \varepsilon \quad (2.1)$$

with

$$\varepsilon = K(\rho - \rho_0)^2 / \rho_0^2. \quad (2.2)$$

The use of this type of potential energy function is common in the treatment of a number of acoustic and hydrodynamic problems.⁵

(a) HYDRODYNAMIC TREATMENT

The Euler equation for the system follows from a variational calculation using the Lagrange function $L = T - U$. It is possible to derive a wave equation to express the density fluctuation modes.

The variation of the kinetic energy

$$T = \frac{1}{2} \int d^3r \rho \mathbf{v} \cdot \mathbf{v} \quad (2.3)$$

yields⁶

$$\delta T = - \int dt \int d^3r \rho [\partial \mathbf{v} / \partial t + (\mathbf{v} \cdot \nabla) \mathbf{v}] \cdot \delta \mathbf{s} \quad (2.4)$$

where $\delta \mathbf{s}$ is related to the variation of \mathbf{v} , $\delta \mathbf{v}$, by

$$\delta \mathbf{v} = \delta(ds/dt) = \frac{d}{dt}(\delta \mathbf{s}). \quad (2.5)$$

The variation of U , eqn (2.1), depends upon

$$\varepsilon' = d\varepsilon/d\rho = 2K(\rho - \rho_0)/\rho_0^2 \quad (2.6a)$$

$$\varepsilon'' = d^2\varepsilon/d\rho^2 = 2K/\rho_0^2. \quad (2.6b)$$

The variation of U now reads

$$\delta U = \rho_0 \int dt \int d^3r \varepsilon' \delta \rho. \quad (2.7)$$

With the use of the equation of continuity expressed as⁶

$$\delta \rho = -\rho \nabla \cdot (\delta \mathbf{s}), \quad (2.8)$$

the final form of δU is

$$\delta U = \rho_0 \int dt \int d^3r \delta s \cdot (\rho \nabla \varepsilon' + \varepsilon' \nabla \rho). \quad (2.9)$$

The second term is the same as $\nabla \varepsilon$. Hence, an alternate expression is

$$\delta U = \rho_0 \int dt \int d^3r \delta s \cdot (\rho \varepsilon'' \nabla \rho + \nabla \varepsilon). \quad (2.10)$$

The Euler equation follows, *viz.*,

$$d\mathbf{v}/dt + (\mathbf{v} \cdot \nabla)\mathbf{v} - \rho_0 \varepsilon \nabla \rho - (\rho_0/\rho) \nabla \varepsilon = 0. \quad (2.11)$$

When the equation of continuity is approximated as

$$d\rho/dt = -\rho_0 \nabla \cdot \mathbf{v}, \quad (2.12)$$

and terms of the order v^2 are ignored, the wave equation follows:

$$d^2\rho/dt^2 - \rho_0^2 \varepsilon'' \Delta \rho = 0 \quad (2.13)$$

where Δ is the nabla operator, ∇^2 . The pressure term $\nabla \varepsilon = \varepsilon' \nabla \rho$ is second order in the density. Hence, it also is ignored.

Only the monopole mode is important in the following discussion; it is one solution to the wave eqn (2.13). This monopole mode corresponds to a symmetric breathing mode, as was mentioned earlier.

Let M be the average mass per particle (solvent molecule). (The mass of the central ion is not included as it is stationary during any symmetric breathing vibration.) Thus, the average mass is in fact simply the solvent mass. The effective velocity of sound is written as

$$u^2 = 2K/M. \quad (2.14)$$

With the use of this quantity the frequency is given by

$$\omega_l^2 = k_l^2 u^2 = 2K z_l^2 / M R_0^2 \quad (2.15)$$

where the eigenvalues [as found in the process of solving the wave eqn (2.13)] are signified by the z_l . R_0 is the solvation radius. The following relation holds: $z_l = k_l R_0$. For the monopole mode, $l = 0$ and $z_0 = 4.493$.⁷ The frequency of the (Raman active) breathing mode is written conveniently (in units of cm^{-1}) as

$$1/\lambda = \frac{1}{2\pi c} \sqrt{2K/M(z_0/R_0)}, \quad (2.16)$$

where c is the velocity of light.

The identification of K and its magnitude is not yet determined. This matter is taken up in the next section, Section 3.

(b) THE FREQUENCY AS DETERMINED WITH THE USE OF MODEL DENSITY FUNCTIONS

There is an alternate, and interesting, route which can be followed in order to determine the values of the frequencies of the symmetric breathing modes. Namely, it is possible to start with the potential energy function given by eqn (2.1) and evaluate this expression with the use of explicit expressions for the distribution of matter in the solvated system. A calculation similar to the one to follow has been used in nuclear physics to examine quasi-molecular optical potential functions.⁸

The physical picture of the solvated ion makes it reasonable to assume that there is an effectively continuous distribution function which has its maximum value in the region where the concentration of solvent molecules about an ion is expected to be the greatest. Two such functions are examined here: first, a Slater-type distribution, and second, a Gaussian distribution.

A simple exponential distribution has the form

$$\rho(r) = N \exp(-r/a) \quad (2.17)$$

where N is a normalization factor and the quantity a is essentially the solvation boundary. It marks the region, measured radially from the ion, where the concentration of solvent is the greatest. Normalization is carried out with respect to the mass of solvent in the primary solvation shell. Thus, N is easily found to be $nM/8\pi a^3$ where n is the coordination number and M is the individual solvent mass.

In the following, the quantity a is the dynamical surface coordinate. Clearly, whenever the solvation system undergoes an expansion or contraction fluctuation, the instantaneous density function, eqn (2.17), must depend upon the instantaneous value of a .

In addition to eqn (2.17), there is a density function which depends upon a_0 , the equilibrium value of a . Thus, we write

$$\rho_0(r) = \frac{1}{8\pi a_0^3} \exp(-r/a_0). \quad (2.18)$$

Eqn (2.17) and (2.18) are substituted into eqn (2.1) and the integration is carried out. The result is

$$U = nK[a_0^6/a^3(2a_0 - a)^3 - 1]. \quad (2.19)$$

Because we are interested in the small, harmonic fluctuations of the density function about a_0 , the potential energy function (2.19) is expanded to second order about a_0 . It is trivially shown that the first order term vanishes at a_0 . The harmonic potential energy function is therefore

$$U = \frac{1}{2}(12nK)(1/a_0^2)(a - a_0)^2. \quad (2.20)$$

For this system, the equation of continuity can be expressed as

$$v = (r/a) da/dt. \quad (2.21)$$

Thus, the kinetic energy is found to be

$$\int d^3r \rho v \cdot v = \frac{1}{2}(12nM)\dot{a}^2. \quad (2.22)$$

The total energy $E = T + U$ is of course the Hamilton function for the oscillator. The frequency is immediately found to be

$$1/\lambda = \frac{1}{2\pi c} \sqrt{2K/M(1/\sqrt{2}a_0)}. \quad (2.23)$$

This frequency will be the same as that of eqn (2.16) if $\sqrt{2}a_0 = R_0/z_0$. If for Li^+ in DMSO, R_0 is the sum of the ionic radius and the solvation diameter, then $R_0 \approx 6 \text{ \AA}$. In this case, a_0 is approximately 0.9 \AA . It would seem to be the case that by choosing the ionic crystallographic radius for a_0 , one may reasonably estimate the breathing mode frequency.

A Gaussian distribution can be handled in a similar manner. The density function is taken to be the form

$$\rho(r) = \frac{nM}{\pi^{\frac{3}{2}}a^3} \exp(-r^2/a^2). \quad (2.24)$$

By means of an analysis which is the same as that above, one finds for the frequency

$$1/\lambda = \frac{1}{2\pi c} \sqrt{2K/M(\sqrt{8}/a_0)}. \quad (2.25)$$

In this case, when $a_0 = \sqrt{8}R_0/z_0$ the value of eqn (2.25) is the same as that of eqn (2.16). For R_0 approximately 6 Å, a_0 is found to be ≈ 3.6 Å. The value of a_0 in a Gaussian distribution appears to approximate the solvation radius.

Finally, it is possible to show that for a general form of the Gaussian distribution

$$\rho_j(r) = \frac{8nM}{\pi^{\frac{3}{2}}(2j+1)!!a^{2j+3}}r^{2j}\exp(-r^2/a^2) \quad (2.26)$$

the value of the predicted frequency is given by eqn (2.25) for any value of $j = 0, 1, 2, \dots$. The proof is straightforward and is not given. The same conclusion does not hold, however, for the simple exponential distribution.

(c) THE FORM OF THE SOLUTIONS TO THE WAVE EQUATION (2.13)

In the subsequent sections of this paper we shall have need to use the specific forms of the eigenfunctions of eqn (2.13). These expressions are summarized here. In addition, the operator form of the breathing mode Hamiltonian function is given.

The density function, which is a solution to eqn (2.13), can be written as

$$\rho(\mathbf{r}, t) = \rho(0)\{1 + \xi(\mathbf{r}, t)\} \quad (2.27)$$

in which the functions $\xi(\mathbf{r}, t)$ describe the density deviations from the equilibrium quantity. When eqn (2.27) is substituted into eqn (2.13),

$$\square_s^2 \xi(\mathbf{r}, t) = 0 \quad (2.28)$$

where \square_s^2 is the acoustic d'Alembertian operator ³

$$\square_s^2 = \nabla^2 + \frac{1}{(iu)^2} \frac{\partial^2}{\partial t^2}. \quad (2.29)$$

The usual course for the separation of variables,

$$\xi(\mathbf{r}, t) = \xi(\mathbf{r}) \exp(-i\omega t), \quad (2.30)$$

yields

$$\nabla^2 \xi(\mathbf{r}) + k^2 \xi(\mathbf{r}) = 0 \quad (2.31)$$

where

$$k^2 = \omega^2/u^2. \quad (2.32)$$

The solutions to eqn (2.31), subject to the boundary condition

$$\mathbf{n} \cdot \mathbf{v} \big|_{R_0} = 0 \quad (2.33)$$

where \mathbf{n} is the normal to the surface, can be written as

$$\xi_{n,l,m}(\mathbf{r}) = F_l^{(n)} j_l(k_l^{(n)} r) Y_{lm}(\hat{\mathbf{r}}) \quad (2.34)$$

in which $j_n(x)$ is the spherical Bessel function of the first kind, and $Y_{lm}(\hat{\mathbf{r}})$ is the spherical harmonic function.⁹ $\hat{\mathbf{r}}$ is a unit vector in r -space. The normalization constant $F_l^{(n)}$ is given by

$$F_l^{(n)} = \frac{\sqrt{2}}{R_0^{\frac{1}{2}}} [j_l(z_l^{(n)}) - j_{l-1}(z_l^{(n)}) j_{l+1}(z_l^{(n)})]^{-\frac{1}{2}}. \quad (2.35)$$

In general terms, the complete solution to eqn (2.29) can be written as

$$\xi(\mathbf{r}, t) = \sum_{n,l} (-1)^l (2l+1)^{\frac{1}{2}} F_l^{(n)} j_l(k_l^{(n)} r) [X^{(n)[l]}(t) \times Y^{[l]}]^{[0]} \quad (2.36)$$

where $X^{[l]}$ is a coordinate variable, and where (in the Fano-Racah ¹⁰ notation)

$$[X^{(n)[l]}(t) \times Y^{[l]}]^{[0]} = \frac{(-1)^l}{(2l+1)^{\frac{1}{2}}} \sum_m (-1)^m X_{lm}^{(n)}(t) Y_{l-m}(\hat{\mathbf{r}}). \quad (2.37)$$

In terms of the general form of the density function, eqn (2.27) with eqn (2.36) and (2.37), the potential energy function U , eqn (2.1), can be written as

$$U = (K\rho/M) \int d^3r |\xi(r, t)|^2 = \frac{1}{2}C \sum_{n,l} (-1)^l (2l+1)^{\frac{1}{2}} [X^{(n)[l]} \times X^{(n)[l]}]^{[0]} \quad (2.38)$$

where the quantity C is defined by

$$C = 2K\rho/M. \quad (2.39)$$

The velocity \mathbf{v} in eqn (2.3) for an irrotational fluid is given by

$$\mathbf{v} = -\nabla\phi \quad (2.40)$$

where ϕ is the velocity potential. The velocity potential also satisfies the Helmholtz equation (2.31). It is possible to show^{3, 7} that for

$$\phi_l^{(n)} = \sum_m (-1)^m S_{lm}^{(n)} \phi_{l-m}^{(n)} \quad (2.41)$$

the equation of continuity gives

$$\dot{X}_{lm}^{(n)} / (k_l^{(n)})^2 = S_{lm}^{(n)}. \quad (2.42)$$

Therefore, the kinetic energy can be expressed as

$$T = \frac{1}{2}\rho \int d^3r \mathbf{v} \cdot \mathbf{v} = \frac{1}{2} \sum_{n,l} \frac{(-1)^l (2l+1)^{\frac{1}{2}}}{B_l^{(n)}} [\Pi^{(n)[l]} \times \Pi^{(n)[l]}]^{[0]} \quad (2.43)$$

where $\Pi^{(n)[l]}$ is the momentum conjugate to $X^{(n)[l]}$ and where

$$B_l^{(n)} = \rho / (k_l^{(n)})^2. \quad (2.44)$$

The frequencies of the density fluctuation modes are given by

$$\omega_l^{(n)} = [C/B_l^{(n)}]^{\frac{1}{2}} = \sqrt{2K/M} (z_l^{(n)}/R_0), \quad (2.45)$$

as before.

Finally, it is possible, by means of an obvious transformation, to write the Hamiltonian function in terms of dimensionless variables:

$$H_d = \frac{1}{2} \sum_{n,l} \hbar \omega_l^{(n)} \{ [p^{(n)[l]} \times p^{(n)[l]}]^{[0]} + [q^{(n)[l]} \times q^{(n)[l]}]^{[0]} \}. \quad (2.46)$$

3. THE ORIGIN OF THE CONSTANT K

A phenomenological constant, signified by K , enters into the analysis which leads to the breathing modes. This constant appears in eqn (2.1) and at this point it has not been identified. In this section we present arguments which suggest a connection between K and the energy D needed to dissociate a single solvent molecule from the complex.

The following identification of K in eqn (2.1) can be made. As is known,¹¹ the Morse potential

$$U = D\{1 - \exp[-(r-r_e)/a]\}^2, \quad (3.1)$$

where D is the dissociation energy, yields the following expression for the vibrations in the harmonic oscillator limit:

$$1/\lambda = \frac{1}{2\pi c} \sqrt{2D/M} \frac{1}{a}. \quad (3.2)$$

For a diatomic molecule, M is the reduced mass. We assume that eqn (3.2) will be the same as eqn (2.16) if

$$nD = K, \quad (3.3)$$

where n is the coordination number, and

$$a = R_0/z_0^{(n)}. \quad (3.4)$$

At this point, we identify K as the energy necessary to strip all the solvent molecules away from the central ion.

As an example, we consider the lithium cation dissolved in dimethylsulphoxide (DMSO). Based on an analysis of a discrete particle system,¹ the breathing mode has been estimated to be 137 cm^{-1} .

We assume here that D is of the order of 1 eV ($1.60 \times 10^{-19}\text{ J}$) and that the coordination number is four for lithium in DMSO.¹ The radius R_0 is taken to be the sum of the ionic (crystallographic) radius and the solvation diameter,¹² $R_0 = 5.7\text{ \AA}$. We find $1/\lambda_{\text{calc}} = 132\text{ cm}^{-1}$ with the use of eqn (3.2)-(3.4). It is unfortunate, however, that for this system there are no data against which to compare this value or the value which was previously calculated.¹

On the other hand, examples exist for which there are data.¹³ One of the earliest studied examples is that of $\text{Zn}(\text{H}_2\text{O})_6^{2+}$.¹³ The Raman spectrum shows a breathing mode at 394 cm^{-1} . If we use $D = 1\text{ eV}$ and $R_0 = 3.9\text{ \AA}$, we calculate a value of 490 cm^{-1} . This value is much too large. However, if the dissociation energy D is reduced to a value of 0.65 eV , good agreement is obtained.

The choice of a value of the order of 1 eV for D is suggested in the activation energies for the solvent exchange as found experimentally and as discussed and tabulated by Basolo and Pearson.¹⁴ To begin, it is reasonable to assume that the dissociation constant D used in eqn (3.2) is of the order of magnitude of the activation energy for a single solvent molecular exchange. The calculations shown above, however, can only be regarded as good guesses, at least at this time.

TABLE 1^a.—LIGAND EXCHANGE ACTIVATION ENERGIES AND FREQUENCIES OF RAMAN-ACTIVE MODES

ion	$E_{\text{a(obs)}}$	$E_{\text{a(calc)}}^b$	$1/\lambda_{\text{obs}}$	$1/\lambda_{\text{calc}}$	$f = E_{\text{a}}/D$
Cr^{3+}	26.7	23.4	490	523	1.14
Mn^{2+}	8.7	15.2	395	299	0.57
Fe^{2+}	8.3	14.8	389	291	0.56
Co^{2+}	8.6	—	—	297	—
Ni^{2+}	12.2	16.0	405	354	0.76
Cu^{2+}	5.6	18.9	440	240	0.30

^a Energies are given in units of kcal mol^{-1} and the frequencies in units of cm^{-1} . ^b This quantity also corresponds to D_{calc} , or just D , which is used in the text and in the last column of the table.

A collection of solvent exchange activation energies and stretching frequencies is listed in table 1. The observed values of both E_{a} and $1/\lambda$ are used to calculate $E_{\text{a(calc)}}$ and $1/\lambda_{\text{calc}}$. In particular, $1/\lambda_{\text{calc}}$ is found with the use of the assumption that $K = 6E_{\text{a(obs)}}$ if $E_{\text{a}} \simeq D$. Similarly, $E_{\text{a(calc)}}$ is found with the use of $1/\lambda_{\text{obs}}$ in the reciprocal sense. Several noteworthy features emerge from this exercise.

First, consistency is not apparent. It is not at all clear that the assumption can be made that K is approximately equal to nD which in turn is approximately equal to nE_{a} . Second, in a restricted sense, there is a short-length consistency in that $1/\lambda_{\text{calc}}$ for Mn^{2+} , Fe^{2+} and Ni^{2+} show the same trend as the observed band maxima. Third, it appears that $E_{\text{a(calc)}} \simeq 1.7 E_{\text{a(obs)}}$ in a number of cases. For the case of Cu^{2+} , however, the difference is much greater. Overall, we conclude that the assumption *cannot* be supported that $D \simeq E_{\text{a}}$ for the solvent exchange.

Nevertheless, this display of the data appears to be both diagnostic and useful in another sense. On closer examination, it is *not* reasonable to assume that D is approximately equal to E_a for the ion in its solvation well. The solvent exchange reaction, along any reaction path, depends upon an adiabatic or quasi-adiabatic potential energy surface. In the quasi-adiabatic limit it is easiest to see that the intersection of two potential energy surfaces, one for the initial and one for the final state, to yield a reaction surface should generally yield a value of $E_a < D$. The quantity D/a^2 , as with the harmonic force constant in general, is a measure of the radius curvature of the potential energy minimum. Thus, with Cu^{2+} as the most extreme and best example in table 1, we can see that the interaction of a steep initial state potential energy function with a final state function can yield a strong splitting. The result, as shown in fig. 1(a), may in fact be effectively an adiabatic potential energy surface for the reaction. On the other hand, a system which has a relatively small vibrational frequency can have a large activation energy if the interaction between the initial and final states is weak. The activation energy in this case also is large effectively because the solvent displacement along the reaction coordinate must be large. This situation is illustrated in fig. 1(b).

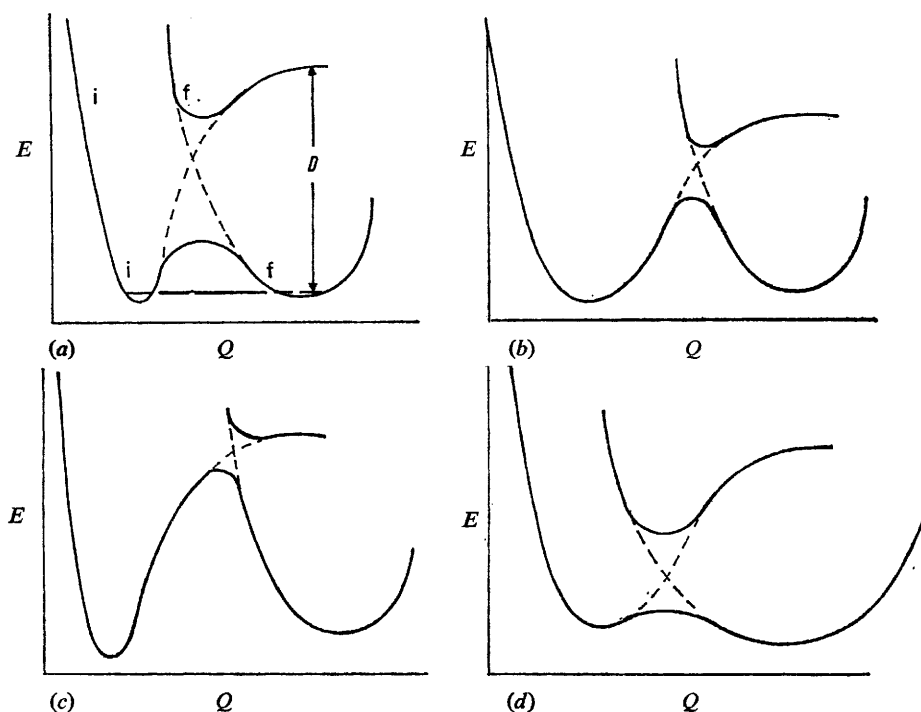


FIG. 1.—Schematic representation of the interaction between the initial and final state potential energy curves for the solvent exchange reaction. Cases: (a) strong interaction (large primary frequency, small activation energy); (b) weak interaction (low primary frequency, relatively large activation energy); (c) weak interaction (large primary frequency, high activation energy); (d) strong interaction (low primary frequency, low activation energy). In (a) the dissociation energy D , in the sense of the Morse potential for the initial state, is indicated. Also in (a) the initial (i) and final (f) state potential energy curves are labelled. The remaining parts of the figure are similar in their implied label to part (a). Finally, Q in (a) is the reaction coordinate. In the case of the solvent exchange reaction, it is essentially the distance directed out from the central ion along which the solvent molecule moves.

The opposite case to that shown in fig. 1(a) is shown in fig. 1(c). Here the vibrational frequency is large, but the interaction with the final state implies a large displacement of the solvent molecule to reach the activation barrier. Effectively, the solvent molecule reaches the dissociation (continuum) limit of the initial state potential energy surface at the time it passes to the final state well. Therefore, for this case it is reasonable to expect that the activation energy E_a is nearly the same as D . Cr^{3+} , in table 1, is an example of this limit.

In fig. 1(d) the case of a strong interaction (small displacement) between intrinsically low frequency curves is shown. In such a system the solvent exchange is expected to be very fast. The examples in table 1, however, do not appear to show a member which would correspond to an example of this type of interpretation.

In view of these considerations, it seems reasonable to define a quantity f as the ratio of the activation energy for solvent exchange to the dissociation limit of the initial state:

$$f = E_a/D. \quad (3.5)$$

Thus, it should be possible to make the identification

$$K = nE_a/f. \quad (3.6)$$

4. SURFACE MODES OF OSCILLATION

The formulation of the surface modes used here is the same as has been considered previously. It is sufficient, therefore, merely to summarize the results in the form of the equations which are to be used here.

The solvation surface is described by an equation of the form

$$R(\mathbf{p}) = R_0 \left\{ 1 + \sum_{L,M} \alpha_{LM} Y_{LM}^*(\mathbf{p}) \right\} \quad (4.1)$$

in which the quantities α_{LM} determine the extent to which the surface deviates from a spherical shape. In the absence of any permanent distortion, the expectation values of all the α_{LM} vanish. These distortion parameters enter the theoretical description of the surface modes essentially as coordinates variables. The associated velocities are $\dot{\alpha}_{LM}$. Thus, the total energy can be written as

$$E_{\text{sur}} = \frac{1}{2} \sum_{L,M} \{ B_L |\dot{\alpha}_{LM}|^2 + C_L |\alpha_{LM}|^2 \} \quad (4.2)$$

with

$$B_L = \rho_0 R_0^5 / L \quad (4.3)$$

and

$$C_L = (L-1) \{ (L+2) \Gamma R^2 - 3e^2 Z^2 / 2\pi(2L+1) R_0 \}. \quad (4.4)$$

The effective surface tension for the solvation surface is given by Γ . B_L and C_L are referred to, respectively, as the inertia and stiffness coefficients.⁷ The charge on the ion is given by Z .

The surface mode frequencies are given by

$$\omega_L = \frac{1}{R_0} \left(\frac{4\pi}{3M} L(L-1) [(L+2) \Gamma R_0^2 - 3Z^2 e^2 / 2\pi(2L+1) R_0] \right)^{\frac{1}{2}} \quad (4.5)$$

It is obvious that ω_0 and ω_1 vanish at this level of approximation.

The Hamiltonian operator (in the quantal sense, or function in the classical sense) can be expressed in terms of dimensionless momenta and coordinates as

$$H_{\text{sur}} = \frac{1}{2} \sum_{L,M} \hbar \omega_L \{ |p_{LM}|^2 - |q_{LM}|^2 \}. \quad (4.6)$$

5. THE MAGNITUDE OF THE EFFECTIVE SURFACE TENSION

The value of Γ , which appears in eqn (4.4), has been discussed previously.¹ It has not been determined experimentally and at present there is no obvious experiment which can be thought of to determine it.

The physical interpretation of the surface tension is simple and obvious. It is simply a parametric statement of the balance of forces at a defined solvation surface. These forces exclude the complete monopolar ion-dipole interactions. The forces in question, therefore, are the forces which preserve the local order of the solvation system as against the forces which cause disorder in the bulk of the system.

It is possible to estimate the surface tension in the following manner. We assume that the solvation surface is spherical. Then the work of expansion from R_0 , the equilibrium value of the solvation radius, to R is given by

$$w = 4\pi\Gamma(R^2 - R_0^2) \quad (5.1)$$

when we assume, further, that Γ is independent of R . This is probably the case for small values of $R - R_0$.

Next, assume that the interaction between the ion and the solvent (apart from the direct ion-dipole interaction) is the same as the interaction between the solvent molecules. The central ion is replaced by a neutral species. This central species interacts with the solvation shell molecules *via* a Stockmayer potential, *viz.*, a combination of the Lennard-Jones and dipole-dipole potentials.¹⁵ With reference to the central species, the solvation shell is allowed to expand by 0.01 Å. The remainder of the system does not change. Thus, for example, for water we find that $\Gamma \approx 130 \text{ dyn cm}^{-1}$ using the data tabulated by Moelwyn-Hughes.¹⁶ This was found by assuming a tetrahedral arrangement of water molecules around a central species. However, this value for the surface tension is too small. It yields an imaginary frequency *via* eqn (4.5). An allowed frequency can be determined if more solvent molecules are included in the calculation. Thus, the expansion of the first and second solvation shells in unison gives a value of $\Gamma \approx 170 \text{ dyn cm}^{-1}$. With this value of the surface tension, the surface mode frequency is predicted to be of the order of 10 cm^{-1} . These surface oscillation modes are about an order of magnitude smaller than the density fluctuation breathing modes.

An alternate way of calculating Γ is to use the harmonic potential energy function, as found for the breathing modes. Thus, if¹

$$V_{\text{br}} = \frac{1}{2}k_{\text{br}}(R - R_0)^2, \quad (5.2)$$

then for a given value of R against R_0 , V_{br} is the work done. For Mn^{2+} in water (*cf.* table 1) we estimate that $\Gamma \approx 100 \text{ dyn cm}^{-1}$. This value also is much too small. There would only be a slight improvement if higher order terms were added to eqn (5.2). Thus, it appears that in order to be able to estimate Γ , it is necessary to consider a solvation surface which surrounds at least the first and second solvation sheaths.

It seems reasonable to expect that these collective solvation shell distortions are low energy degrees of freedom.

6. THE COUPLING BETWEEN THE SURFACE AND BREATHING MODES

The general form of the structure of the coupling between the symmetric density fluctuations and the surface modes can be established easily. We follow a form used in nuclear physics.^{7, 17} As we are interested mostly in the monopolar breathing modes

as they couple to the surface quadrupole oscillations, it is necessary only to consider terms of the form

$$H_{\text{int}} = \sqrt{5}K_1[X^{[0]} \times [\alpha^{[2]} \times \alpha^{[2]}]^{[0]}]^{[0]} + \frac{1}{2}\sqrt{5}K_2[[\Pi^{[0]} \times \Pi^{[0]}]^{[0]} \times [\alpha^{[2]} \times \alpha^{[2]}]^{[0]}]^{[0]} + \frac{1}{2}\sqrt{5}K_2[[X^{[0]} \times X^{[0]}]^{[0]} \times [\alpha^{[0]} \times \alpha^{[2]}]^{[0]}]^{[0]} \quad (6.1)$$

where the momenta $\Pi^{[0]}$ are conjugate to the generalized density fluctuation coordinates $X^{[0]}$.

It is useful to consider the transformation to a principal axis, or intrinsic, coordinate system:

$$a_{2\mu} = \sum_{\nu} D_{\nu\mu}^2(\theta_i) \alpha_{2\nu} \quad (6.2)$$

where the $D_{\nu\mu}^2(\theta_i)$ are elements of the rotation matrix and θ_i ($i = 1, 2, 3$) are the Euler angles. Thus, the scalar quantity

$$[\alpha^{[2]} \times \alpha^{[2]}]^{[0]} = \frac{1}{\sqrt{5}}(a_{20}^2 + 2a_{22}^2). \quad (6.3)$$

For the principal axis system it is required that

$$a_{2\pm 1} = 0$$

and by symmetry

$$a_{2-2} = a_{22} \equiv a_2.$$

We also write $a_{20} \equiv a_2$.

In the sense of the Born-Oppenheimer separation, the quantities a_0 and a_2 are parameters which are freely adjusted in calculations which serve to determine the density oscillations. Once these density terms have been found, it is possible to determine the force field for the surface modes.

The density fluctuation Hamiltonian and the interaction term can be combined to write

$$H_d + H_{\text{int}} = \frac{1}{2} \sum_n \{1/B_0^{(n)} + \bar{K}_2(a_0^2 + 2a_2^2)\}(\Pi_{00}^{(n)})^2 + \frac{1}{2} \sum_n \{C_0^{(n)} + K_2(a_0^2 + 2a_2^2)\}(X_{00}^{(n)})^2 + K_1 \sum_n \bar{X}_{00}^{(n)}(a_0^2 + 2a_2^2). \quad (6.4)$$

The term which is linear in $X_{00}^{(n)}$ can be removed by means of a simple definition of a new coordinate $Q_{00}^{(n)}$:

$$Q_{00}^{(n)} = X_{00}^{(n)} - \bar{X}_{00}^{(n)} \quad (6.5)$$

where

$$X_{00}^{(n)} = -\frac{K_1(a_0^2 + 2a_2^2)}{C_0^{(n)} + K_2(a_0^2 + 2a_2^2)}. \quad (6.6)$$

The transformed momenta are identical to the old quantities. Thus,

$$H_d + H_{\text{int}} = \frac{1}{2} \sum_n \{1/B_0^{(n)} + K_2(a_0^2 + 2a_2^2)\}(\Pi_{00}^{(n)})^2 + \frac{1}{2} \sum_n \{C_0^{(n)} + K_2(a_0^2 + 2a_2^2)\}(Q_{00}^{(n)})^2 - F(a_0, a_2) \quad (6.7)$$

with

$$F(a_0, a_2) = \frac{K_1^2(a_0^2 + 2a_2^2)^2}{2[C_0^{(n)} + K_2(a_0^2 + 2a_2^2)]}. \quad (6.8)$$

In the following discussion it is assumed that $K_1 \simeq 0$. This is consistent both with arguments concerning adiabaticity and with the fact that matter is constrained not to move across the solvation boundary. It remains therefore to determine K_2 and \bar{K}_2 . This is done in a manner which follows a similar calculation given by Urbas and Greiner¹⁷ for a nuclear hydrodynamic problem.

For the monopolar modes the following variational equation can be used

$$(k_{00}^{(n)})^2 = \min \frac{\int_v d^3r \nabla \eta^* \cdot \nabla \eta}{\int_v d^3r \eta^* \eta} \quad (6.9)$$

where η is a trial function which can be constructed of monopole density solutions as well as higher order density fluctuation terms. [This type of variational principle is discussed in ref. (7) and (17).] However, it is adequate (especially when considering only small surface perturbations) to use the spherical monopolar terms in (6.9) and to include account of the deformed surface. The integrations in eqn (6.9) are taken over the actual surface. Thus, in the intrinsic system

$$R(\hat{r}) = R_0 \{1 + a_0 Y_{20}(\hat{r}) + a_2 [Y_{2-2}(\hat{r}) + Y_{22}(\hat{r})]\} \quad (6.10)$$

and

$$\eta(r) = \frac{1}{\sqrt{4\pi}} j_0(k_0^{(n)} r). \quad (6.11)$$

The general form of the integrals in eqn (6.9) is written as

$$I(a) = \int_{4\pi} d\Omega \int_0^{R(\hat{r})} dr F(r) = \int_{4\pi} d\Omega f(a) \quad (6.12)$$

where $F(r)$ is either $r^2 j_1^2(k_0^{(n)} r)$ for the numerator or $r^2 j_0^2(k_0^{(n)} r)$ for the denominator.

As we have to deal only with small surface contributions, it is sufficient to consider the expansion of $f(a)$ in eqn (6.12) in a MacLaurin series to the second order in a_0 and a_2 . Thus,

$$\begin{aligned} f(a) = & \int_0^{R_0} dr F(r) + \sum_m a_m (\partial R(a) / \partial a_m) |_{a_m \rightarrow 0} F(R_0) + \\ & \frac{1}{2} \sum_m a_m \{ (\partial^2 R(a) / \partial a_m^2) F(R_0) + (\partial R(a) / \partial a_m) (\partial F(R_0) / \partial a_m) \} |_{a_m \rightarrow 0} + \\ & \frac{1}{2} \sum_{m,m'} a_m a_{m'} \{ (\partial R(a) / \partial a_m) (\partial F(R_0) / \partial a_{m'}) + \\ & (\partial R(a) / \partial a_{m'}) (\partial F(R_0) / \partial a_m) + 2(\partial^2 R(a) / \partial a_m \partial a_{m'}) F(R_0) \} |_{a_m \rightarrow 0}. \end{aligned} \quad (6.13)$$

where the Leibnitz rule for differentiating an integral has been used.

When the various terms have been evaluated, we find

$$(k_{00}^{(n)})^2 = (k_0^{(n)})^2 \frac{G_1(z_0^{(n)}) + 2A_1(a_0^2 + 2a_2^2)}{G_0(z_0^{(n)}) + 2A_0(a_0^2 + 2a_2^2)} \quad (6.14)$$

in which

$$G_l(z_0^{(n)}) = j_l^2(z_0^{(n)}) - j_{l-1}(z_0^{(n)}) j_{l+1}(z_0^{(n)}) \quad (6.15)$$

which arises from the normalization integral, and

$$A_l = j_l^2(z_0^{(n)}) + z_0^{(n)} j_l(z_0^{(n)}) j_l'(z_0^{(n)}) \quad (6.16)$$

where $j'_n(x)$ is the derivative of the Bessel function with respect to x . Because of the boundary condition

$$j'_0(k_0^{(n)}r)|_{r \rightarrow R_0} = 0 \quad (6.17)$$

it is easy to see that $A_1 = 0$ and $A_0 = j'_0(z_0^{(n)})$. Therefore,

$$(k_{00}^{(n)})^2 = (k_0^{(n)})^2 \frac{1}{1 + 2(a_0^2 + 2a_2^2)} \quad (6.18)$$

and

$$k_{00}^{(n)} \simeq k_0^{(n)} \{1 - a_0^2 - 2a_2^2\}. \quad (6.19)$$

In terms of the dimensionless coordinates for the density modes, we write

$$\bar{H}_d = \frac{1}{2} \sum_n \hbar \omega_{00}^{(n)}(a_0, a_2) \{ (p_{00}^{(n)})^2 + (q_{00}^{(n)})^2 \} \quad (6.20)$$

where

$$\omega_{00}^{(n)}(a_0, a_2) = u k_0^{(n)} (1 - a_0^2 - 2a_2^2). \quad (6.21)$$

Eqn (6.7) is converted to a dimensionless form. On comparison with eqn (6.21) we find

$$\frac{1}{2} \{ \hbar \omega_0^{(n)} B_0^{(n)} \bar{K}_2 + (\hbar / B_0^{(n)} \omega_0^{(n)}) K_2 \} = -\hbar \omega_{00}^{(n)} = K (\hbar / B_0^{(n)} \omega_0^{(n)}). \quad (6.22)$$

If \bar{K} is suppressed, which can be done as a reasonable approximation, then

$$K_2 \simeq -2C_0^{(n)}. \quad (6.23)$$

7. COUPLING BETWEEN SURFACE MODES AND IONIC VIBRATIONS

We have shown previously¹ that the small amplitude vibrations of the ion within its solvation cage can be well represented in terms of the spherical harmonic oscillator potential. The harmonic force constant is found in terms of the electrostatic, polarization and repulsion interactions which operate between the ion and the solvent molecules in the primary solvation shell. It was shown² subsequently that deformations along and about the C_3 and C_2 symmetry axes, respectively, can be handled in a straightforward manner. It was noted that the distortions in a tetrahedral solvation system, for example, are of the form of elliptic distortions of the solvation shell. However, this point was not pursued further in ref. (2). In the following paragraphs the relationship between the elliptic distortions of the solvation system and the vibrations of the solvated ion are explored.

The spherical oscillator potential energy function which applies to the ionic part of the system is expressed as

$$V(r) = \frac{1}{2} k r^2 = \frac{1}{2} m \omega^2 r^2 \quad (7.1)$$

where $\omega = \sqrt{k/m}$ and m is the ionic reduced mass with respect to the solvent in the primary solvation shell or to the solvent in the complete system [cf. ref. (1) for a discussion of this point]. For a light ion, such as lithium, m is effectively the ionic mass.¹

Assume that the potential depends upon the surface coordinate parameters $\alpha_{2\mu}^*$. Thus, to the first order in a Taylor series expansion one finds

$$V(r) = V_0(r) - m \omega^2 r^2 \sum_{\mu} \alpha_{2\mu}^* Y_{2\mu}(\hat{r}) \quad (7.2)$$

where $V_0(r)$ is given by eqn (7.1) with no further dependence upon the $\alpha_{2\mu}^*$ implied. In a principal axis system, we have

$$\begin{aligned} V(r) &= V_0(r) - m\omega^2 r^2 \{a_0 Y_{20}(\hat{r}) + a_2 (Y_{2-2}(\hat{r}) + Y_{22}(\hat{r}))\} \\ &= V_0(r) - m\omega^2 \sqrt{5/4\pi} \{ \frac{1}{2} a_0 (3z^2 - r^2) + \sqrt{3/8} a_2 (x^2 - y^2) \}. \end{aligned} \quad (7.3)$$

Thus,

$$a_0 = 2\sqrt{4\pi/3}(3a_{zz} - a_{rr}) \quad a_2 = 2\sqrt{8\pi/15}(a_{xx} - a_{yy}). \quad (7.4)$$

It is clear from the general form of the expression (7.3) that the surface parameters a_0 and a_2 must include an account of the forces which come into play when the solvation shell is deformed.

The problem of the vibrations inside the distorted solvation shell has already been considered² and does not need to be considered further. It is possible to compare the treatment of the distortion in the discrete system with this parametric treatment to be able to identify the quantities a_0 and a_2 in terms of forces acting in the system and the positions of the solvent particles. However, the quantities a_0 and a_2 are surface "coordinates" which take on a much broader meaning when more than one solvation shell is considered. This has been discussed in Section 5. It is reasonable, for example, to expect changes in the near solvation structure (*i.e.*, changes in the primary and secondary solvation shells) in a number of instances. In particular, with reference to the electron transfer reaction and with reference to ionic transport in solution, substantial changes in the solvation structure can be expected as part of the activation process. As much less is known about the secondary solvation structure than is known about the primary structure, it is useful to be able to treat this part of the system in a parametric manner.

8. SURFACE DEFORMATION IN RESPONSE TO IONIC DISPLACEMENT

BORN-OPPENHEIMER CONSIDERATIONS

In many instances the density fluctuations are expected to be of the same order of magnitude as the ionic vibrations. This, of course, is reasonable to expect because the density oscillations, as symmetric stretching modes, involve basically the same species and forces as the ionic vibrations (dipole, infrared active) within the solvation cage.¹ It is also clear from the analyses of the tetrahedral, *etc.*, molecular systems in the vacuum state that these frequencies should be close.¹⁸ Therefore, there is no point in attempting to separate the density monopole fluctuation mode from the dipolar ionic vibrations. A normal mode analysis in a discrete system accomplishes the desired separation. In this semicontinuum analysis the separation is implied in the separate handling of the ionic and density vibrations.

Nevertheless, it is certainly possible to consider an ionic vibration inside an excited solvation shell. The effect of a symmetric excitation of the solvation structure on the ionic vibrations is handled parametrically in an adequate fashion simply by noting the dependence of the ionic frequencies upon the solvation radius.¹ Clearly, as the radius increases, the frequency decreases. More complicated forms of coupling are not likely to be of much importance.

An important factor which does need to be considered is the following. Within the context of the Born-Oppenheimer adiabatic separation scheme, as it may apply to the ionic system and its solvation surface vibrations, we need to examine the consequences on the solvation surface states of an excited ionic vibrational state. That is, we need to determine how changes in the state and location of the ion in its solvation

shell influence the solvation surface. In particular, it is clear, for example, that an external charge can shift an ion within its (rigid) solvation cage.² This shifting of the ion can be viewed in terms of virtual excitations of the ionic vibrational states. The effect is simple. The displacement of the ion gives rise to coupling terms of the form of eqn (7.3) where now the x , y and z variables are replaced by the permanent shifts x_0 , y_0 and z_0 . (In a quantum-mechanical sense, of course, these quantities are merely the root-mean-square values of the coordinates evaluated as expectation values.) These shift quantities may be expressed in terms of the magnitude of the external charge.

Assume that the ion is displaced along the z -axis. Thus, we can write the contribution to the surface mode potential energy function as

$$V_{\text{int}} = -m\omega^2 \sqrt{5/4\pi(3/2)} a_0 z_0^2 \quad (8.1)$$

in which z_0 is the extent of the shift of the ion in the presence of the external charge. Because the interaction is linear in a_0 , it is easy to see that the surface also shifts, or distorts, away from a spherical shape. In particular,

$$\begin{aligned} H_{\text{sur}} &= \frac{1}{2B_2} p_0^2 + \frac{1}{2} C_2 a_0^2 - m\omega^2 \sqrt{5/4\pi} \frac{3}{2} z_0 a_0 \\ &= \frac{1}{2B_2} p_0^2 + \frac{1}{2} C_2 (a_0 - \bar{a}_0)^2 - \frac{45m^2\omega^4 z_0^2}{32\pi C_2} \end{aligned} \quad (8.2)$$

with

$$\bar{a}_0 = \frac{3m\omega^2}{2C_2} \sqrt{5/4\pi} z_0^2 \quad (8.3)$$

and \bar{a}_0 defines a new equilibrium position for the surface. As $\bar{a}_0 \geq 0$, the solvation spheroid is distorted into a prolate ellipsoid.

The Born–Oppenheimer adiabatic analysis applies to the solvated ionic system in the following sense. The ionic vibrations are assumed adiabatically to follow distortions of the solvation surface. Thus, as has been done,² it is possible to examine these vibrational states for the solvated system in various states of distortion of the solvation shell. For a given state of ionic vibration, just as with the molecular vibronic problem, it is possible to determine the associated states of vibration of the solvation surface. However, as the simple calculation shown above indicates, it is also possible to examine the states of the surface vibrations with reference to the system ground state. Thus, the vibrational Hamiltonian function for the surface modes in a system in which the ion is displaced from its equilibrium position in the spheroidal ground state can be handled in terms of states of excitation in the uniform system. It is possible therefore to analyse the changes which take place in a system which is subject to complicated forces in terms of the virtual excitations which have been determined with reference to the simpler, uniform system.

9. THE INTERACTION BETWEEN DYNAMICALLY SOLVATED IONS

In order to complete this analysis of the dynamically solvated ionic system, it is necessary to determine the form of the interaction between two solvated ionic species. The purpose of this section is to derive a potential energy function which expresses the direct interaction between two ions. In addition, this function gives the form of the interaction between an ion and the solvation shell on another ion. Finally, there appear terms which express the coupling between the solvation shell oscillations for the two species.

In Section 2(b) we consider the form of the density fluctuation modes derived from

a continuous distribution function. In this section we follow a similar line of reasoning. Here, use is made of the continuous charge density functions of the Slater and Gaussian types. These functions have been used, with success, in the determination of the free energy of solvation of ions.¹⁹

The interaction between two charge distributions can be calculated with the use of the Carlson-Rushbrooke formula:²⁰

$$1/r_{12} = \sum_{\{l,m\}} \frac{(-1)^{m_1+m_2} r_1^{l_1} r_2^{l_2}}{R^{l_1+l_2+1}} B_{l_1 l_2}^{m_1 m_2} Y_{l_1+m_1}(\hat{r}_1) Y_{l_2+m_2}(\hat{r}_2) \quad (9.1)$$

with

$$B_{l_1 l_2}^{m_1 m_2} = \frac{(4\pi)^{\frac{1}{2}} (-1)^{m_1+m_2}}{[(2l_1+1)(2l_2+1)(2l_1+2l_2+1)]^{\frac{1}{2}}} \times \frac{((l_1+l_2+m_1+m_2)!(l_1+l_2-m_1-m_2)!)^{\frac{1}{2}}}{((l_1+m_1)!(l_1-m_1)!(l_2+m_2)!(l_2-m_2)!)^{\frac{1}{2}}} \quad (9.2)$$

Generally, it is sufficient to let $\hat{R} = 0$ (i.e., $\theta = 0$, $\phi = 0$). Eqn (9.1) then reduces to

$$1/r_{12} = 4\pi \sum_{\{l,m\}} \frac{(-1)^{l_1} r_1^{l_1} r_2^{l_2}}{R^{l_1+l_2+1}} b_{l_1 l_2}^{m_1} Y_{l_1 m_1}(\hat{r}_1) Y_{l_2 - m_1}(\hat{r}_2) \quad (9.3)$$

with

$$b_{l_1 l_2}^{m_1} = \frac{(l_1+l_2)!}{[(2l_1+1)(2l_2+1)(l_1+m_1)!(l_1-m_1)!(l_2+m_1)!(l_2-m_1)!]^{\frac{1}{2}}} \quad (9.4)$$

We now consider a 1s-type Gaussian charge distribution:¹⁹

$$\rho(r) = \frac{Ze}{\pi^{\frac{3}{2}} a^3} \exp(-r^2/a^2) \quad (9.5)$$

where Z is the charge. This charge distribution is not quantum mechanical,¹⁹ however, it does mimic some of the important features of an actual quantum mechanical description of an ionic system.²¹ The distance quantity has been referred to as "an effective Bohr radius".¹⁹ It is a quantity which has been found to correspond reasonably well with the crystallographic ionic radius. In the following discussion, we make the assumption that a is angle-dependent:

$$a(r) = a_0 [1 + \sum_{\lambda, \mu} \alpha_{\lambda \mu} Y_{\lambda \mu}^*(\hat{r})]. \quad (9.6)$$

The interaction energy is given by

$$\begin{aligned} V(R) &= \int d^3 r_1 \int d^3 r_2 (1/r_{12}) \rho_a(r_1) \rho_b(r_2) \\ &= 4\pi \sum_{\{l,m\}} (-1)^{l_2} b_{l_1 l_2}^{m_1} \frac{1}{R^{l_1+l_2+1}} \int d^3 r_1 r_1^{l_1} Y_{l_1 m_1}(\hat{r}_1) \rho_a(r_1) \times \\ &\quad \int d^3 r_2 r_2^{l_2} Y_{l_2 - m_1}(\hat{r}_2) \rho_b(r_2). \end{aligned} \quad (9.7)$$

Consider the general integral

$$\begin{aligned} \int d^3 r r^l Y_{lm}(\hat{r}) \rho(r) &= \frac{Ze}{\pi^{\frac{3}{2}}} \int d\Omega Y_{lm}(\hat{r}) \frac{1}{a^3} \int_0^\infty dr r^{l+2} \exp(-r^2/a^2) \\ &= (Ze/\pi) \frac{(l+1)!}{2^{2+l/2}} \int d\Omega Y_{lm}(\hat{r}) a(\hat{r})^l \\ &= Ze \frac{(l+1)!! a_0^l}{\pi 2^{2+l/2}} \int d\Omega Y_{lm}(\hat{r}) [1 + \sum_{\lambda, \mu} \alpha_{\lambda \mu} Y_{\lambda \mu}^*(\hat{r})]^l. \end{aligned} \quad (9.8)$$

By using the binomial expansion to the second order in the surface variables, we find

$$\int d^3r r^l Y_{lm}(\hat{r}) \rho(r) = Ze \frac{(l+1)!! a}{2^{2+l/2}} \left(\sqrt{4\pi} \delta_{l,0} + l \alpha_{lm} + \frac{l(l-1)}{2} \sum \alpha_{\lambda\mu} \alpha_{\lambda'\mu'} (\lambda|l|\lambda') (\lambda\lambda'\mu\mu'|lm) + \dots \right) \quad (9.9)$$

where $(\lambda\lambda'\mu\mu'|lm)$ is the Clebsch-Gordan coefficient²² and where

$$(\lambda|l|\lambda') = \left(\frac{(2\lambda+1)(2l+1)}{4\pi(2\lambda'+1)} \right)^{\frac{1}{2}} (\lambda\lambda'00|l0). \quad (9.10)$$

Therefore, the interaction is expressed as

$$V(R) = \frac{Z_a Z_b e^2}{4\pi R} \sum_{\{l,m\}} b_{l_1 l_2}^m \frac{(-1)^{l_2} a_0^{l_1} b_0^{l_2}}{2^{(l_1+l_2)/2} R^{l_1+l_2}} [\sqrt{4\pi} \delta_{l_1,0} + l_1 \alpha_{l_1 m} + \frac{1}{2} l_1 (l_1 - 1) \sum (\lambda|l_1|\lambda') (\lambda\lambda'\mu\mu'|l_1 m) \alpha_{\lambda\mu} \alpha_{\lambda'\mu'}] [\sqrt{4\pi} \delta_{l_2,0} + l_2 \beta_{l_2 m} + \frac{1}{2} l_2 (l_2 - 1) \sum (\lambda|l_2|\lambda') (\lambda\lambda'\mu\mu'|l_2 m) \beta_{\lambda\mu} \beta_{\lambda'\mu'}] \quad (9.11)$$

where the β -quantities apply to the b -species.

For a Slater-type distribution¹⁹

$$\rho(r) = \frac{Ze}{8\pi a^3} \exp(-r/a) \quad (9.12)$$

the interaction can be written as

$$V(R) = \frac{Z_a Z_b e^2}{16\pi R} \sum_{\{l,m\}} b_{l_1 l_2}^m \frac{(-1)^{l_2} (l_1 + 2)! (l_2 + 2)! a_0^{l_1} b_0^{l_2}}{R^{l_1+l_2}} \times \{ \dots \text{same as in eqn (9.11)} \dots \}. \quad (9.13)$$

It is clear from the structure of eqn (9.11) that the interaction considered in the last section is duplicated here. Considering only the surface quadrupole modes, eqn (9.11) can be expanded to give

$$V(R) = \frac{Z_a Z_b e^2}{R} \left(1 + \frac{1}{\sqrt{5\pi} R} [a_0^2 \alpha_{20} + b_0^2 \beta_{20}] + \frac{a_0^2 b_0^2}{4\pi R^4} \sum_m b_{22}^m \alpha_{2m} \beta_{2m} + \frac{1}{4\sqrt{\pi} R^2} \sum_{m,\mu,\mu'} \times \{ a_0^2 [(2|2|2)(22\mu\mu'|2m) + (2|4|2)(22\mu\mu'|4m)(a_0/R)^2] \alpha_{2\mu} \alpha_{2\mu'} + b_0^2 [(2|2|2)(22\mu\mu'|2m) + (2|4|2)(22\mu\mu'|4m)(b_0/R)^2] \beta_{2\mu} \beta_{2\mu'} \} \right). \quad (9.14)$$

The first term is of course the direct interaction between the ions. The second term is the interaction between the ion and the surface modes of the neighbouring species. The third term expresses the coupling between the surface modes on the separate centres to the lowest order, bilinear interaction. Finally, the last term expresses the effect of the interaction on the force constants (or stiffness coefficients) for the surface modes. In addition, this same term indicates that the presence of a neighbouring ion causes a mixing of the various quadrupole modes on the individual solvated species.

It is possible to see that as a result of the combination of the interaction between solvated ionic species, together with the internal interactions discussed in the last two sections, the configuration of solvent about an ion should be different from that of a simple spheroid.

10. DISCUSSION

It is important to note the distinction between this work and the previously reported completely continuous hydrodynamic treatment of solvation.^{3, 4} This distinction has been mentioned, but bears repeating for emphasis.

The treatment presented in this paper, together with the last two papers,^{1, 2} is a semicontinuous one. The discrete vibrations of the centrally located, solvated ion are handled specifically by means of an appropriate analysis. In particular, these vibrations are those of a discrete mass which is trapped inside a spherical harmonic oscillator well.^{1, 2}

On the other hand, the solvation structure is handled in this paper as a continuum. It is a continuum in the sense of a fluid drop. First, the breathing modes of the solvation structure are handled as hydrodynamic density fluctuations. Second, there are considered oscillations of the solvation surface. These oscillations are volume-conserving and are superimposed upon a stationary density state of the system. The surface oscillations are low energy modes. However, they are very important to any consideration of the deformation of the solvation structure.

In contrast to the treatment presented here, previously^{3, 4} the ionic dipolar oscillations within the solvation shell and the breathing modes were considered within the framework of a single continuum, hydrodynamic treatment. In that particular analysis the model of the system was that of two inter-penetrating fluids, one charged and one electrically neutral. Although that treatment allowed similar interpretations of the vibrational spectra of the solvated alkali metal cations,³ it is clear from this work^{1, 2} that the discrete representation of the central ion provides greater flexibility and, more important, it is more accurate. It is reasonable therefore to replace the previous continuum treatment with a semi-continuum one, as we have done here. The fluid in this case is the conceptually simpler single component solvent. The continuum solvent fluid (which is, nevertheless, distinct from the bulk of the solution system) and the ion interact with one another. This interaction is a reflection of the locally special character of the state of solvation of the ion.

It is reasonable to treat the solvation structure as a continuum. Most of the dynamical aspects of ionic and molecular solvation, as they are important to various transport and rate processes, do not reflect any discrete character of the solvation structure. Indeed, it is arguable just how extensive and organized the solvation structure really is. Thus, the continuum treatment of the solvation shell is sufficiently flexible to be able to include account of several molecular layers when the solvation structure is that extensive. Locally compact solvation structures may still require a discrete molecular vibrational analysis in terms of normal modes, *etc.* This should be the case for transition metal solvo-complexes in which the primary solvation shell molecules are covalently bonded to the central ion. The secondary solvation shell probably is of a loose structure in these cases. Therefore, the semi-continuum treatment implies a normal mode analysis for the molecular solvo-complex and a continuum treatment of the remaining solvation structure. Such a situation has not been considered here. The analysis of the interaction between the molecular system and the continuum solvation structure can be generated by means of a straightforward extension of the analysis presented here; such an analysis, however, will be much more complicated in view of the increased number of discrete-continuum interactions which must be considered.

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