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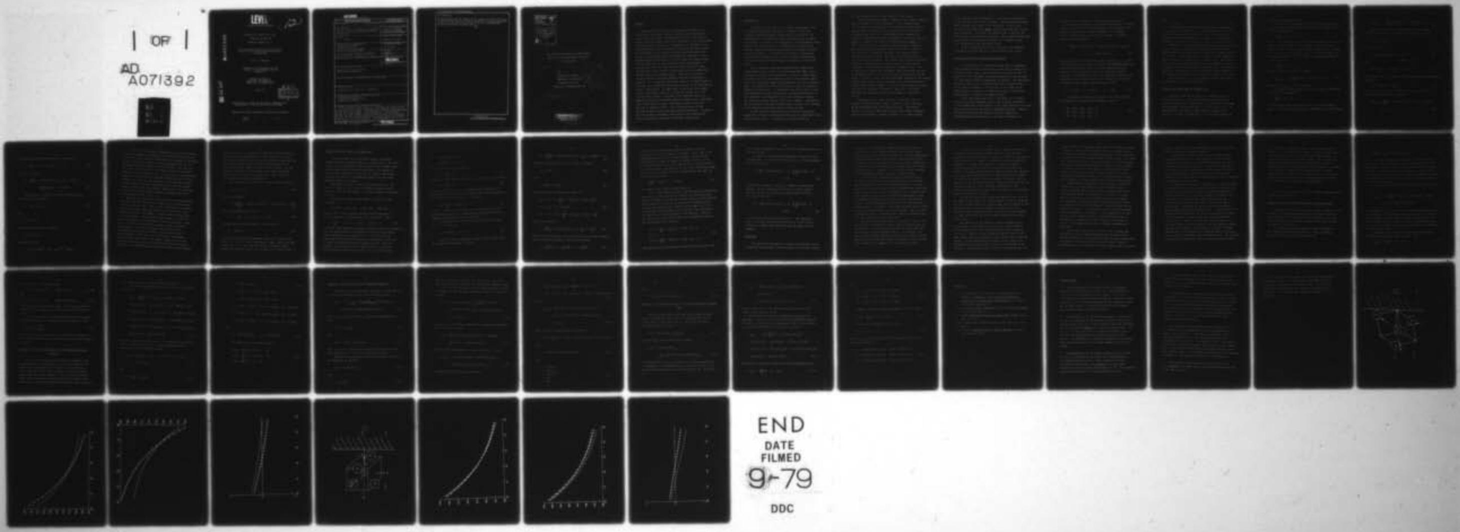

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The Vibrational Spectrum of Alkali Metal Cations in Distorted Solvation Shells: A Prediction

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The purpose of this paper is to examine the effect of the distortion of the primary solvation shell upon the vibrations of an ion within this shell. In addition, the effect of an external charge (or image charge) on the vibrations is investigated. We find that distortions (including the presence of an external charge) can cause a splitting of the solution phase far infrared band into two or three new bands. The frequencies of the band

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maxima depend upon the nature of the solvation shell distortion. It appears that the far infrared vibrational spectrum may prove to be a tool to probe the structure and the intermolecular forces of adsorbed, solvated ions.

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Abstract

The purpose of this paper is to examine the effect of the distortion of the primary solvation shell upon the vibrations of an ion within this shell. In addition, the effect of an external charge (or image charge) on the ionic vibrations is also investigated. An objective of this work is to see whether it is possible to use predicted changes in the far infrared vibrational spectrum to probe the alterations in the solvation structure which take place when an ion is incorporated into the metal/solution interface. In the solution phase the vibrations of the ion within the solvation shell yield a single band, as was discussed in the previous paper. It is shown here that this single band can split into two or three new bands due to the presence of distortion of the solvation shell and the effect of an external charge. The case of the lithium cation dissolved in dimethylsulphoxide with four-coordination is examined. It is found that an external charge or an image charge in the metal has a pronounced effect upon the extent of the splitting of the far infrared band. An image charge in the metal, for example, yields a splitting of about 16 cm^{-1} when the lithium ion is 2 Å from the metal surface. Distortion of the solvation shell, for moderate deviations from uniform spherical symmetry, has a relatively small effect upon the system. Nevertheless, these distortions may have an important effect in the activation process of the electron transfer reaction and other transport processes. It appears that far infrared vibrational spectroscopy of the interface may be able to probe the structure of adsorbed, solvated ions.

Introduction

The purpose of this paper is to examine what happens to the far infrared vibrational spectrum of a solvated ion when the solvation structure undergoes various kinds of distortion. The incorporation of a solvated ion into the metal/solution interface, for example, is expected to be accompanied by some deformation of the primary ionic solvation shell. In addition, the presence of an external charge or an image charge outside the solvation structure can have an effect. It is therefore of interest to investigate these distorted systems to see if the far infrared spectrum might provide a tool for the investigation of interfacial structure and forces.

The far infrared vibrational spectrum of the symmetrically solvated alkali metal cations in dimethylsulphoxide (DMSO) (and in other polar solvent) can be understood in terms of a simple model. The model, which was investigated in detail in the previous paper,[1] consists of the cation trapped inside a primary, or inner, solvation cage. The vibrations of the ion are those of a mass in a spherical harmonic oscillator well. In the harmonic oscillator limit, it was shown that the classical electrostatic, ion-dipole interactions do not contribute to the magnitude of the force constant as long as the solvation structure retains simple cubic symmetry. Consequently, the far infrared vibrational spectra provide a probe of the structure of the repulsion forces which operate in these systems.

We show that the distortion of the solvation structure can produce two or three new vibrational bands from the single band of the solution phase species. In addition, an external charge or an image charge exerts a strong influence on the system.

The lithium cation in DMSO is examined. The primary solvation cage is assumed to be four-coordinated. In the solution phase it is assumed to be tetrahedral.[1] At the metal/solution interface an image charge produces most of the splitting if the solvation structure changes only by a few hundredths of an angstrøm unit. Two types of uniform distortion are examined: (1) uniform distortion along a C_3 symmetry axis, and (2) uniform distortion about a C_2 axis. In the first case, a single solvent molecule is allowed to move in or out of the solvation structure along the C_3 symmetry axis which passes through the molecule. The external charge is located on the same C_3 axis. This type of distortion leads to a splitting into two new bands. The second type of uniform distortion allows two solvent molecules to move in or out of the solvation structure to the same extent along their tetrahedral radii. The C_2 symmetry axis bisects the tetrahedral angle enclosed by the radii of the moving species. It is also the axis upon which the external charge is placed. In this case the vibrational spectrum of the original solution phase species splits into three bands with or without the presence of an external charge. Two of the bands, however, typically are very close together in frequency. Hence, it is not likely that they can be resolved in the solution phase or interfacial system.

The presence of an image charge in a metal due to an ion located 2 Å from the metal surface is shown to yield a splitting of the vibrational band of the order of 16 cm^{-1}. This result applies to a system in which the solvation shell remains unchanged from its solution phase, uniform structure. As is shown, changes in the solvation shell structure, i.e., distortions, can increase or decrease the extent of the splitting. Compressional distortions tend to decrease the extent of the splitting. In these cases the ionic vibrational modes appear little changed from the solution phase vibrations. Distortions of expansion tend to increase the extent of the vibrational band splitting. Thus, enhanced vibrational splitting may be looked upon as evidence for a tendency toward ionic desolvation in the interfacial state.

In the following sections these conclusions are documented by means of a detailed analysis of the distorted ionic system.

Vibrations Inside the Distorted Solvation Shell

It was pointed out in the previous paper that the potential energy function for the solvated ionic system must be expressed in a suitable form.[1] Thus, several expansions were used in order to express the small amplitude vibrational excursions of the ion about its equilibrium position in appropriate coordinates. The equilibrium position of the ion in a uniform, symmetrically solvated shell is at the centre of symmetry. In this case, it is natural to use spherical polar coordinates to analyse the single (s-type) vibrational degree of freedom in the harmonic limit.

On the other hand, when there is distortion, it is simpler to use a cartesian coordinate system. The system of coordinates is still appropriate to the analysis of the small amplitude vibrational excursions of the ion away from the equilibrium position. However, the centre about which the harmonic oscillator expansion is constructed need not necessarily be the centre of symmetry (if one exists), nor need it even be the equilibrium position.

The simplest procedure to follow when dealing with a distorted system is to consider the distortion effects with reference to the symmetric, solution phase system. Therefore, it is possible to write a general (cartesian) form of the harmonic oscillator potential energy function as

$$V = \frac{1}{2}(k_{xx}x^2 + k_{yy}y^2 + k_{zz}z^2) + k_{xy}(xy) + k_{xz}(xz) + k_{yz}(yz) + X_s x + Y_s y + Z_s z \qquad (1)$$

The quantities k are the (tensorial) force constants. X_s, Y_s, and Z_s are the shift forces which are related to the magnitude and direction of the displacement of the new equilibrium position with reference to the coordinate origin of the expansion system of coordinates. [Throughout this paper, the coordinate system for the expansion in terms of the Taylor series is taken to be the centre of symmetry of the solvated, uniform system.] Thus,

$$x_0 = -X_s/k_{xx}, \quad y_0 = -Y_s/k_{yy}, \quad z_0 = -Z_s/k_{zz}. \qquad (2)$$

The equations of motion for the ion in the three cartesian directions are of course easy to determine. They are

$$\begin{aligned} m\ddot{x} &= -k_{xx}x - k_{xy}y - k_{xz}z - X_s \\ m\ddot{y} &= -k_{yx}x - k_{yy}y - k_{yz}z - Y_s \\ m\ddot{z} &= -k_{zx}x - k_{zy}y - k_{zz}z - Z_s \end{aligned} \qquad (3)$$

and

$$k_{xy} = k_{yx}, \tag{4}$$

etc. For the purpose of determining the vibrational frequencies, it is possible to ignore the X_s, Y_s, and Z_s quantities in eqn (3). Thus, the vibrational problem reduces to one of finding three eigenvalues for the three degrees of freedom. The equilibrium position of the ion in the distorted system is given by eqn (2).

Although the vibrational equations of motion (3) are extremely simple in form, the major effort in solving the problem is the determination of the functional form of the force constants and the shift forces. In the next section we examine a simple system for which an analytical solution can be obtained easily. The system is that of a tetrahedrally solvated ion which is uniformly distorted by moving a solvent dipole along a C_3 symmetry axis. Following this analysis we will examine a system in which two solvent molecules are allowed to move uniformly in and out with respect to a C_2 axis.

The derivations of the force constants and the shift forces are considered in a series of appendices.

Uniform Distortion Along a C_3 Symmetry Axis

The model system and the system of coordinates used are illustrated in Fig. 1. The solvent molecules are labelled (1) to (4) with molecule (4) lying on the C_3 axis which passes through the coordinate origin and the points (-1,-1,1) and (1,1,-1). An external charge (or metallic image charge) is located at the point (c,c,-c) where $c=R_i/\sqrt{3}$, and R_i is the distance between the charge and the coordinate origin.

For tetrahedral solvation, the sum of the electrostatic contributions to the potential energy function from the dipoles (1) to (3) is (see appendix 2)

$$-\frac{3}{2}\frac{\mu e}{R_e^4}(-xy + xz + yz)$$

where μ is the magnitude of the solvent dipole moment, and where the location of the molecule (1), for example, is given by (a,a,a) with $a = R_e/\sqrt{3}$. A single displaced dipole on the C_3 axis is located at (-b,-b,b) with $b = R_d/\sqrt{3}$ where R_d is the distance along C_3 the ion has been displaced. The ion-dipole interaction contribution from this term is

$$-\frac{3}{2}\frac{\mu e}{R_d^4}(xy - xz - yz).$$

The sum of these two terms is written as

$$V_{dist(i)} = -\frac{3}{2}\frac{\mu e}{R_e^4}[(R_e/R_d)^4 - 1](xy - xz - yz). \qquad (5)$$

When $R_d = R_e$, $V_{dist(i)} = 0$, as required.

The external charge located at (c,c,-c) yields a contribution of the form (see appendix 1)

$$\frac{Ze^2}{R_i^3}(xy - xz - yz).$$

Z is the charge on the external species. This term is added to eqn (5) to give the total electrostatic contribution to the potential:

$$V_{\mathrm{dist(el)}} = -\left\{\frac{3}{2}\,\frac{\mu e}{R_e^4}\,[(R_e/R_d)^4 - 1] - Ze^2/R_i^3\right\}(xy - xz - yz). \tag{6}$$

Next, we consider the contribution from the ion-solvent repulsion interactions. The potential is written in the form

$$V = V_0 + V_{\mathrm{dist(r)}} \tag{7}$$

with (see appendix 3)

$$V_0 = \frac{1}{2}\{3p(R_e) + p(R_d)\}(x^2 + y^2 + z^2) \tag{8}$$

$$= \frac{1}{2}k(x^2 + y^2 + z^2)$$

and

$$p(R) = \frac{B}{3\rho^2}(1 - 2\rho/R)\exp[-(R - R_e)/\rho]. \tag{9}$$

The constants B and ρ are found in the general form of the exponential repulsion[1]

$$V_r(R) = B\exp[-(R - R_e)/\rho]; \tag{10}$$

B is of the order of 2.3×10^{-13} erg and ρ is 1.9×10^{-9} cm. The distortion contribution is given by

$$V_{\mathrm{dist(r)}} = \frac{B}{3\rho}\left\{\frac{1}{R}(1 + \rho/R)\exp[-(R - R_e)/\rho] - (1 + \rho/R_e)/R_e\right\}$$

$$\times(xy - xz - yz) \tag{11}$$

The complete potential energy function is expressed as

$$V = \frac{1}{2}k(x^2 + y^2 + z^2) + f_c(xy - xz - yz) \tag{12}$$

where f_c is given by

$$f_c = \frac{B}{3\rho}\left\{\frac{1}{R}(1 + \rho/R)\exp[-(R-R_e)/\rho] - \frac{1}{R_e}(1 + \rho/R_e)\right\}$$

$$- \frac{3}{2}\frac{\mu e}{R_e^4}[(R_e/R_d)^4 - 1] + Ze^2/R_i^3. \tag{13}$$

The equations of motion (3) yield the following secular equation for the frequencies:

$$x^3 - 3f_c x + 2f_c^3 = 0 \tag{14}$$

with

$$x = m\omega^2 - k. \tag{15}$$

The solutions to (14) are well known;[2]

$$x = 2f_c, -f_c, -f_c,$$

from which we write

$$\omega = [\omega_0^2 + 2f_c/m]^{1/2}, \quad [\omega_0^2 - f_c/m]^{1/2} \quad \text{(twice)}.$$

Figs. 2 and 3 illustrate the dependence of the two frequencies on the displacement of the fourth solvent dipole along the C_3 axis. It can be seen that when the solvent dipole is displaced a sufficient distance inward, the vibrations of the ion along the C_3 axis are of a higher frequency than the vibrations normal to the same axis. For the ion in the absence of an external charge, this behaviour changes at the point where $R_d = R_e$. As R_d increases, the vibrations along the C_3 axis decrease in frequency compared to the vibrations normal to the exis. The same behaviour is seen when the external or image charge is present (provided of course that the external charge is opposite the ionic charge). When there is an attraction between the ion and the external charge, the change-over point in the behaviour occurs for $R_d < R_e$.

When the solvation shell is distorted, the ionic equilibrium position shifts from the centre of symmetry of the solution phase system to a new position. Note, in these calculations the distance between the external charge and the centre for the Taylor series expansion (to obtain the harmonic oscillator terms) has been kept a constant quantity. [The distance between charges is about 5 Å which corresponds to the electrostatic interaction between a charge and its image in a metal where the charge is about 2 Å from the metal surface.] The actual distance between the ion at its instantaneous location and its image or the external charge is given inherently in this work. The shift forces, the harmonic terms, and additional terms in the Laplace expansion of 1/r when all taken into account give the actual interaction for the actual separation. In constructing the harmonic oscillator system potential energy function, it is possible to eliminate the linear terms by means of a simple diagonalization. Thus, there arise constant terms in the complete expression for the potential energy function which together with the terms expressed here account for the interaction between charges for their actual locations. For the harmonic oscillator problem, however, these terms vanish upon differentiation leading to the force terms. Hence, they are not displayed, nor are they needed here.

The shift forces, cf. eqn (2), for this system are given by

$$X_s = Y_s = -Z_s = f_s \tag{18}$$

with (see appendix 4)

$$f_s = \frac{1}{\sqrt{3}}\left\{2\frac{\mu e}{R_e^8}[1 - (R_e/R_d)^3] + (B/\rho)(1 - \exp[-(R-R_e)/\rho] - e^2/R_i^2\right\} \tag{19}$$

The new equilibrium positions are

$$x_0 = - f_s/k, \quad y_0 = -f_s/k, \quad z_0 = f_s/k. \tag{20}$$

The magnitude of the displacement is given simply by

$$R_s = \sqrt{3}|f_s|/k \tag{21}$$

and the direction of the displacement (along C_3) is given by the sign of f_s. If $f_s > 0$, the displacement is <u>away</u> from the external charge. As Fig. 4 shows, when the dipole is displaced inward toward the coordinate origin, the ion tends also to move in with it.

Uniform Distortion About a C_2 Symmetry Axis

A second soluble distortion model involves the uniform distortion about (instead of along) a C_2 symmetry axis. The result of this type of distortion is the splitting of the original single solution phase band into three separate bands. The analytical forms for the frequencies in this case are simple in appearance, and can be derived in a straightforward manner from the system discussed in the last section.

The geometry of the system is illustrated in Fig. 5. The y-axis is chosen as the C_2 axis of reference; obviously, any C_2 axis will yield the same results. An external charge is located at $(0,R_i,0)$.

The positions of the solvent dipoles are seen to be the following:

$$(0,a,\sqrt{2}a), \quad (0,a,-\sqrt{2}a), \quad (-\sqrt{2}a,-a,0), \quad (\sqrt{2}a,-a,0)$$

with $a = R/\sqrt{3}$. These locations can be generated from those of Fig. 1 by means of a rotation about the y-axis of 45°. Thus,

$$x \rightarrow \frac{1}{\sqrt{2}}(x' - z'), \quad y \rightarrow y', \text{ and } \quad z \rightarrow \frac{1}{\sqrt{2}}(x' + z') \tag{22}$$

in the new frame (henceforth we drop the prime on the new coordinates). The same transformations can be applied directly to the potential energy function for the system of Fig. 1. In order to get an appropriate representation for this new system, however, some care is needed to consider the correct grouping of terms. Thus, for example, with reference to Fig. 1, the ion-dipole interactions for the dipoles located at (a,a,a) and $(-a,a,-a)$ can be written as

$$-\frac{3}{2}(\mu e/R^4)(xy + xz + yz)$$

$$-\frac{3}{2}(\mu e/R^4)(-xy + xz - yz).$$

The sum of these terms is obviously

$$V_1 = -3\frac{\mu e}{R_1^4}(xz) \qquad (23)$$

Similarly, for the dipoles located at (a,-a,-a) and (-a,-a,a) one gets

$$V_2 = +3\frac{\mu e}{R_2^4}(xz)\ . \qquad (24)$$

If $R_1 = R_2$, then $V_1 + V_2 = 0$, as required in the symmetric case. However, here we allow $R_1 \neq R_2$, and further apply the transformations (22) to the sum of (23) and (24). The result is

$$V_{id} = \frac{3}{2}\frac{\mu e}{R_e^4}[1 - (R_e/R_d)^4](x^2 - z^2) \qquad (25)$$

in the C_2 system of Fig. 5. [Note, the transformations (22) are vibrational principal axis transformations which have the effect of diagonalizing the potential energy function.]

The contribution to the potential from the external charge (of Z = -1) is written as

$$V_e = (e^2/2R_i^3)(x^2 - 2y^2 + z^2). \qquad (26)$$

Finally, by means of arguments similar to those already used, the repulsion contribution is written as

$$V_r = \frac{B}{3\rho}\left\{\frac{1}{R_d}(1 + \rho/R_d)\exp[-(R_d-R_e)/\rho] - \frac{1}{R_e}(1 + \rho/R_e)\right\}(x^2 - z^2). \tag{27}$$

With p(R) defined by eqn (9), the r^2 term is written as

$$V_{sym} = \frac{1}{2}kr^2 \tag{28}$$

with

$$k = 2p(R_e) + 2p(R_d) \tag{29}$$

Thus, the equations of motion are found to be

$$m\ddot{x} = -F_x x = -\left\{k + 3\frac{\mu e}{R_e^4}[1 - (R_e/R_d)^4] + e^2/R_i^3 + 2f_r\right\}x$$

$$m\ddot{y} = -F_y y = -\left\{k - 2e^2/R_i^3\right\}y \tag{30}$$

$$m\ddot{z} = -F_z z = -\left\{k - 3\frac{\mu e}{R_e^4}[1 - (R_e/R_d)^4] + e^2/R_i^3 - 2f_r\right\}z$$

where f_r is defined by

$$f_r = \frac{B}{3\rho}\left\{\frac{1}{R_d}(1 + \rho/R_d)\exp[-(R_d-R_e)/\rho] - \frac{1}{R_e}(1 + \rho/R_e)\right\}. \tag{31}$$

Because of the differences in the expressions for the force constants, three vibrational frequencies clearly can be defined:

$$\omega_x = \frac{1}{2\pi}\sqrt{F_x/m}, \quad \omega_y = \frac{1}{2\pi}\sqrt{F_y/m}, \quad \omega_z = \frac{1}{2\pi}\sqrt{F_z/m}\ . \tag{32}$$

In the absence of an external charge, and when $R_d = R_e$, the frequencies (32) are all equal one to another. Note, *that in the* configuration of Fig. 5 the solvent molecules between the ion and the external charge (or image) are allowed to move. As the two solvent molecules leave the solvation cage in the direction of the external charge, the vibrations in the x and y directions change. There is a point at which these two frequencies are the same, but for which $R_d \neq R_e$; when

$$3\,\frac{\mu e}{R_e^4}[1 - (R_e/R_d)^4] = -\,2f_r(R_d) \tag{33}$$

the system of three *bands* collapses into two.

It is a simple matter to reverse the situation just considered. That is, it is easily possible to maintain the solvent molecules which lie between the ion and the external charge in fixed positions and to examine the effect of the vibrational frequencies as the solution-side molecules move further into the cage or out of it. Retaining the external charge on the positive y-axis at $(0,R_i,0)$, but allowing the solvent molecules at the positions $(-\sqrt{2}a,-a,0)$ and $(\sqrt{2}a,-a,0)$ to move radially along their tetrahedral radii, we get the following force constants:

$$\begin{aligned}
F_x' &= k - 3\frac{\mu e}{R_e^4}[1 - (R_e/R_d)^4] + e^2/R_i^3 - 2f_r = F_z \\
F_y' &= F_y \\
F_z' &= k + 3\frac{\mu e}{R_e^4}[1 - (R_e/R_d)^4] + e^2/R_i^3 + 2f_r = F_x .
\end{aligned} \tag{34}$$

The roles of F_x' and F_z' are merely reversed from the previous case.

This second arrangement is more in line with the model discussed in the last section.

It remains to consider the displacement of the ion in this configuration. For the situation shown in Fig. 5, the displacement force is found to be

$$Y_s = \frac{2}{\sqrt{3}}(B/\rho)\left\{\exp[-(R_d-R_e)/\rho] - 1\right\} + \frac{4}{\sqrt{3}}\frac{\mu e}{R_e^3}[(R_e/R_d)^3 - 1]$$

$$- e^2/R_i^2. \qquad (35)$$

There are no components X_s and Z_s, as symmetry considerations dictate. For the configuration in which the solvent dipoles which lie between the ion and the external charge are fixed, it is easy to see that

$$Y'_s = -\frac{2}{3}(B/\rho)\left\{\exp[-(R_d-R_e)/\rho] - 1\right\} - \frac{4}{3}\frac{\mu e}{R_e^3}[(R_e/R_d)^3 - 1]$$

$$- e^2/R_i^2. \qquad (36)$$

As in the last section, here as well, $y'_0 = - Y'_s/k$ indicates a shift of the ionic equilibrium position closer to the external charge for a compressional distortion, and the opposite for an expansion.

Discussion

The vibrational structure of a solvated electroactive species is important in particular in the activation of an electron transfer reaction. The displacement of the electroactive species to a position closer to or farther away from another active centre will have an effect on the rate of reaction. Clearly, deformations of the solvation structure which enable charge transfer species to approach closer than would be the case for rigid, symmetrical solvation will assist the transfer by allowing the system greater overlap potential. Therefore, it is necessary to have knowledge of the vibrational structure of these solvated systems.

The most likely experimental system in which to observe the effects of solvation shell deformations on the vibrational spectrum appears to be the metal/solution interface. For this reason, the preceeding discussion and the examples have been given with reference to this system. Nevertheless, it is equally clear that distortion effects may be important in homogeneous systems. For example, the transfer of an electron between electroactive species in the solution phase may depend in part upon transient, deformed states of solvation. Such states, however, are not likely to be observed due to their very short lifetimes. Thus, it would seem that the primary information about solvation deformation must come from studies of the interfacial state.

In this section several matters are discussed. Some of the discussion is an elaboration of the results presented in the last two sections. Some of the discussion concerns conclusions which can be drawn from the preceeding results. In particular, the nature of the solvation deformation observed here suggests further modeling which can take into account the dynamics of the solvation shell as well as the dynamics of the ion within the shell.

As the results of the analyses clearly show, the vibrational spectrum of an ion within a deformed solvation shell can only reveal the forces which operate between the ion and the surrounding solvent dipoles. The analyses presented here were based upon the assumption of solvent configurations. It certainly cannot be stated that one form of distortion is necessarily favoured over another. The answer to that question requires further the consideration of the interaction between the solvent dipoles, their images, the rest of the solution, and their images in the metal. Such an analysis has not yet been carried out. However, on the basis of the behaviour of the ion in the structures displayed here, some tenative conclusions can be made even in the absence of a definitive interfacial solvation structure.

We note that unless the solvated ion approaches very close to the metal surface, there is no strong tendency present to desolvate. The ion is shifted inside its solvation cage in the direction of the attractive image. However, assuming a configuration of close packing of solvent molecules on the metal surface, there probably is little liklihood an ion will be found in contact with the bare metal surface.

The expansion of the solvation structure brought about by the departure (or the tendency to depart) of a solvent molecule on the solution side of the interfacial system tends to take the ion with it. That is, a loose solvation structure normal to the metal surface favours an increased distance between the ion and the surface. If the solvent molecule actually leaves, however, the ion generally will remain in the vicinity of the remainder of the structure. The remaining forces of attraction between the ion, its image, the other solvent dipoles are likely to hold the ion in the interface as another solvent molecule moves in from the solution to build up the solvation structure once again. On the other hand, a compressed solvation structure favours a more compact system with the ion displaced closer to the metal surface. It is not possible, of course, to determine which type of structure (loose or compact) is likely on the basis of the analyses presented in this paper. However, in view of the possible solvent dipole-image dipole interactions which are possible, it is not unreasonable to expect that a compact, distorted structure may be found in the interface.

Unfortunately, the analysis of the two types of distortion (along the C_3 axis and about the C_2 axis) indicate that for compact structures the splitting of the vibrational band of the solution phase system is not as great as it would be if there were no distortion or if the solvation system were to expand. For lithium, for example, the mobile solvent group would have to be compressed 0.1 Å in the direction of the metal surface for the splitting to vanish. It is difficult to say at this time whether such a displacement is reasonable. As was indicated in the introduction, if the solvation structure remains unaltered from its solution phase configuration, the splitting is of the order of 16 cm^{-1}. A splitting of this order is probably experimentally observable.

In any case, whether or not the distortion is present and observable in the far infrared spectrum, the distortion of the solvation structure (if it exists) will enter into any consideration of the process of activation of an electron transfer reaction. The dynamics of ionic vibration inside the solvation cage, as worked out here, apply to the electron transfer reaction system, and to other solution phase transport processes.

The examples discussed in the last two sections assumed tetrahedral solvation. It is not difficult to derive similar expressions which apply to the octahedral solvation case and to other possible solvation structures. Indeed, in the appendices to follow, the various contributions to the harmonic oscillator limit potential energy function are expressed in sufficient generality to be applicable to any distribution of solvent molecules in the primary solvation shell.

An important consequence of these analyses is the following. The harmonic oscillator limit implies for these systems that the various distortions can be viewed as ellipsoidal deformations. Thus, in both cases, i.e., distortion along C_3 or about C_2, an expansion of the solvation shell effectively distorts the spherical system into a prolate shape, a compression into an oblate shape. The dynamics of the solvation shell definitely have not been taken into consideration here. In the spirit of the Born-Oppenheimer separation, the ion has been allowed to vibrate within a stationary solvent cage in any state of deformation. In real systems, clearly, the solvation structure alters as the ion moves through the solution medium. The ion probably responds adiabatically to changes in the solvation structure. The fact that the form of the distortion is ellipsoidal makes it possible to simplify the consideration of the combined system. The solvation structure can be regarded as that of a vibrating liquid surface.[2]

It is possible to formulate a theory of the deformation of this surface. It is also possible to examine the effect of the surface on the vibrations of the ion contained within the surface. An adequate treatment of the solvation surface, and its vibrations, requires the consideration of the primary and the secondary solvation shells. Such a treatment is now in progress. It suffices at this point to conclude by noting that once the solvation structure and its dynamics have been specified, it is possible to predict the nature of the ionic vibrations inside the solvation shell with the use of the analysis presented here.

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Appendix 1: Vibrations in the Presence of an External Charge

The simplest type of distortion to consider is that due to the presence of a single external charge placed outside the primary solvation cage. This charge can arise, for example, as an image charge in a metal or it might be a counter ion of some form held in place in a rigid lattice.

We consider an expansion about the centre of symmetry for the isolated, symmetrically solvated ion. Thus, the Laplace expansion of the free space Green function is[3]

$$\frac{1}{|\underset{\sim}{r}-\underset{\sim}{R}|} = 4\pi \sum_{\ell,m} (2\ell+1)^{-1} Y^{*}_{\ell m}(\hat{R}) Y_{\ell m}(\hat{r}) r^{\ell}/R^{\ell+1} \tag{1.1}$$

and R > r. $Y_{\ell m}(\hat{r})$ is the spherical harmonic function[3] with $\hat{r}$ the unit vector. The second order term ($\ell=2$) contributes directly to the harmonic oscillator terms in the vibrational potential energy function. The first order terms are associated with the actual displacement of the ion away from the centre of symmetry associated with the symmetrically solvated ion. These first order terms will be considered in appendix 4.

The second order electrostatic contribution can be expressed as

$$V_{2(el)} = (Z_1Z_2)\frac{e^2}{R^5}\Big\{\frac{3}{4}(X^2-Y^2)(x^2-y^2) + 3[(XY)(xy) + (XZ)(xz) + (YZ)(yz)] + \frac{1}{4}(3Z^2-R^2)(3z^2-r^2)\Big\} \tag{1.2}$$

The coordinates (X,Y,Z) locate the position of the external charge with reference to the coordinate origin at the centre of symmetry of the solvated ion. The location of the ion with respect to the same coordinate origin is given by (x,y,z). Upon differentiation of these ionic coordinates (x,y,z), the contributions to the force field are easily found.

The simplest case to consider places the external charge along the principal axis: viz., at R on z. Thus,

$$V_{2(el)} = Z_1Z_2\frac{e^2}{R^3}[z^2 - \frac{1}{2}(x^2 + y^2)] \tag{1.3}$$

As a result, it is possible to write

$$k_+ = k_0 + 2Z_1Z_2e^2/R^3 \qquad \text{(along the z-axis)} \tag{1.4a}$$

and

$$k_- = k_0 - Z_1Z_2e^2/R^3 \qquad \text{(normal to the z-axis)} \tag{1.4b}$$

where the k are force constants, and k_0 is the force constant with reference to the symmetric system in the absence of the external charge.

Assume, for example, that the additional charge is an image charge in the metal for a solvated ion in the interface. Then,

$$\begin{aligned} k_+ &= k_0 - e^2/8D^3 \\ k_- &= k_0 + e^2/16D^3 \end{aligned} \tag{1.5}$$

where D is the distance between the ion and the metal surface. If D is 2 Å, the original lithium band splits into two bands separated by 16 cm^{-1}.

Appendix 2: Ion-Dipole Contributions to the Harmonic Oscillator Potential

It was shown in a previous paper[1] that for symmetric, cubic solvation there is no second order ($\ell=2$, r^2) contribution to the potential energy function arising from classical electrostatic terms. This ceases to be the case when the solvation structure departs from simple cubic symmetry. In this section, the general formula for the second order contribution to the potential which arises from the interaction between an arbitrarily placed dipole and ion located near the coordinate origin is presented.

The Carlson-Rushbrooke[4] expression to order $O(r^2)$ was given earlier[1] as

$$\begin{aligned} V_{2(CR)} = {} & \frac{(4\pi)^{3/2}}{\sqrt{3.5.7}} e\mu(r^2/R^4) \Big\{ Y_{2-2}(\hat{r})[-\sqrt{15}Y_{1-1}(\hat{a})Y_{33}(\hat{R}) \\ & + \sqrt{5}Y_{10}(\hat{a})Y_{32}(\hat{R}) - Y_{11}(\hat{a})Y_{31}(\hat{R})] + Y_{22}(\hat{r})[-\sqrt{15}Y_{11}(\hat{a})Y_{3-3}(\hat{R}) \\ & + \sqrt{5}Y_{10}(\hat{a})Y_{3-2}(\hat{R}) - Y_{1-1}(\hat{a})Y_{3-1}(\hat{R})] + Y_{2-1}(\hat{r})[\sqrt{10}Y_{1-1}(\hat{a})Y_{32}(\hat{R}) \\ & - \sqrt{8}Y_{10}(\hat{a})Y_{31}(\hat{R}) + \sqrt{3}Y_{11}(\hat{a})Y_{31}(\hat{R})] + Y_{21}(\hat{r})[\sqrt{10}Y_{11}(\hat{a})Y_{3-2}(\hat{R}) \\ & - \sqrt{8}Y_{10}(\hat{a})Y_{3-1}(\hat{R}) + \sqrt{3}Y_{1-1}(\hat{a})Y_{30}(\hat{R})] + Y_{20}(\hat{r})[-\sqrt{6}Y_{1-1}(\hat{a})Y_{31}(\hat{R}) \\ & + 3Y_{10}(\hat{a})Y_{30}(\hat{R}) - \sqrt{6}Y_{11}(\hat{a})Y_{3-1}(\hat{R})] \Big\} \end{aligned} \tag{2.1}$$

where $\hat{a}$ is the dipolar unit vector, μ is the magnitude of the dipole which is located at $\underset{\sim}{R} = (X,Y,Z)$. The transformation of this equation to cartesian coordinates yields

$$\begin{aligned} V_{2(CR)} = {} & \frac{3}{2}\frac{\mu e}{R^4}\Big\{(a' - c/2)x^2 - (a' + c/2)y^2 + cz^2 + 2\alpha xy \\ & + 2bxz + 2\beta yz\Big\} \end{aligned} \tag{2.2}$$

with

$$a' = \tfrac{1}{2}[XA_1 - YA_2]/aR^3 \tag{2.3}$$

$$\alpha = \frac{1}{2}[XA_1 + YA_2]/aR^3 \tag{2.4}$$

$$A_1 = a_x(3X^2 - 2Y^2 - 2Z^2) + 5a_yXY + 5a_zXZ$$

$$A_2 = 5a_xXY + a_y(3Y^2 - 2X^2 - 2Y^2) + 5a_zYZ$$

$$c = [(a_xX + a_yY)(4Z^2 - X^2 - Y^2) + a_zZ(2Z^2 - 3X^2 - 3Y^2)]/aR^3$$

$$b = [a_xZ(4X^2 - Y^2 - Z^2) + 5a_yXYZ + a_zX(4Z^2 - X^2 - Y^2)]/aR^3$$

$$\beta = [5a_xXYZ + a_yZ(4Y^2 - X^2 - Z^2) + a_zY(4Z^2 - X^2 - Y^2)]/aR^3$$

and

$$a = \sqrt{a_x{}^2 + a_y{}^2 + a_z{}^2}, \qquad R = \sqrt{X^2 + Y^2 + Z^2} \tag{2.5}$$

The contribution to the force field is

$$F_{x(CR)} = 3\frac{\mu e}{R^4}[(c/2 - a')x - \alpha y - bz]$$
$$F_{y(CR)} = 3\frac{\mu e}{R^4}[-\alpha x + (a' + c/2)y - \beta z] \tag{2.6}$$
$$F_{z(CR)} = 3\frac{\mu e}{R^4}[-bx - \beta y - cz].$$

Appendix 3: Contributions from the Exponential Repulsion

Given the Fourier transform of a function, it is possible to express the second order Taylor series expansion term as[1]

$$t_2(\underset{\sim}{r}) = -\frac{1}{\pi}r^2 \sum_{\ell,\nu}\sum_{L,M}(-i)^L\left\{\frac{2\lambda+1}{4\pi(2\ell+1)(2L+1)}\right\}^{1/2}(1100|\ell 0)^2$$

$$\times(\lambda\ell 00|L0)(\lambda\ell\mu\nu|LM)Y_{LM}(\hat{r}_0)Y^*_{\ell\nu}(\hat{r})I_L(r_0) \tag{3.1}$$

where $\underset{\sim}{r}_0$ is the expansion point. The Fourier transform has the form

$$f(\underset{\sim}{k}) = Y_{\lambda\mu}(\hat{k})g_\lambda(k) \tag{3.2}$$

and

$$I_L(r_0) = \int_0^\infty dk\; k^4\; g_\lambda(k)j_L(kr_0) \tag{3.3}$$

where $j_n(x)$ is the spherical Bessel function of the first kind,[3] and $(\ell_1\ell_2m_1m_2|\ell_3m_3)$ is the Clebsch-Gordan coefficient.[5]

The form of the repulsion interaction used in the last paper was exponential of the form[1]

$$V_r(\underset{\sim}{r}) = B\exp[-(R-a)/\rho] \tag{3.4}$$

where

$$B = 2e\mu\rho/R_e^3 \tag{3.5}$$

and ρ is a constant of the order of 1.9×10^{-9} cm. R_e is the equilibrium solvation radius for the symmetrically solvated system.

If we consider an expansion of the repulsion about the centre of symmetry for the bulk phase solvated ion, then $r_0 = 0$, and in general,[1]

$$t_2(r) = 2\pi r^2 (B/\rho^2) \exp(R_e/\rho) \sum_{\ell,\lambda,\mu} \left(\frac{2\lambda+1}{2\ell+1}\right)^{1/2} (1100|\ell 0)^2$$

$$\times (\lambda\ell 00|00)(\lambda\ell\mu{-}\mu|00) Y_{\lambda\mu}(\hat{R}) Y_{\ell-\mu}(\hat{r}) [(R/\rho)k_{\lambda+1}(R/\rho)$$

$$- (3+\lambda)k_\lambda(R/\rho)] \qquad (3.6)$$

where $k_n(x)$ is the modified spherical Bessel function of the third kind.[3] For $\ell=0$, $\lambda=0$, and

$$t_{2(0)} = \frac{1}{6} r^2 (B/\rho^2) \exp(R_e/\rho) [(R/\rho)k_1(R/\rho) - 3k_0(R/\rho)]$$

$$= \frac{1}{6} r^2 (B/\rho^2)(1 - 2\rho/R) \exp[-(R-R_e)/\rho] \qquad (3.7)$$

The only other contribution to t_2 comes from $\ell=2$, $\lambda=2$. Thus,

$$t_{2(2)}(r) = 2\pi r^2 (B/\rho^2)(1100|20)^2 (2200|00)[(R/\rho)k_3(R/\rho)$$

$$- 5k_2(R/\rho)] \sum_\mu (22\mu{-}\mu|00) Y_{2\mu}(\hat{R}) Y_{2-\mu}(\hat{r}) \qquad (3.8)$$

The summation in eqn (3.8) can be written as

$$(22\mu\text{-}\mu|00)Y_{2\mu}(\hat{R})Y_{2-\mu}(\hat{r}) = \frac{3\sqrt{5}}{16\pi}\{(X^2 - Y^2)(x^2 - y^2)$$

$$+ (3Z^2 - R^2)(3z^2 - r^2) + 4[(XY)(xy) + (XZ)(xz) + (YZ)(yz)]\}/R^2r^2 \tag{3.9}$$

Hence,

$$t_{2(2)}(\underset{\sim}{r}) = \frac{1}{2}(B/\rho R^3)(1 + \rho/R)\exp[-(R-R_e)/\rho]\{(X^2-Z^2)x^2$$

$$+ (Y^2-Z^2)y^2 + (3Z^2-R^2)z^2 + 2[(XY)xy + (XZ)xz$$

$$+ (YZ)yz]\} \tag{3.10}$$

When this term is combined with $t_{2(0)}$, we find

$$t_2(\underset{\sim}{r}) = \frac{1}{2}[(p+q)x^2 + (p+r)y^2 + (p+s)z^2] + \delta xy + \varepsilon xz + \zeta yz \tag{3.11}$$

with

$$p = (B/3\rho^2)(1-2\rho/R)\exp[-(R-R_e)/\rho] \tag{3.12}$$

and

$$\begin{aligned} q &= f(X^2-Y^2) \\ r &= f(Y^2-Z^2) \\ s &= f(3Z^2-R^2) \\ \delta &= fXY \\ \varepsilon &= fXZ \end{aligned} \tag{3.13}$$

$$\zeta = fYZ$$

with

$$f = (B/\rho R^3)(1+\rho/R)\exp[-(R-R_e)/\rho]. \qquad (3.14)$$

Appendix 4: The Equilibrium Position of the Ion Inside the Solvation Cage

The first order Taylor series term for the repulsion interaction is calculated with the use of the integral form of the Taylor series as discussed in ref. 1. Thus, with the Fourier transform of eqn (3.4) given by

$$v(\underset{\sim}{k}) = 8\pi B \exp(R_e/\rho)\ \frac{1}{\rho(1/\rho^2+k^2)^2} \qquad (4.1)$$

the first order Taylor series term is given by

$$t_1(\underset{\sim}{r}) = \underset{\sim}{r}\cdot[\nabla_r V_r(\underset{\sim}{r},\underset{\sim}{R})]\Big|_{\underset{\sim}{r}=\underset{\sim}{r}_0}$$

$$= -\frac{i}{(2\pi)^3}\ \underset{\sim}{r}\cdot\int d^3k\ \underset{\sim}{k}\ v(\underset{\sim}{k})\ \exp[-i\underset{\sim}{k}\cdot(\underset{\sim}{r}-\underset{\sim}{R})]\Big|_{\underset{\sim}{r}=\underset{\sim}{r}_0} \qquad (4.2)$$

As was discussed in ref. 1, we make use of separate expansions of the arguments in the exponential in the second line of eqn (4.2). The resulting integration can be carried out directly. The result is

$$t_1(r) = -\frac{4\pi}{3}(B/\rho)\exp(R_e/\rho)\,r \, {}_{m} Y^{*}_{1m}(\hat{r})Y_{1m}(\hat{R})[3k_1(R/\rho)$$

$$- (R/\rho)k_2(R/\rho)]$$

$$= (B/\rho R)\exp[-(R-R_e)/\rho](Xx + Yy + Zz). \tag{4.3}$$

Note, the value of R_e is the equilibrium solvation radius with respect to the symmetric system.

The electrostatic terms are somewhat more complicated in appearance. Again, use is made of the Carlson-Rushbrooke expansion[4] to express the shift terms in an appropriate form. The first order (ℓ=1,r) term contributes to the shift; it is given by

$$V_{1(CR)} = -\mu e\frac{r}{R^3}\frac{(4\pi)^{3/2}}{3\sqrt{5}}\{Y_{1-1}(\hat{r})[\sqrt{6}Y_{1-1}(\hat{a})Y_{22}(\hat{R})$$

$$- \sqrt{3}Y_{10}(\hat{a})Y_{21}(\hat{R}) + Y_{11}(\hat{a})Y_{20}(\hat{R})] + Y_{11}(\hat{r})[Y_{1-1}(\hat{a})Y_{20}(\hat{R})$$

$$- \sqrt{3}Y_{10}(\hat{a})Y_{2-1}(\hat{R}) + \sqrt{6}Y_{11}(\hat{a})Y_{2-2}(\hat{R})] + Y_{10}(\hat{r})[-\sqrt{3}Y_{1-1}(\hat{a})Y_{21}(\hat{R})$$

$$+ 2Y_{10}(\hat{a})Y_{20}(\hat{R}) - \sqrt{3}Y_{11}(\hat{a})Y_{2-1}(\hat{R})]\}. \tag{4.4}$$

Rewriting this expression in terms of cartesian coordinates gives

$$V_{1(CR)} = -\frac{\mu e}{R^3}[d_X x + d_Y y + d_Z z] \tag{4.5}$$

with

$$d_X = [a_x(2X^2-Y^2-Z^2) + 3a_yXY + 3a_zXZ]/aR^2$$
$$d_Y = [3a_xXY + a_y(2Y^2-X^2-Z^2) + 3a_zYZ]/aR^2 \qquad (4.6)$$
$$d_Z = [3a_xXZ + 3a_yYZ + a_z(2Z^2-X^2-Y^2)]/aR^2$$

Finally, an external charge Ne located at (X',Y',Z') yeilds

$$V_{1(ex)} = \frac{Ne^2}{(R')^3}[X'x + Y'y + Z'z]. \qquad (4.7)$$

Thus, upon combining terms, we can write

$$V_1 = X_sx + Y_sy + Z_sz \qquad (4.8)$$

where X_s, Y_s, and Z_s stand for the shift forces; these forces are given specifically by

$$X_s = (B/\rho R)\exp[-(R-R_e)/\rho]X - \mu ed_X/R^3 + Ne^2X'/(R')^3$$
$$Y_s = (B/\rho R)\exp[-(R-R_e)/\rho]Y - \mu ed_Y/R^3 + Ne^2Y'/(R')^3 \qquad (4.9)$$
$$Z_s = (B/\rho R)\exp[-(R-R_e)/\rho]Z - \mu ed_Z/R^3 + Ne^2Z'/(R')^3.$$

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Figure Captions:

1. The configuration of a solvated ion with a coordination number of 4 at the surface of a metal. The solvent molecules S_1 to S_3 lie in a plane coplanar with the surface. The C_3 axis is normal to the surface and passes through the ion and the solvent molecule S_4. D is the distance between the ionic expansion centre and the metal surface. The actual location of the ion depends upon the shift forces (see text for details).

2. The dependence of the vibrational frequencies in the system of Fig. 1 as a function of the distance the solvent molecule S_4 is displaced along the C_3 axis. These frequencies have been calculated for the system in the absence of an image or external charge. The line --Δ-- is associated with the vibrations along the C_3 axis. The other (two-fold degenerate) vibrations are normal to the C_3 axis. The frequencies are three-fold degenerate at the solution phase equilibrium point for the distance between the ion and the solvent.

3. The dependence of the vibrational frequencies in the system of Fig. 1 as a function of the distance the solvent molecule S_4 is displaced along the C_3 axis. These frequencies have been calculated for the system in the presence of an image charge located at a constant distance from the metal of 2 Å. The frequencies associated with the line --Δ--are those along the C_3 axis.

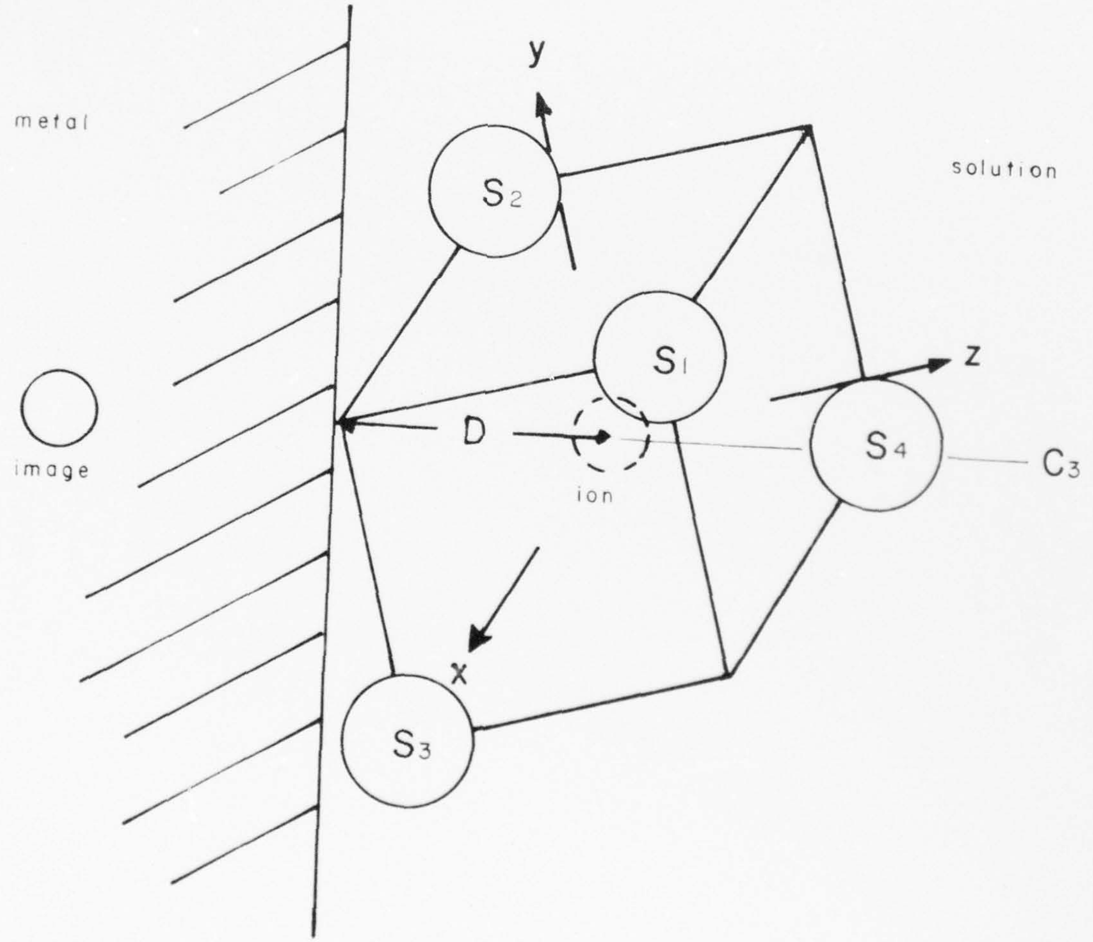
4. The displacement of the ion with reference to the centre of symmetry of the solution phase system. The displacement along the line --Δ-- is associated with the system in the presence of an image or external charge.

5. The configuration of solvent molecules about the ion in the case where the C_2 axis (colinear with the system y-axis) is normal to the metal surface. Two of the solvent molecules lie in a plane which is coplanar with the metal surface and which lies between the surface and the ion. The other two solvent molecules, on the solution side of the ion, lie also in a plane coplanar with the surface. As in Fig. 1, D is the distance between the ionic expansion point and the surface.

6. The dependence of the vibrations of the system of Fig. 5 as a function of the displacement of the solvent molecules in pairs. The solid line ---- represents the vibrations in the y-direction along the C_2 axis. The vibrations along the line --+-- are along the x-axis and --Δ-- are along the z-axis. This applies to the case for which the molecules between the ion and the surface move. If the solvent-side molecules are displaced in pairs, then the vibrations along --+-- correspond to vibrations in the z-direction and along --Δ-- correspond to vibrations in the x-direction.

7. The dependence of the vibrations of the system of Fig. 5 in the presence of an image charge. The interpretation of the lines is the same as in Fig. 6.

8. The displacement of the ion as a function of solvent molecule displacement. Curve --Δ-- indicates the displacement of the ion in the system in the absence of an image charge. The solid line indicates the displacement in the system in the presence of an image charge. In both cases, the solvent-side molecules of Fig. 5 are mobile.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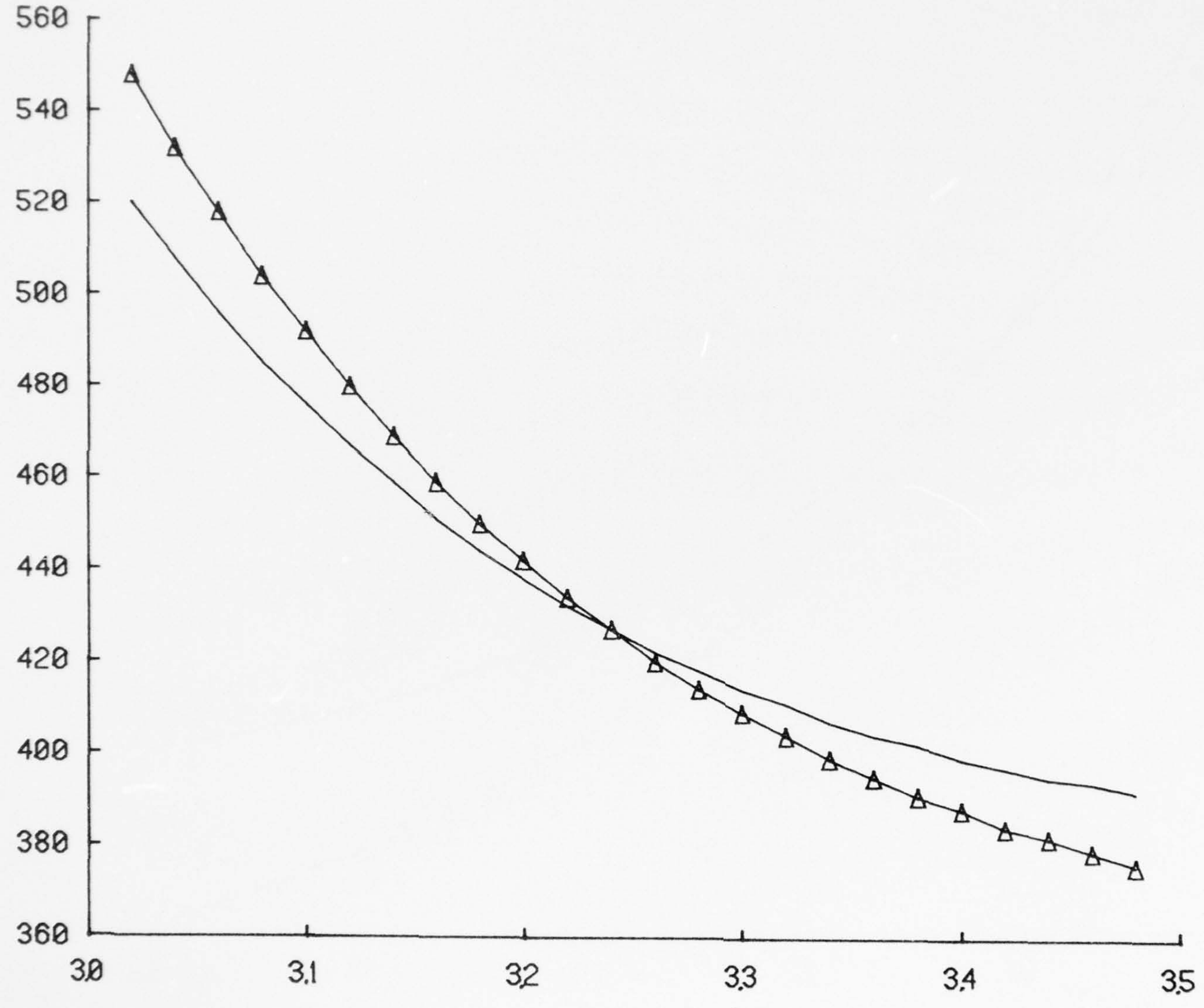
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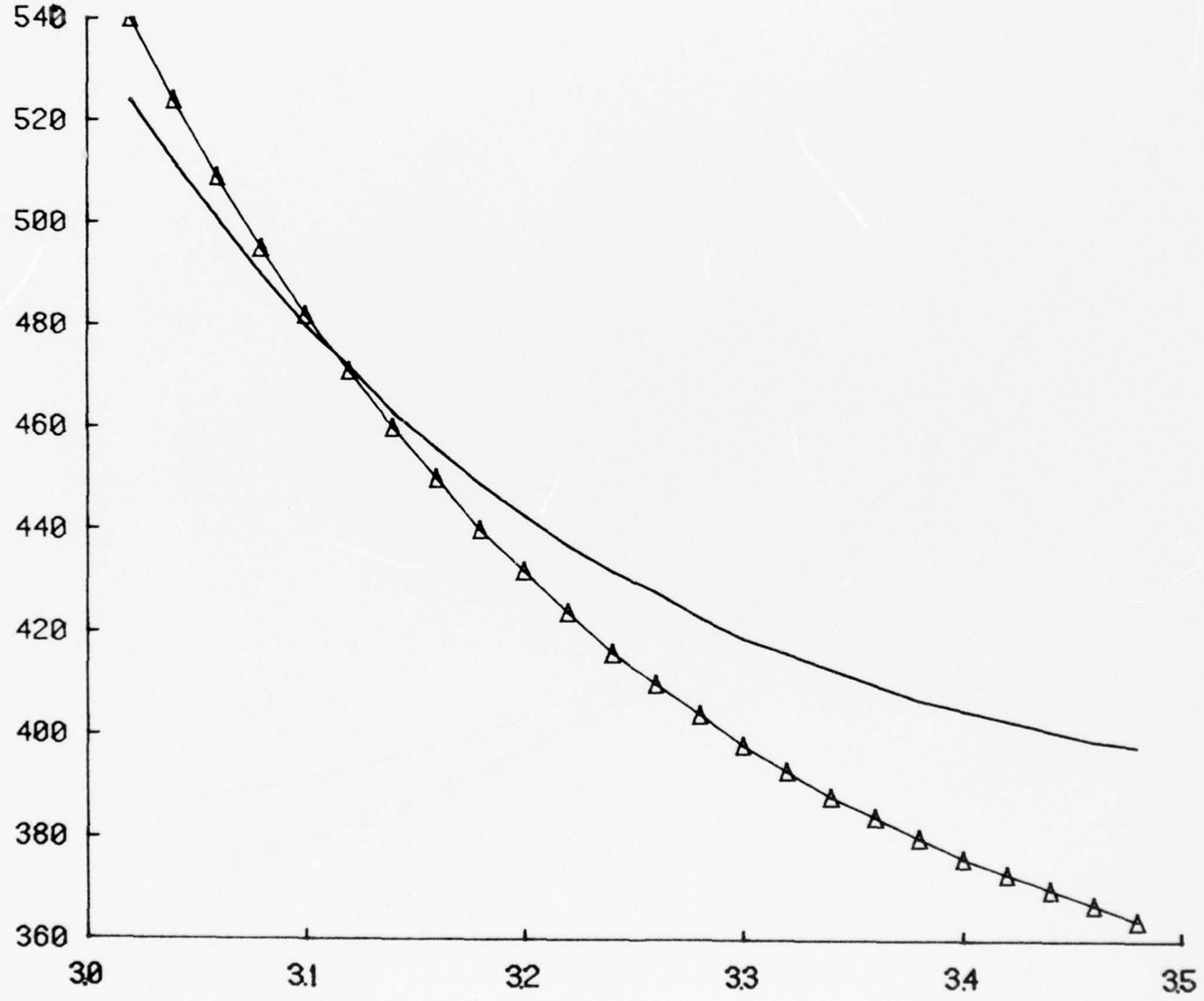
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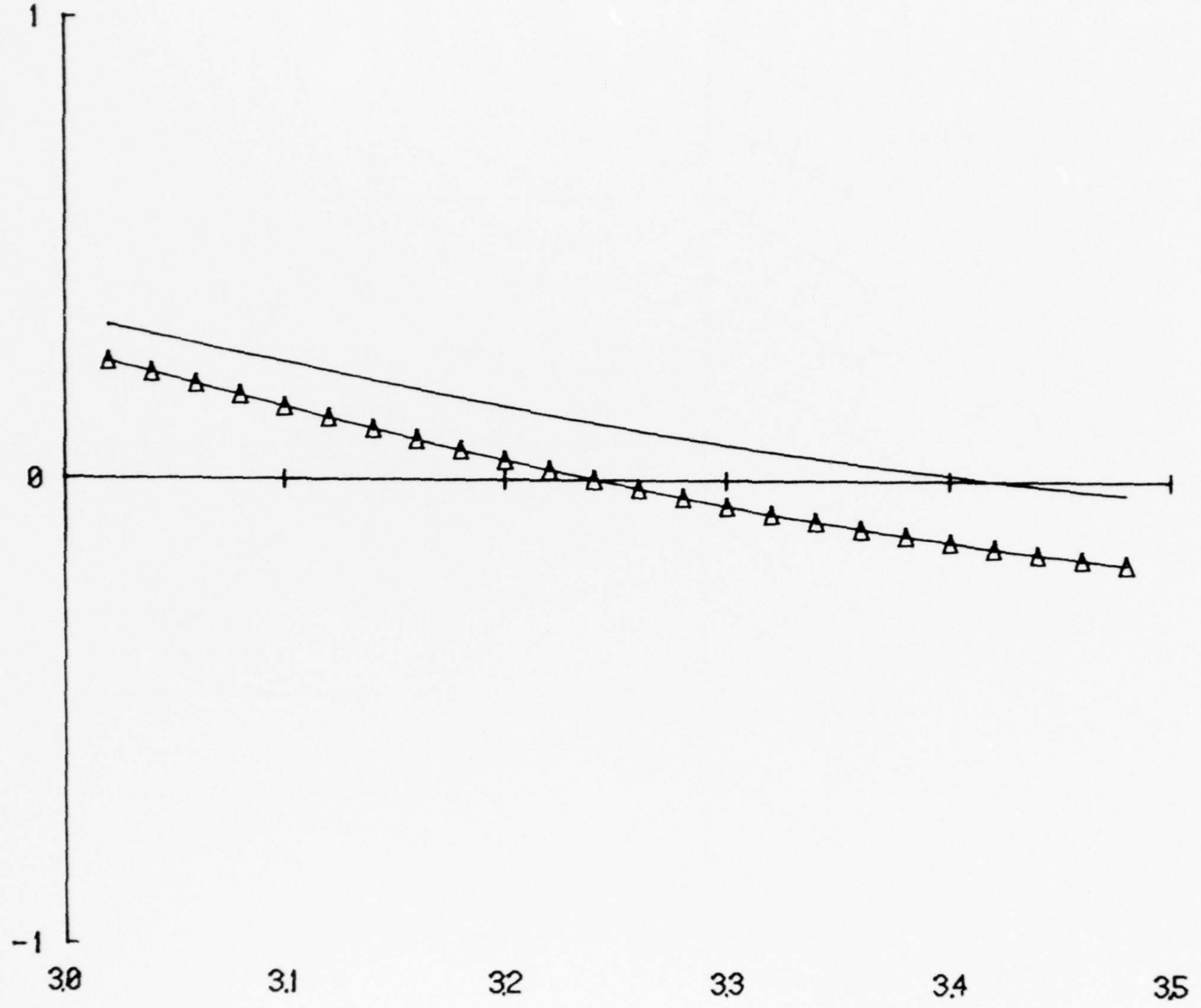
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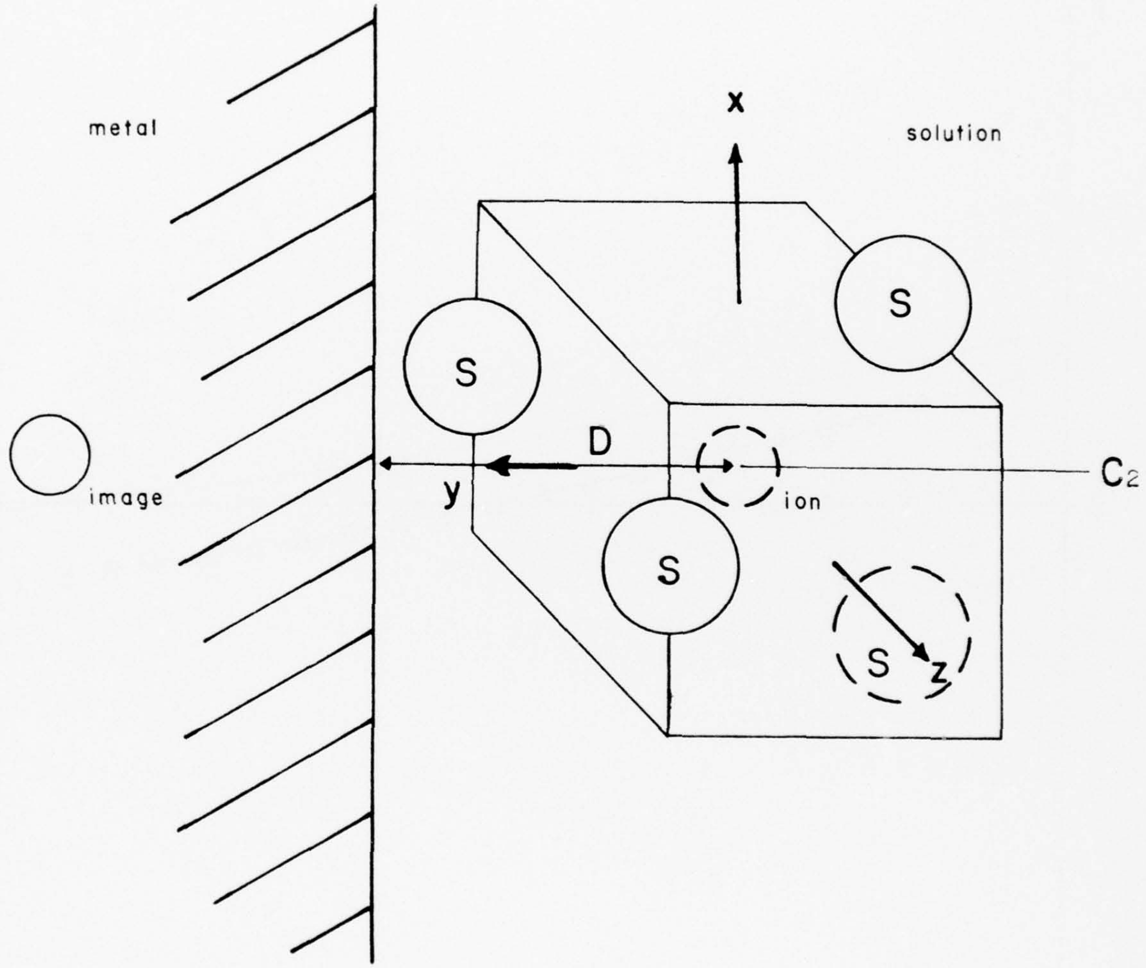

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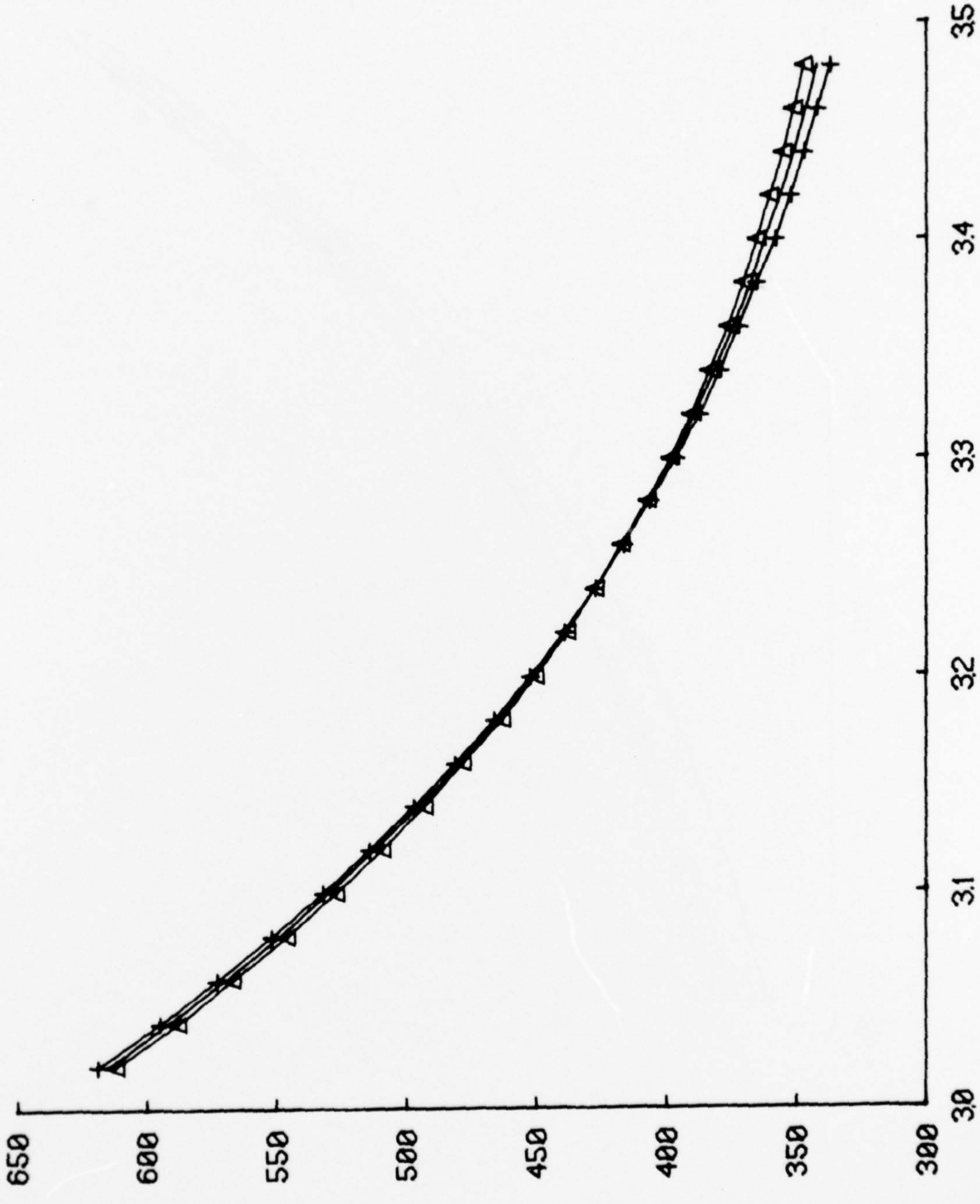

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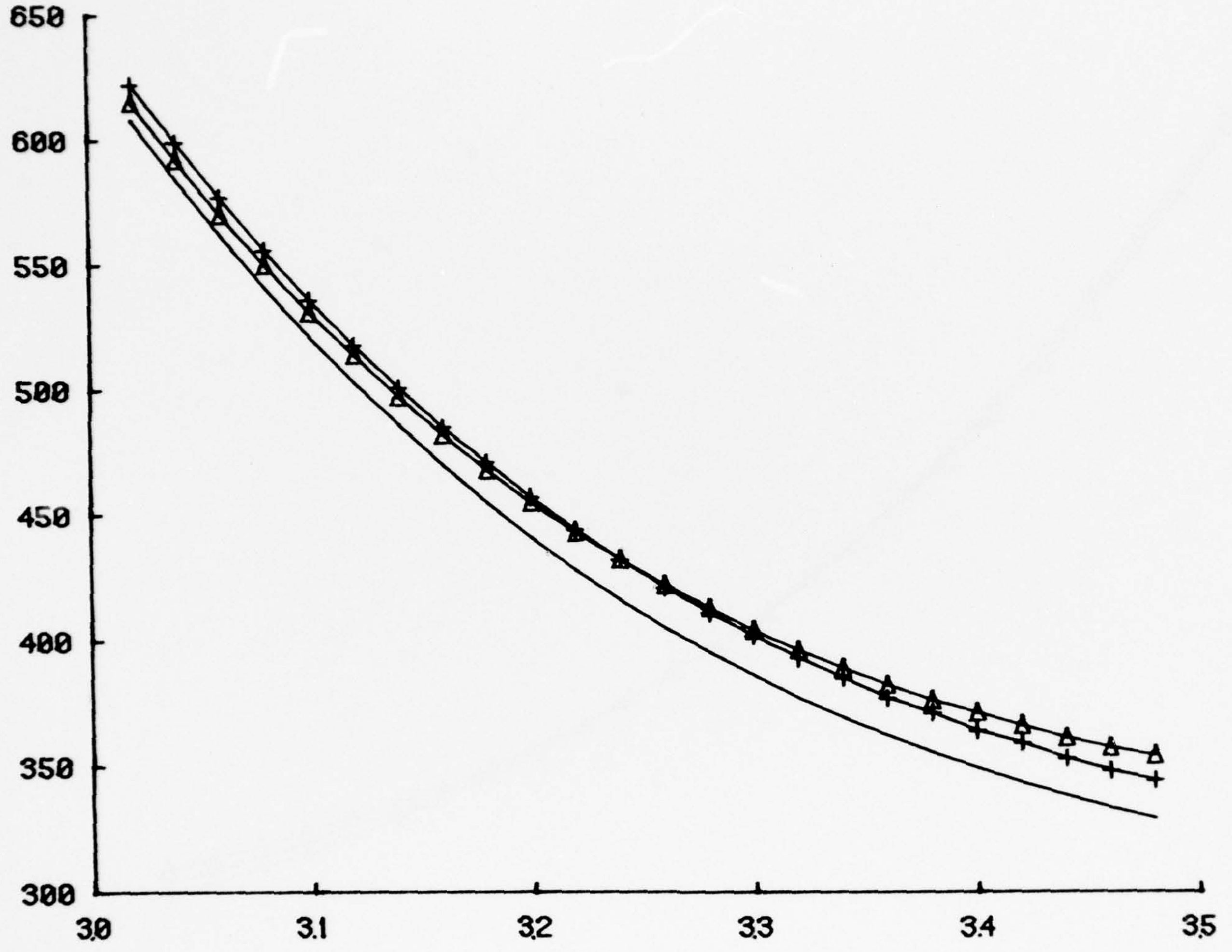
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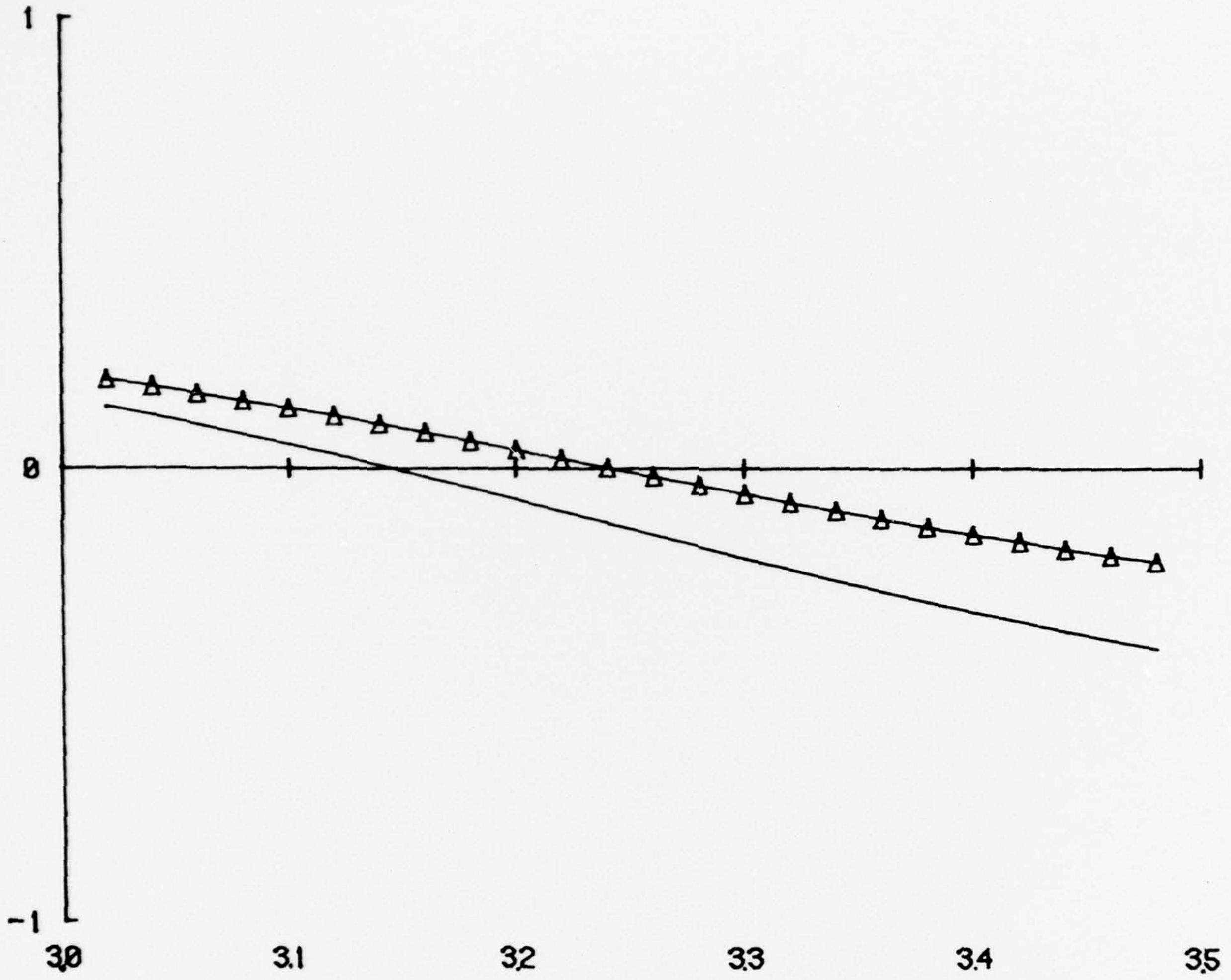
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