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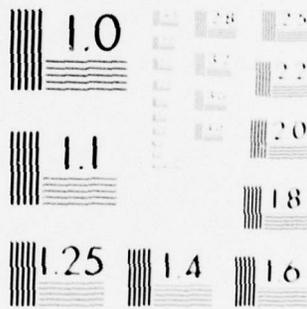
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AN ANALYSIS OF THE VIBRATIONAL SPECTRUM OF SYMMETRICALLY SOLVAT--ETC(U)  
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An Analysis of the Vibrational Spectrum of Symmetrically Solvated Alkali Metal Cations

by P. P. Schmidt and B. S. Pons

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a probe of the repulsion interaction which operates in the system. Our study shows that the ions of lithium, sodium, and potassium can be regarded as classical point charges. The far infrared spectra of the ions of rubidium and cesium, on the other hand, depend upon dispersion forces (dispersion is treated with the use of the Morse function). Finally, lithium and sodium may be considered to be trapped inside an infinitely massive solvent cage. For the remaining ions, reduced mass effects must be considered.

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An Analysis of the Vibrational Spectrum of Symmetrically Solvated  
Alkali Metal Cations

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Abstract

This paper presents the results of an analysis of the vibrational spectrum of the solvated alkali metal cations in dimethyl sulphoxide (DMSO). The purpose of this study is to determine more about the structure of the primary solvation shell and to formulate a clearer picture of the vibrational states of these species. The ionic systems are investigated with the use of a potential energy function which consists basically of an ionic term and an exponential repulsion. Dispersion interactions, where they apply, are accounted for with the use of the Morse function. We show that for systems with cubic symmetry there is no dependence in the force constant upon electrostatic terms. Thus, the far infrared spectrum provides a probe of the repulsion interaction which operates between the ion and the solvent. On the other hand, the breathing modes depend upon all contributions in the potential function. Our study shows that the ions of lithium, sodium, and potassium can be regarded as classical point charges. Dispersion effects are not important for these ions. The far infrared spectra of the ions of rubidium and cesium, on the other hand, depend upon dispersion forces. Finally, the ions of lithium and sodium may be regarded as atomic masses trapped inside an infinitely massive solvent cage. For the remaining alkali metal ions, reduced mass effects are important in the determination of the vibrational frequencies.

## Introduction

A knowledge of the mechanics of ionic solvation is important for the understanding of a number of phenomena. For example, the deformation of the solvation sheath about an ion contributes to the electrophoretic effect.<sup>1</sup> An adjustment of the solvation sheath about an ion or electroactive species often contributes to the activation of an electron transfer transition in an oxidation-reduction reaction.<sup>2</sup> The elastic deformation of the solvation structure can be expressed in terms of the vibrations of the system. Thus, a knowledge of the vibrational modes of solvated ionic and molecular species is needed in order to understand a number of transport and kinetic processes.

Because of the relative simplicity of the electronic structure of the alkali metals and their cations, they are potentially excellent systems to investigate in order better to understand many of the features of the electron transfer reaction. Electrochemistry can be carried out on the alkali metal cations in dimethyl sulphoxide (DMSO) as well as in other solvents.<sup>3</sup> All of the available alkali metal cations are soluble in DMSO to some extent. Thus, for these systems there is the greatest amount of information from spectroscopic experiments. Thus, we concentrate our attention on these systems in this paper. In particular, we are interested in the vibrational spectra of the metal cations in DMSO.

Edgell et al.<sup>4</sup> and Popov and his colleagues<sup>5,6</sup> have carried out extensive investigations of the far infrared vibrational spectra of the alkali metal cations in DMSO. Thus, their data form

the basis of our investigation.

Edgell et al.<sup>4</sup> and Popov<sup>5,6</sup> in examining their data have constructed potential energy functions in order to try to determine the force constants for the vibrations in these systems. Generally, their analyses have been based upon the use of much simplified models of the primary state of solvation. In particular, both groups have examined a linear triatomic model in which the ion is sandwiched between two solvent molecules. This model is not adequate in that it does not usually consider enough of the solvent which surrounds the ion. Specifically, a linear triatomic model predicts that the force constant will depend upon an electrostatic contribution which arises from the ion-dipole interactions. In the following paragraphs we present a refined solvation model which can account for more complicated states of solvation. We show that whenever the geometry of solvation satisfies simple cubic symmetry requirements, there will be no electrostatic contribution to the force constant for the far infrared vibrational modes. The conclusion reached by Edgell et al., that the repulsion interactions are important in the determination of the magnitude of the vibrational force constants survives in our treatment. Indeed, it is strengthened. We assert, in fact, that the far infrared, dipole allowed transitions of the ion vibrating within the solvent cage provide a direct probe of these repulsion interactions.

The potential energy function for a system of an ion with a shell of solvent molecules (as dipoles) can be constructed from four basic parts. The first, and obvious, part consists of the electrostatic interactions which operate between the ion and the solvent dipoles which surround it. The second part consists of

the intermolecular repulsion interactions. Third, dispersion interactions enter to a lesser or greater degree depending upon the degree of polarizability of the ion and the solvent. Finally, if the ion and its first solvation shell are immersed in a polar solvent system, it is necessary to consider the influence of the remainder of the solvent system on the central ion.

For the solvated ionic system there are two distinct kinds of force constant which operate. The far infrared, vibrationally active transitions depend upon the oscillation of the central ion within its cage of solvent molecules. For this degree of freedom the interaction between the solvent molecules in the solvation shell and the interaction between the solvent and outer solvent molecules is unimportant. Indeed, as we show later, electrostatic interactions in general are important only as cubic or higher order corrections to the basic spherical harmonic oscillator potential energy function.

On the other hand, the symmetric stretching, Raman active mode depends upon a number of factors. In particular, it depends upon the electrostatic terms which operate within the primary solvation system, i.e., the ion and its first solvation shell, as well as the interaction between the system and the outer solvent. The secondary interaction between the primary solvated ion and the remaining solvent system in part can be handled in terms of electrical image interactions. Specifically, the solvated ion resides in a spherical cavity. The charged ion and the solvent dipoles all have images in the surrounding continuum dielectric. In addition, there is a repulsion force which acts to keep the solvent molecules within the cavity. As a consequence, although

the breathing mode is simple with respect to symmetry, the mechanical interactions which determine the strength of the oscillation are much more complicated than is the case with the infrared active vibration of the central ion.

There are indeed other modes of vibration which are possible. Many of these modes, however, are expected to be of very weak intensity and low frequency. Nevertheless, they can be important in the activation process for an electron transfer reaction. In particular, the simultaneous stretching along one axis and the contraction along another, can be important. This type of elliptic deformation has been discussed before in connection with the hydrodynamic, collective model of ionic solvation.<sup>7</sup> It represents effectively a volume conserving, surface oscillation. In this paper, however, we do not examine this particular vibrational mode. On the one hand, there is no direct experimental evidence which can be attributed to such vibrations. On the other hand, it may well be the case that such vibrational modes represent collective oscillations of the secondary solvation shell. In spite of a lack of direct experimental evidence for the existence of these vibrations, they are nevertheless important to the electron transfer process. They will be considered more in detail in a separate paper.

The basic form of the interaction between the ion and its collection of solvent molecules is through the ion-dipole interaction. However, in order to be able to describe the small vibrational excursions which the ion can make away from its equilibrium position at the centre of the solvation cage, it is necessary to consider the expansion of the interaction in appropriate terms.

This can be done in terms of the Carlson-Rushbrooke formula.<sup>8</sup>

The reason for using the Carlson-Rushbrooke expansion is the following. In a system in which the ion moves with respect to a fixed set of solvent dipoles, it is necessary to be able to specify the interaction between the ion and each of the dipoles with reference to one point. Clearly, for an ion with some form of symmetric solvation, the reference point for the ion is at the centre of symmetry. The use of the Carlson-Rushbrooke expansion formula [see appendix 1 for details] enables us to express the ion-dipole interaction in terms of coordinates which are appropriate to the analysis of the vibrations of the ion in the cage. This has not been done in other treatments.<sup>4-6</sup> Our use of this type of expansion allows us to consider the types of caged ion vibrations which occur in condensed systems, but not necessarily in the gas phase.

In the following section we present the various forms of the potential energy function. The force constants which are derived from these functions are summarized. The details of many of the calculations are presented later in this paper in a series of appendices. There, a number of technical points are developed. These matters, pertaining to computation, are important in the analysis of the activation of the electron transfer reaction. The application of the force constants to the analysis of the spectrum of the solvated alkali metal cations in DMSO is considered in the third section.

Potential Energy Functions and Vibrational Force Constants

In this section we present potential energy functions for two basic types of solvated ionic system: a four-coordinated, tetrahedral solvation, and a six-coordinated, octahedral solvation. Mention is made of the eight-coordinated, cubic solvation case.

For an arrangement of solvent dipoles (in a sense to ensure an attractive interaction) at the vertices of a regular tetrahedron, the Carlson-Rushbrooke<sup>8</sup> expansion yields

$$V_t = -4 \frac{\mu e}{R^2} \left[ 1 + i \frac{5}{9} \sqrt{10\pi/7} [Y_{3,2}(\hat{r}) - Y_{3,-2}(\hat{r})] (r/R)^3 \right] \quad (1)$$

in which  $Y_{\ell m}(\hat{r})$  is the spherical harmonic function. The vector  $\underline{r} = (x, y, z)$  defines the position of the ion with reference to the centre of symmetry. The distance  $R$  is the distance between the centre of symmetry and the solvent molecules. In the regular array, each molecule has the same value of  $R$ . The molecular dipole moment is given by  $\mu$ .

An octahedron with dipoles at the vertices yields the following:

$$V_o = -6 \frac{\mu e}{R^2} \left[ 1 + (35/18) \sqrt{\pi/3} (r/R)^4 \left\{ Y_{4,0}(\hat{r}) + \sqrt{5/14} [Y_{4,4}(\hat{r}) + Y_{4,-4}(\hat{r})] \right\} \right] \quad (2)$$

Another form which is possible, but probably not common, places the dipoles at the vertices of a regular cube. In this case the first term past the zeroth order contribution depends upon  $O(r^4)$ .

It is obvious that the equilibrium position is located at  $\underline{r} = \underline{0}$ , i.e., at (0,0,0). It is equally clear that in both eqn (1) and (2) there is no contribution to the potential of order  $O(r^2)$ . Hence, when the harmonic oscillator limit is sought (through the use of a Taylor series expansion) in the complete potential energy function, there will be no electrostatic contribution. This is not true if the solvation is linear. For linear solvation, however, two distinct caged ion vibrational modes are predicted; this is considered further in an appendix. The non-involvement of electrostatic terms in the force constants applies only to the infrared, dipole allowed transitions in a point charge system.

There are several acceptable expressions for the usually short ranged, repulsion interaction which operates between atomic and molecular species. Although the repulsion term ( $R^{-12}$ ) in the Lennard-Jones potential is perhaps best known and most widely used, an exponential form, used extensively by Born,<sup>9</sup> can also be employed. There are obvious computational advantages to the use of the Lennard-Jones potential for many applications. However, for the centro-symmetric systems we investigate here, the Lennard-Jones function has the disadvantage of not allowing an appropriate Laplace-type expansion. Thus, for the repulsion which operates between species, we make use of the exponential representation.

The dispersion interaction, as it is contained in the Morse potential function, is also given in an exponential form.

The Born repulsion has the simple exponential form

$$V_r = B \exp[-(r-r_e)/\rho] \quad (3)$$

where B and  $\rho$  are constants. When dispersion is also considered, the Born term is expanded into the Morse function:<sup>10</sup>

$$V_m = D\{1 - \exp[-\kappa(r-r_e)]\}^2 \quad (4)$$

where, as usual, D is the dissociation energy and  $\kappa$  is a constant with the units of inverse distance.

The Laplace expansion of the exponential function (3) is given by (see appendix 3)

$$V_r = -4\pi B \exp(r_e/\rho) \sum_{\ell, m} Y_{\ell m}^*(\hat{r}) Y_{\ell m}(\hat{R}) \{ (2\ell+1) i_\ell(r/\rho) k_\ell(R/\rho) + (r/\rho) i_{\ell+1}(r/\rho) k_\ell(R/\rho) - (R/\rho) i_\ell(r/\rho) k_{\ell+1}(R/\rho) \}. \quad (5)$$

The functions  $i_n(x)$  and  $k_n(x)$  are respectively the modified spherical Bessel functions of the first and second kinds.<sup>11</sup> This expansion is valid only as long as  $r < R$ . A more general expression can easily and obviously be written (see appendix 3).

For a four-coordinated, tetrahedral system the contribution from eqn (3) through (5) to the system potential energy function is given by

$$V_r = B \left[ 4\sqrt{4\pi} Y_{00}(\hat{r}) f_0(r, R) + i\frac{3}{4}\sqrt{35/8\pi} [Y_{3-3}(\hat{r}) - Y_{33}(\hat{r})] f_3(r, R) \right] \quad (6)$$

with

$$f_{\ell}(r,R) = -(2\ell+1)i_{\ell}(r/\rho)k_{\ell}(R/\rho) + (r/\rho)i_{\ell+1}(r/\rho)k_{\ell}(R/\rho) \\ - (R/\rho)i_{\ell}(r/\rho)k_{\ell+1}(R/\rho) \quad (6a)$$

The Laplace expansion of the Morse function follows that already shown for the exponential repulsion. Apart from a constant factor  $D$ , the dissociation energy, the expansion is the same (see appendix 3). It can be written as

$$V_m = D - 4\pi D \sum_{\ell,m} Y_{\ell m}^*(\hat{r}) Y_{\ell m}(\hat{R}) F_{\ell}(r,R) \quad (7)$$

with

$$F_{\ell}(r,R) = \exp(\kappa R_e) \left\{ (2\ell+1) [\exp(\kappa R_e) i_{\ell}(2\kappa r) k_{\ell}(2\kappa R) \right. \\ - 2i_{\ell}(\kappa r) k_{\ell}(\kappa R)] + 2(\kappa r) [\exp(\kappa R_e) i_{\ell+1}(2\kappa r) k_{\ell}(2\kappa R) \\ - i_{\ell+1}(\kappa r) k_{\ell}(\kappa R)] - 2(\kappa R) [\exp(\kappa R_e) i_{\ell}(2\kappa r) k_{\ell+1}(2\kappa R) \\ \left. - i_{\ell}(\kappa r) k_{\ell+1}(\kappa R)] \right\} \quad (8)$$

It is evident that because of the functional form of the repulsion interactions (and in the Morse function, the dispersion contribution) there is a non-vanishing second order contribution to the Taylor series evaluated about  $\underline{r}$  (with  $\underline{r}_e = 0$ ). Thus, as noted above, although the force constant does not depend upon any electrostatic contributions, there are contributions from

the repulsion terms and from the dispersion interaction (as it is expressed in the Morse function).

In the limit in which dispersion interactions play little or no role, and where there are only repulsion contributions, the expressions for the force constants in the harmonic oscillator limit are the following: the four-coordinated, tetrahedral system,

$$k_4 = (4B/3\rho^2)(1 - 2\rho/R_e); \quad (9a)$$

the six-coordinated, octahedral system,

$$k_6 = (2B/\rho^2)(1 - 2\rho/R_e); \quad (9b)$$

and the eight-coordinated, cubic system,

$$k_8 = (8B/3\rho^2)(1 - 2\rho/R_e). \quad (9c)$$

In contrast, a system potential which is a simple combination of an electrostatic term and a Morse function (i.e., dispersion included) yields the following expressions for the force constants:

$$k_4 = 8D\kappa^2/3 \quad (10a)$$

$$k_6 = 4D\kappa^2 \quad (10b)$$

$$k_8 = 16D\kappa^2/3 \quad (10c)$$

Moelwyn-Hughes<sup>10</sup> points out that for small deviations about an equilibrium position the Lennard-Jones potential and the Morse potential are equivalent. Thus,  $\kappa$  can be replaced by  $6/R_e$ , and eqn (1) can be expressed as

$$k_4 = 96D/R_e^2 \quad (11a)$$

$$k_6 = 144D/R_e^2 \quad (11b)$$

The force constants are seen to vary as  $R_e^{-2}$  as the equilibrium solvation radius changes. There is also a radial dependence in the dissociation constant  $D$ . Altogether, as we shall show in the next section, the force constants depend upon  $R_e$  as  $R_e^{-8}$ .

Finally, it is necessary to consider the fact that the solvated ion occupies space, effectively in a cavity, inside the bulk of a continuum dielectric. However, because we have found that the image contributions to the breathing mode force constants amount only to a small change in the frequencies, we defer our discussion of these contributions to an appropriate appendix. It is clear that as far as we are concerned with the harmonic oscillator limit for the infrared active, ionic vibrations within the primary solvation cage, the image effects (also electrostatic) will be non-contributing. The image contribution, as we will show, depends importantly upon the size of the cavity within which the ion resides. If the cavity dimensions change, then there can be an important image contribution. [We do not consider this effect in this paper.]

The system potential energy function which is a combination of the electrostatic, repulsive, and dispersion terms can be

differentiated with respect to  $R$ , the solvation radius, to obtain the force constants for the breathing modes. In addition to the terms which have been mentioned, the breathing modes depend upon the solvent dipole-dipole interactions as well as upon an intermolecular repulsion of the Born type. For a tetrahedral system, we can write

$$V_{br} = - \frac{4\mu e}{R^2} + 4B \exp[-(R-R_e)/\rho] + 6B' \exp[-(2\sqrt{2/3}R-R'_e)/\rho'] + (15/4)\sqrt{3/2}(\mu^2/R^3) \quad (12)$$

in which the constants  $B'$  and  $\rho'$  account for the possibility that the intermolecular interaction may differ from the ion-solvent interaction. We assume that the two types of interaction are roughly similar. Therefore, the force constant for the breathing mode is obtained directly (note, this term does not include any account of the electrical image interactions)

$$k_{br} = - \frac{24e\mu}{R_e^4} + 45\sqrt{3/2} \frac{\mu^2}{R_e^5} + 20B/\rho^2 \quad (13)$$

In the next section we consider the application of these results to the examination of the vibrational spectra of the alkali metal cations in DMSO.

Discussion of the Solvation Spectra

The data of Maxey and Popov<sup>5</sup> on the far infrared spectra of the alkali metal cations in DMSO are reproduced in Table 1. These experimental data form the basis of our discussion .

A preliminary analysis of these data is needed in order to extract the force constants. We assume that the harmonic oscillator limit applies: viz.,

$$1/\lambda = \frac{1}{2\pi C} \sqrt{k/\mu} \quad (14)$$

is the relationship between the frequency (in wave numbers), the mass  $\mu$  and the force constant  $k$ ;  $C$  is the velocity of light.

At this point it is necessary to specify the form of the mass quantity which is to be used in eqn (14). In general, the expression for the reduced mass of the ion (mass  $m_i$ ) which oscillates with respect to  $c$  neighbouring solvent molecules (each  $m_s$ ), is

$$\mu = cm_s m_i / (cm_s + m_i) \quad (15)$$

In the limit of large  $c$ , the reduced mass is the same as the ionic mass. This limit also applies to the case of an infinitely massive solvent system. In other words, the ion vibrates within a cage of rigidly fixed solvent molecules.

With the reduced mass as specified by eqn (15), it is possible to obtain values for the force constants for the ions under the assumption of various degrees of coordination. The force constants

are listed in Table 2. From the table it appears that the lithium cation has a frequency which is at odds with the rest for any type of coordination. The cations of sodium and potassium seem to pair and the cations of rubidium and cesium likewise seem to form a pair. We show shortly, however, that the frequency of the lithium system is wholly consistent with the frequencies of sodium and potassium. The frequencies of the rubidium and cesium systems are distinct from the rest. In any case, it is clear from the table that it is not reasonable to assume that the force constants are uniform for the ionic systems of the group. Such an assumption was made by Maxey and Popov.<sup>4</sup>

In order to make the comparison between the data and the formulae for the force constants presented in the last section, it is necessary to specify the values of the solvation radii. We assume, as have Abraham and Liszi,<sup>12</sup> that the solvation radius can be expressed as the sum of the ionic, Goldschmidt radius and the radius of the solvent. Abraham and Liszi<sup>12</sup> calculated the solvent radius from the liquid partial molar volumes with the use of the Stearn-Eyring formula.<sup>13</sup> The values of the radii are listed in Table 3.

First, we compare the experimental results with the theoretical expressions for the force constants obtained under the assumption that dispersion plays a minor role. Thus, the force constants of eqn (9) apply.

When the simple exponential repulsion is used, the two parameters  $B$  and  $\rho$  must be specified. The work of Huggins and Mayer<sup>14</sup> on the alkali halide crystals indicates that  $\rho$  for those systems is essentially a constant. It seems reasonable to make a similar

assumption here for the solvated ionic systems. There is no reason, however, to expect that it should be the same constant.

The parameter B can be eliminated in favour of other quantities which are more easily determined, viz., the ionic charge, the solvent dipole moment, and the equilibrium separation between the ion and the solvent molecules. Following Born's treatment<sup>9</sup> of the crystalline alkali halides, we write

$$V = -c\{e\mu/R^2 - B \exp[-(R-R_e)/\rho]\} \quad (16)$$

where again c is the coordination number. The simple equilibrium condition  $dV/dR_e = 0$  yields

$$B = 2e\mu\rho/R_e^3. \quad (17)$$

We find that an optimal value of  $\rho$  is  $1.9 \times 10^{-9}$  cm. With the use of this value of  $\rho$  together with the values of the solvation radii, we determined the values of the force constants which are listed in Table 4.

The results shown in Table 4 indicate a clear grouping of effects. Indeed, the theoretical results indicate that lithium belongs with sodium and potassium in its behaviour. The force constants and the associated frequencies are reasonably accurately predicted for the series of ions lithium, sodium, and potassium under the assumption of four-coordination. It is clear from the results that six-coordination for these three ions is inconsistent with the experimental data. It is worth noting from the table the fact

that with the use of the infinite mass assumption for the solvent, the best agreement with experiment is found for lithium. That is, lithium, which has a small mass and very small polarizability, shows negligible dispersion and reduced mass effects. At the other extreme, potassium, which has a mass about half the mass of the solvent, begins to show a definite dependence upon the choice of the appropriate reduced mass. The results for sodium indicate that this ion is better handled with the assumption that the cage is rigid. The value of  $206 \text{ cm}^{-1}$  for the vibrational frequency compares favourably with the experimental value.

Turning to the ions of rubidium and cesium, it seems that four-coordination is inconsistent with the experimental data. The assumption of six-coordination brings the theoretical results more into an agreement with the experimental results. However, the unmistakable fact that the theoretically predicted force constants decrease from rubidium to cesium is at odds with the experimental fact that the force constants increase in this direction. The fault lies with the neglect of the polarizability of these larger ionic systems.

As we have indicated in the last section, the Morse potential can be used to bring an account of the dispersion interactions into the analysis. For small amplitude oscillations it is possible to argue the transformation from the Lennard-Jones to the Morse potential. The quantity  $D$  in the Morse potential is the dissociation energy for a single solvent-ion couple. By means of an argument outlined by Moelwyn-Hughes,<sup>10</sup> it is possible to identify the dissociation energy further in terms of the London force which operates between the ion and the solvent molecule. Thus, the dissociation

energy can be expressed as

$$D = \frac{C}{2R_e^6} \quad (18)$$

where C is a constant which can be identified by comparing eqn (18) with the London interaction:<sup>15</sup>

$$V_{\text{London}} = - \frac{3I_s I_i \alpha_s \alpha_i}{2R^6 (I_s + I_i)} \quad (19)$$

In this expression  $I_s$  and  $I_i$  are respectively the ionization potentials of the outermost electron in the solvent and the ion. The polarizabilities of the solvent and the ion are expressed by the terms  $\alpha_s$  and  $\alpha_i$ . In eqn (19) it is apparent that the ionization potential for the outermost electron in the ion is a quantity which generally will be much larger than the ionization potential for the outermost electron in the solvent. Therefore, we can simplify eqn (19) by writing

$$V_{\text{London}} \approx - \frac{3}{2} \frac{I_s \alpha_s \alpha_i}{R^6} \quad (20)$$

The dissociation energy now is expressed as

$$D = \frac{3}{4} \frac{I_s \alpha_s \alpha_i}{R_e^6} \quad (21)$$

When this expression for D is substituted into the expressions for the force constants, we find

$$k_4 = 72 \frac{I_s \alpha_s \alpha_i}{R_e^8} \quad (22)$$

and

$$k_6 = 108 \frac{I_s^{\alpha} s^{\alpha} i}{R_e^8} . \quad (23)$$

In some instances it is difficult to determine the ionization potential of a particular solvent molecule. Information about the ionization potential of DMSO is scarce. Nevertheless, these expressions for the force constant still can be used in a slightly modified sense. In particular, we are interested to see if it is possible to predict the value of the force constant for another species (in a homologous series) given the experimental value of an ion in the series. To do this, we simply form the ratio of the force constants:

$$k_2/k_1 = (R_1/R_2)^8 (\alpha_2/\alpha_1) . \quad (24)$$

This ratio holds as long as both species have the same coordination. The comparison between force constants for four- and six-coordinated species is the following:

$$k_{(6)}/k_{(4)} = \frac{3}{2} (R_{(4)}/R_{(6)})^8 (\alpha_{(6)}/\alpha_{(4)}) . \quad (25)$$

In order to test eqn (24) we make use of the ionic refractions (related to the polarizabilities by a common constant factor) given by Smyth;<sup>16</sup> they are reproduced in Table 5. The results are shown in Table 6. It can be seen from the Table 6 that for sodium and potassium, as determined from lithium, there is no agreement with experiment. The inclusion of any account of dispersion

interaction is not appropriate for these systems. On the other hand, the agreement between the calculated and experimental values for the force constants for cesium as calculated from the rubidium force constants is very good. The increase in the value of the force constant for all values of the coordination is correctly predicted.

Eqn (24) reasonably accurately predicts the force constant for rubidium from potassium; this implies the coordination remains the same. The ratio of the force constants (9b) to (9a) is 1.5. As we discussed earlier, this ratio also gives a reasonably accurate prediction of the rubidium force constant from that of potassium. In this case, however, the agreement is not quite as good as that found with eqn (24). On the other hand, if we use eqn (25) to attempt to predict the change in force constant in going from potassium to rubidium, the predicted force constant is 30,000 dynes/cm<sup>2</sup> too large. As Symth notes,<sup>16</sup> the ionic refractions are not very accurate quantities. Thus, there may be some uncertainty associated with their use in this case. In any event, the coordination of the ions of rubidium and cesium remains a cloudy issue.

We summarize the far infrared vibrational analysis as follows. Lithium and sodium behave as classical point charges which vibrate within rigid solvent cages. The magnitudes of the force constants for these two systems are determined entirely by the form of the short-ranged repulsion interactions which operate between the ion and the solvent molecules. Potassium also behaves as a classical point charge. Its force constant depends only upon the short ranged repulsion interactions. However, potassium has a mass

which is approximately half the mass of the solvent. Hence, it is appropriate to consider the reduced mass in determining the value of the ionic vibrational frequency. Rubidium and cesium appear to be six-coordinated in DMSO, but, as noted immediately above, this cannot be a definitive coordination on the basis of the spectroscopic data alone. These ions of rubidium and cesium depend importantly upon the operation of the dispersion forces of the London type. The fact that the force constant increases in going from rubidium to cesium is accounted for accurately when the polarization of the ions is taken into account. In effect, the importance of these dispersion interactions simply points to the fact that these ions cannot be regarded as simple classical point charges. Quantum mechanical effects enter and must be considered.

Finally, we turn to a consideration of the breathing modes for these systems. Unfortunately, the experimental picture is not clear.  $\text{LiClO}_4$  has been examined in acetone.<sup>17</sup> In the Raman spectrum there is a shoulder on the active line of acetone which is about  $14 \text{ cm}^{-1}$  greater than the 789 acetone line. If we assume that this is due to a symmetrical stretching breathing mode, then for acetone we calculate the force constant to be  $6.2 \times 10^5 \text{ dynes/cm}^2$ . Using the general formula for calculating the frequency for a symmetric stretching mode,<sup>18</sup>

$$\nu^2 = k/m_s \tag{26}$$

where  $m_s$  is the mass of the solvent molecule in a tetrahedral  $\text{XY}_4$  system, we determine that the frequency should be  $134 \text{ cm}^{-1}$ . Agreement with the assumption that the  $14 \text{ cm}^{-1}$  shoulder is a

symmetric stretch is apparently not good. However, it is not necessarily reasonable to expect to be able to use the simple solvent mass in this case. The symmetric stretch is a volume non-conserving mode. Thus, the expansion against the remainder of the system may, in effect, amount to an expansion of a much larger effective mass. An effective mass of about 5384 gm gives agreement, assuming that the value of the force constant is accurate. In any case, the experimental situation is not definitive enough for us to make any clear statement about these breathing modes.

One conclusion we can make, however, is that in the image approximation, the effect of the image terms on the breathing modes is insignificant. The variation of the force constant versus the ionic solvation radius is shown for the cavity and the cavity plus its image contributions in Figure 1. As can be seen, there is very little difference. Consequently, we believe that these terms, which are an additional burden to calculate, can be ignored. It should be noted, nevertheless, that in certain applications, in particular in the calculation of electron transfer activation energies, these image contributions need to be considered. For the vibrational problem alone, they are small.

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Appendix 1: Electrostatics of ionic solvation

The derivation of the Carlson-Rushbrooke expansion has been discussed in detail by these authors.<sup>8</sup> Buehler and Hirschfelder<sup>19</sup> were the first to point out, however, the fact that the original expansion is not a general formula. Further discussion and generalization of the original expansion, therefore, has been given by Buehler and Hirschfelder,<sup>19</sup> by Ruedenberg,<sup>20</sup> by Sack,<sup>21</sup> and by Kay, Todd, and Silverstone.<sup>22</sup> For our purposes, the original expansion suffices. We are therefore limited to a region of applicability such that the sum of the distance magnitude of the dipole (viz.,  $\mu/e$ ) and the distance of the ion from its equilibrium position is less than the distance between any solvent molecule and the centre of symmetry. This limit is made mathematically clear below.

The general formula is given by

$$1/r_{12} = \sum_{\substack{\ell, m \\ \ell', m'}} (-1)^{\ell'} B_{\ell\ell'}^{mm'} Y_{\ell m}(\hat{r}_1) Y_{\ell' m'}(\hat{r}_2) Y_{\ell+\ell', m+m'}(\hat{R}) \frac{r_1 r_2^{\ell'}}{R^{\ell+\ell'+1}} \quad (1.1)$$

and  $R > r_1 + r_2$ . The B-coefficient is given by

$$B_{\ell\ell'}^{mm'} = \frac{(-1)^m (4\pi)^{3/2}}{\sqrt{(2\ell+1)(2\ell'+1)(2\ell+2\ell'+1)}} \left[ \frac{(\ell+\ell'+m+m')! (\ell+\ell'-m-m')!}{(\ell+m)! (\ell-m)! (\ell'+m')! (\ell'-m')!} \right] \frac{1}{2} \quad (1.2)$$

The coordinate system applicable to eqn (1.1) is shown in Fig. 2.

When one of the interacting particles is a point dipole of magnitude  $\mu = er_2$ , for example, the expression can be applied to the types of systems we have discussed in the main body of this paper. The remaining coordinate  $r_1$  now specifies the location of the ion with respect to the origin as shown in Fig. 2. This is precisely the type of coordinate which is needed in order to specify the vibrational excursions of an ion away from its centre of symmetry in the solvated system.

For a system with tetrahedral solvation, we outline the steps necessary to determine the form of the electrostatic contribution to the system potential energy function.

The B-coefficient in this case is specifically

$$B_{12}^{m'm} = \frac{(4\pi)^{3/2}}{\sqrt{3 \cdot 5 \cdot 7}} b(m'm) \quad (1.3)$$

where

$$b(m'm) = \left\{ \frac{(3+m+m')! (3-m-m')!}{(1+m')! (1-m')! (2+m)! (2-m)!} \right\}^{1/2} \quad (1.4)$$

The b-coefficients are listed in Table 7.

For the tetrahedral system it is convenient to place the solvent dipoles at the following locations:

$$(1,1,1) \quad (-1,-1,1) \quad (1,-1,-1) \quad (-1,1,-1)$$

By means of scaling, the solvation radius can be inserted into the potential energy function. In the same order as locations are listed, the direction cosines for the dipoles are chosen to be

$$(-a, -a, -a) \quad (a, a, -a) \quad (-a, a, a) \quad (a, -a, a)$$

where

$$a = 1/\sqrt{3} .$$

The first contribution to the electrostatic part of the potential energy function is the obvious one:  $-4\mu e/R^2$ . The next contribution which can be considered is order  $\ell = 2$  (which would give  $r^2$ , harmonic terms for the ion with respect to the centre of symmetry) and  $\ell + 1 = 3$  in  $Y_{3m}(\hat{R})$ . As a result, we find that the contribution to the potential due to the interaction between the ion and the solvent dipole at (1,1,1) is

$$V_{111} = - \frac{\mu e}{R^3} \frac{3}{\sqrt{2}} (xy + xz + yz) . \quad (1.5)$$

The remaining terms follow easily by symmetry:

$$V_{-1-11} = - \frac{\mu e}{R^3} \frac{3}{\sqrt{2}} (xy - xz - yz) \quad (1.6)$$

$$V_{1-1-1} = - \frac{\mu e}{R^3} \frac{3}{\sqrt{2}} (-xy - xz + yz) \quad (1.7)$$

$$V_{-11-1} = - \frac{\mu e}{R^3} \frac{3}{\sqrt{2}} (-xy + xz - yz) . \quad (1.8)$$

The net second order contribution is the sum of (1.5) to (1.8). Thus, there is no second order contribution.

The next order contribution is third order in  $r$ . The result is given in the text of the paper, eqn (1). The values of  $b(m', m)$  needed in that calculation are listed in Table 8.

Cubic solvation (eight-coordination) can be shown easily to yield a zero third order term. The vertices of a regular cube

can be regarded in terms of the vertices of two inter-penetrating, identical tetrahedra. The rotation about any  $C_3$  axis takes one tetrahedron into the other. The sum of the contributions from the two tetrahedra cancel. Thus, the first order contribution in the cubic system is of order  $O(r^4)$ .

The remaining general type of solvation to consider is that of the linear "triatomic" type considered before by Edgell, et al.,<sup>4</sup> and by Maxey and Popov.<sup>5</sup> Although the authors indicate that the use of this model is to an extent suggestive only of the types of forces which need to be considered, Maxey and Popov<sup>5</sup> give linear solvation considerable credence on the basis of their NMR solvation study.<sup>23</sup> Their analysis suggests that in DMSO  $Li^+$  is strongly associated with two molecules of the solvent. Their analysis also suggests that for the ions of sodium through cesium, the coordination is less well defined.

There are difficulties associated with the use of a linear solvation model which have to do with the problem of the agreement between theory and experiment. In particular, the linear solvation model yields two non-vanishing contributions of order  $O(r^2)$  to the system potential energy function. One of these contributions is an exponential repulsion term, and the other is electrostatic. Specifically, the electrostatic contribution can be written as

$$V_{es.lin} = 3ue(x^2 + y^2 - 2z^2)/R^4, \quad (1.9)$$

omitting the zeroth order contribution. The repulsion contribution has a similar functional dependence on the coordinate variables.

It is clear from the form of this potential function that it already contains the appropriate harmonic oscillator potential terms. Moreover, it is clear that there are two infrared active vibrational modes for the solvation system. The vibration along the axis of symmetry is one mode, and the motion of the ion perpendicular to the axis about the bond mid-point is the other mode. Consequently, this model predicts that the experimental spectrum of the solvation system should show two vibrational peaks associated with the solvation structure. Although it is possible that the second peak is present (with perhaps very weak intensity), the authors who have examined these spectra have not reported any additional structure. It seems to us, therefore, that in spite of the suggestion that the solvation number of the lithium cation in DMSO is two,<sup>23</sup> this conclusion does not seem to be substantiated by the far infrared spectrum.

The analysis in this paper is based on the assumption that the electrostatic interactions can be modelled in terms of the familiar point charge interactions. It is possible to test the reasonableness of this assumption by comparison with a potential energy function which is derived on the basis of the assumption that the charge distributions have a diffuse nature. In this manner it is possible to enter further account of the ionic polarizability into the potential energy function. It will be evident from the form of the potential function that there are non-vanishing electrostatic contributions to the force constant. Here, in the remaining paragraphs of this appendix, we consider only the general form of the interaction. The derivation of the electrostatic contributions to the force constant is considered later in appendix 4.

The form of the interaction between a continuous charge distribution and a point dipole located at the centre of a conducting sphere of radius  $a$  is developed with the use of the Fourier convolution theorem as discussed by Silverstone.<sup>24</sup> The general form of the interaction can be expressed as

$$V(\underline{r}_{12}) = \frac{1}{2\pi^2} \int d^3k \, k^{-2} \rho_{\text{soft}}^*(\underline{k}) \rho_{\text{dipole}}(\underline{k}) \exp(i\underline{k} \cdot \underline{r}_{12}), \quad (1.10)$$

where  $\underline{r}_{12}$  is the vector separation between an element of charge in the continuous distribution and the point dipole. The Fourier transforms of the charge densities are signified by the  $\rho$ -quantities. The general expression for the transform is

$$\rho(\underline{k}) = \int d^3r \, \rho(\underline{r}) \exp(i\underline{k} \cdot \underline{r}). \quad (1.11)$$

In the following discussion we assume that the continuous charge distribution is modelled as a Slater-type distribution, as has been discussed in connection with the free energy of ionic solvation elsewhere (cf. ref. 25). Thus, the transform of the charge density can be expressed as<sup>25</sup>

$$\rho_{\text{soft}}(\underline{k}) = p^4 / (p^2 + k^2)^2 \quad (1.12)$$

corresponding to a coordinate-space distribution of

$$\rho_{\text{soft}}(\underline{r}) = \frac{p^3}{8\pi} \exp(-pr) \quad (1.13)$$

where

$$p = 2/b \quad (1.14)$$

and  $b$  is the effective Bohr radius for the distribution.<sup>25</sup>

The transform for the dipolar distribution can be expressed as

$$\rho_{\text{dipole}}(\underline{k}) = 4\pi i(\mu/a)j_1(ka) \sum_m Y_{1m}^*(\hat{a})Y_{1m}(\hat{k}) \quad (1.15)$$

where  $j_1(ka)$  is the spherical Bessel function of the first kind of order 1.<sup>11</sup>

When the above transform expressions are substituted into the expression for the interaction, we find

$$V(r_{12}) = \frac{2i\mu p^4}{a} \sum_m Y_{1m}^*(\hat{a}) \int d^3k \frac{j_1(ka)}{k^2(p^2+k^2)^2} Y_{1m}(\hat{k}) \exp(i\mathbf{k} \cdot \underline{r}_{12}). \quad (1.16)$$

We now consider the expansion of this function with respect to two arbitrary centres  $O$  and  $S$  (for the origin of the centre of symmetry and the location of the solvent). Thus, if  $\underline{R}$  is the vector from  $O$  to  $S$  and  $\underline{r}$  is the vector from  $O$  to the location of the centre of the charge density, we can write  $\underline{r}_{12} = \underline{R} - \underline{r}$ . The exponential function in (1.16) now can be written as a product of exponentials. The Rayleigh expansion can be used for each of these exponential functions:<sup>11</sup>

$$\exp(i\mathbf{k} \cdot \underline{x}) = 4\pi \sum_{\ell, m} i^\ell Y_{\ell m}^*(\hat{x}) Y_{\ell m}(\hat{k}) j_\ell(kx). \quad (1.17)$$

The angular integrations can be carried out easily. As a result,

$$V = \frac{8\sqrt{\pi}}{a} \pi i \sum \left\{ \frac{3(2\ell_2+1)}{2\ell_1+1} \right\}^{1/2} (1\ell_2 00 | \ell_1 0) (1\ell_2 m m_2 | \ell_1 m_1) \times$$

$$i^{\ell_1 - \ell_2} Y_{1m}^*(\hat{a}) Y_{\ell_2 m_2}^*(\hat{r}) Y_{\ell_1 m_1}(\hat{R}) \int_0^\infty dk \frac{j_1(ka) j_{\ell_1}(kr) j_{\ell_2}(kR)}{(p^2 + k^2)^2}. \quad (1.18)$$

The k-space radial integral has a pole at  $k=0$ . The contribution of this part of the integral to the whole expression is identical to the Carlson-Rushbrooke<sup>8</sup> expression as we have used it for dipolar systems. The remaining terms arise from the pole at  $k=ip$ . As a result, denoting by  $V'$  all terms different from the Carlson-Rushbrooke expansion, we can write

$$V' = - (4\pi)^{3/2} \frac{4\pi}{2a} \sum Y_{1m}^*(\hat{a}) Y_{\ell_1 m_1}^*(\hat{r}) Y_{\ell_2 m_2}(\hat{R}) \left\{ \frac{3(2\ell_1+1)}{2\ell_2+1} \right\}^{1/2}$$

$$\times (1\ell_1 00 | \ell_2 0) (1\ell_2 m m_1 | \ell_2 m_2) \left\{ (\ell_1 + \ell_2) i_1(ap) i_{\ell_1}(rp) k_{\ell_2}(Rp) \right.$$

$$+ (ap) i_2(ap) i_{\ell_1}(rp) k_{\ell_2}(Rp) + (rp) i_1(ap) i_{\ell_1+1}(rp) k_{\ell_2}(Rp)$$

$$\left. - (Rp) i_1(ap) i_{\ell_1}(rp) k_{\ell_2+1}(Rp) \right\}. \quad (1.19)$$

The angular dependence of this expression is the same as the Carlson-Rushbrooke expansion. However, there is an important distinction between this term and the Carlson-Rushbrooke formula in that the zeroth order contribution is non-vanishing in its  $r$ -dependence. Thus, as we show in appendix 4, there is an electrostatic contribution to the force constant.

Appendix 2: Electrostatic image effects

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In discussing ionic solvation, so far we have concentrated only on the vibrational degrees of freedom which exist for the system of the ion and its primary solvation shell. This subsystem is considered to be located inside a cavity within the bulk of the solvent. In this section we examine the consequences of adding electrostatic image effects to the basic cavity interaction terms.

Friedman<sup>26</sup> has considered the image approximation to the dielectric reaction field. His approximation methods are particularly useful for the consideration of complicated collections of solvent and ions within a solvation cavity. Although Friedman considered the image approximation to the monopole field in detail, he only quotes the results for the dipolar field. For the sake of completeness in our discussion, we outline the electrostatics of the dipolar reaction field and the application of the image approximation to it.

Consider a single charge  $q$  located at  $s$  on the  $z$ -axis inside a spherical cavity of radius  $a$ . The potential due to this charge inside the cavity is given by<sup>26,27</sup>

$$\phi_{in}(r, \theta) = \sum_{\ell} \left[ \frac{qs^{\ell}}{r^{\ell+1}} - \frac{\epsilon-1}{\epsilon+\ell/(\ell+1)} \frac{qs^{\ell}r^{\ell}}{a^{2\ell+1}} \right] P_{\ell}(\cos\theta), \quad a > r > s \quad (2.1)$$

where  $P_n(x)$  is the Legendre polynomial of order  $n$ . Outside the spherical cavity, the potential is

$$\phi_{\text{out}}(r, \theta) = \sum_{\ell} \frac{2\ell+1}{\ell+\epsilon(\ell+1)} \frac{qs^{\ell}}{r^{-(\ell+1)}} P_{\ell}(\cos\theta). \quad (2.2)$$

We now imagine a single image charge  $q_{\text{im}}$  placed at  $z = r_{\text{im}} > a$ . The potential produced by this charge at  $r < a$  is given by

$$\phi_{\text{im}} = \sum_{\ell} \frac{q_{\text{im}} r^{\ell}}{r_{\text{im}}^{\ell+1}} P_{\ell}(\cos\theta). \quad (2.3)$$

We would like to make the identification

$$\begin{aligned} \frac{q_{\text{im}}}{r_{\text{im}}^{\ell+1}} &= - \frac{\epsilon-1}{\epsilon+\ell/(\ell+1)} \frac{qs^{\ell}}{a^{2\ell+1}} \\ &= - \frac{\epsilon-1}{\epsilon+\ell/(\ell+1)} q(a/s) \frac{s^{\ell+1}}{a^{2\ell+1}}. \end{aligned} \quad (2.4)$$

This identification will be valid for all sufficiently large values of  $\ell$ . Thus,  $r_{\text{im}}$  and  $q_{\text{im}}$  can be identified as

$$r_{\text{im}} = a^2/s \quad (2.5)$$

and

$$q_{\text{im}} = - \frac{\epsilon-1}{\epsilon+1} \frac{a}{s} q \quad (2.6)$$

Alternatively, Friedman<sup>26</sup> has noted that

$$\frac{\epsilon-1}{\epsilon+\ell/(\ell+1)} = \frac{\epsilon-1}{\epsilon+1} \sum_{k=0}^{\infty} \frac{1}{(\epsilon+1)^k (\ell+1)^k}. \quad (2.7)$$

Thus, the identifications (2.5) and (2.6) amount to the assumption

that only the  $k=0$  term in (2.7) needs to be considered. It is equivalent to say that for sufficiently large values of  $\ell$ , the  $k=0$  term is the dominant contribution. It should be noted, however, that also for sufficiently large values of the dielectric constant  $\epsilon$  the  $k=0$  term also suffices regardless of the size of  $\ell$ .

If we consider only the  $k=0$  contribution to (2.7), eqn (2.3) can be written as

$$\phi_{im} = - \frac{\epsilon-1}{\epsilon+1} (a/s) \frac{q}{(a^2/s)} \sum_{\ell} (r/a^2 s)^{\ell} P_{\ell}(\cos\theta) \quad (2.8)$$

which, as Friedman has pointed out,<sup>26</sup> is equivalent to the Laplace expansion of

$$q_{im} / |r - r_{im}|$$

for  $r < r_{im}$ .

In order to consider a dipole located in the cavity and its image, we next consider the superposition to two solutions: one,  $\phi_1$  is the potential produced by  $q_1 = +q$  located at  $z=s$ , and two,  $\phi_2$  is the potential produced by  $q_2 = -q$  located at  $z=s-\delta$ . The potential inside the cavity produced by  $q_1$  is given by eqn (2.1). The potential produced by  $q_2$  is

$$\phi_{2in} = \sum \left[ \frac{-q(s-\delta)^{\ell}}{r^{\ell+1}} + \frac{\epsilon-1}{\epsilon+\ell/(\ell+1)} \frac{q(s-\delta)^{\ell} r^{\ell}}{a^{2\ell+1}} \right] P_{\ell}(\cos\theta). \quad (2.9)$$

The total potential inside the cavity is

$$\phi_{total(in)} = (\phi_1 + \phi_2)_{in} \quad (2.10)$$

which is the sum of (2.1) and (2.9). Now, we write

$$s^\ell - (s-\delta)^\ell = s^\ell \left\{ \ell(\delta/s) - \frac{1}{2!} \ell(\ell-1)(\delta/s)^2 + \dots \right\}, \quad (2.11)$$

and

$$\lim_{\ell \rightarrow 0} [s^\ell - (s-\delta)^\ell] = \ell \delta s^{\ell-1}. \quad (2.12)$$

Thus,

$$\phi_{\text{total(im)}} = \sum_{\ell} \left\{ \frac{\ell q \delta s^{\ell-1}}{r^{\ell+1}} - \frac{\epsilon-1}{\epsilon+\ell/(\ell+1)} \frac{\ell q \delta r^{\ell} s^{\ell-1}}{a^{2\ell+1}} \right\} P_{\ell}(\cos\theta). \quad (2.13)$$

Turning now to the image, we superimpose a second image charge  $q_{2im} = -q_{im}$  at  $z = r_{im} - \delta_{im}$ . The potential produced by the second image charge is

$$\phi_{2im} = \sum_{\ell} \frac{-q_{im} r^{\ell}}{(r_{im} - \delta_{im})^{\ell+1}} P_{\ell}(\cos\theta). \quad (2.14)$$

The potential produced by the two image charges is

$$\begin{aligned} \phi_{\text{total(im)}} &= \sum_{\ell} q_{im} r^{\ell} \left[ 1/r_{im}^{\ell+1} - 1/(r_{im} - \delta_{im})^{\ell+1} \right] P_{\ell}(\cos\theta) \quad (2.15) \\ &= q_{im} (r^{\ell}/r_{im}^{\ell+1}) P_{\ell}(\cos\theta) \{ 1 - [1 - (\ell+1)(-\delta_{im}/r_{im}) \\ &\quad + \frac{1}{2!} (\ell+1)(\ell+2)(-\delta_{im}/r_{im})^2 + \dots] \} \end{aligned}$$

In the limit as the distance between the charges vanishes, an image dipole moment is defined. The potential can be written as

$$\lim_{\delta_{im} \rightarrow 0} \phi_{total(im)} = - \sum_{\ell} (\ell+1) \frac{q_{im} \delta_{im} r_{im}^{\ell}}{r_{im}^{\ell+2}} P_{\ell}(\cos\theta) \quad (2.16)$$

As before with eqn (2.3) and the identification (2.4), here we want to establish a similar means of identifying the dipole image and location in terms of the dipole moment and location inside the cavity. Thus, in eqn (2.13) we add and subtract the same quantity:

$$\begin{aligned} \phi_{total(in)} = & \sum_{\ell} \left[ \frac{\ell q \delta s^{\ell-1}}{r^{\ell+1}} - \frac{\epsilon-1}{\epsilon+\ell/(\ell+1)} (\ell+1) \frac{q \delta r_{im}^{\ell} s^{\ell-1}}{a^{2\ell+1}} \right. \\ & \left. + \frac{\epsilon-1}{\epsilon+\ell/(\ell+1)} \frac{q \delta r_{im}^{\ell} s^{\ell-1}}{a^{2\ell+1}} \right] P_{\ell}(\cos\theta) . \end{aligned} \quad (2.17)$$

The second term is identified as the image dipole:

$$\begin{aligned} \frac{q_{im} \delta_{im}}{r_{im}^{\ell+2}} &= \frac{\epsilon-1}{\epsilon+\ell/(\ell+1)} \frac{q \delta s^{\ell-1}}{a^{2\ell+1}} \\ &= \frac{\epsilon-1}{\epsilon+\ell/(\ell+1)} q \delta (a/s)^3 \frac{s^{\ell+2}}{a^{2\ell+4}} . \end{aligned} \quad (2.18)$$

As before for the monopole case, in the limit of large  $\ell$  or  $\epsilon$ , the location of the image is given by

$$r_{im} = a^2/s \quad (2.19a)$$

and the dipole moment of the image is, given by

$$q_{im} \delta_{im} = \frac{\epsilon-1}{\epsilon+1} (a/s)^3 q \delta . \quad (2.19b)$$

Finally, the third term in (2.17) is identified as an added image

charge

$$q'_{im} = \frac{\epsilon-1}{\epsilon+1}(a/s^2)q\delta. \quad (2.19c)$$

The purpose of the image approximation is to simplify the calculations involving the use of the reaction field. This is done by replacing the complicated solutions to the Laplace equation by simpler expressions which involve the interaction of discrete charges or multipoles. The image approximation amounts, simply, to the assumption of the  $k=0$  term in eqn (2.7).

The energy of interaction of a charge with its own image, or more exactly its reaction field, defines the self energy of that charge with respect to the dielectric. The self energy is<sup>26,27</sup>

$$V_{self} = -\frac{1}{2}q\phi_{im}. \quad (2.20)$$

The interaction of any other charge with this image charge can be expressed as

$$V' = q'\phi_{im}. \quad (2.21)$$

Thus, we are now in a position to calculate the image contribution to the ionic potential energy function for the solvated ion. In this manner we can approximate the contribution of the remainder of the solution system to the vibrational modes of the ion and its primary solvation system.

In the following, we illustrate the image approximation with the use of the tetrahedral solvation model.

Within the solvation cavity, the terms which contribute to the breathing mode force constant are the following: (1) the ion-dipole interaction, (2) the dipole-dipole interaction, (3) the short-ranged interactions (repulsions) which operate between the species in a pair-wise sense, and (4) the interaction between the solvent molecules and the cavity surface. Outside the cavity, in the bulk of the dielectric, the various image quantities are located. We consider first the electrostatic interactions which operate between species within the cavity.

The ion-dipole interaction has been discussed earlier. For the tetrahedral solvation it is simply

$$V_{id(c)} = -4\mu e/R^2. \quad (2.22)$$

We next calculate the dipole-dipole interaction which operates between each pair of solvent molecular dipoles within the cavity. To carry out this calculation, we assume that the dipoles can be regarded as ideal point dipoles. Thus, the general form of the interaction is given by

$$V_{dd} = \underline{\mu}_1 \cdot \underline{\mu}_2 / R^3 - 3(\underline{\mu}_1 \cdot \underline{R})(\underline{\mu}_2 \cdot \underline{R}) / R^5 \quad (2.23)$$

and the vector  $\underline{R}$  is given by

$$\underline{R} = \underline{R}_1 - \underline{R}_2. \quad (2.24)$$

The vectors  $\underline{R}_1$  and  $\underline{R}_2$  are referred to a common origin at the centre of symmetry for the system.

Each solvent dipole has the same magnitude. Furthermore, the angle between each pair of dipoles is the same, the tetrahedral angle of  $109.47^\circ$ . Consequently, each scalar product  $\underline{\mu} \cdot \underline{R}$  is easily calculated. The interaction for any pair of dipoles is

$$\frac{5\sqrt{3}}{8} \frac{\mu^2}{R^3} .$$

This interaction is a repulsion. There are six terms of this type which contribute to the total. Hence,

$$V_{DD}(c) = \frac{15\sqrt{3}}{4} \frac{\mu^2}{R^3} . \quad (2.25)$$

In addition, between each solvent molecule operates a short-ranged repulsion interaction. The general form of the interaction we use in our calculations is exponential. In fact, in the spirit of the Stockmayer model of an electrolyte,<sup>28,29</sup> we assume, for simplicity, that the repulsion between the solvent molecules is the same as the repulsion which operates between the ion and the solvent molecules.

There is a repulsion interaction which operates between the solvent molecules and the wall of the cavity. Because it is possible for solvent molecules to penetrate the cavity wall with reasonable ease, it is not reasonable to assume that this repulsion term is very large. A reasonable expression to approximate this interaction, therefore, is the Woods-Saxon potential<sup>30</sup> which is used extensively in dealing with collective models of the atomic nucleus. The form of the potential is

$$V_{\text{wall}} = \frac{V_0}{1 + \exp[(R-A)/a]} \quad (2.26)$$

where  $A$  is the cavity radius and  $a$  is the half width of the barrier. The thickness of the barrier, and the extent of its influence into the cavity, is determined by the magnitude of the constant  $a$ . For a value of  $V_0$  of the order of several eV (a magnitude which corresponds roughly to the solvation well depth), the effect of the potential term (2.26) is very small. Its effect on the breathing mode force constant is even less.

The contribution of these cavity potential terms to the solvation shell harmonic breathing mode force constant is easily found by direct differentiation. Thus,

$$k_c = -24 \frac{\mu e}{R_0^4} + 45\sqrt{3}/2 \frac{\mu^2}{R_0^5} + 20B/\rho^2 + 4 \frac{V_0}{a^2} \frac{\exp[(R_0-A)/a]-1}{(\exp[(R_0-A)/a]+1)^3} \quad (2.27)$$

where  $B$  and  $\rho$ , associated with the repulsion interaction, are defined in the text: cf. eqn (3).

We now turn to a consideration of the image contributions to the potential energy function and to the force constant. These terms show a complicated structure, and their ultimate effect on the force constant is small. Thus, we will show that they generally need not be considered further, especially when one is interested only in the vibrational structure of the system.

There are a number of contributions to the potential energy function for the system which arise from the interaction of the ion and the solvent dipoles with images in the bulk of the solution. Two of the interactions yield no contribution to the harmonic force

force constant, although they may be of considerable importance in matters concerned with solvation and free energy changes. In particular, the ionic self energy (the interaction of the ion with its image) depends only upon the solvation shell radius  $A$ . Also, the interaction between the ion inside the cavity and the images of the dipoles yields no contribution to the force constant. These terms, and others, will be illustrated in the following paragraphs.

For the classical, non-spatially and temporally disperse dielectric, the ionic self energy is given by the Born expression

$$V_{i(s)} = -(1-1/\epsilon) \frac{e^2}{2A} \quad (2.28)$$

In the image approximation of this expression, we find<sup>26</sup>

$$V_{i(s)} \approx - \frac{1}{2} \frac{\epsilon-1}{\epsilon+1} \frac{e^2}{A} \quad (2.29)$$

For DMSO, for example, the image approximation differs from the Born self energy by about 2.5%. For water, the image approximation differs from the Born self energy by only 1.3%. Thus, for polar solvent systems, the image approximation is reasonable. In any case, it is clear from the form of eqn (2.28) and (2.29) that there can be no contribution arising from these terms to the force constant.

In the image approximation, the self energy of the dipole is relatively easy to determine. Making use of the location of the dipole image, we can write the vector separation between any dipole and its image as

$$\underline{R}_{12} = (1 - A^2/R^2)\underline{R} \quad (2.30)$$

where  $\underline{R}$  is the vector drawn from the centre of symmetry to the dipole in the cavity. The image dipole, and its source, lie along the vector  $\underline{R}$  (and its extensions), but these dipoles are directed in the opposite sense. From the general form of the dipole-dipole interaction, we find

$$V_{dd(i)}(s) = - \frac{\epsilon-1}{\epsilon+1} \frac{\mu^2 A^3}{(A^2-R^2)^3} \cdot \quad (2.31)$$

As we discussed above, and as Friedman also notes,<sup>26</sup> co-located with the dipole image is an effective charge with a magnitude given by

$$e_i = \frac{\epsilon-1}{\epsilon+1} \mu \frac{A}{R^2} \cdot \quad (2.32)$$

The interaction between the source dipole and this part of the image can be written as

$$V_{de(i)}(s) = - \frac{\epsilon-1}{\epsilon+1} \frac{\mu^2}{2A^3} \frac{1}{(1-R^2/A^2)^2} \cdot \quad (2.33)$$

When (2.33) is combined with (2.31), we can write

$$V_{dd(s)} = - \frac{1}{2} \frac{\epsilon-1}{\epsilon+1} \frac{\mu^2}{A^3} \frac{1+x^2}{(1-x^2)^3} \quad (2.34)$$

in which  $x$  is defined by

$$x = R/A. \quad (2.35)$$

This quantity is always less than or at worst equal to unity.

By means of a direct differentiation (with respect to R) of (2.34) we find that this term contributes

$$k_{i(s)} = - \frac{1}{2} \frac{\epsilon-1}{\epsilon+1} \frac{\mu^2}{A^5} \frac{16}{(1-x^2)^5} [20x^4 + 11x^2 - 1] \quad (2.36)$$

to the force constant. Interestingly enough, this term contributes maximally (viz., zero) to the force constant when  $R = 0.28A$ . Generally, however, a solvation radius as small as  $0.28A$  is unlikely.

The interaction between the ion and the dipole images is easily found. It is given by

$$V_{id(i)} = - 4 \frac{\epsilon-1}{\epsilon+1} \frac{\mu e}{A^3}. \quad (2.37)$$

As remarked earlier, this term does not make a contribution to the force constant (it is independent of R).

Next, we consider the interaction between the ion and the effective charges associated with the dipole images. This term is given simply by

$$V_{ii(i)} = \frac{\epsilon-1}{\epsilon+1} \frac{e\mu}{AR}. \quad (2.38)$$

The interaction between a dipole and the dipolar image which arises from another dipole in the cavity is fairly complicated.

The derivation is sketched as follows. The distance between any dipole and the image of any other dipole is given by

$$R_{12} = [3(A^4 + R^4) + 2A^2R^2]^{1/2} / \sqrt{3}R. \quad (2.39)$$

For a system of tetrahedral solvation, the scalar product of the dipole with the other-dipole-image is

$$\underline{\mu}_1 \cdot \underline{\mu}_2 = \frac{\epsilon - 1}{\epsilon + 1} (A/R)^3 \frac{\mu^2}{3}. \quad (2.40)$$

The scalar product of the image dipole moment with the radius vector between the dipole and the other image is

$$\underline{\mu}_1' \cdot \underline{R}_{12} = \frac{\epsilon - 1}{\epsilon + 1} \mu R (A^2/R^2 + 1/3) (A/R)^3. \quad (2.41)$$

Similarly, for the cavity dipole we find

$$\underline{\mu}_2 \cdot \underline{R} = \mu R \left[ \frac{1}{3} (A/R)^2 + 1 \right]. \quad (2.42)$$

The general dipole-dipole interaction is now evaluated to give

$$V_{dd'}(i) = - 2\sqrt{3} \frac{\epsilon - 1}{\epsilon + 1} \mu^2 A^3 \frac{3A^4 + 14A^2R^2 + 3R^4}{(3A^4 + 2A^2R^2 + 3R^4)^{5/2}}. \quad (2.43)$$

Finally, in a similar manner, we find that the interaction between a dipole inside the cavity and the effective charge co-located with the dipolar image arising from a separate dipole in the cavity is given by

$$V_{de(i)} = \sqrt{3} \frac{\epsilon-1}{\epsilon+1} \frac{\mu^2}{A^3} \frac{x^2(x^2+3)}{(3+2x^2+3x^4)^{5/2}} \quad (2.44)$$

The quantity  $x$  is defined by eqn (2.35).

From all these contributions to the potential energy function, we find the image contribution to the force constant is given by

$$k_i = -4 \frac{\epsilon-1}{\epsilon+1} \frac{\mu^2}{A^5} \left\{ \frac{2}{(1-x_0^2)^2} (20x_0^4 + 11x_0^2 - 1) - \frac{2e\mu A}{x_0^3} + \sqrt{3} [2f''(x_0) - g''(x_0)] \right\} \quad (2.45)$$

where

$$f''(x_0) = \frac{1}{A^2 (3+2x_0^2+3x_0^4)^{5/2}} \left[ 4(7+9x_0^2) - \frac{1}{(3+2x_0^2+3x_0^4)} \left( 40x_0^2(1+3x_0^2) \times (7+3x_0^2) + 10 \frac{(3+14x_0^2+3x_0^4) [(1+9x_0^2)(3+2x_0^2+3x_0^4) - 14x_0^2(1+3x_0^2)^2]}{(3+2x_0^2+3x_0^4)} \right) \right] \quad (2.46)$$

and

$$g''(x_0) = \frac{6}{(3+2x_0^2+3x_0^4)^{3/2}} \left[ 2x_0^2 + 1 - \frac{x_0^2}{(3+2x_0^2+3x_0^4)} \left( 3(5+24x_0^2+11x_0^4) + 10 \frac{x_0^2(3+19x_0^2+33x_0^4+9x_0^6)}{(3+2x_0^2+3x_0^4)} \right) \right] \quad (2.47)$$

The quantity  $x_0$  is  $R_0/A$  where  $R_0$  is the equilibrium solvation radius.

The difference between the cavity contributions to the force

constant and the total form of the force constant as a function of the solvation radius of a tetrahedral solvation system is illustrated in Figure 1. The difference is not significant. The image contributions to the force constant for the breathing mode are small, and probably can be ignored in most cases.

Appendix 3: The Laplace expansion of the exponential repulsion

As we indicated earlier in this paper, in order to be able properly to consider the vibrational modes associated with the motion of an ion within its solvation shell, it is necessary to make use of an appropriate form of the potential energy function. For the electrostatic terms the Carlson-Rushbrooke<sup>8</sup> expansion was used. The scalar exponential repulsion which operates between the ion and any of the solvent molecules can be expanded in a similar appropriate manner. It is the purpose of this appendix to outline the construction of this expansion.

The scalar exponential, Born repulsion has the form

$$V(r_{12}) = B \exp[-(r_{12}-a)/\rho]. \quad (3.1)$$

The expansion of this function in terms of the coordinates  $r_>$  and  $r_<$  (where  $r_>$  is the greater of  $r_1$  and  $r_2$ ) is carried out in a manner similar to that of Ruedenberg,<sup>20</sup> and others,<sup>21,22</sup> for the Laplace expansion of the free-space Green function (viz.,  $1/r_{12}$ ).

We make use of the Fourier transform of eqn (3.1) which is given by

$$v(\underline{k}) = 8\pi B \exp(a/\rho) \frac{1}{\rho(1/\rho^2 + k^2)^2}. \quad (3.2)$$

Given

$$f(\underline{k}) = \int d^3r F(\underline{r}) \exp[i\underline{k} \cdot \underline{r}], \quad (3.3)$$

it is well known that one can write

$$F(\underline{r}-\underline{R}) = \frac{1}{(2\pi)^3} \int d^3k f(\underline{k}) \exp[-i\underline{k} \cdot (\underline{r}-\underline{R})] \quad (3.4)$$

Thus, for example, if  $f(\underline{k}) = 4\pi/k^2$  and the exponential function in eqn (3.4) is written as a product of two exponential functions, then the Rayleigh expansion can be used in place of each exponential. When, in the resulting expression, the various integrations are carried out, one recovers the familiar Laplace expansion of  $1/|\underline{r}-\underline{R}|$ .

We now make use of  $v(k)$  in place of  $f(k)$  in eqn (3.4) to write

$$V(\underline{r}-\underline{R}) = 16 \frac{B}{\rho} \exp(a/\rho) \sum_{\ell, m} Y_{\ell m}^*(\hat{r}) Y_{\ell m}(\hat{R}) \int_0^\infty dk k^2 \frac{j_\ell(kr) j_\ell(kR)}{(1/\rho^2 + k^2)^2} \quad (3.5)$$

There is no pole at  $k=0$ . Therefore, we need only evaluate the residue of the radial integral at  $k=i/\rho$ . The general form of the expansion of (3.1) now is written as

$$V(\underline{r}-\underline{R}) = -4\pi B \exp(a/\rho) \sum_{\ell, m} Y_{\ell m}^*(\hat{r}) Y_{\ell m}(\hat{R}) \left\{ (2\ell+1) i_\ell(r_{<}/\rho) k_\ell(r_{>}/\rho) + (r_{<}/\rho) i_{\ell+1}(r_{<}/\rho) k_\ell(r_{>}/\rho) - (r_{>}/\rho) i_\ell(r_{<}/\rho) k_{\ell+1}(r_{>}/\rho) \right\} \quad (3.6)$$

where  $r_{>}$  is the larger of  $r$  and  $R$ .

The expansion of the Morse potential is merely an application of eqn (3.6). The Morse potential function is given by

$$\begin{aligned} V_M &= D\{1 - \exp[-(r-r_e)/a]\}^2 \\ &= D\{1 - 2 \exp[-(r-r_e)/a] + \exp[-2(r-r_e)/a]\}. \end{aligned} \quad (3.7)$$

The Fourier transform of the first term,  $D$ , yields the Dirac delta function. Consequently, the inverse transform yields the constant  $D$  in return. The remaining terms in eqn (3.7) behave in a manner identical to the Born-type repulsion. Thus, the expansion of these terms is accomplished directly with the use of eqn (3.6). When the contributions from the two exponential terms are grouped, the form of the expansion given in eqn (7) results.

Appendix 4: Harmonic force constants

Given a potential energy function for a system, the second order term in the Taylor series expansion defines the harmonic oscillator potential energy function. This second order term is determined by the differentiation of the original function, followed by the evaluation of the resulting expression in terms of the equilibrium values of the coordinates. This is the obvious route to the force constant quantities.

However, for a number of complicated functional forms of the potential, the use of differentiation can be cumbersome. In particular, when one seeks the form of the oscillator potential which operates on the ion inside the rigid cage, the differentiation of the complicated angular dependencies is not necessarily straightforward. Indeed, if, instead of the symmetric, regular systems considered in this paper, one were to consider systems in which the solvent molecules were arbitrarily placed in the solvation cavity, the determination of the oscillator potential would be extremely difficult. Such differentiations, as would be carried out by this method, could be pursued with the use of the formula derived by Rose.<sup>31</sup>

On the other hand, as we have shown in Appendices 1 and 3, often the potential energy function can be expressed in terms of the Fourier convolution integral. In this case it is simpler to differentiate the integral. The analysis then proceeds with the evaluation of the integral. We will show that in this manner the calculation often can be simplified.

In the following paragraphs we will derive the integral representation of the second order Taylor series term. The first order term can be found in a similar manner. However, here only the result will be quoted.

Given a function which can be expressed in the form

$$G(\underline{r}) = F(\underline{r}) Y_{\lambda\mu}(\hat{\underline{r}}), \quad (4.1)$$

we wish to find an integral representation of the second order term which can be expressed as

$$t_2(\underline{r}) = \lim_{\underline{a} \rightarrow \underline{r}_0} \frac{1}{2} (\underline{r} \cdot \nabla_{\underline{a}})^2 G(\underline{a}), \quad (4.2)$$

where  $\underline{r}_0$  is the equilibrium value of  $\underline{r}$ . The notation implies simply that in  $G(\underline{r})$ ,  $\underline{r}$  is replaced by  $\underline{a}$ , but the functional form remains unchanged. The differential operators now operate only on the function  $G$ . As a result, it is possible to write

$$t_2(\underline{r}) = \lim_{\underline{a} \rightarrow \underline{r}_0} \frac{1}{2} \underline{r} \underline{r} : \nabla_{\underline{a}} \nabla_{\underline{a}} G(\underline{a}) \quad (4.3)$$

As the effect of the differential operators now has been established, we can drop the distinction between the coordinates  $\underline{a}$  and  $\underline{r}$  without risk of confusion.

The Fourier transform of  $G(\underline{r})$  is written as  $f(\underline{k}) Y_{\lambda\mu}(\hat{\underline{k}})$ . Thus, equn (4.3) can be written as

$$t_2(\underline{r}) = \frac{1}{2} \underline{r} \underline{r} : \left\{ \frac{1}{(2\pi)^3} \int d^3 \underline{k} \underline{k} \underline{k} f(\underline{k}) Y_{\lambda\mu}(\hat{\underline{k}}) \exp[-i \underline{k} \cdot \underline{r}] \right\}. \quad (4.4)$$

The integral is evaluated at  $r_0$ . It is clear that the functional form of this result also can include additional coordinate dependencies as long as these coordinates are independent of  $r$ .

The vector  $\underline{k}$  can be expressed in terms of the basis vectors for the spherical tensors:<sup>31</sup>

$$\underline{k} = \sqrt{4\pi/3} k \sum_{m=-1}^1 (-1)^m Y_{1m}(\hat{k}) \hat{\xi}_{-m}. \quad (4.5)$$

The product of the  $k$ -vectors can be expressed in terms of the product of the summations in eqn (4.5). The use of the Rayleigh expansion (1.17) together with the contraction formula<sup>31</sup>

$$Y_{\ell_1 m_1} Y_{\ell_2 m_2} = \sum_{\ell_3} \left\{ \frac{(2\ell_1+1)(2\ell_2+1)}{4\pi(2\ell_3+1)} \right\}^{1/2} (\ell_1 \ell_2 00 | \ell_3 0) (\ell_1 \ell_2 m_1 m_2 | \ell_3 m_3) \times Y_{\ell_3 m_3} \quad (4.6)$$

allows us to write

$$\begin{aligned} V_r V_r G(r) &= - \frac{1}{2\pi^2} \sum_{L, \ell, M, m, m'} (-i)^{L+2(m+m')} \hat{\xi}_{-m} \hat{\xi}_{-m'} \left( \frac{2\lambda+1}{2L+1} \right)^{1/2} \\ &\times Y_{LM}(\hat{r}) (11mm' | \ell m+m') (1100 | \ell 0) (\lambda \ell \mu m+m' | LM) (\lambda \ell 00 | L0) \\ &\times I_L(r) \end{aligned} \quad (4.7)$$

where

$$I_L(r) = \int_0^\infty dk k^{\lambda} f(k) j_L(kr). \quad (4.8)$$

The evaluation of the dyad product gives

$$\begin{aligned}
 t_2(\underline{r}) = & -\frac{r^2}{3\pi} \sum_{L, \ell, M, m, m'} (-i)^L Y_{LM}(\hat{r}_0) Y_{1m}^*(\hat{r}) Y_{1m'}^*(\hat{r}) \\
 & \times \left[ \frac{2\lambda+1}{2L+1} \right]^{1/2} (1100|\ell 0) (11mm'|\ell, m+m') (\lambda \ell 00|L 0) (\lambda \ell 1m+m'|LM) \\
 & \times I_L(r_0). \tag{4.9}
 \end{aligned}$$

The contraction equation (4.6) can be used to write

$$\begin{aligned}
 t_2(\underline{r}) = & -\frac{r}{\pi} \sum_{\ell, L} (-i)^L \left[ \frac{2\lambda+1}{4\pi(2L+1)(2\ell+1)} \right]^{1/2} (1100|\ell 0)^2 \\
 & \times (\lambda \ell 00|L 0) I_L(r_0) \sum_{M, \nu} (\lambda \ell \nu \nu|LM) Y_{LM}(\hat{r}_0) Y_{\ell \nu}^*(\hat{r}). \tag{4.10}
 \end{aligned}$$

It is evident from the Clebsch-Gordan coefficients that for any value of  $\lambda$  the index  $\ell$  can only have the value of 0 or 2. Moreover,  $\ell + \lambda + L = \text{even}$ . Consequently, eqn (4.10) can be separated into two parts:

$$\begin{aligned}
 t_2(\underline{r}) = & -\frac{r^2}{6\pi} \frac{1}{3/2} i^\lambda Y_{\lambda 0}(\hat{r}_0) Y_{\lambda 0}(\hat{r}) I_\lambda(r_0) \\
 & -\frac{r^2}{3\sqrt{5}\pi} \frac{1}{5/2} \sum_{L, M, \nu} (-i)^L \left[ \frac{2\lambda+1}{2L+1} \right]^{1/2} (\lambda 200|L 0) (\lambda 2\nu \nu|LM) \\
 & \times Y_{LM}(\hat{r}_0) Y_{2\nu}^*(\hat{r}) I_L(r_0). \tag{4.11}
 \end{aligned}$$

Generally, for the systems we consider, and their associated potential energy functions, only the first term in eqn (4.11) is needed. We illustrate this with the exponential repulsion and

with the interaction between the continuous charge distribution and the point dipole which was discussed in Appendix 1.

The Fourier transform of the exponential repulsion is given by eqn (3.2). We are interested in the harmonic term with respect to the  $\underline{r}$ -variable in the general expression  $v(\underline{r}-\underline{R})$ : cf., eqn (3.4) and (3.5). Thus, we write

$$V(\underline{r}-\underline{R}) = \frac{1}{(2\pi)^3} \int d^3k [v(\underline{k}) \exp(i\underline{k} \cdot \underline{R})] \exp(-i\underline{k} \cdot \underline{r}). \quad (4.12)$$

Differentiating this expression twice with respect to  $\underline{r}$  yields

$$\nabla_{\underline{r}} \nabla_{\underline{r}} V(\underline{r}-\underline{R}) = - \frac{1}{(2\pi)^3} \int d^3k \underline{k} \underline{k} [v(\underline{k}) \exp(i\underline{k} \cdot \underline{R})] \exp(-i\underline{k} \cdot \underline{r}). \quad (4.13)$$

The integral in (4.13) has the same form as the integral expression in eqn (4.4). Subsequent evaluation of eqn (4.13) proceeds with the expansion of the exponential term. Thus,

$$\begin{aligned} [v(\underline{k}) \exp(i\underline{k} \cdot \underline{R})] &= \sum_{\lambda, \mu} f_{\lambda}(\underline{k}) Y_{\lambda\mu}(\hat{\underline{k}}) \\ &= 32\pi^2 B \exp(a/\rho) \frac{1}{\rho(1/\rho^2 + k^2)^2} \sum_{\lambda, \mu} i^{\lambda} Y_{\lambda\mu}^*(\hat{\underline{R}}) Y_{\lambda\mu}(\hat{\underline{k}}) \\ &\quad \times j_{\lambda}(kR). \end{aligned} \quad (4.14)$$

The  $I_L(r_0)$  defined by eqn (4.8) now has the specific form

$$I_L(r_0) = 32\pi^2 B \exp(a/\rho) \sum_{\lambda, \mu} i^\lambda Y_{\lambda\mu}^*(\hat{R}) \int_0^\infty dk k^4 \frac{j_L(kr_0) j_\lambda(kR)}{(1/\rho^2 + k^2)^2} \quad (4.15)$$

The integral is evaluated for  $r_0 < R$ , which will always be true (the limit is taken as  $r_0 \rightarrow 0$ ). There is no pole at  $k=0$  unless  $\lambda > L+4$ , which will not happen. As a result, we find

$$\int_0^\infty dk k^4 \frac{j_L(kr_0) j_\lambda(kR)}{(1/\rho^2 + k^2)^2} = i^{L-\lambda} \frac{\pi}{4\rho} \{ (3+L+\lambda) i_L(r/\rho) k_\lambda(R/\rho) + (r/\rho) i_{L+1}(r/\rho) k_\lambda(R/\rho) - (R/\rho) i_L(r/\rho) k_{\lambda+1}(R/\rho) \}. \quad (4.16)$$

The equilibrium value of  $r_0$  is 0. As a result, the integral (4.16) vanishes for all values of  $L \neq 0$ . Consequently, there is only one term  $I_0(r_0)$ :

$$I_0(r_0) = 8\pi^2 (B/\rho^2) \exp(a/\rho) \sum_{\lambda, \mu} Y_{\lambda\mu}^*(\hat{R}) \{ (3+\lambda) k_\lambda(R/\rho) - (R/\rho) k_{\lambda+1}(R/\rho) \} \quad (4.17)$$

However, the first term in (4.11) is  $I_\lambda(r_0)$ . That is, the first term in (4.11) corresponds to  $L=\lambda$ . But, since  $L=0$ , only one term in (4.17) contributes. Thus, the first term in (4.11), evaluated for this system, is

$$t_2^0(r) = r^2 (B/6\rho^2) \exp[-(R-a)/\rho] (1-2\rho/R). \quad (4.18)$$

When this quantity is evaluated at the system equilibrium point of  $R=a=R_{eq}$ , we find

$$t_2^0(r) = r^2 (B/6\rho^2) (1-2\rho/R_{eq}). \quad (4.19)$$

The second term in eqn (4.11), evaluated for this repulsion, has the form

$$t_{\tilde{2}}^2(\tilde{r}) = \frac{\pi r^2}{3\sqrt{5}} (B/\rho^2) \exp(a/\rho) \sum_{\lambda, \mu} \sqrt{2\lambda+1} (\lambda 2 0 0 | 0 0) (\lambda 2 \mu - \mu | 0 0) \\ \times Y_{\lambda \mu}^*(\hat{R}) Y_{2-\mu}^*(\hat{r}) \{ (R/\rho) k_{\lambda+1}(R/\rho) - (3+\lambda) k_{\lambda}(R/\rho) \}. \quad (4.20)$$

Clearly, the sum collapses to one term, the term for  $\lambda=2$ . For any system with simple cubic symmetry, the summation of the repulsion terms, in the same sense as the summation of the dipole terms in the electrostatic case, yields a zero contribution. Hence, only the zeroth order term survives; that term is given by eqn (4.19).

The application of this analysis to the Morse potential is straightforward. We proceed from eqn (4.19).

The Morse potential can be seen to yield two terms to the force constant. The force constant contribution associated with the attraction term we label  $k_+$ , the term associated with the repulsion contribution we label  $k_-$ . Thus,

$$k_+ = - \frac{2Da^2}{3} (1-2/aR) \quad (4.21)$$

and

$$k_- = \frac{4Da^2}{3} (1-1/aR). \quad (4.22)$$

The sum of these two terms gives

$$k = 2Da^2/3 \quad (4.23)$$

We turn now back to a consideration of the interaction between the soft ionic charge distribution and the collection of point solvent dipoles which was discussed in the first appendix. At this point we need to assess the contribution this type of electrostatic interaction makes to the force constant.

In eqn (1.16) we expand the exponential,  $\exp(i\mathbf{k} \cdot \mathbf{r}_{12})$ , in terms of  $\mathbf{r}$  and  $\mathbf{R}$ :  $\mathbf{r}_{12} = \mathbf{R} - \mathbf{r}$ . Therefore, consistent with eqn (4.4), we write

$$\begin{aligned} & \frac{16\pi^2 i \mu p^4}{a} \sum_m Y_{1m}^*(\hat{a}) Y_{1m}(\hat{k}) \frac{j_1(ka)}{k^2(p^2+k^2)^2} \exp(i\mathbf{k} \cdot \mathbf{R}) \\ &= \frac{64\pi^3 i \mu p^4}{a} \sum_{\lambda, \mu} \sum_m \sum_{j, k} \left( \frac{3(2j+1)}{4\pi(2\lambda+1)} \right)^{1/2} (1j00|\lambda 0) (1jmk|\lambda \mu) i^\lambda Y_{1m}^*(\hat{a}) \\ & \times Y_{jk}^*(\hat{R}) Y_{\lambda\mu}(\hat{k}) \frac{j_1(ka) j_j(kR)}{k^2(p^2+k^2)^2} \quad (4.24) \\ &= \sum_{\lambda, \mu} f_\lambda(k) Y_{\lambda\mu}(\hat{k}). \end{aligned}$$

The radial quantity  $I_L(r_0)$  is

$$\begin{aligned} I_L(r_0) &= \frac{2^7 \pi^3 i \mu p^4}{a} \sum_m \sum_{j, k} \left( \frac{3(2j+1)}{4\pi(2\lambda+1)} \right)^{1/2} (1j00|\lambda 0) (1jmk|\lambda \mu) i^j \\ & \times Y_{1m}^*(\hat{a}) Y_{jk}^*(\hat{R}) \int_0^\infty dk k^2 \frac{j_1(ka) j_j(kR) j_L(kr_0)}{(p^2+k^2)^2}. \quad (4.25) \end{aligned}$$

We now evaluate the first term in eqn (4.11). Here, as with the repulsion term examined above, we note that  $I_L(r_0)$  vanishes as  $r_0 \rightarrow 0$  for  $L \neq 0$ . Note, however, that the integral in eqn (4.25) does not depend upon  $\lambda$ . Nevertheless, the first term in eqn (4.11) requires that  $L=\lambda=0$ . We find that the first term in (4.11) yields

$$t_{\frac{0}{2}}^0(r) = 2\pi r^2 \frac{\mu p^3}{3a} [Y_{11}(\hat{a})Y_{1-1}(\hat{R}) - Y_{10}(\hat{a})Y_{10}(\hat{R}) + Y_{1-1}(\hat{a})Y_{11}(\hat{R})] \\ \times \{3i_1(ap)k_1(Rp) + (ap)i_2(ap)k_1(Rp) - (Rp)i_1(ap)k_2(Rp)\}. \quad (4.26)$$

For a tetrahedral system, this becomes

$$t_{\frac{0}{2}}^0(r) = 2 \frac{\mu p^3}{a} \{3i_1(ap)k_1(Rp) + (ap)i_2(ap)k_1(Rp) \\ - (Rp)i_1(ap)k_2(Rp)\}. \quad (4.27)$$

There is another possible contribution to the force constant for the case when  $L=0$ ,  $\ell=\lambda=2$ . However, it is relatively easily shown that the form is similar to the Carlson-Rushbrooke expression for  $\ell=2$ . Thus, for simple cubic systems, these additional terms vanish by symmetry.

The behaviour of the force constant contribution (4.27) as a function of solvation radius is shown in Table 10. The first three values, which correspond roughly to the solvation radii for lithium, sodium and potassium, can be seen to be decreasing. On the other hand, the last two values, which correspond approximately to the solvation radii for rubidium and cesium, increase. The

contribution to the force constant has a negative value as a result of the attraction between the soft charge and the point dipoles. The repulsion contribution will continue to be a positive valued contribution to the force constant. This term generally will decrease with increasing solvation radius. As a result, the first three force constants for lithium, sodium, and potassium will be expected to decrease, as observed. However, because the electrostatic contribution increases from rubidium to cesium, the overall force constant for these two species should at worst decrease slower than is the case for lithium to potassium, and at best, they should increase, as the experimental data indicate.

This soft charge contribution to the force constant does support the results of our analysis. The softness of the charge distribution is connected to the polarizability of the atom or ion. Hence, the result we find for this electrostatic contribution is not surprising.

Finally, to complete this discussion of force constant problems, we quote the integral form of the first order Taylor series term. This term generally is needed any time a particular distribution of solvent dipoles deviates from the equilibrium symmetry and arrangement of some reference state.

The first order contribution to the Taylor series expansion is written as

$$t_1(\underline{r}) = \frac{r}{2\pi^2} \sqrt{4\pi/3} \sum_{L,M,m} (-i)^{L+1} Y_{1m}^*(\hat{r}) Y_{LM}(\hat{r}_0) \left( \frac{2\lambda+1}{2L+1} \right)^{1/2} (1\lambda 00 | L0) \\ \times (1\lambda m\mu | LM) H_L(r_0), \quad (4.28)$$

$$H_L(r_0) = \int_0^{\infty} dk \, k^3 \, f_\lambda(k) j_L(kr_0) \quad (4.29)$$

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Table 1: Experimental vibrational frequencies (in units of  $\text{cm}^{-1}$ )  
from Maxey and Popov.<sup>5</sup>

Ion (and counter ion)	frequency ( $\text{cm}^{-1}$ )
Li(I)	429±2
Na(I)	198±3
K(I)	153±3
Rb(I)	123±3
Cs(I)	110±4

Table 2: Force constants (units:  $\text{dynes/cm}^2$ ) for coordination numbers  
 $c$  from 4 to infinity

Ion	$c = 4$	$c = 6$	$c = 8$	$c = \infty$
Li	74307	74849	75902	75935
Na	49497	50652	51253	53148
K	47837	49672	50652	53811
Rb	60121	64785	67398	79204
Cs	66506	73888	78188	94856

Table 3: Solvation radii

Ion	radius (Å)
Li	3.24
Na	3.56
K	3.79
Rb	3.91
Cs	4.12

Table 4: Calculated force constants according to eqn (9a) and (9b).

The results are presented in the following manner: the first number is the force constant; the first number in parentheses is the calculated vibrational frequency (in  $\text{cm}^{-1}$ ) using the reduced mass associated with the coordination; the second number in parentheses is the calculated frequency assuming a rigid solvation cage ( $c = \infty$ ).

Ion	4-coordination	6-coordination
Li	75181(432)(427)	112772(527)(---)
Na	57353(213)(206)	86092(258)(---)
K	47877(153)(144)	71815(184)(---)
Rb	43752(105)(---)	65627(124)(114)
Cs	37602( 83)(---)	56403( 96)( 85)

Table 5: Ionic refractions (after Smyth<sup>16</sup>)

Ion	refraction
Li	0.2
Na	0.5
K	2.2
Rb	3.6
Cs	6.3

Table 6: Calculated force constants with the use of eqn (24).

Ion	$c = 4$	$c = 6$	$c = 8$	$c = \infty$
Li(e)	74307	74849	75092	75935
Li(c)	87443	88082	88368	89360
K(c) <sup>a</sup>	233168	(all large)		
K(c) <sup>b</sup>	131983	(all large)		
Rb(e)	60121	64785	67398	79204
Cs(e)	66506	73888	78188	94856
Cs(c)	69231	74602	77611	91206

(e) is the experimental value; (c) is a calculated value.

a: calculated from lithium

b: calculated from sodium

Table 7: values of  $b(m',m)$  for  $B_{12}^{m'm}$

$m' \backslash m$	-2	-1	0	1	2
-1	$-\sqrt{15}$	$\sqrt{10}$	$-\sqrt{6}$	$\sqrt{3}$	-1
0	$\sqrt{5}$	$-\sqrt{8}$	3	$-\sqrt{8}$	$\sqrt{5}$
1	-1	$\sqrt{3}$	$-\sqrt{6}$	$\sqrt{10}$	$-\sqrt{15}$

Table 8: values of  $b(m',m)$  for  $B_{13}^{m'm}$

$m' \backslash m$	-3	-2	-1	0	1	2	3
-1	$2\sqrt{7}$	$-\sqrt{21}$	$\sqrt{15}$	$-\sqrt{10}$	$\sqrt{6}$	$-\sqrt{3}$	1
0	$-\sqrt{7}$	$\sqrt{12}$	$-\sqrt{15}$	4	$-\sqrt{15}$	$\sqrt{12}$	$-\sqrt{7}$
1	1	$-\sqrt{3}$	$\sqrt{6}$	$-\sqrt{10}$	$\sqrt{15}$	$-\sqrt{21}$	$2\sqrt{7}$

Table 9: values of  $b(m',m)$  for  $B_{14}^{m'm}$

$m' \backslash m$	-4	-3	-2	-1	0	1	2	3	4
-1	$-3\sqrt{5}$	6	$-2\sqrt{7}$	$\sqrt{21}$	$-\sqrt{15}$	$5/\sqrt{2}$	$-\sqrt{6}$	$\sqrt{3}$	-1
0	3	-4	$\sqrt{21}$	$-2\sqrt{6}$	5	$-2\sqrt{6}$	$\sqrt{21}$	-4	3
1	-1	$\sqrt{3}$	$-\sqrt{6}$	$5/\sqrt{2}$	$-\sqrt{15}$	$\sqrt{21}$	$-2\sqrt{7}$	6	$-3\sqrt{5}$

Table 10: The relative contribution of the "soft" electrostatic interaction to the force constant (normalized to lithium).

R (solvation radius)	$k/ k_{Li} $
3.26	-1.00
3.46	-1.23
3.66	-1.25
3.86	-1.18
4.06	-1.08

Figure Captions:

Figure 1: A comparison of the variation of the breathing mode force constant with solvation radius for (a) cavity contributions alone and (b) with dielectric image effects included.

Figure 2: The relationship between the various vector quantities used in the bipolar, Carlson-Rushbrooke expansion of the free space Green function  $1/r_{12}$ . For the systems we consider,  $O$  is the origin at the centre of symmetry and  $S$  is the location of a solvent molecule.

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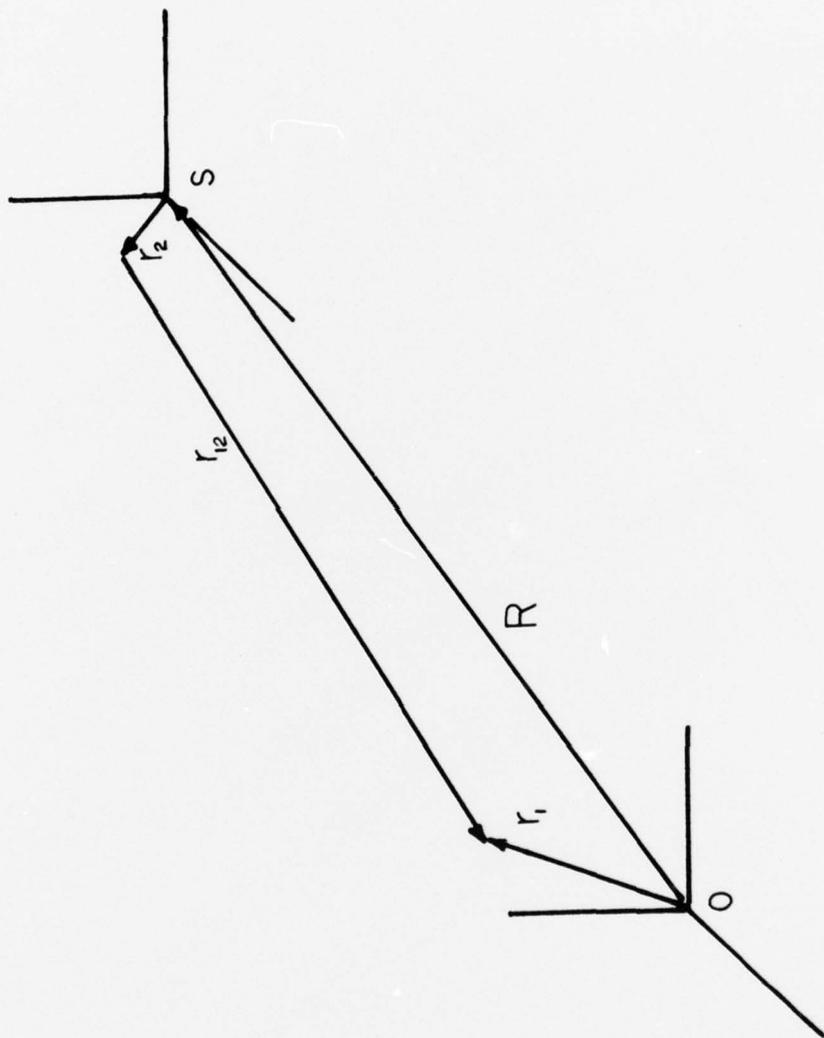
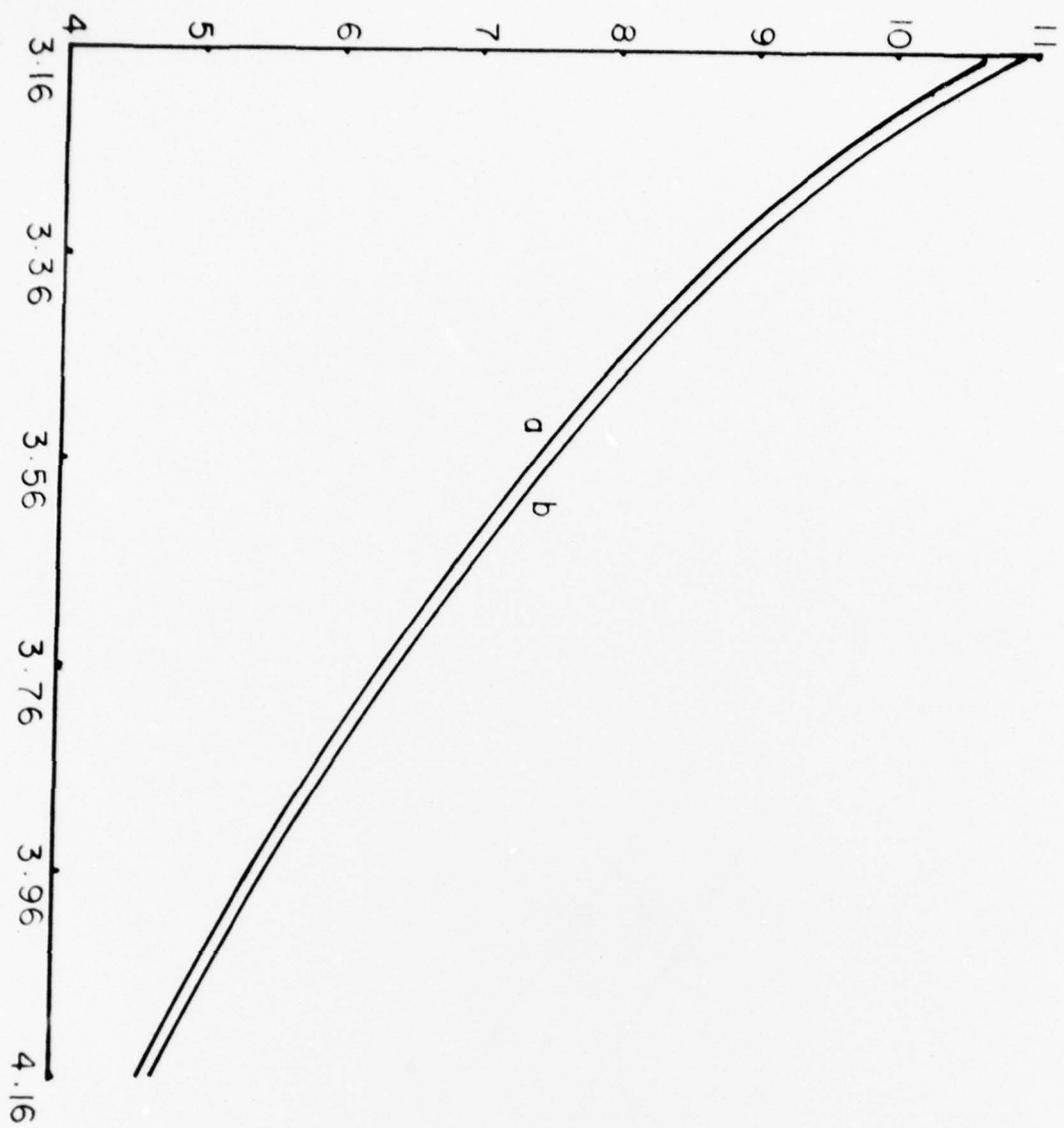


Figure 5



$t/A$

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