The Intermolecular Vibration of Ions in Solution[1]

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Abstract: The infrared spectrum of tetrahydrofuran solutions of a number of alkali metal salts has been observed between 90 and 600 cm^{-1}. Some measurements were made in other solvents (dimethyl sulfoxide, pyridine, and piperidine). In every case, a band was observed which could be associated with alkali ion vibration. The frequency shows a dependence upon anion in THF as well as a dependence upon solvent. The effect of pressure to 20 kbar, frequency shift with Li^+ isotope substitution, the variation of band intensity with concentration, and Raman spectra were studied for selected salts in THF. The results suggest that the infrared band arises from motion in the solutions which is similar to that which occurs on the excitation of a highly localized phonon at an impurity center in crystals. The motion may be approximated as the alkali ion vibrating in a cage, under the influence of electrostatic and repulsion forces. The anion is a cage component in THF solutions while only solvent molecules are involved in DMSO. The force constant for the net force resisting the displacement of the alkali ion was calculated from the experimental results. Force constants of the same magnitude arise from a solution model in which the electrostatic terms are expressed on a molecular basis and repulsion by exponential terms.

Little is known about the dynamics of monatomic ions in electrolytic solutions in the very short time range. Yet knowledge of this kind can provide information about such fundamental solution properties as the short-range forces and the details of solution structure at these ions. The importance of these aspects of solvation to an understanding of chemical reactivity is well known; see, for example, Cram, *et al.*[2]

In a short communication,[3] we have indicated that an infrared band which is observed at longer wavelengths in the infrared spectrum of the alkali metal salts of $Co(CO)_4^-$ dissolved in THF arises from the vibration of the alkali ion in a cage formed by solution components. At essentially the same time, Evans and Low[4] reported a band in the same region of the infrared spectrum of tetraalkylammonium chlorides and bromides in benzene, which they attribute to a ring stretching vibration of the salt dimer in solution. Soon Popov and coworkers[5] observed bands for alkali salts dissolved in sulfoxides and pyrolidones, which they assign to the vibration of the alkali ion in a cage of solvent molecules. Recently, French and Wood[6] reported a study of the alkali salts of BPh_4^- for the most part in pyridine, and interpret their band in terms of the vibration of a "diatomic" type of ion pair species.

In this paper, we give the results of some studies designed to obtain information about the general nature of the alkali ion vibration together with the details behind our earlier communication.

Results and Discussion

A broad band of medium intensity, which can be assigned to alkali ion vibration, appeared in the infrared spectrum of each salt solution studied. The Li^+ salt solutions showed a band near 400 cm^{-1}, the Na^+ salt solutions near 200 cm^{-1}, and the K^+ salt solutions near 150 cm^{-1}. Table I shows the frequencies for each absorption maximum. Much of the work was carried out in THF, as an example of a solvent of modest solvating power. In connection with an examination of the effect of solvent upon band position and characteristics, some studies were made in DMSO, a solvent of high solvating power, and in pyridine and piperidine—solvents more like THF.

Table I. Frequencies (cm^{-1}) of Alkali Ion Vibrations

	Li^+ Salts in THF		
$Co(CO)_4^-$	413	Cl^-	387
NO_3^-	407	Br^-	378
BPh_4^-	412	I^-	373
	Na^+ Salts in THF		
$Co(CO)_4^-$	192	I^-	184
BPh_4^-	198		
	K^+ Salts in THF		
$Co(CO)_4^-$	142		
	Li^+ Salts in DMSO-d_6		
NO_3^-	425	Br^-	424
Cl^-	425	I^-	424
	Na^+ Salts in DMSO		
$Co(CO)_4^-$	199	$Cr_2(CO)_{10}^{2-}$	200[a]
BPh_4^-	203	NO_3^-	200
$HCr_2(CO)_{10}^-$	200[a]	I^-	194
	$NaCo(CO)_4$ in Other Solvents		
Piperidine	183 (274)	Pyridine	180

[a] Taken from the Ph.D. thesis of N. Pauuwe, Purdue University, June 1968.

Several of the salts examined in DMSO in this study were also studied by Maxey and Popov in that solvent. Our values for these agree with those of the latter work within the limits of uncertainty established in both

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[1] Based in part upon the Ph.D. thesis of J. Lyford, IV, Purdue University, Aug 1969, and the M.S. thesis of R. Wright, Purdue University, Aug 1968, with some contribution from the Ph.D. thesis of W. Risen, Jr., Purdue University, Aug 1966.

[2] D. J. Cram, J. L. Mateos, F. Hanck, A. Langemann, K. R. Kopecky, W. D. Nielsen, and J. Allinger, *J. Amer. Chem. Soc.*, **81**, 5774 (1959).

[3] (a) W. F. Edgell and A. T. Watts, Abstracts, Symposium on Molecular Stucture and Spectroscopy, Ohio State University, June 1965, p 85; (b) W. F. Edgell, A. T. Watts, J. Lyford, IV, and W. Risen, Jr., *J. Amer. Chem. Soc.*, **88**, 1815 (1966).

[4] J. C. Evans and G. Y. Low, *J. Phys. Chem.*, **69**, 3223 (1965).

[5] (a) B. W. Maxey and A. I. Popov, *J. Amer. Chem. Soc.*, **89**, 2230 (1967); (b) *ibid.*, **91**, 20 (1969); (c) private communication.

[6] M. J. French and J. L. Wood, *J. Chem. Phys.*, **49**, 2358 (1968).

studies. However, French and Wood report the Na^+ band of $NaBPh_4$ at 175 cm⁻¹ in several solvents including THF. Our measurements yield 198 cm⁻¹ for this band in THF with an uncertainty of ±3 cm⁻¹.

Effect of Anion on Frequency. A series of measurements was made with different anions in order to explore the environment in the near neighborhood of a cation. Consider the salts in THF first. Only Li^+ salts are extensively soluble in this liquid and more data were obtained for this cation than for others. The value found for $LiCo(CO)_4$ was 413 cm⁻¹ and this shifts progressively through six anions to 373 cm⁻¹ for LiI. Since the uncertainty range on these particular values is about ±3 cm⁻¹, it is clear that these values indicate a pronounced shift of frequency with anion for Li^+ salts in THF. The uncertainties for $NaCo(CO)_4$ and $NaBPh_4$ are also ±3 cm⁻¹, while that for NaI is perhaps twice as large. Thus, the frequencies of Na^+ salts in THF also vary with anion although the shifts are not as large as with the Li^+ salts. Solubility difficulties prevented us from establishing an anion effect for K^+ salts in THF.

The measurements for salts in DMSO are plagued by solvent absorption near the alkali ion bands. With the Na^+ salts, increased solvent absorption occurs as one moves through the low-frequency half of the band. As a result, the tabulated Na^+ values are uncertain by ±4 cm⁻¹. DMSO has strong absorption bands very close to the Li^+ band maximum. Since solvent absorption was substantial at the Li^+ band maximum, it is difficult to eliminate its effect upon the frequency of the maximum by any techniques. These solvent absorptions occur at lower frequency in DMSO-d_6 and the overlap problem is much alleviated if one works in this solvent. Consequently, the lithium salts were measured in the deuterated solvent. The bands for LiCl, LiBr, LiI, and $LiNO_3$ were all superimposable and the absorption maximum occurred at 425 ± 3 cm⁻¹. These results show that the frequency of an alkali ion vibration in DMSO is independent of the salt anion.

Effect of Solvent on Frequency. Solvent molecules will be a part (if not all) of the near-neighbor environment of alkali ions in solution. This is not the same thing as saying that solvent molecules will significantly influence the force felt by the alkali ion and the other solution components moving in the vibration. We sought information on this effect in two types of measurements. In the first, representative salts were compared in THF and DMSO. As can be seen in Table I, pronounced changes were found for the Li^+ salts, *e.g.*, LiBr from 376 to 424 cm⁻¹ and LiI from 373 to 425 cm⁻¹. The same thing occurred for the Na^+ salts although the changes are smaller here.

In the second type of measurements, the alkali ion vibration of $NaCo(CO)_4$ was observed in THF, pyridine, piperidine, and DMSO. The frequency shifts from 199 cm⁻¹ in DMSO to 180 cm⁻¹ in pyridine. Thus, the solvent has a role in determining the force resisting the displacements in this far-infrared vibration.

General Solution Structure at the Cation. Perhaps the salient thing about these results is that they exist at all, for this means there must be structure at the cation, which exists over a period of time, which is significant in terms of the vibrational phenomena. For the present, we shall place a lower limit on the lifetime of such structure as the period of vibration, namely 10^{-13} sec. On the other hand, the rate of ligand attachment to alkali ions suggests an upper limit for such structures of perhaps 10^{-7} sec.[7]

The variation of cation frequency with the anion of the salt indicates that the cation is associated with the anion in an intimate way in THF solutions. The simplest form that this association could take is the contact ion pair.[3] Whatever the form this intimate association takes, one also expects the cation to have solvent molecules in its near-neighbor environment on geometrical grounds. The fact that the frequency of the vibration varies with solvent implies that the solvent also contributes to the force on the alkali ion. Thus, one is led to the view that the cation vibrates in a cage composed of anion and solvent molecules in THF solutions and that all elements of this cage contribute (although not necessarily equally) to the factors which determine the band frequency. In general, a similar situation can be expected to obtain in other solvents of modest solvating power.

As the solvating power of the solvent increases, contact ion pairs are expected to become less stable. In solvents of high solvating power, solvent molecules can be expected to predominate in the near-neighbor environment of the cation. The lack of variation of cation frequency with anion shown in Table I supports such a solution structure for the alkali salts in DMSO, as do the data of Maxey and Popov, who reached the same conclusion for this solvent.

Variation of Band Intensity with Concentration. The experimental evidence cited above favors an intimate association of cation and anion for the alkali salts in THF. The simplest cation environment consistent with this finding is the contact ion pair. But other cation environments may also be present at the same time in these THF solutions, *e.g.*, solvent-separated ion pairs, free ions, high aggregates, etc. In the case of $NaCo(CO)_4$ in piperidine, two separate infrared bands have been observed. But the existence of one alkali band in a THF solution does not necessarily mean that only one cation environment exists in that solution. For example, the infrared band could arise from only one of the environments present.

If there is more than one cation environment in solution, the concentration variation of each with the change in concentration of the salt will depend upon the equilibria involved. Since the absorbance of an infrared band arising from a given cation environment would be proportional to the concentration of that environment, a study of band intensity *vs.* salt concentration should yield information about this point. To this end, the intensity of the Na^+ band of $NaCo(CO)_4$ in THF has been studied over a concentration range of 0.04–0.32 *M* with the results shown in Table II and plotted in Figure 1. As can be seen, the absorbance of the Na^+ band varies linearly with salt concentration within the accuracy of the experiments. There are two situations which could lead to this result. First, virtually all of the cation might be present in a single environment. Second, several cation environments might be present in substantial

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(7) M. Eigen, "Coordination Chemistry: Seventh International Conference," Butterworth and Co. Ltd., London, 1963.

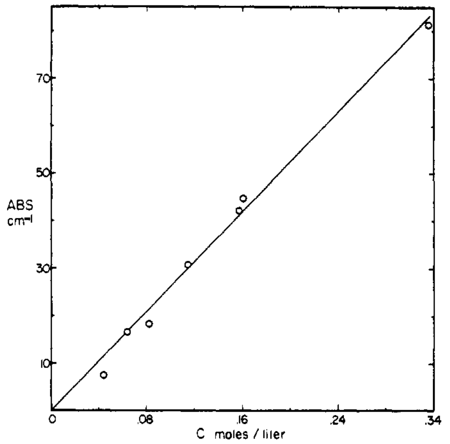

Figure 1. The integrated absorbance *vs.* concentration of the Na^+ vibration for $NaCo(CO)_4$ in THF.

amounts in the solution as long as the concentration of each (one or more) of those that contribute to the band is proportional to the salt concentration. A realistic example of the second case would be the presence of both contact and solvent-separated ion pairs in the solution.

Table II. The Variation of the Intensity of the Na^+ Band of $NaCo(CO)_4$ in THF with Concentration

$M \times 10^2$	Abs, cm^{-1}
31.5	8.12
16.0	4.47
15.7	4.22
11.5	3.07
8.1	1.83
6.4	1.66
4.4	0.76

A nonlinear variation of absorbance with salt concentration is expected in the case where the ratio of two environments contributing to the band would change with salt concentration. This latter result depends upon the expectation that the molar absorbance of one cation environment would be different from that of another. But is the molar absorbance of a cation vibrating in a contact ion pair expected to be different from that of the cation vibrating in a solvent-separated ion pair (or, more generally, in a solvent-surrounded cation)? To gain an insight into the answer to this question, we have compared the molar absorbance (Abs) expected for the cation band in these two cases for the simple models of the motions discussed below and the assumption of point charges. Then

$$\begin{aligned} &\text{Contact ion pair:} \\ &\qquad \text{Abs} = Ke^2(M + A + S)/M(A + S) \\ &\text{Solvent-surrounded cation:} \\ &\qquad \text{Abs} = Ke^2 2S/M(M + 2S) \end{aligned} \qquad (1)$$

M, A, and S are the mass of the cation, anion, and solvent molecule, respectively, and e is the electron charge. This leads to an expected ratio of about 1.3 for the absorbance of the Na^+ vibration in a contact ion pair to that of the Na^+ as a solvent-surrounded cation for $NaCo(CO)_4$ in THF.

It is worthwhile noting that $A + S \approx M + A + S$ and $2S \approx M + 2S$. Then eq 1 leads one to expect that the intensity of the alkali ion bands would be approximately inversely proportional to alkali ion mass. Qualitative observations on these bands are in agreement with this expectation.

Laser Raman Spectra. Plane and coworkers[8,9] have shown that heavy metal ions bond water molecules in aqueous solutions with forces that have a strong covalent component. This is shown by the fact that the vibrations of the water molecules against the stationary metal ion are readily observed in the Raman effect. To what extent are the forces on the alkali ion of covalent nature? To answer the question, we have examined the Raman spectra of $NaCo(CO)_4$, $Na_2Cr_2(CO)_{10}$, and $NaHCr_2(CO)_{10}$ in THF and DMSO solutions, as well as the first salt in DMF, all without observing a Raman line which could be assigned to a Na^+ vibration. Further, long photographic exposures were made on THF solutions of LiCl in an effort to find Raman lines associated with the salt, but without success. The carbon–chlorine stretching mode of CCl_4 at 459 cm^{-1} is a good example of a vibration involving the stretching of a covalent bond to a chlorine atom. As such, it serves as a standard for the evaluation of the LiCl results. CCl_4 was dissolved in THF and the intensity of the 459-cm^{-1} line measured as a function of concentration. This line disappeared when the CCl_4 concentration was $^1/_{150}$th of the salt concentration used in the LiCl runs. This means that the polarizability change in the Li^+ vibration is at least an order of magnitude ($\sqrt{150}$) smaller than that for the CCl_4 vibration. One concludes that covalent forces are small and that these alkali ion vibrations take place essentially under the influence of ionic forces.

Pressure Effect on the Li^+ Vibration. Ferraro, Mitra, and Postmus[10] have studied the effect of pressure on the vibration of ionic crystals at long wavelengths. They find that internal modes of vibration of polyatomic ions (*e.g.*, NO_3^-, SO_4^{2-}) are relatively insensitive to pressure—the change being about 0.0–0.2 cm^{-1}/kbar of applied pressure.[10,11] On the other hand, large shifts in frequency were observed for external (lattice) modes, *e.g.*, 0.7–1.9 cm^{-1}/kbar.

The principle involved in these results can be applied to the determination of an important aspect of the alkali ion vibrations. Suppose the Li^+ vibration for LiCl in THF were the vibration of a simple contact ion pair LiCl (*i.e.*, a diatomic species). Then the forces between the Li^+ and nearby solvent molecules and between the Cl^- and nearby solvent molecules would be small compared to those between the ions and one could speak of the LiCl species in a solvent cavity. In this case, the pressure response of the Li^+ frequency would be characteristic of an internal mode of vibration, *i.e.*, small. On the other hand, if the forces between the Li^+ and nearby solvent molecules and between the Cl^- and nearby solvent molecules were similar in magnitude to those between the two

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[8] R. Hester, R. Plane, and G. Walrafen, *J. Chem. Phys.*, **38**, 249 (1963).

[9] R. Hester and R. Plane, *Inorg. Chem.*, **3**, 768 (1964).

[10] J. Ferraro, S. Mitra, and C. Postmus, *Inorg. Nucl. Chem. Lett.*, **2**, 269 (1966).

[11] C. Postmus, K. Nakamoto, and J. Ferraro, *Inorg. Chem.*, **6**, 2194 (1967).

ions, the frequency of the Li^+ would be sensitive to pressure like a lattice mode of a solid salt.

The effect of pressure on the frequency of the Li^+ vibration for LiCl in THF has been studied over a range of applied pressure from 0 to 20 kbar. The results are shown in Table III and Figure 2. The average value of $\partial\nu/\partial P$ from those measurements is 1.5 cm^{-1}/kbar of applied pressure. This value is characteristic of a lattice mode in an ionic solid and means that we are dealing with the second case discussed above. It means that solvent molecules must also be displaced in the vibration as well as Li^+ and Cl^- ions. Moreover, it would seem that this pressure result implies that solvent molecules beyond those in contact with the Li^+ ion are also displaced. Otherwise, the increase in pressure would decrease the distance between the solvent molecules in the solvent region but not that between the Li^+ and those solvent molecules directly in contact with (and "bound" to) it. The implication, however, is that the displacement of the solvent molecules in the vibration drops off (rapidly) as the distance from the Li^+ increases. Then, the motions in the vibration are similar to those which occur at an impurity center in a crystal when a localized phonon is excited.

Table III. Variation of Li^+ Frequency of LiCl in THF with Pressure

Pt gasket 1		Pt gasket 2		Mo gasket	
P, kbar	ν, cm^{-1}	P, kbar	ν, cm^{-1}	P, kbar	ν, cm^{-1}
1	385	1	382	9.8	385
12	406	6	389	16.2	395
		12	398	31.6	402

Isotope Effect. Confirming evidence is sought in this section for the participation of solvent molecules in the vibration. Linear momentum is conserved in vibrational motion. Consequently, the amplitude of the alkali ion displacement will depend upon whatever other entities take part in the vibration and upon the relative extent of their participation. Thus, the frequency variation which results from isotopic alkali ion substitution will depend upon this factor and can be used to investigate it.

This point was studied by comparing ^7LiCl and ^6LiCl spectra in THF.[12] As will be shown below, the conclusions depend upon the value the isotopic shift takes within a range of 5 cm^{-1}. This is particularly small in view of the uncertainties in these frequencies as indicated above. To reduce the uncertainty, we have examined the region near the transmission minimum for LiCl and ^6LiCl with an expanded scale (3×) and retraced each spectrum seven times. By drawing an average curve through this composite of seven spectra much of the large amount of noise present in a single spectrum is eliminated. In this way, we find the transmission minimum for $^7Li^+$ (LiCl) at 391 cm^{-1} and that for $^6Li^+$ (^6LiCl) at 420 cm^{-1} with an estimated uncertainty of ±2 cm^{-1}.[13]

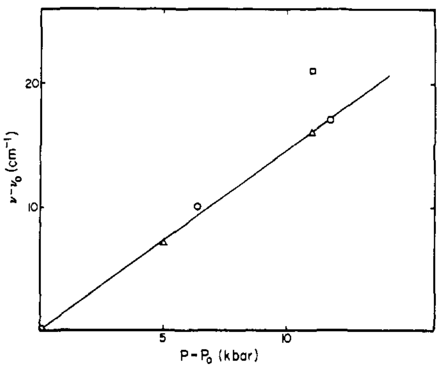

Figure 2. Effect of pressure on the Li^+ band of LiCl in THF. $P - P_0$ = pressure increment after pressure was transmitted to solution, $\nu - \nu_0$ = corresponding frequency increment, Δ is the common first point for each run.

Now, if the vibration were confined to the Li^+ and Cl^- ions alone, the frequency ratio ν_7/ν_6 would be given by the expression $(\mathrm{Li}\ (\mathrm{Li}' + \mathrm{Cl})/\mathrm{Li}'\ (\mathrm{Li} + \mathrm{Cl}))^{1/2}$. Here Li′ is the mass of the heavy lithium isotope and the other symbols follow. Then the value computed for ν_7 from the observed value of ν_6 is 394 cm^{-1}. The lowest value that the ν_7/ν_6 ratio could have is $(\mathrm{Li}/\mathrm{Li}')^{1/2}$, which would correspond to the case in which a large number of solvent molecules moved with the Cl^- in opposition to the Li^+. The computed value of ν_7 for this case is 389 cm^{-1}. The experimental value for ν_7 is seen to be between these numbers. While the uncertainty in ν_7 is essentially as large as the range in its theoretical value, the results are consistent with the pressure finding.

Net Force on the Alkali Ion. The alkali ion is subject to forces from a number of components of the solution. It is, of course, not possible to evaluate these several forces separately from the single frequency of vibration. However, it is possible to evaluate the composite of these forces or, more precisely, the net force resisting the displacements of the vibration per unit displacement of the alkali ion (evaluated for small displacements). This net force constant is a valid parameter to describe the alkali ion environment in the solution. It is directly related to the potential energy of interaction of the alkali ion with the other components of solution. Moreover, it will give significant information about short-range forces in electrolytic solutions. And it is just these short-range forces which have proved so difficult to obtain from thermodynamic and conductance measurements.

To be sure, to compute the net force constant for a vibration from the observed frequency requires a knowledge of the displacements of the several components which move in the vibration. The importance of knowledge of this value makes it worthwhile to approximate. However, as the isotope study above shows, these modes are so dominated by the alkali ion motion in the solutions studied here that the net force constants computed from a variety of models consistent with this localization do not differ much from one another. For the present purpose, we chose the simplest model for this vibration. Figure 3a shows the

(12) Since ordinary Li^+ is 92% $^7Li^+$ and the frequency of the $^6Li^+$ is 30 cm^{-1} away, the observed frequency of the transmission minimum in Li^+ can be taken as the $^7Li^+$ value. Any small shift in the minimum which would result from $^6Li^+$ overlapping would move it above the true $^7Li^+$ value. This would increase the amount of solvent participation as discussed in this section.

(13) These composites revealed some asymmetry in the LiCl and ^6LiCl bands. The value given above is for the band minimum in each case. This asymmetry was not clear in the individual runs and the value for LiCl in Table I represents the band center.

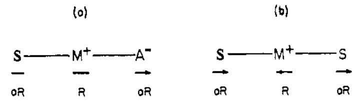

Figure 3. Simple model displacements for the alkali ion vibration: a, contact ion pair; b, solvent surrounded cation.

model for the contact ion pair in THF. Here $a = M/(A + S)$ and is determined by the conservation of momentum condition; M, A, and S are the alkali ion, anion, and solvent masses, respectively. Figure 3b shows the model for the solvent-surrounded cation environment, as found in DMF, DMSO, etc. In this case, $a = M/2S$. The net force constant for the vibration is given by the expression

$$K_{\text{net}} = 4\pi^2c^2\omega^2T_{\text{net}} \tag{2}$$

where ω is the frequency of vibration in cm^{-1} and T_{net} is the kinetic energy constant defined through the relation, kinetic energy = $T_{\text{net}}R^2/2$. R is the alkali ion displacement in terms of which all other displacements are expressed, as illustrated in Figure 3. For the models of Figure 3

$$\text{Contact ion pair:}\quad T_{\text{net}} = M(A + S + M)/(A + S) \tag{3}$$
$$\text{Solvent-surrounded cation:}\quad T_{\text{net}} = M(2S + M)/2S$$

Applying eq 2 and 3 to the frequency data of Table I gives the net force constants found in Table IV.[14]

Table IV. The Force Constant K_{net} (mdyn/Å) for the Alkali Ion Vibrations

	THF Solutions		
$LiCo(CO)_4$	0.72	$LiNO_3$	0.71
$NaCo(CO)_4$	0.55	LiCl	0.65
$KCo(CO)_4$	0.54	LiBr	0.61
		LiI	0.59
NaI	0.51	$LiBPh_4$	0.71
$NaBPh_4$	0.56		
	DMSO Solutions		
Li^+ salts	0.77	Na^+ salts	0.62

On the Origin of K_{net}

It is the purpose of this section to show that these measurements have an important role in determining short-range forces in electrolytic solutions. We shall show that they are understandable in terms of standard theory.

Potential energy expressions (U) for ion pairs have been written by several authors.[15–18] They contain the dielectric constant D in the denominator. Since D for DMSO is greater than that for THF by a factor of 6, one would expect the force constants in DMSO to be much less than those in THF if expressions of this type were valid for the short-range forces. This is clearly not the case. Improved models of ion solvation have been formed by summing the specific electrostatic interaction of the ion with the solvent molecules in the near-neighbor shell while considering the remaining as a dielectric continuum.[19–21] We have modified this kind of model by replacing its hard-shell feature by adding repulsion terms between the relevant entities. As an example, consider the vibration of Li^+ in DMSO using the model of Figure 3b. Each solvent molecule is represented as a dipole μ with polarizability α, which has its repulsion center located a distance b from the dipole center. Then

$$K_{\text{net}} = [(2S + M)/2S]^2\{(2A/\rho^2)\exp[-(r - b)/\rho] - 12e\mu/r^4 - 20e^2\alpha/r^6 - 144\alpha_i\mu^2/r^8\} \tag{4}$$

We take $A = 1300$ eV from an estimation of the oxygen atom radius in DMSO (r_i) and the Li^+ radius (r_j) together with the relation between A and ($r_i + r_j$) found earlier for gaseous alkali halides.[1] For DMSO, $\mu = 4.3$ D, $\alpha = 7 \times 10^{-24}$ cm^3, and $b = 0.9$ Å; for Li^+, $\alpha_i = 0.03 \times 10^{-24}$ cm^3, and ρ is given its nearly universal value of 0.32 Å. Then eq 4 yields $K_{\text{net}} = 0.64$ mdyn/Å of Li^+ displacement in agreement with the observed value of 0.72 mdyn/Å. This force constant can be understood as arising from the electrostatic and repulsion forces of the solution. The same conclusion has been reached from calculations for the kind of contact ion pair suggested by this work.

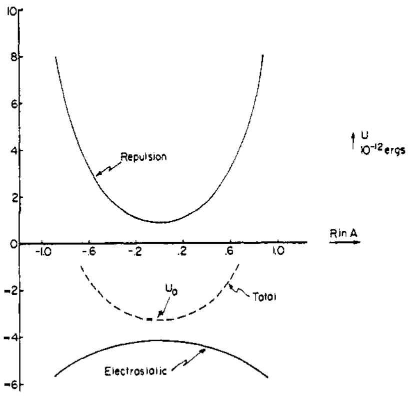

Figure 4. The various contributions to the energy U for Li^+ in DMSO plotted *vs.* the alkali ion displacement in the cation mode.

The above calculation for Li^+ in DMSO can be used to illustrate an important role for the measurement of intermolecular vibration in solution of ions. Figure 4 shows a plot of the potential energy (dashed line) as a function of the displacement (R) of the alkali ion from its equilibrium position in the mode of Figure 3b. Its value at $R = 0$ gives the potential energy of the Li^+ at its equilibrium position. It can be seen from this figure that the major part of U_0 comes from the electrostatic terms. Since U_0 leads directly to the energy of solvation of the ion, it follows that solvation measurements will be a primary source of information about the electrostatic terms. This is well known.

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(14) If one assumes that all the forces resisting the motions of the vibration depend only on the change in the M–A and M–S distances shown, one can relate K_{net} to force constants k_A and k_S for the M–A and M–S distances, respectively. Thus, for the motion of Figure 2a, $K_{\text{net}} = (k_A + k_S)(A + S + M)^2/(A + S)^2$; and of Figure 2b, $K_{\text{net}} = k_S(2S + M)^2/2S^2$.

(15) N. Bjerrum, *Kgl. Danske Videnskab Selskab*, 7, No. 9 (1926).

(16) R. M. Fuoss and F. Accascina, "Electrolytic Conductance," Interscience Publishers, New York, N. Y., 1959.

(17) J. Dennison and J. Ramsey, *J. Amer. Chem. Soc.*, 77, 2615 (1955).

(18) L. Pettit and S. Bruckenstein, *ibid.*, 88, 4783 (1966).

(19) J. D. Bernal and R. H. Fowler, *J. Chem. Phys.*, 1, 515 (1933).

(20) D. D. Eley and M. G. Evans, *Trans Faraday Soc.*, 34, 1093 (1938).

(21) A. D. Buckingham, *Discuss. Faraday Soc.*, 24, 15 (1957).

Figure 5 shows a plot of the curvature of U (dashed line) against R. Its value at the equilibrium position is K_{net}. As can be seen, the major contribution to K_{net} comes from the *repulsion terms.* It follows that these vibration studies should be a primary source of information about the repulsion terms in U_0. As far as we know, this fact has not been recognized. Since U_{rep} is not a negligible part of U_0, its inclusion in U_0 should lead to an improvement over hard shell models. And one can hope that a combination of the data from vibrational and solvation studies will lead to a balanced determination of the parameters of U_0.

Conclusions

The results of this study indicate that structure exists at the alkali ion in solution and this structure has a sufficiently long lifetime to form a cage in which the cation vibrates. Two kinds of cation cages have been found—one in which the cation is surrounded by solvent molecules and one in which the cage contains an anion in intimate contact with the cation in addition to solvent molecules. More than one kind of cation cage is possible in the same solution. When the cation moves in vibration, several cage elements, including solvent, respond in a type of motion which appears to be similar to that which occurs at an impurity site in crystals when a localized phonon is excited. Thus, the contact ion pair does not appear to be well represented by a "diatomic species" M^+A^- in a solvent cavity. Net force constants may be calculated for the vibration in terms of simplified models of the motion. It is possible to compute net force constants of the same general magnitude from potential energy expressions which add repulsion terms to the molecular model type of electrostatic terms. The repulsion terms make a much larger contribution to the net force constant than do the electrostatic terms and hence this type of measurement should be a useful source of such information.

Experimental Section

Since some of the compounds used in this work were extremely oxygen-sensitive, and since the presence of any traces of moisture in the solutions was undesirable, rigorous precautions were taken to ensure that both anaerobic and extremely dry conditions were maintained at all times. To this end, all manipulations were carried out either on a vacuum line or in an atmosphere of dry nitrogen, and all solvents were thoroughly dried and deaerated before use. The THF was dried and deoxygenated by a sequential procedure involving storage over Na ribbon, distillation in a stream of dry N_2, deaeration on a vacuum line, and distillation *in vacuo* onto Linde 4A molecular sieves. Prior to use, the sieves were activated by heating to at least 300° and pumping on the vacuum line. The DMSO ("Baker Analyzed" reagent) and DMSO-d_6 (Stohler Isotope Chemicals, 99.5% D) were placed directly onto the molecular sieves and were deaerated on the vacuum line.

The $NaBPh_4$ (Baker Analyzed reagent, 99.5% pure) was dried at 140° and was used without further purification. It also served as the starting material for the preparation of the $LiBPh_4$.[22] The $NaCo(CO)_4$ was prepared in tetrahydrofuran by a reaction similar to that reported[23] to occur between $Co_2(CO)_8$ and alcoholic base. In this procedure NaOH (Mallinckrodt analytical reagent), which had been heated on the vacuum line prior to use, was stirred with $Co_2(CO)_8$ (Alfa Inorganics) in a THF solution. When the reaction had gone to completion, the resulting solution was filtered, and the solvent was removed on the vacuum line to yield a white solid.

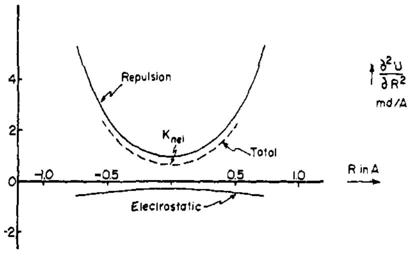

Figure 5. The various contributions to the energy curvature ($\partial^2 U/\partial R^2$) for Li^+ in DMSO plotted *vs.* the alkali ion displacement in the cation mode.

The $LiCo(CO)_4$ was prepared by a reaction analogous to the one used for the $LiBPh_4$ preparation. A solution of LiCl (Baker Analyzed reagent) in THF was added to a solution containing a stoichiometric amount of $NaCo(CO)_4$ in THF. Following precipitation of the insoluble NaCl, the solution was filtered. Since it did not prove feasible to remove the solvent (the solid decomposed to a brown material when most of the solvent had been removed), the resulting solution of $LiCo(CO)_4$ was used as such.

Whenever an accurate concentration of a $Co(CO)_4^-$ solution was desired, the nitroso-R salt method for the determination of Co was used. The application of this procedure to these solutions has been described.[24] The other salts were dried at 140° before use, but otherwise they were subjected to no further purification. The sources of these compounds were LiCl and NaI, Baker Analyzed reagent; LiBr, Matheson Coleman and Bell; $LiNO_3$, Fisher Certified reagent; and LiI, K and K Laboratories. The ^{6}LiCl was prepared from ^{6}LiOH (95%, Oak Ridge National Laboratories) by treating a water solution of the base with a stoichiometric amount of HCl in water followed by removal of the water. The last stages of the dehydration were carried out by heating on a vacuum line.

The infrared spectra were measured in the region between 33 and 600 cm^{-1} with a Beckman IR-11 infrared spectrometer. The cells were of dense polyethylene (Phillips Petroleum) and constructed in this labotatory.[25] In general, two types of runs were made. In the first, the salt solution in the sample beam was run against dry air in the reference beam. Then the same cell filled with solvent was run in the sample beam against air in the reference beam. The per cent transmission curve for the salt in the solution was calculated in the usual way from these data. The second type of run was made in a similar manner except that a cell of about the same thickness and filled with solvent was placed in the reference beam for both runs. In the quantitative measurements of intensity, the ln (I_0/I) was plotted against wave number and the area under the band determined. The integrated absorbance, Abs $= \int \ln (I_0/I)\, d\nu = cl \int \epsilon(\nu)\, d\nu$, obtained in this way for the Na^+ vibration for $NaCo(CO)_4$ in THF is plotted against salt concentration in Figure 1. These measurements were made in cells with a nominal thickness of 20 mils. This cell thickness and the slope of Figure 1 permit one to estimate the integrated absorption coefficient for the vibration.

The infrared measurements on the LiCl solutions at high pressures were performed at Argonne National Laboratories with a Perkin-Elmer Model 301 double beam far-infrared spectrophotometer. The modifications which have been made to this instrument to adapt it to these pressure measurements have been discussed elsewhere.[10] The high-pressure diamond cells which were used in these studies have also been described.[26] Gaskets for containing the solution between the diamond anvils of the cell were made of either platinum or molybdenum. The solutions themselves were viewed with an optical microscope both before and after all measurements to ensure that the increase in pressure had not caused crystallization. Applied pressures were determined by measuring the compression of the spring of the diamond cell. A pressure of 9.8 kbar was required to compress the Mo gasket to the point that pressure was actually transmitted to the solution. Furthermore, the gasket would eventually rupture as the pressure was increased.

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[22] D. N. Bhattocharyya, C. L. Lee, J. Smid, and M. Szwarc, *J. Phys. Chem.*, **69**, 608 (1965).

[23] W. Hieber, J. Sedlmeier, and W. Abeck, *Chem. Ber.*, **86**, 700 (1953).

[24] W. F. Edgell, M. T. Yang, and N. Koizumi, *J. Amer. Chem. Soc.*, **87**, 2563 (1965).

[25] J. Lyford, IV, and W. F. Edgell, *Appl. Spectrosc.*, 22, 582 (1968).

[26] (a) E. E. Weir, E. R. Lippincott, A. Van Valkenburg, and E. N. Bunting, *J. Res. Nat. Bur. Stand.*, *A*, 63, SS (1959); (b) E. R. Lippincott, C. E. Weir, A. Van Valkenburg, and E. N. Bunting, *Spectrochim. Acta*, **16**, 58 (1960); (c) E. R. Lippincott, F. E. Welsh, and C. E. Weir, *Anal. Chem.*, **33**, 137 (1961); (d) E. R. Lippincott, L. S. Whatley, and H. C. Duecker in "Applied Infrared Spectroscopy," D. N. Kendall, Ed., Reinhold Publishing Corp., New York, N. Y., 1966, p 435.

The Raman spectra were recorded photographically on a grating instrument constructed in this laboratory. A Spectra-Physics Model 125 He–Ne laser was used for the excitation source, and the use of a Spectra-Physics Model 310 polarization rotator made the identification of the polarized lines a straightforward matter. By using a Corning filter, No. SPO-98565, in front of the slit, it was possible to obtain Raman spectra above 200 cm^{-1} from the exciting line, although the maximum transmission of the Corning filter is not reached until 400 cm^{-1}. Several Rowland ghosts appear in the region between 200 and 400 cm^{-1} but they are weak and do not interfere. On the other hand, the region below 200 cm^{-1} is heavily populated with ghosts. A special Baird filter permitted one to obtain high transmission from about 40 to 200 cm^{-1} while removing all the ghosts. However, the constant presence of lines at 63 and 91 cm^{-1} was observed.

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The Microscopic Mechanism for Diffusion and the Rates of Diffusion-Controlled Reactions in Simple Liquid Solvents[1]

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Abstract: Standard theoretical treatments of chemical reaction kinetics generally neglect any mean interaction potentials or "excluded volume" effects that might interfere with the relative diffusion of a pair of reactant molecules in solution. Analyses of the computer-generated simulation data for a model dense fluid of Lennard-Jones disks have shown that the microscopic mechanism for diffusion in simple liquids is largely "cooperative" in nature, and that short-range correlations associated with this cooperative mechanism tend to slow the relative diffusion of pairs of molecules approaching to within three–four diameters of each other. In this paper we examine the impact of these results upon the theoretical prediction of diffusion-controlled reaction rates and the physical interpretation of several other very fast chemical processes in solution.

The use of diffusion models to treat the kinetics of fast reactions in solution was first proposed by Smoluchowski[3] and has more recently been reviewed by Noyes.[4] Although this approach is widely used and frequently provides satisfactory order-of-magnitude predictions of rate constants, several fundamental difficulties remain. These difficulties appear to stem primarily from a lack of detailed information regarding the microscopic mechanism for diffusion in liquids. In particular, the manner in which this mechanism might affect the *relative* motions of molecules in a liquid is not well understood.

In Smoluchowski-type treatments of chemical reaction kinetics, it is frequently assumed that the relative diffusion of molecules of two reactant species is described by a coefficient that is just the sum of the bulk diffusion coefficients for the two species in solution. This assumption is equivalent to a supposition that no correlation exists between the time-dependent relative displacements of two solute molecules and their relative positions and motions at previous times. It is not altogether clear that this supposition is valid for molecules that are separated by only short distances, and indeed a deviating behavior—the so-called "solvent cage effect"—was long ago suggested by Rabinowitch.[5] The results obtained by Noyes and coworkers from their investigations of iodine atom recombination rates[6,7] and the wavelength dependence of the quantum yield for iodine photodissociation[8–10] in solution also suggest that these short-range correlations may have a measurable effect upon the kinetics of certain very fast chemical processes.

In order to obtain additional information regarding the microscopic structure and kinetics characteristic of simple liquids, one of the authors (P. L. F.) has recently completed a series of computer calculations simulating the dynamics of a two-dimensional dense fluid of Lennard-Jones disks. Two previous papers have presented the results from some preliminary analyses of the simulation data[11] and a detailed investigation of the mechanism for diffusion and relative diffusion in the model fluid.[12] The purpose of this paper is to examine the

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(3) M. von Smoluchowski, *Z. Phys. Chem.*, 92, 129 (1917).

(4) R. M. Noyes in "Progress in Reaction Kinetics," Vol. 1, G. Porter, Ed., Pergamon Press, New York, N. Y., 1961, p 128.

(5) E. Rabinowitch, *Trans. Faraday Soc.*, 33, 1225 (1937); W. C. Wood, *ibid.*, 32, 1381 (1936).

(6) H. Rosman and R. M. Noyes, *J. Amer. Chem. Soc.*, 80, 2410 (1958).

(7) R. M. Noyes, *ibid.*, 86, 4529 (1964).

(8) R. M. Noyes, *ibid.*, 77, 2042 (1955).

(9) L. F. Meadows and R. M. Noyes, *ibid.*, 82, 1872 (1960).

(10) R. M. Noyes, *Z. Elektrochem.*, 64, 153 (1960).

(11) P. L. Fehder, *J. Chem. Phys.*, 50, 2617 (1969).

(12) P. L. Fehder, C. A. Emeis, and R. P. Futrelle, "The Microscopic Mechanism for Self-Diffusion and Relative Diffusion in Simple Liquids," manuscript in preparation.