

Ion–Ion–Solvent Interactions in Solution

Part 4.—Raman Spectra of Aqueous Solutions of Some Nitrates with Monovalent Cations

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The profile of the band due to the symmetric stretching of the nitrate ion in the Raman spectra of solutions of NH_4NO_3 , $\text{Me}_4\text{N}\cdot\text{NO}_3$, LiNO_3 , KNO_3 and RbNO_3 has been component analysed. For the cations NH_4^+ and Me_4N^+ only one component was present. The bandwidth indicates that the ammonium ion causes enhanced dephasing while the tetramethylammonium ion produces essentially no perturbation. Solutions of LiNO_3 gave evidence of four concentration-dependent species identified as aquated ions, solvent-separated ion pairs, contact ion pairs and ion aggregates. Solutions of KNO_3 and RbNO_3 gave evidence of three species identified as aquated ions, ion pairs and ion aggregates. It was not possible to distinguish between contact ion pairs and solvent-separated ion pairs. Association quotients calculated for LiNO_3 solutions were $K_1(1 \text{ mol dm}^{-3}) = 1.34 \text{ dm}^3 \text{ mol}^{-1}$ and $K_2(6 \text{ mol dm}^{-3}) = 1.5$, for KNO_3 solutions $K(1 \text{ mol dm}^{-3}) = 2.0 \text{ dm}^3 \text{ mol}^{-1}$ and for RbNO_3 solutions $K(1 \text{ mol dm}^{-3}) = 1.0 \text{ dm}^3 \text{ mol}^{-1}$.

Nitrates having monovalent cations produce a variety of effects in aqueous solution. Ammonium nitrate solutions give little indication of disturbance of the anion by the cation^{1,2} and it has been assumed that the ammonium ion, with a tetrahedral shape, fits well into the hydrogen-bonded network of water. Solutions of the related salt tetramethylammonium nitrate³ gave little evidence for a concentration-dependent disturbance of the nitrate ion but the structural disturbance by the large cation was reflected in the infrared spectrum. Spectra of the NO_3^- ion in solutions of lithium nitrate showed a concentration-dependent splitting of the band due to the antisymmetric stretching vibration (ν_3) in the Raman spectra,⁴ appearance of a second band in the spectral feature due to the in-plane bending vibration (ν_4) at 738 cm^{-1} in water⁵ and 734 cm^{-1} in D_2O ,⁶ and at high concentrations asymmetry in the band due to the symmetrical stretching vibration (ν_1).⁷ The spectra of the nitrate ion in solutions of potassium nitrate show a splitting of ν_3 which is less than for solutions of LiNO_3 or NaNO_3 .⁴ In addition, although ν_4 shows some asymmetry no new features are evident. Studies of the band profile of the ν_1 band in the Raman spectra^{8,9} have shown that the vibrational relaxation time is almost independent of concentration when the cations are NH_4^+ or K^+ but for Na^+ and Li^+ the value of τ_v decreases with concentration, with $\text{Li}^+ > \text{Na}^+$.

In this study the Raman band due to the symmetrical stretching vibration was studied for aqueous solutions of the salts LiNO_3 , KNO_3 , RbNO_3 , NH_4NO_3 and $\text{Me}_4\text{N}\cdot\text{NO}_3$ from dilute solution to saturation. Using the techniques described in the previous paper these spectra have been component band analysed. This analysis will be described for each solute and then the overall trends in results will be examined.

EXPERIMENTAL

The salts were all recrystallised twice from water, dried at 110 °C for 48 h and stored over P_2O_5 . All other experimental details and methods of data treatment were as described in the previous paper.¹⁰

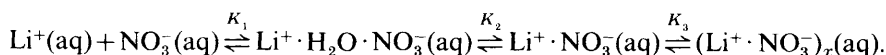
RESULTS AND DISCUSSION

SOLUTIONS OF $LiNO_3$

The time correlation functions for solutions of $LiNO_3$ are shown in fig. 1 A, which includes the transform for a Lorentzian profile of half-width 3.4 cm^{-1} . The imaginary part of the transform is appreciable and increases rapidly with concentration. This behaviour is compatible with a band composed of more than one component in which the component(s) growing at higher concentrations have a greater half-width than the dilute solution band. The correlation functions at various concentrations also give evidence of weak minima, and in particular the transforms of 8 and 10 mol dm^{-3} solutions have minima at 3.5-4 ps, indicating two components separated by $4\text{--}5\text{ cm}^{-1}$.

The time variation of the θ function derived from the real and imaginary parts of the transform is shown in fig. 1 B. In 1 mol dm^{-3} solution the θ function already lies above that of the dilute solution band and the point of intersection is beyond the range of the figure at *ca.* 7-8 ps, corresponding to a separation between components of $2\text{--}2.4\text{ cm}^{-1}$. The curves for concentrations of 2, 4 and 6 mol dm^{-3} all give evidence of a second minimum at *ca.* 4 ps, corresponding to a peak separation of *ca.* 4 cm^{-1} , while at the highest concentrations a weak inflection at short times, 1.5-2.5 ps, indicates a separation of *ca.* 10 cm^{-1} . On this basis the initial band components were positioned at 1047.6, 1050 and 1052 cm^{-1} with allowance for a fourth component at higher energy.

The results of the component analysis of the spectroscopic band at various concentrations are given in table 1 with the variation in band intensity (band area) as a function of concentration being shown in fig. 2. The four components are at 1047.6, 1050.0, 1053.0 and 1065 cm^{-1} , and all are dominantly Lorentzian with the half-width increasing from 3.4 cm^{-1} for the lowest-energy band to 6.2 cm^{-1} for the highest-energy band. As for solutions of $NaNO_3$ these results are compatible with a three-stage concentration-dependent set of equilibria



The values for K_1 and K_2 are included in table 1. In dilute solution the obtained value of K_1 of $1.8\text{ dm}^3\text{ mol}^{-1}$ is smaller than for solutions of $NaNO_3$ and similarly the concentration-dependent values for K_2 are lower than corresponding values for $NaNO_3$ solutions. These comparisons will be discussed in more detail later in the paper.

The component-band characteristics illuminate the nature of the association process. The energy and band profile of the component assigned to the solvent-separated ion pair is the same as in solutions of $NaNO_3$ but the half-width for $LiNO_3$ solute is significantly greater ($\tau_v = 1.32\text{ ps}$). This means that the average coulombic field perturbing the NO_3^- and the nature of the relaxation process is the same for both solutes but the symmetry perturbation imposed on the nitrate ion is greater for the lithium cation. This is in accord with the observation that even at low concentrations the splitting of the ν_3 band is greater in solutions of $LiNO_3$ than in solutions of $NaNO_3$. The paradox of the nitrate ion in the solvent-separated ion pair having the same

coulombic perturbation but a greater symmetry perturbation can be resolved by considering the dynamic nature of the solution. Because of its small size the lithium ion is more strongly hydrated than the sodium ion. This means that the residence time for water in the hydration sheath is longer. This in turn means that when the anion

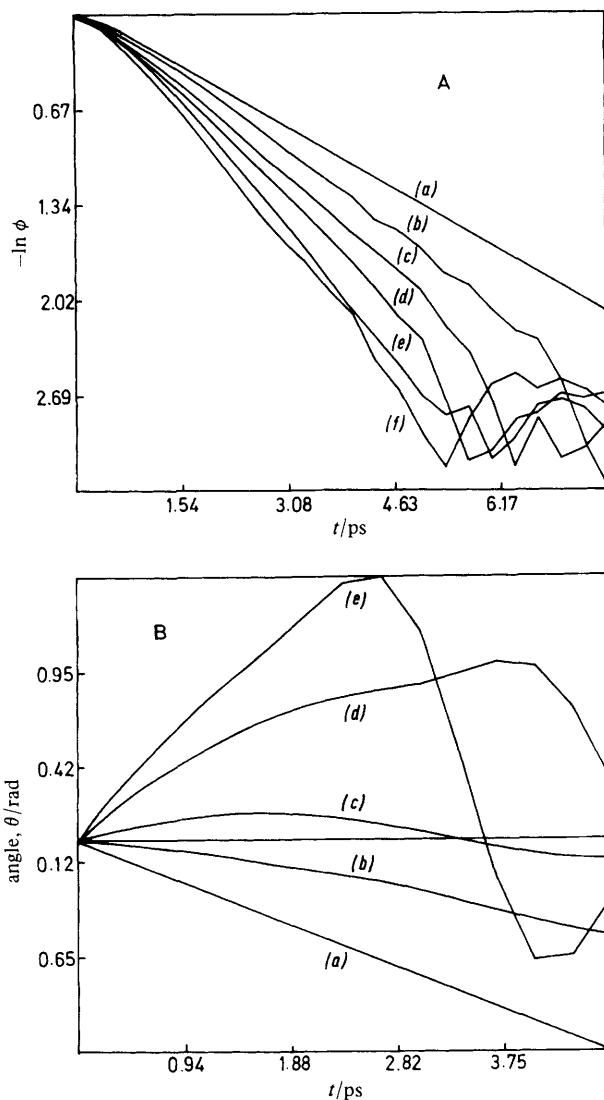


FIG. 1.—A, Time correlation functions [concentration/ mol dm^{-3} : (a) 0.05; (b) 0.5; (c) 4; (d) 6; (e) 8; (f) 10] and B, theta functions [concentration/ mol dm^{-3} : (a) 0.1; (b) 1; (c) 14; (d) 8; (e) 10] from A'_1 spectral bands of aqueous solutions of LiNO_3 .

and cation have a common hydration layer the cation exchanges more slowly and so has a stronger localised perturbation. However, because of the mediation of the water the cation does not have a preferred orientation with regard to the anion and so the coulombic perturbation is still averaged. The stronger aquation of the cation will also

TABLE 1.—SECOND MOMENT, MODULATION TIMES AND RELAXATION FOR AQUEOUS (GROUP I) NITRATE SOLUTIONS

electrolyte	concentration /mol dm ⁻³	ν_x/cm^{-1}	ν_y/cm^{-1}	$M_{2,x}/(\text{cm}^{-1})^2$	$(\Sigma b/a) \times 100$	τ_c/ps	$\tau_c M_2^2/2\pi c$	$\tau_v(\omega_2^2)/\text{ps}$	$\tau_v(\text{e}^{-1})/\text{ps}$
LiNO ₃	1.0	1048.3	1048.3	63.0	-0.84	0.76	0.80	1.38	1.19
	2.0	1048.7	1048.9	68.0	+1.70	0.69	0.75	1.29	1.21
	4.0	1049.0	1049.8	73.2	+3.9	0.64	0.73	1.14	1.06
	6.0	1050.1	1050.8	85.6	+4.4	0.62	0.77	1.07	0.95
	8.0	1050.8	1051.3	95.0	+8.4	0.77	0.99	0.92	0.77
KNO ₃	10.0	1051.9	1052.5	96.0	+11.9	0.78	1.00	0.81	0.76
	0.5	1048.2	1048.4	58.0	+0.91	0.87	0.88	1.36	1.12
	1.0	1048.7	1048.9	58.0	+0.63	0.88	0.90	1.36	1.10
	2.0	1048.9	1049.1	62.0	-4.02	0.84	0.88	1.31	1.08
	2.75	1049.1	1049.4	64.0	-2.50	0.83	0.89	1.30	1.08
RbNO ₃	1.0	1048.0	1047.0	56.2	-1.15	0.96	0.96	1.34	1.05
	2.0	1048.7	1049.1	66.0	-1.22	0.95	1.02	1.34	1.05
	3.0	1048.9	1049.0	56.2	-0.89	0.96	1.01	1.34	1.05
CsNO ₃	0.5	1048.3	1048.6	59.0	-0.80	0.93	0.95	1.36	1.06
	1.0	1048.7	1049.0	59.0	-0.44	0.93	0.95	1.30	1.06

favour the formation of isolated ions, a tendency which is evident from the relative concentrations of aquated nitrate ions in the two solutes. The band assigned to the contact ion pair species indicates that both the coulombic and symmetry perturbations are greater for the Li^+ counter-ion than for Na^+ . However, the band remains much more Lorentzian than for NaNO_3 solute indicating that crystal-type damping is less important for LiNO_3 solute. The strong aquation of the cation is again a possible cause of these differences. In the contact ion pair the relative orientation of the cation and anion is going to be influenced by the constraint of a common aquation shell. The strong aquation of the lithium ion may well constrain the cation to take up a position

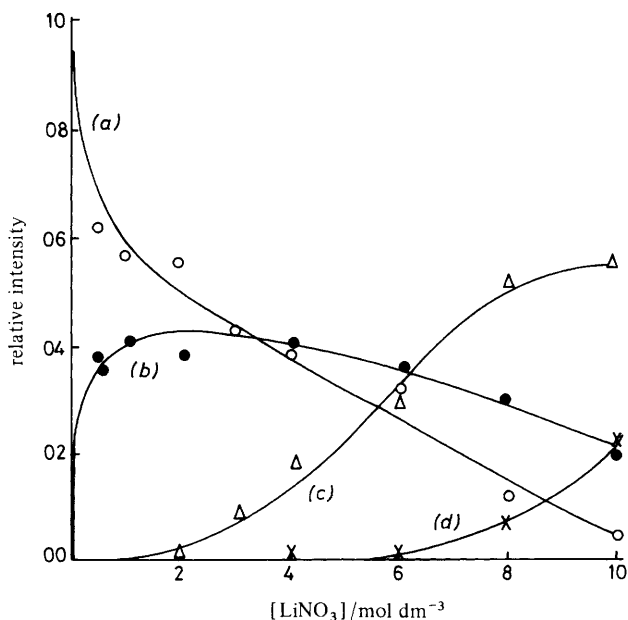


FIG. 2.—Variation of component-band intensities for the A_1' spectral bands from fig. 1: (a) aquated-nitrate band (1047.6 cm^{-1}), (b) solvent-separated-ion-pair band (1050 cm^{-1}), (c) contact-ion-pair band (1053 cm^{-1}), (d) ion-aggregate band (1065 cm^{-1}), \times = data from ref. (5).

which is incompatible with crystal packing. This in turn will make the contact ion pair less favourable than the ion aggregate at high concentrations, as is observed. In fig. 2 the previous estimates^{5, 6} of the concentration of 'ion pairs' in this system are included and they are seen to coincide with the intensity of the ion-aggregate band.

SOLUTIONS OF KNO_3 AND RbNO_3

The time correlation functions obtained on Fourier transformation of the isotropic profile are similar for these two solutes. The functions for potassium nitrate solutions are given in fig. 3A. There is little variation with concentration and no minima are obvious. This means that if there is more than one component the band half-widths are little different and the components will not be widely separated. The theta functions shown in fig. 3B show deviation from the dilute-solution band at all concentrations with a clearly developed inflection at *ca.* 6.5 ps which corresponds to a band separation of *ca.* 2.4 cm^{-1} .

Band component analysis yielded the results collected in table 1, from which the similarity between the two systems is obvious. For both systems there are two main

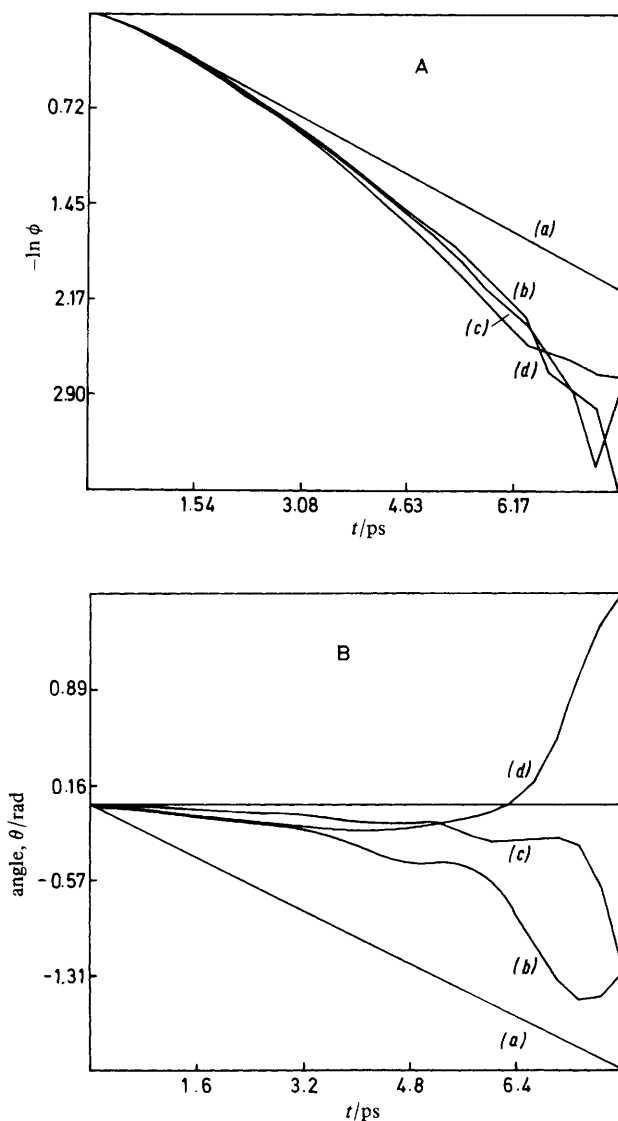


FIG. 3.—A, Time correlation functions [concentration/mol dm⁻³: (a) 0.01; (b) 0.05; (c) 1; (d) 2] and B, theta functions [concentration/mol dm⁻³: (a) 0.01; (b) 0.5; (c) 1; (d) 2] from A'_1 spectral bands of aqueous solutions of KNO₃.

components at 1047.6 and 1050.0 cm⁻¹ and a weak component at much higher energy. The variation of intensity of the three components with concentration for solutions of KNO₃ is shown in fig. 4. The presence of two rather than three major bands signals behaviour in these solutions which is distinctly different from that in solutions of LiNO₃ or NaNO₃. The two band components are similar in shape with the higher-energy band a little broader. As the size of the cation increases the position of the contact-ion-pair band decreases and so it would be expected that there would be little difference in position of the solvent-separated-ion-pair band and the contact-ion-pair band in solutions of KNO₃ and RbNO₃. Because the band at 1050.0 cm⁻¹ has a half-width

which is of the magnitude expected for a solvent-separated ion pair and because this half-width does not change with concentration, the associated species can be described with some confidence. The change in energy from 1047.6 cm^{-1} [$\text{NO}_3^-(\text{aq})$] to 1050.0 cm^{-1} [$\text{NO}_3^-(\text{assoc})$] can in the first instance be associated with the change in coulombic field with water in the second hydration shell is replaced by K^+ . The next stage would be the replacement of an H_2O molecule in the primary hydration shell with a K^+ ion. The coulombic perturbation for these two configurations is clearly similar. However, the symmetry perturbation imposed by a mixed primary shell would certainly cause an increased dephasing and a broadening of the 1050.0 cm^{-1} band as the concentration increases. That such an increase in half-width is not observed indicates that the relative exchange rates for water and K^+ ions with the nitrate ion

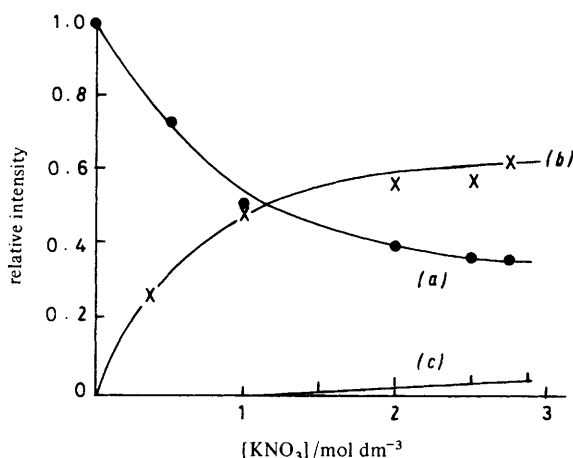
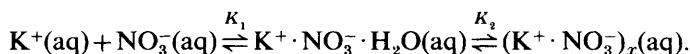


FIG. 4.—Variation of component-band intensities for the A'_1 spectral bands from fig. 3: (a) aquated-nitrate band (1057.6 cm^{-1}); (b) ion-pair band (1050 cm^{-1}), (c) ion-aggregate band (1067 cm^{-1}).

are similar and they are probably also similar to the exchange rates of water molecules in the hydration shell of the K^+ ion. This gives rise to a situation where the two species $\text{K}^+\cdot\text{H}_2\text{O}\cdot\text{NO}_3^-(\text{aq})$ and $\text{K}^+\cdot\text{NO}_3^-\cdot\text{H}_2\text{O}(\text{aq})$ are not distinguishable. Entropic considerations will then lead to the most random arrangement. At higher concentrations the weak driving force towards aquated ions leads to the formation of ion aggregates and low solubility.

The solution behaviour can be described in terms of a two-step equilibrium



The constant K_1 is not really comparable with K_1 or K_2 for solutions of NaNO_3 and LiNO_3 . The values for KNO_3 solutions are significantly greater than for RbNO_3 solutions, which indicates that association is weaker for the larger cation, as might be expected intuitively.

SOLUTIONS OF NH_4NO_3 AND $\text{Me}_4\text{N}\cdot\text{NO}_3$

These two solutes demonstrate distinctly different behaviour to any of the others so far examined. As shown in table 2 neither solute produces a concentration-dependent shift in the band maximum although the band position for $\text{Me}_4\text{N}\cdot\text{NO}_3$ is lower at 1046.6 cm^{-1} than that any of the other solutes. The time correlation functions and

TABLE 2.—COMPONENT-BAND ANALYSIS FOR THE ISOTROPIC BANDS OF GROUP I NITRATES

electrolyte	concentration /mol dm ⁻³	aquated-nitrate band			solvent-separated- ion-pair band				
		$\nu_M \pm 0.1$ /cm ⁻¹	$\omega_2 \pm 0.01$ /cm ⁻¹	shape ratio ± 0.001	area ± 0.01	ν_M /cm ⁻¹	ω_2^1 /cm ⁻¹	shape ratio	area
LiNO ₃	0.5	1047.6	3.397	0.852	0.621	1050.0	3.95	0.899	0.380
	1.0	1047.6	—	—	0.561	1050.0	3.96	0.844	0.421
	2.0	1047.6	—	—	0.575	1050.0	4.01	0.844	0.388
	4.0	1047.6	—	—	0.37	1050.0	4.03	0.844	0.38
	6.0	1047.6	—	—	0.327	1050.0	4.03	0.844	0.353
	8.0	1047.6	—	—	0.115	1050.0	4.03	0.844	0.297
	10.0	1047.6	—	—	0.042	1050.0	4.03	0.844	0.198
KNO ₃	0.5	1047.6	3.395	0.851	0.725	0.725	—	—	—
	1.0	1047.6	—	—	0.504	—	—	—	—
	2.0	1047.6	—	—	0.398	—	—	—	—
	2.75	1047.6	—	—	0.347	—	—	—	—
RbNO ₃	1.0	1047.6	3.395	0.852	0.602	—	—	—	—
	2.0	1047.6	—	—	0.504	—	—	—	—
	3.0	1047.6	—	—	0.465	—	—	—	—

TABLE 2. (cont.)

electrolyte	concentration /mol dm ⁻³	contact-ion-pair band				ion-aggregate band			
		ν_{M_1}/cm^{-1}	$\omega_2^1/\text{cm}^{-1}$	shape ratio	area	ν_{M_1}/cm^{-1}	$\omega_2^1/\text{cm}^{-1}$	shape ratio	area
LiNO ₃	0.5	1053.0	3.60	0.920	0.001	—	—	—	—
	1.0	1053.0	3.52	0.889	0.001	—	—	—	—
	2.0	1053.0	3.46	0.848	0.0385	—	—	—	—
	4.0	1053.0	4.90	0.850	0.24	1065.0	6.01	0.80	0.01
	6.0	1053.0	5.22	0.862	0.3046	1065.0	6.42	0.81	0.03
	8.0	1053.0	5.32	0.800	0.529	1065.0	6.41	0.83	0.057
KNO ₃	10.0	1053.0	5.16	0.863	0.5496	1065.0	6.12	0.763	0.207
	0.5	1050.0	3.7	0.852	0.275	—	—	—	—
	1.0	1050.0	3.7	0.852	0.496	1067.0	7.00	0.80	0.001
	2.0	1050.0	3.7	0.852	0.387	1067.0	7.05	0.81	0.015
	2.75	1050.0	3.7	0.852	0.623	1067.0	7.07	0.80	0.022
	1.0	1050.0	3.69	0.861	0.376	1057.5	6.56	0.76	0.01
RbNO ₃	2.0	1050.0	3.69	0.861	0.479	1057.5	6.60	0.76	0.013
	3.0	1050.0	3.69	0.861	0.531	1057.5	6.60	0.76	0.016
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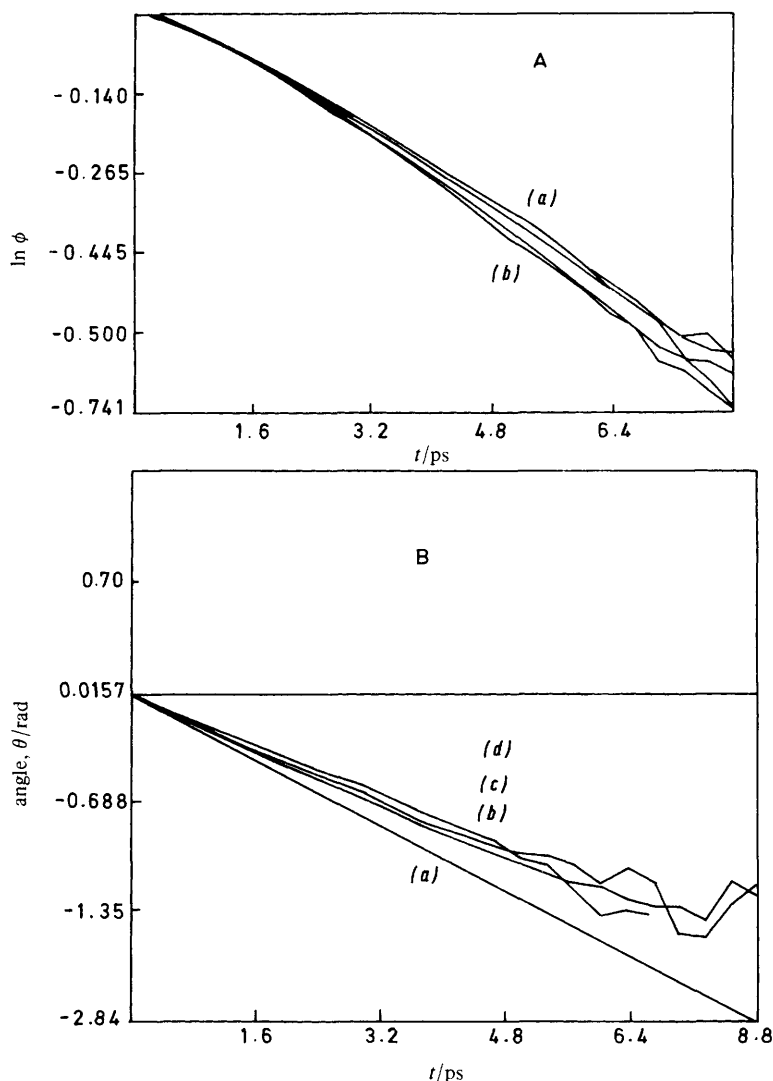


FIG. 5—A, Time correlation functions [concentration/mol dm^{-3} : (a) 2; (b) 10] and B, theta functions [concentration/mol dm^{-3} : (a) 0.01; (b) 1; (c) 2; (d) 4] from A'_1 spectral bands of aqueous solutions of NH_4NO_3 .

theta functions obtained on Fourier-transforming the isotropic band profile for solutions of NH_4NO_3 are shown in fig. 5. The time correlation functions show little change with concentration and the theta functions are essentially invariant for concentrations of 1–6 mol dm^{-3} while for 8 and 10 mol dm^{-3} the functions deviate and have an intersection at *ca.* 13 ps, which corresponds to a peak separation of *ca.* 1.2 cm^{-1} . Because the experimental isotropic spectra showed almost no concentration dependence and the time correlation functions and theta functions were simple, a band component analysis is not reported for these two solutes. For solutions of ammonium nitrate the band half-width of 3.95 cm^{-1} is greater than that for the dilute-solution band, 3.4 cm^{-1} , and this indicates that the ammonium ion enhances the dephasing

TABLE 3.—BAND PARAMETERS FOR THE A'_1 SYMMETRICAL STRETCHING VIBRATION FOR AQUEOUS SOLUTIONS OF AMMONIUM NITRATE AND
TETRA-ALKYLAMMONIUM NITRATE

electrolyte	concentration /mol dm ⁻³	ν_a /cm ⁻¹	ν_b /cm ⁻¹	$M_{2,a}/(\text{cm}^{-1})^2$	$(\Sigma b/a) \times 100$	τ_c /ps	$\tau_c M^{\frac{1}{2}}/2\pi c$	$\tau_v(\omega_2^2)/\text{ps}$	$\tau_v(\text{e}^{-1})/\text{ps}$
NH ₄ NO ₃	1.0	1047.6	1048.0	58.0	-0.47	0.85	0.86	1.34	1.14
	2.0	1047.7	1048.1	58.0	-0.48	0.86	0.88	1.36	1.12
	4.0	1047.7	1048.1	58.0	-0.40	0.87	0.88	1.36	1.12
	6.0	1047.7	1048.1	58.0	-0.48	0.89	0.90	1.36	1.09
	8.0	1047.8	1048.1	76.0	+0.82	0.68	0.78	1.34	1.07
	10.0	1047.8	1048.1	90.0	+0.90	0.57	0.72	1.34	1.09
N(CH ₃) ₄ NO ₃	1.0	1046.6	1046.8	50.0	+4.7	0.79	0.74	1.53	1.45
	2.0	1046.6	1046.8	52.0	+4.4	0.73	0.70	1.58	1.48
	3.0	1046.8	1046.9	56.0	+1.5	0.65	0.65	1.54	1.54
	4.0	1046.8	1046.9	56.0	+1.9	0.64	0.64	1.54	1.58

process, probably through an environment perturbation. For tetramethylammonium nitrate solute, on the other hand, the half-width corresponds closely to that of the dilute-solution band. The band position, however, is moved to lower energy by *ca.* 1 cm^{-1} . This movement of the band maximum may reflect the perturbation to the water structure by the large cation.

In the group of electrolytes studied three different patterns of interaction can be identified. For the two non-metallic cations the charge is diffused over the ion and the interactions are dominated by size and ability to form hydrogen bonds. The ammonium ion is characterised by a tetrahedral shape which permits its acceptance into the water structure with only a small symmetry disturbance to the nitrate ion, which appears as band broadening. Only at very high concentrations does the anion-cation interaction produce any change in the spectrum. The tetramethylammonium cation disturbs the water structure through its hydrophobic nature. It has been previously suggested that this allows preferential solvation of the anion.⁸ The shift of the nitrate band to lower energy may reflect this change in structure of the hydration shell which is unique to these large hydrophobic cations. The bandwidth in these solutions is the same as that we characterise for the aquated nitrate ion in the absence of cationic perturbation. Note that band component analysis was attempted for both of these solutes but no improvement in fit was obtained. The absence of additional components in these solutions supports the view that the changes we observe are not experimental artifacts but represent real trends.

The four remaining solutes give either two (KNO_3 and RbNO_3) or three (LiNO_3 and NaNO_3) main concentration-dependent band components. If the influence of change in water structure is ignored there will be three interactions of importance which are the aquation of the cation, the aquation of the anion and the anion-cation contact interaction. The water-lithium interaction will be the strongest and this is reflected in the dominance of the aquated nitrate ion (which implies a corresponding concentration of isolated aquated cation) at low concentrations. For the sodium cation aquation forces will be less strong and the nitrate takes a position in the second hydration sphere at low concentrations, becoming the dominant species at 1 mol dm^{-3} as against 4 mol dm^{-3} for lithium nitrate solute. The strong aquation of the lithium ion also retards the formation of contact ion pairs which dominate the spectrum of NaNO_3 solutions from 4 mol dm^{-3} while for LiNO_3 solute it does not dominate until 8 mol dm^{-3} .

For the cations potassium and rubidium the solvent molecules are more weakly held, which causes the exchange rate to be more rapid. The aquation of the nitrate ion, however, is not influenced by the change of cation. The energy of the second band for the potassium and rubidium cations indicates that the perturbation of the nitrate either by a water molecule shared with a cation or by a cation in contact are similar. In terms of exchange rates this is compatible with the water of solvation and the cation having similar exchange rates. This prevents the identification of the solvent-separated ion pair as a distinct species. In dilute solution the associated species is more likely to be a solvent-separated ion pair than a contact ion pair. The appearance of an ion-aggregate species in appreciable concentration, however, makes it likely that anion-cation contact is present in the associated species.

The value of the association quotient at 1 mol dm^{-3} concentration reflects the influence of aquation described above. The value for LiNO_3 solute of $1.35\text{ dm}^3\text{ mol}^{-1}$ is lower than for either NaNO_3 solute or KNO_3 solute. The strong aquation of Li^+ , the influence of which extends past the first hydration shell, is undoubtedly responsible for the preferred species not being closely associated with the anion. The remaining three cations show a regular decrease in the association quotient with increasing cation size, which follows the expected trend.

The measurement of association quotients for the association equilibria opens the way to study the energy changes in the association equilibria. Some preliminary studies will be examined in the following paper together with the influence of a variety of anions with a range of solution properties.

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