

SOLUTE-SOLUTE INTERACTIONS IN LIQUID AMMONIA SOLUTIONS :
A VIBRATIONAL SPECTROSCOPIC VIEW

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Abstract - Multicomponent bands are observed in the Raman spectra of solutions in liquid ammonia of salts of all multiatomic anions except ClO_4^- and BF_4^- . The positions and the variations of relative intensities of these component bands with changing cation, concentration, and temperature indicate that a range of discrete ion paired species coexist in equilibria.

Bands due to the "free" solvated anion have been unambiguously assigned in all vibrational regions for CN^- , NCS^- , NO_2^- , NO_3^- , NCO^- and N_3^- ; in a given region these are usually found at the lowest vibration frequency. The frequency dependence of its band on the counter cation identifies the presence of a discrete 1:1 contact ion pair in alkali metal, alkaline earth and Al^{3+} salt solutions. The intensity variation of bands associated with contact ion pairs with changing concentration and temperature indicates equilibria between linkage isomers of these "inner-sphere" associates found in CN^- and NO_2^- solutions. The extent of contact ion-pairing is greatest with the largest cations and decreases markedly with decreasing ionic radius: $\text{Cs}^+ > \text{Rb}^+ > \text{K}^+ > \text{Na}^+ > \text{Li}^+$, and $\text{Ba}^{2+} > \text{Sr}^{2+} > \text{Ca}^{2+} > \text{Mg}^{2+}$.

The intensities of bands due to inner-sphere association are very low for solutions of Li^+ salts, some alkaline earth metal salts, and $\text{Be}(\text{CN})_2$ and $\text{Al}(\text{CN})_3$. Their spectra indicate the formation of a stable solvation shell around these small highly polarising cations, almost to the exclusion of the ligand anion. Bands, close in frequency to that of the free solvated anion, are a manifestation of the solvent-shared (outer-sphere) ion pairs which can be seen to exist in these solutions.

Higher ion-aggregates, sometimes triplets $\text{M}^+\text{X}^-\text{M}^+$, sometimes dimers of ion pairs $(\text{M}^+\text{X}^-)_2$, or even larger species can be identified in the Raman spectra of some solutions (usually the Na^+ salts) by bands of higher frequency.

The methods used to investigate the nature of the species present, and their structures, in electrolyte solutions can be broadly categorised into three main areas; thermodynamic measurements on bulk solutions, various forms of spectroscopy of the solutions, and theoretical calculations based upon electrostatics and molecular dynamics.

Electrochemical methods such as ion conductance, ion activity determinations *etc.* have now been carried out for the greater part of a century. Although these methods give an excellent picture of the bulk behaviour of an electrolyte solution they usually fail completely with regard to the question of how the solute electrolyte is structured within the solution. To advance at all in this area using bulk thermodynamic methods it is necessary to fit the observed data to a specific model based on theoretical calculations on electrostatics and/or molecular dynamics. Up to date such advances have been somewhat limited.

Some of our previous studies concerning the measurement of bulk properties of solutions have been aimed at determining the degree of non-ideality of electrolyte solutions in liquid ammonia at varying concentrations. Naturally it is interesting to compare this with the degree of non-ideality found in aqueous

solutions (1). It is seen from Fig. 1 how similar conductance/concentration behaviour occurs for 1:1 salts in liquid ammonia and 2:2 salts in water. suggesting that the electrostatic situation in the two systems could be substantially identical.

When we consider the mean ion activity coefficients γ_{\pm} , for ions in liquid ammonia (Fig. 2) we see they are unexpectedly low, much lower than those obtained for 2:2 salts in water (2), and much lower than can be accounted for by any sensible extension of the Debye-Hückel approach. However, if it is assumed that the lowering of γ_{\pm} beyond that predicted by the extended Debye-Hückel law is due to the presence of ion-paired species an ion-pairing constant, $K_{ip} \sim 500 \text{ kg mol}^{-1}$, is obtained for ammonium nitrate and iodide solutions (3). An even better fit of the calculated data with the observed results is obtained if a small constant K_T is included to represent the formation of ion triplets. Some confidence in the result obtained by this procedure is provided from the fact that the values of K_{ip} obtained from conductance measurements on 1:1 salts in liquid ammonia (4,5) are of the same order of magnitude, as that for aqueous MgSO_4 solutions (6).

Two problems are paramount in the approach from bulk measurements. Firstly, no adequate theory is currently available by which these properties can be correlated with specific species existing in electrolyte solutions. This is particularly true of non-aqueous solutions not only in the moderately concentrated solutions ($> 10^{-2}$ molal) but also in the very dilute solutions which have been studied (10^{-5} - 10^{-4} molal). Secondly, established theory has, broadly speaking, been found to be grossly inadequate for most non-aqueous systems. All the so-called improvements and modifications to the Debye-Hückel and Bjerrum approaches throughout the past 50 years have done little to improve the real state of understanding with regard to the structure of these solutions. A new attack on the theoretical front on both the middle concentration range and those solvents with medium and low dielectric constants is therefore long awaited.

To consider the ionic species which may be present in a salt solution we believe that a good (but oversimplified) electrostatic picture can be obtained by consideration of the Bjerrum critical distances, $q = z_+z_-e^2/\epsilon kT$ for ions in different solvents. For 1:1 salts in water at 298 K and ammonia at 233 K we obtain values of 350pm and 1900pm respectively. It is thus easy to see that, using the Bjerrum approach, any pair of oppositely charged ions closer than 1900pm in ammonia must be considered as an ion-pair. On the other hand only those ions closer than 350pm are to be regarded as paired in water. This theory would lead us to the belief (perhaps somewhat erroneous!) that the only species to be regarded as pairs in aqueous solutions are those in actual physical contact. For liquid ammonia, however, the large critical distance forces us to accept that a much larger range of species must be regarded as ion pairs; contact ion pair (or inner-sphere complex), solvent-shared ion pair (or outer-sphere complex) and solvent-separated ion pair (in which two or more solvent molecules are interposed between cation and anion). Also, with such a large sphere of interaction, the presence of discrete species formed by the electrostatic interaction between 3, 4 or more ions (aggregates) must be considered.

The concept of ion triplets quadruplets and higher aggregates was introduced to account for the minima in the conductance/concentration curves of salts dissolved in solvents of low dielectric constant (7). Ammonia with its medium range dielectric constant (25 at 203 K to 15 at 298 K) is a likely solvent in which many or all of these species might be observed (8,9). Clearly spectroscopy might assist in the observation of these species. In his plenary lecture (10) at IV.ICNAS, and in many other papers, Popov (10) provided an insight into the use of *n.m.r.* and *i.r.* techniques as a tool in this area.

One of the problems which confronts the researcher in this field is that of selecting a *suitable* solute concentration. Solution concentrations suitable for *n.m.r.* and vibrational spectroscopic studies have always been too great to allow direct comparison of the results with those of electrochemistry. One valuable study relating both the conductances and the Raman spectra of AgNO_3 solutions was reported recently (11), and it is clear that major advances will be enhanced by the study, using different methods, of the same solutions under identical conditions.

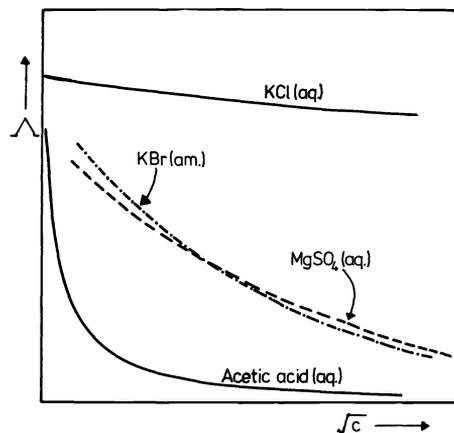


Fig. 1. Variation of conductance of electrolytes in liquid ammonia and in water.

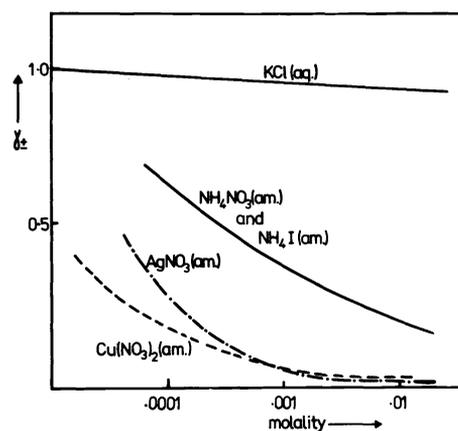


Fig. 2. Variation of mean ion activity coefficients for salts in liquid ammonia compared with those for KCl in water.

Vibrational spectroscopy, particularly in the form of Raman spectroscopy, is ideally suitable for the study of solutions in liquid ammonia. Like water the Raman spectrum of liquid NH_3 , shown in Fig. 3, contains wide "windows" between its bands. Unlike nearly all other non-aqueous solvents, with the exception of SO_2 , HCN and the hydrogen halides, the vibrations of simple multiatomic uncharged anions can be clearly viewed within these "windows" and usually can be conveniently analysed without serious interference from underlying solvent features.

Throughout the past decade or so Irish and his co-workers (12,13) have carried out extensive studies of the Raman spectra of aqueous electrolyte solutions. Their spectra have, in general, indicated ion pairing in these solutions to be relatively free from complications. Our Raman studies on liquid ammonia solutions commenced about 8 years ago with a general survey of the solvation of cations. In an initial study we followed the trends in the $\nu(\text{M-N})$ symmetric stretching frequencies in the $150\text{--}500\text{ cm}^{-1}$ region to establish the solvation numbers for solvent molecules in the inner coordination spheres of cations (14). From this work it became apparent that all the NO_3^- ion

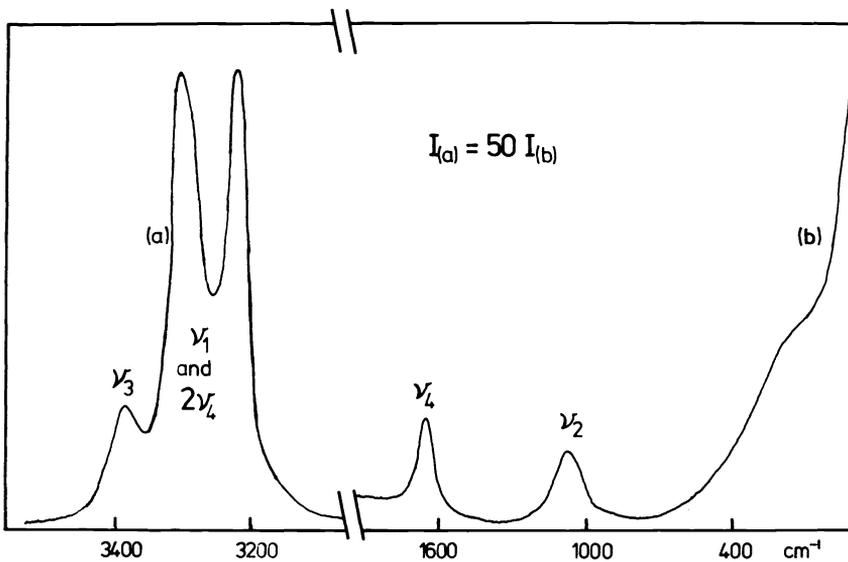


Fig. 3. Raman spectrum of liquid ammonia. (I = Intensity)

stretching and bonding regions exhibited complex multicomponent structures as illustrated for a LiNO_3 solution in Fig. 4. The striking feature of all the spectra was that the band profiles were exceedingly sensitive to the counter cation, the concentration and the temperature. Accordingly a programme was embarked upon which involved the analysis of the Raman spectra of a wide range of solutions at various concentrations and temperatures. Among the uncharged anions studied have been CN^- , NO_2^- , NO_3^- , NCS^- , NCO^- , N_3^- , ClO_4^- and BF_4^- in solutions with the alkali and alkaline earth metal cations. Other

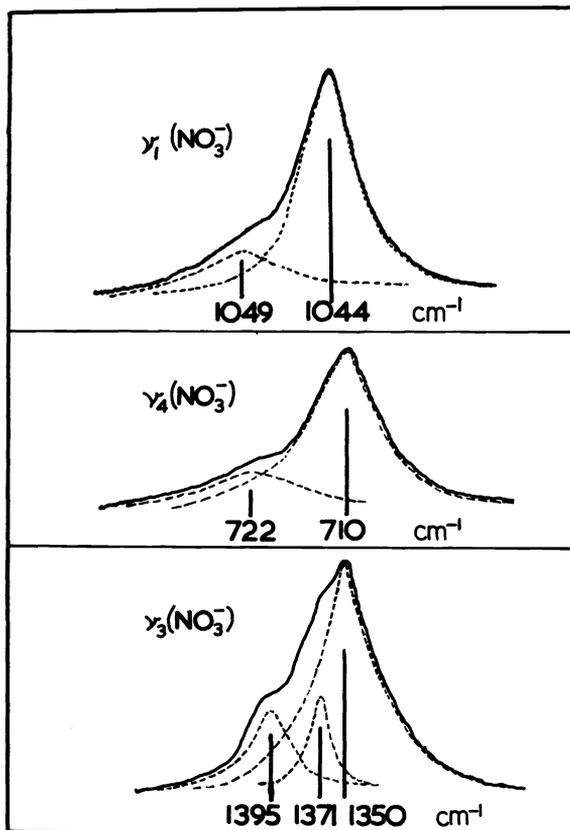


Fig. 4. The ν_1 , ν_3 and ν_4 vibration regions of the Raman spectra of LiNO_3 solutions in liquid NH_3 . $R = 50$.

cations used were: Al^{3+} , Zn^{2+} , Cd^{2+} , Hg^{2+} , Pb^{2+} , Tl^+ , Ag^+ , NH_4^+ and methyl-substituted ammonium. Ion pairing phenomena have been observed for all the anions studied except the tetrahedral ones, ClO_4^- , and BF_4^- .

Concurrently with our work two groups in France, under the separate leadership of Chabanel and Corset, have been investigating the vibrational spectra and the ion pairing behaviour of alkali cyanides, cyanates and thiocyanates in solvents such as DMF and DMSO. Solutions in liquid ammonia have already received some attention by the Raman spectroscopic method. Lagowski *et al.* have reported on the spectra of alkali metal and ammonium nitrates and thiocyanates from two points of view; one with regard to the effect of the solute on the nature of the solvent spectrum (15,16), and the other an investigation of interionic (17) and cation-solvent interactions (17,18). Similarly Lundeen and Tobias (19) studied the multicomponent spectra of alkali metal and silver nitrate solutions, following an earlier study by Hester *et al.* (20) on the Raman spectra of solutions of LiNO_3 and NH_4NO_3 in ammonia. More recently Straughan and his colleagues have reported an interesting Raman spectroscopic study of TlNO_3 solutions in ammonia (21). In these solutions the Raman-forbidden $\nu_2(\text{NO}_3^-)$ vibration at 830 cm^{-1} can be observed in solutions at $R < 30$ (Note a). Their proposal that this band results from a "sideways-on" interaction between the Tl^+ cation and the π -system of the NO_3^- anion might be consistent with the results of the ^{205}Tl *n.m.r.* work on the $\text{Tl}^+ \dots \text{NO}_3^-$ pairing in liquid ammonia (22); it is possible that the Tl^+ ion is coordinated by 3 solvent molecules in this ion paired species.

Whilst we are generally in agreement with the spectroscopic results of most of the ion pairing work for liquid ammonia solutions mentioned above we have had the distinct advantages of both better spectroscopic resolution and improved procedures for computer-aided curve analysis. There is no doubt, however, that the advances made in our general understanding of ion pairing in liquid ammonia have chiefly emerged by virtue of the study of a very large number of salt solutions over wide concentration ranges (from $R = 1.5$, when possible, to $R = 4000$) and over a wide temperature range (203 K to 355 K).

COMPUTER RESOLUTION

Throughout the spectra have mainly been analysed into component bands by computer-aided resolution. The best fit is obtained of the band profile using underlying component bands with a Lorentz-Gauss sum function shape, $I_\nu = h\{(1-f)/[1 + (2(\nu - \nu_0)/w)^2] + f \exp[-\ln 2 + (2(\nu - \nu_0)/w)^2]\}$, where f = fraction of Gaussian contribution, h = height, w = width at half-height, and ν_0 = position of a component (23,24).

To avoid the unacceptable inclusion of "computer bands" in the analyses we have always adopted the following criteria. A component band must either (a) be evident as an inflection or asymmetry on the spectral profile, or, if not, (b) its position and intensity must vary in a consistent manner as the temperature and/or the solute concentration are/is changed.

We have been aided considerably by the recent development (25,26) of a curve-smoothing and differentiation technique based on the use of B-splines of degree from 3 to 7. The signal/noise deterioration obtained on differentiation of the experimental data is normally significantly less than that normally obtained by the widely-used Savitzky-Golay method (27). Resolution enhancement by the 2nd derivative technique has enabled the identification (together with the positions) of a number of the more elusive component bands in some of our spectra. It has been used almost exclusively to establish the species present in the complicated equilibrium system obtained by the complexation of Ag^+ with CN^- ions in liquid ammonia which will be reported in the near future.

DISCUSSION

In the space of a short lecture it is clearly impossible to give an account of the details of all the examples we have studied. When the spectra of (a) different anions, and (b) different cations with the same anion, are surveyed

Note a: Solution concentrations are normally expressed as mole ratios, i.e. $R = \text{no. of moles of solvent}/\text{no. of moles of solute}$.

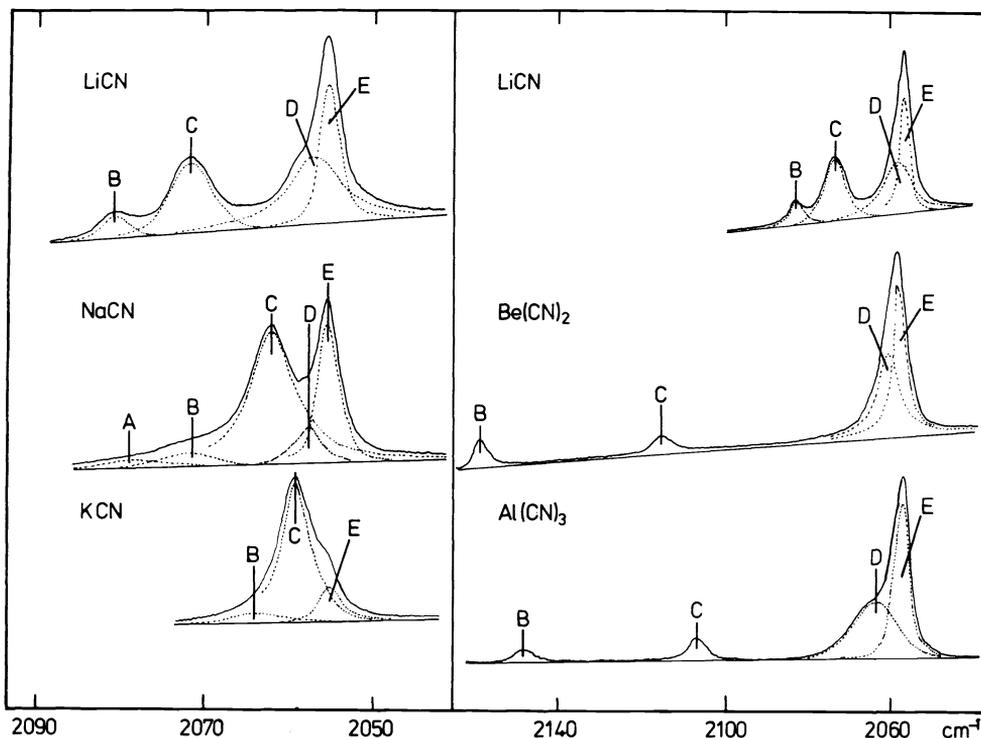


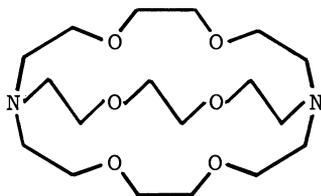
Fig. 5. The $\nu(\text{CN})$ region of the Raman spectra of cyanide solutions in liquid ammonia at 298 K. LiCN ($R = 20$), NaCN ($R = 46$), KCN ($R = 175$), $\text{Be}(\text{CN})_2$ ($R = 65$), $\text{Al}(\text{CN})_3$ ($R = 50$).

specific trends can be observed. These trends in the relative intensities of underlying components and their positions appear to follow common patterns across the range of anions. Also some common trends are observed for sets of cations associated with a given anion. These allow us to assess the relative extent of different forms of ion pairing from one cation to another (28). The study of a vast number of systems and their spectra has provided a large amount of circumstantial evidence which collectively allows our conclusions to be presented with a high degree of confidence. Of course, there are also some features in the spectra which can only be regarded as dependent upon the specific behaviour of an individual ion or pair of ions. For simplicity, a few examples have been chosen from which some of the salient features which emerge from our work can be illustrated.

The complexity observed in any series of Raman spectra of solutions which exhibit ion pairing is well illustrated in Fig. 5 which shows the $\nu(\text{CN})$ stretching frequency region for five different cyanide solutions. In cyanide solutions the solubility restricts the study of KCN to $R > 100$ and prevents a serious concentration variation study of RbCN and CsCN. However, most of the general trends in the component band patterns can be seen in the group of spectra of the *simple* cyanide ion in solution which, if isolated, can only consist of a single band at $\sim 2050 \text{ cm}^{-1}$. Some time ago we made a claim (29) that the multicomponent spectra observed in NaCN and KCN solutions were due to the presence of a number of *discrete* ion paired species which coexist in equilibrium. Whilst we now accept that there were some errors in our initial assignments of the bands to individual species types we still hold firmly to our main thesis that individual bands can be identified with "free" solvated anions, 1:1 contact ion pairs (or inner-sphere complexes), solvent-shared ion pairs (or outer-sphere complexes) and higher ion aggregates (which may be composed of triplets, quadruplets or even higher species).

With the exception of a limited number, including all Li^+ salt solutions, the relative intensities of the component bands in a region vary markedly with changes in both solute concentration and temperature. This is evidenced in the spectra of NaCN and KCN solutions by the increase in relative intensity of band E (and the decrease in all others) when the salt concentration is decreased or the temperature is raised. Thus it is immediately attractive to

identify band E with the "free" (unpaired) solvated anion and the bands A, B, C and D with various forms of ion paired species. Additional support comes from the invariance in the position of band E irrespective of cation, concentration or temperature. Unambiguous confirmation of this assignment has been made (30) by sequestering the cation into an inclusion complex within the framework of a cryptand, C222,



Solutions of $[\text{Na}(\text{C222})]^+[\text{CN}]^-$ give spectra with a single sharp band E at 2056 cm^{-1} .

The free solvated anion bands for all the other anions have been similarly identified. It is apparent that when a cation is encapsulated within the cryptand its effective perturbing field upon the counter anion is enormously reduced, because of both the increase in overall cation size and also the increased cation-anion distance, to a level at which no ion-pairing is observable in the spectra. When fully (but not partially) alkyl-substituted ammonium ions are used as the counter cations similar single band anionic spectra indicate the absence, or a low degree of ion pairing. Complexation of the cation by crown ethers does not prevent ion pairing, it merely reduces it slightly because coordination sites perpendicular to the crown ring remain open for occupation by the ligand anion. In nearly all spectra the band at the lowest frequency is associated with the free solvated anion. However, changes in the band width with changing concentration and temperature suggest that this "free" anion band is best regarded as a composite band deriving from species in which the interaction energies between anion and cation are very low and consequently whose frequencies differ only marginally from those of the truly "free" solvated anions. Such species must include the solvent-separated ion pairs in which anion and cation, although to a small extent are under the influence of each other's fields, are separated by several solvent molecules. Evidence of this comes from the observed variations in band widths of these free anion bands as the solute concentrations and solution temperatures are varied.

Contact ion pairs. At higher frequencies a series of bands is observed, all of which increase in relative intensity with increasing concentration and temperature, and whose positions are extremely cation sensitive. These must all be attributed to ion paired species. The extent of ion pairing must increase with both increasing concentration, and also as a result of the substantial decrease in solvent dielectric constant which occurs with increasing temperature. For a given counter cation these bands remain at invariant positions regardless of the concentration and temperature.

We believe that the bands B and C (Fig. 5) can be identified with 1:1 contact ion pairs. It is only to be expected that the frequency shift, $\Delta\nu$, from the invariant position of the free anion band will be dependent upon both the size and the charge of the cation with which the anion is in contact. In all the systems studied the shift $\Delta\nu$ is seen to decrease in the expected order, $\text{Li}^+ > \text{Na}^+ > \text{K}^+ > \text{Rb}^+ > \text{Cs}^+$. We have also found that within a group of similarly charged cations a linear empirical relationship exists between $\Delta\nu$ and z_+/r_+^2 , where r_+ is the crystallographic radius of the cation. Fig. 6 illustrates the plot for the frequency shift, $\Delta\nu_{A-B}$, between bands A and B in the $\nu(\text{CS})$ stretching region of the spectra of the alkali metal thiocyanates in ammonia solutions (shown in Fig. 7). We take the compliance of the frequency shift to this simple empirical rule, held throughout all our anionic spectra, to be an indicator of the bands which can be assigned to 1:1 contact ion pairs.

Both the bands marked B and C in Fig. 5 are attributable to species of the same stoichiometry and both can therefore be assigned to 1:1 contact ion pairs. Addition of a common cation, e.g. LiClO_4 to LiCN solution, causes an equivalent increase in the relative intensities of both B and C. Similar but smaller effects are observed in the case of the NaCN system when NaClO_4 is

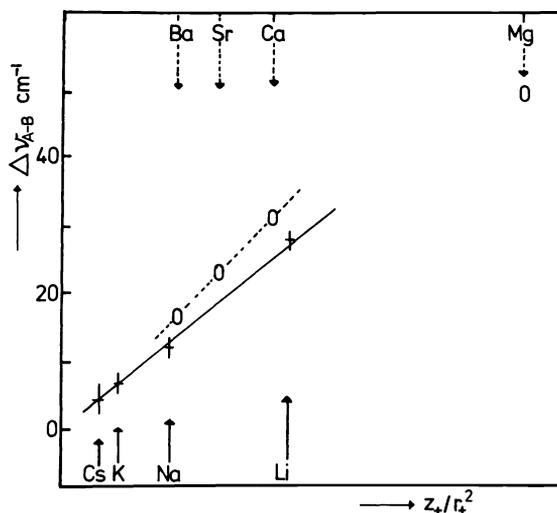


Fig. 6. Frequency shift, $\Delta\nu_{A-B}$, of the ion pair band A from the free anion band B for thiocyanate solutions in liquid ammonia.

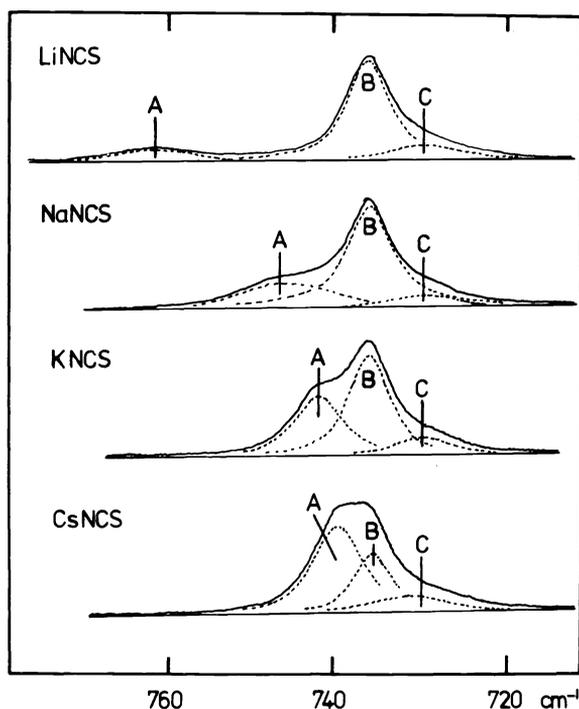


Fig. 7. The $\nu(\text{CS})$ region of the Raman spectra of alkali metal thiocyanate solutions in liquid ammonia at 298 K. $R \sim 50$.

added. The only feasible explanation of two bands, both attributable to a 1:1 species, is the existence of an equilibrium between the two linkage isomers $\text{Li}^+ \dots \text{CN}^-$ and $\text{Li}^+ \dots \text{NC}^-$. Hitherto linkage isomerism in solutions of simple ionic cyanides seems to have been virtually undiscovered but the intensity variation between bands B and C with concentration, and particularly with temperature provides excellent evidence of their equilibrium existence.

The specific assignments of the bands due to these isomers poses a problem and is still not much more than an intuitive guess. It is not unreasonable, following the *hard-soft* concept, to decide that the more intense band C should be associated with the $\text{M}^+ \dots \text{NC}^-$ form. Other evidence might be used in support

of this assignment. When bonded at its N-end to Si (31), and to B (32,33) the C-N group has a lower frequency than when bonded at its C-end. Further work subsequent to our preliminary report on the cyanide complexes of Ag(I) in liquid ammonia (34) is also consistent with this assignment.

Isomerism between 1:1 contact ion pairs is not unique to cyanides. The ν_2 bending region of the Raman spectra of the alkali nitrates all have a free anion band at 796 cm^{-1} . Bands C, due to a contact ion pair, probably the $M^+ \dots NO_2^-$ isomer, appear at 810 cm^{-1} (Li^+), 801 cm^{-1} (Na^+), 800 cm^{-1} (K^+), 799 cm^{-1} (Rb^+) and 798 cm^{-1} (Cs^+). A third band B, seen in the $NaNO_2$ solution spectrum at 807 cm^{-1} in Fig. 8, must also be assigned to a contact ion pair; probably the $M^+ \dots ONO^-$ isomer. The fourth band A at 814 cm^{-1} which becomes an important feature of the spectrum at very high concentrations ($R \sim 4-5$), could be due to the third possible isomer with the NO_2^- entering the cation's inner-sphere as a bidentate ligand. The appearance of a band of high relative intensity at this frequency on addition of $NaClO_4$ raises the question, however, as to whether this band indicates the presence of a higher aggregated species. It is an interesting point to note that the Raman spectra of aqueous alkali metal nitrites have failed to provide evidence for ion-pairing in water (35). Not unexpectedly spectroscopic evidence has indicated the equilibrium existence in aqueous solutions of both bound and free forms of nitrite ion with the doubly charged cations (36,37).

In the alkali azide series the ν_1 symmetric stretching region exhibits three bands; for NaN_3 solutions, 1321 , 1327 and 1338 cm^{-1} . The attribution of the middle of these to a contact ion pair is in accord with the analysis of the Raman spectra of NaN_3 solutions in DMSO carried out by Chabanel *et al.* (38). The high frequency band must be assigned to a triplet or higher aggregate.

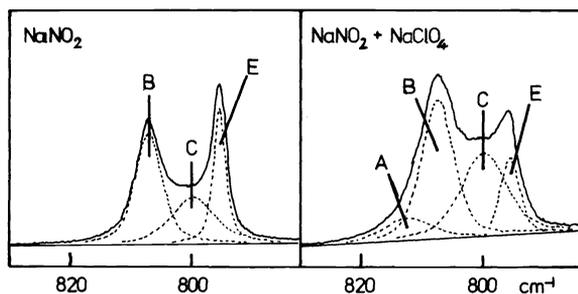


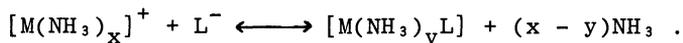
Fig. 8. The ν_2 region of the Raman spectrum of $NaNO_2$ solution in liquid ammonia at 298 K. $R \sim 40$. $[ClO_4^-]/[NO_2^-] \sim 5$.

Alkali thiocyanate solutions are worthy of some discussion. Unfortunately the $\nu(CN)$ region yields little information because the bands are too closely spaced for analysis, though the addition of C222 results in the isolation of a very sharp free anion band at 2060 cm^{-1} . The $\nu(CS)$ region is much more informative because all the spectra (Fig. 7) contain three resolvable bands. Because band B can be unambiguously assigned to the free anion we initially thought that bands A and C should be assigned to the isomeric 1:1 contact ion pairs. The assignment of band A to a 1:1 contact ion pair is beyond question (Fig. 6) and because its frequency is higher than that of the free SCN^- ion frequency (28,39) we have assigned it to the $M^+ \dots NCS^-$ species. A lowering of the $\nu(CS)$ frequency is associated with S-bonding to the metal in thiocyanate complexes and, at first, attribution of band C to the $M^+ \dots SCN^-$ species seemed appropriate. Closer investigation of the spectra with added C222 revealed that band C is associated with the free NCS^- anion; its position is invariant and we must now refute our original suggestion made at VI. ICNAS (40) that bands B and C derive from differently solvated forms of the anion in equilibrium. The most acceptable explanation of the spectra is for band C to be attributed to a "hot" or upper stage band of the free anion. This is consistent with the interpretation presented by Chabanel and Rannou (41) to account for a similar low intensity feature on the low frequency side of the free anion band in the $\nu(CN)$ region of the spectrum of the NCO^- ion in alkali cyanates in DMSO. That the observed intensity ratio I_B/I_C follows the theoretically predicted values for a set of temperatures provides convincing support for this interpretation.

The degree of formation of contact ion pairs always increases in the perhaps unexpected order $\text{Li}^+ < \text{Na}^+ < \text{K}^+ < \text{Rb}^+ < \text{Cs}^+$. This is clearly seen in both the cyanide (Fig. 5) and the thiocyanate (Fig. 7) series by following the intensity ratio trends between the free ion and the contact ion pair bands. Stoichiometric contact ion pairing constants have been obtained (assuming similar band intensity coefficients and neglecting ion activity coefficients) for the thiocyanate series (40): CsNCS , 4.3, KNCS , 1.2; NaNCS , 0.4; and LiNCS , 0.1 kg mol^{-1} . It should be noted that these constants, K_{ip} 's for contact ion pairs, are more than two orders of magnitude lower than those obtained for overall ion pairing in uni-unicharged salts in ammonia from conductance and activity data.

Lithium salts appear to behave somewhat differently from the others. Their ion-pairing ability is not only relatively low but, as illustrated by the cyanide, azide and nitrite ions, the bands associated with ion associates show little tendency to change their relative intensities with changes in either concentration or temperature. Also for LiNO_3 and LiNCS , as seen in the $\nu_4(\text{NO}_3^-)$ bending and in the $\nu(\text{CS})$ stretching regions respectively, the degree of ion pairing is very low except at very high concentrations *i.e.* when $R < 8$.

The spectra clearly exhibit a competition between the solvent molecules and the anions for a site in the inner coordination sphere of the cation. Thus an equilibrium of the following form must apply:



The high solvation energy of Li^+ in ammonia is clear from its ability to form the extremely concentrated Divers' solutions which are normally associated with NH_4 salts but also occur with some Na^+ salts. The low ion-pairing ability of lithium salt solutions and the low sensitivity of their spectra to concentration and temperature finds its explanation in the ability of the small Li^+ cation to form a highly energetically favourable $\text{Li}(\text{NH}_3)_4^+$ solvated cation, almost to the exclusion of the ligand anion. The solvation enthalpies of the alkali metals in ammonia decrease in the order $\text{Li}^+ > \text{Na}^+ > \text{K}^+ > \text{Rb}^+ > \text{Cs}^+$ (42), and on electrostatic reasoning, the ligation enthalpies are expected to follow the same order. On descent of the group the ability of the cations of increasing radius to form strongly covalent solvates must decrease at a greater rate than the ability of those same cations to form the more electrostatic ligation interactions.

Solvent-shared ion pairs. The spectra illustrated in Fig. 5 for LiCN , $\text{Be}(\text{CN})_2$ and $\text{Al}(\text{CN})_3$ solutions contain a component band D very close to that of the free solvated anion band E. A band D in a similar position is also found in the spectra of NaCN solutions in the low to middle concentration range ($R = 100-1000$). There are two possible explanations. That of its assignment to an ion triplet of the form $\text{X}^-\dots\text{M}^+\dots\text{X}^-$ is discounted on the grounds of the small frequency shift and also the band intensity/solution concentration relationship. The band comes up to maximum intensity in those solutions in which the metal cations (those cations which form the most thermodynamically stable primary solvation sheaths) are expected to be completely enclosed inside a layer, one molecule thick, of solvating ammonias. Accordingly we can identify this band with a solvent-shared ion-paired species. The spectra of LiNO_2 and LiN_3 support this assignment because a band situated close to the free anion band, and on its high frequency side exhibits a very similar behaviour pattern to band D in the LiCN spectra.

Perhaps the existence of solvent-shared species is best illustrated by the spectra of the Group II metal thiocyanate solutions (Fig. 9) where it appears as band B. In these spectra bands A, C and D can be interpreted, as in the alkali thiocyanate solutions, as deriving from a 1:1 contact ion pair (A) and a free SCN^- anion (C and D). Descending the group band B demonstrates a small frequency shift ($\sim 3 \text{ cm}^{-1}$) from being easily resolved for the small Mg^{2+} ion to being virtually irresolvable for the large Ba^{2+} ion (when B has merged with C). A smaller frequency shift would be expected for the 1:1 solvent-shared ion pair than for the 1:1 contact ion pair because the alteration of the cation's perturbing field must reduce the $\nu(\text{CS})$ frequency shift considerably.

There is a feasible but less attractive assignment for band B - to a 2:1 species, $\text{SCN}^-\dots\text{M}^{2+}\dots\text{NCS}$ because here the perturbation of the $\nu(\text{CS})$ frequency would not be as great as for the 1:1 contact ion pair. It is the band intensity trends, in particular I_A/I_B , which force us to conclude that band B corresponds to a solvent-shared species. In both the Mg and the Ca

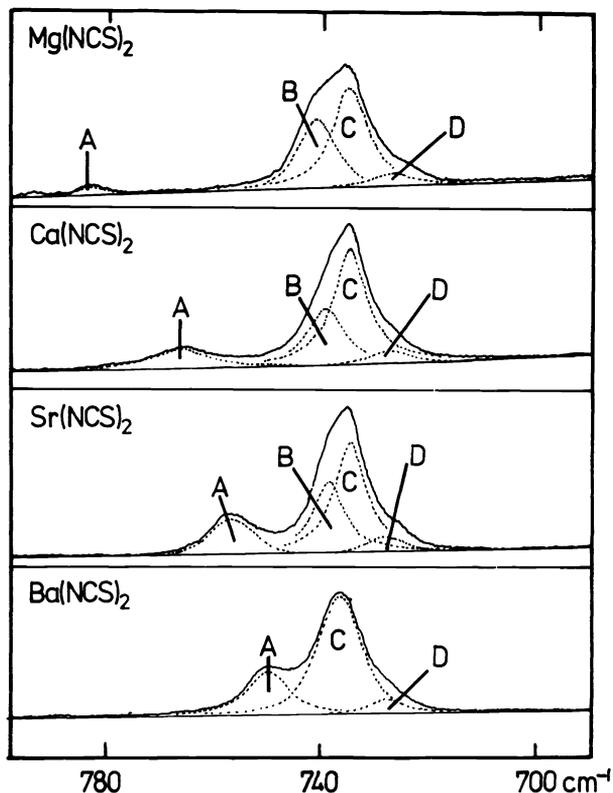


Fig. 9. The $\nu(\text{CS})$ region of the Raman spectra of alkaline earth metal thiocyanate solutions in liquid ammonia at 298 K. $\text{Mg}(\text{NCS})_2$, $R = 180$. $\text{Ca}(\text{NCS})_2$, $R = 360$. $\text{Sr}(\text{NCS})_2$, $R = 360$. $\text{Ba}(\text{NCS})_2$, $R = 30$.

cases the relative intensities of band A are low and invariant with concentration (4% and 10% respectively). $\text{Mg}(\text{NCS})_2$ solutions cannot be studied at $R < 40$ for solubility reasons but on dilution up to $R \sim 1000$ the ratio $I_B/I_A \sim 10$. More concentrated solutions of $\text{Ca}(\text{NCS})_2$ can be studied. In the range $R = 15$ to 700 it is invariant at about 10%. Band B does not appear until $R \sim 50$, but has a maximum relative intensity ($\sim 40\%$) between $R = 100$ to 250 which falls to about 25% at $R = 700$. This behaviour is far more consistent with the assignment to a solvent-separated ion pair than to a 2:1 triplet.

In the early years of our work we were greatly puzzled by the failure of some nitrate solutions to exhibit ion-pairing phenomena in their vibrational spectra. The Raman spectra of AgNO_3 , $\text{Pb}(\text{NO}_3)_2$, $\text{Zn}(\text{NO}_3)_2$, $\text{Cd}(\text{NO}_3)_2$ and $\text{Hg}(\text{NO}_3)_2$ solutions are all substantially symmetrical in their ν_1 and ν_4 regions. This can now be best explained in terms of the thermodynamically very stable solvation shells formed by these cations in liquid ammonia. In all these cases the solvent molecule is a better competitor for a place in the inner coordination sphere than the rival ligand anion. Thus if ion pairing is to occur at all it will be, at best, in the form of the solvent-shared species. In the cases of $\text{Pb}(\text{NO}_3)_2$ and AgNO_3 this proposal can be supported by ion mobility studies (2,43).

Ion aggregation. The spectra we have observed provide good evidence for the existence of discrete ion aggregates in liquid ammonia solutions. Usually the spectra of Na^+ salt solutions are found to be the most complex. Perhaps this is because the Na^+ cation occupies an intermediate position between the high charge density Li^+ ion which readily forms solvent-shared ion pairs and the larger and lower charge density cations which favour the formation of contact ion pairs. The spectra of $\text{NaN}_3(\nu_1)$, NaCN and $\text{NaNO}_2(\nu_1 \text{ and } \nu_2)$ solutions all show high frequency bands which must be assigned to ion aggregates.

Ion aggregation has been much discussed by Chabanel (38,41,44,45,46) and Corset (47,48,49,50). Both these groups have separately worked on the problem through both *i.r.* and Raman studies on a number of salts of NCO^- ,

NCS^- , Br^- , ClO_4^- , CF_3COO^- and CN^- in DMF and dimethylthioformamide, DMSO, acetonitrile and a number of organic solvents. Both groups tend towards the formation of ion triplets in the systems they have studied.

In the spectra of liquid ammonia solutions of NaCN (Fig. 5) band A must be attributed to an aggregated species. The band increases in relative intensity on increase of temperature, concentration and on addition of common cation as NaClO_4 , but is absent from the spectra at 293 K at $R > 100$. Although attractive we believe the assignment of this band to the $\text{Na}^+\dots\text{CN}^-\dots\text{Na}^+$ triplet would be erroneous. Mass balances in the respective equilibrium steps demand that the addition of excess Na^+ ion would cause a concentration increase in the species defined as either $\text{Na}^+\dots\text{CN}^-\dots\text{Na}^+$ or $(\text{Na}^+\text{CN}^-)_2$. The equilibrium positions change markedly with temperature. (Fig. 10). Band A is a main feature of the spectrum at 363 K and the free cyanide band E disappears completely. If mass and electrical balances are to be maintained a feature due to either free CN^- , or the triplet $\text{CN}^-\dots\text{Na}^+\dots\text{CN}^-$, must appear in the spectrum if band A is due to the triplet $\text{Na}^+\dots\text{CN}^-\dots\text{Na}^+$. The evidence is thus in favour of the aggregate being overall uncharged, probably the dimer of the 1:1 contact ion pair, $\text{Na}^+\dots\text{CN}^-\dots\text{Na}^+\dots\text{CN}^-$. This proposal is consistent with the presence of an $(\text{AgCN})_2$ species found in equilibrium with other cyanoargentates in solutions of silver(I) cyanide in ammonia (51).

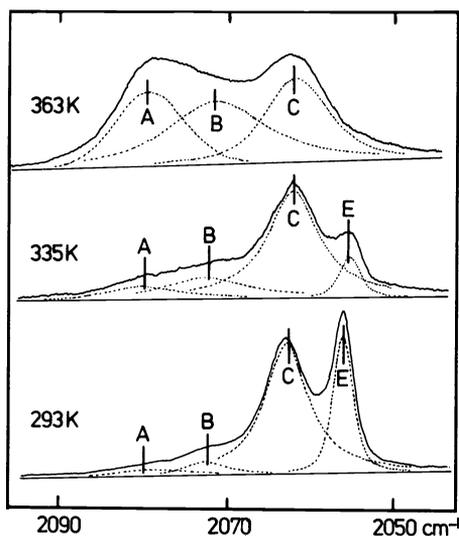
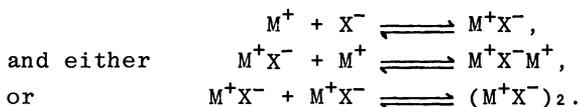


Fig. 10. Temperature variation of the $\nu(\text{CN})$ region of the Raman spectrum of a liquid ammonia solution of NaCN. $R = 45$.

In the spectra of NaNO_2 solutions (Fig. 8) bands at 808(B), 800(C) and 795(D) cm^{-1} in the ν_2 region are assigned to isomeric contact ion pairs (B and C) and the free NO_2^- ion (D). Band A can be extracted from the profile only as an extremely weak feature but it appears at substantial intensity on addition of NaClO_4 and also at very high concentration (30% relative intensity at $R < 10$). The presence of free NO_2^- in the solution is indicative of the formation of the ion triplets, $\text{Na}^+\dots\text{ONO}^-\dots\text{Na}^+$, though on the evidence as it exists, the attribution of band A to a third contact ion pair isomer involving bidentate complexation through the O's of NO_2^- to the Na^+ cation cannot be ruled out.

The ν_1 symmetric stretching vibration of NaN_3 solutions contains 3 bands; 1339(A), 1327(B) and 1320(D) cm^{-1} . Bands B and D are due to the $\text{Na}^+\dots\text{N}_3^-$ contact ion pair and the free N_3^- anion respectively. Addition of NaClO_4 causes the relative intensity of band A to increase to a greater extent than that of band B. At elevated temperatures band A increases in intensity but D always remains in the spectrum. Like the assignment made by Chabanel *et al.* (38) for the N_3^- bands in DMSO solutions we are inclined to ascribe band A to the ion triplet, $\text{Na}^+\dots\text{N}_3^-\dots\text{Na}^+$.

Some attempts have been made - unfortunately with little success - to determine the stoichiometry of the aggregated species by the calculation of the equilibrium constants for the steps,



Several factors contribute to the failure of this approach: the extremely non-ideal behaviour of the solutions at high and medium concentrations and a lack of the data which relates this non-ideality to solution concentration; the degree of accuracy obtainable in computer-assisted curve resolution; and assumptions concerning the relationships between the species present and their band intensity coefficients.

Nitrate solutions

At first sight the spectra of nitrate solutions would be expected to provide an excellent source of data for the study of the ion pairing phenomenon. Three vibrations ν_1 , ν_3 and ν_4 are all observed in the Raman spectra of the solutions. The ν_1 symmetric stretching region is extremely intense and sharp, $\omega_1 \sim 2 \text{ cm}^{-1}$, so sharp that the slight asymmetries observed are impossible, or at best very difficult, to resolve. The ν_3 asymmetric and the ν_4 bending regions have proved to be far more informative. As mentioned above the Raman-forbidden out-of-plane vibration has only been observed in one case, that of concentrated $TlNO_3$ solutions (21) where it indicates the unusual sideways-on interaction between the Tl^+ cation and the π -orbital of the NO_3^- anion.

Irish and his co-workers have studied aqueous nitrate solutions extensively by Raman spectroscopy and have proposed the existence of a wide variety of ion paired associates including contact and solvent-shared ion pairs (52,53), ion triplets and "roll-on" complexes (54). A quasi lattice structure was proposed for $LiNO_3$ solutions (55).

In ammonia solutions of alkali nitrates only two bands in the ν_4 region have been observed corresponding to the free solvated NO_3^- ion and contact ion pairs; 708 cm^{-1} (free NO_3^-), and 720 cm^{-1} ($Li^+NO_3^-$) and 717 cm^{-1} ($Na^+NO_3^-$). The ν_4 region for the alkaline earth metal nitrate solutions is more complicated and some data for these solutions are listed in Table 1. Results for $Mg(NO_3)_2$ solutions are not included among these because, whilst the salt is soluble at 213 K (it is virtually insoluble at 298 K), the spectrum consists of a single sharp band at 708 cm^{-1} .

Table 1. Relative % intensities of the component bands of the ν_4 region of the Raman spectra of alkaline earth metal nitrate solutions in liquid ammonia.

		% Relative intensity of bands at frequency/cm ⁻¹			
		Temperature/K			
Ca(NO ₃) ₂		A(732)	B(727)	C(708)	
		22	14	64	
	R = 52	273	9	21	70
		253	-	6	94
		233	-	-	100
Sr(NO ₃) ₂		A(724)		C(708)	
		38		62	
	R = 40	273	29	71	
		253	11	89	
		233	7	93	
	213	-	-	100	
Ba(NO ₃) ₂		A(719)		C(708)	
		44		56	
	R = 48	273	35	65	
		233	17	83	

Bands A are due to the 1:1 contact ion pairs $M^{2+} \dots NO_3^-$. This type of ion pairing, which increases in degree from Ca^{2+} to Ba^{2+} , is greatly reduced by decrease of temperature and is not observed at all at 213 K. An easily resolved band B, of intermediate frequency is present in the spectra of $Ca(NO_3)_2$ solutions at higher temperatures. Because this band appears with increasing concentration and temperature it could be assigned to a 1:1 solvent-shared ion pair.

The ν_3 region has a very complex band profile in all spectra. Unfortunately it suffers from a serious resolution problem. It is a long spectral region ($150-200\text{ cm}^{-1}$), relatively weak with respect to the ν_2 and ν_4 solvent ammonia bands at $\sim 1050\text{ cm}^{-1}$ and $\sim 1650\text{ cm}^{-1}$, and lies in a trough between these two solvent bands. Previous workers have commented upon the same base-line difficulties (17,19). We are forced, therefore, for the present time, to compare only the underlying band positions listed in Table 2. An attempt at correlation of component bands in the ν_3 and ν_4 regions is illustrated in Fig. 11.

Table 2. Band positions in the ν_3 region of the Raman spectra of alkali and alkaline earth metal nitrates in liquid ammonia solutions.

	Temperature/K		Band position/ cm^{-1}			
LiNO ₃	293		1405	1371	1355	
	253		1395	1370	1348	
NaNO ₃	293		1399	1374	1349	
	233		1392	1373	1355	
KNO ₃	293		1382		1346	
	233		1379		1350	
	203		1378		1352	
Mg(NO ₃) ₂	253		A	B	C	D
	213		-	-	1375	1345
Ca(NO ₃) ₂	353				1370	1328
	293		1430	1427	1373	1337
	213		1444	-	1365	1350
Sr(NO ₃) ₂	353		1420	-	-	1332
	293		1422	1408	1374	1339
	213		-	-	1365	1348
Ba(NO ₃) ₂	353		1410	-	-	1332
	293		-	1405	1373	1337
	253		-	1400	1370	1350

Bands A and B of the ν_3 region are both cation dependent. This dependency shows band A as due to the contact ion pair, $M^{2+} \dots NO_3^-$. The frequency shift of band B relative to band C (invariant in position and assigned to the free NO_3^- ion) does not follow the normal relationship found for other 1:1 contact ion pairs. Also the observed trend (qualitative) in band area *versus* solution concentration suggests a possible attribution to the 2:1 contact ion pair, $NO_3^- \dots M^{2+} \dots NO_3^-$. However, the alternative assignment to a solvent-shared ion pair, following the assignments made in the $\nu_4(NO_3^-)$ region, is not unreasonable. The lowest frequency band D (shown dotted) shifts to some extent with both cation and temperature. It seems best explained in terms of solvent splitting of the ν_3 vibration of the *free* NO_3^- anion as suggested also

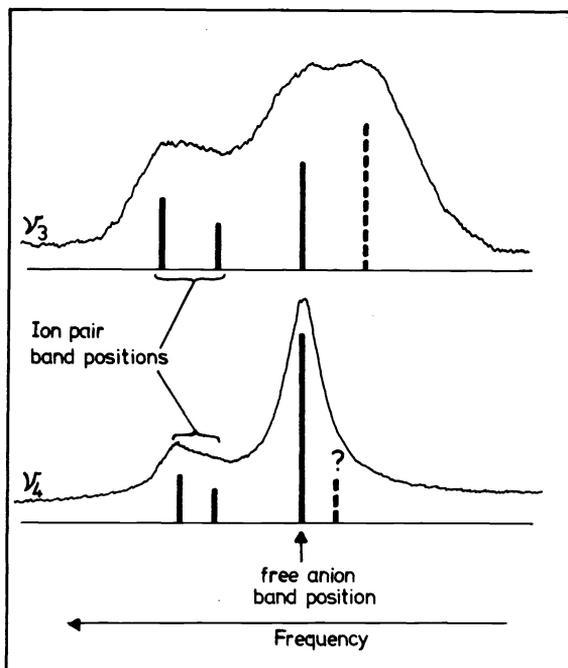


Fig. 11. Correlation of component bands in the ν_3 and ν_4 regions of the Raman spectra of nitrate solutions in liquid ammonia.

by other workers (12,13,17,19). Symmetry considerations ought to demand a similar splitting in the ν_4 region. Whilst we have been unable to resolve such a band in that region the ν_4 profiles suggest that there could be an underlying feature of low intensity (shown dotted? at $\sim 702 \text{ cm}^{-1}$) of about $6\text{--}8 \text{ cm}^{-1}$ lower frequency than the free NO_3^- anion band.

It is important to note here that the $\nu_3(\text{NO}_3^-)$ regions of the spectra of solutions of Zn^{2+} , Cd^{2+} , Hg^{2+} , Pb^{2+} , Ag^+ and Tl^+ (those cations which demonstrate little tendency to form contact ion pairs) contain only two bands, C and D, around 1373 and 1345 cm^{-1} respectively. Both these bands appear to be cation independent thus supporting the assignments made above.

In spite of the vast amount of data now available to us in respect of nitrate solutions, from three different regions of the NO_3^- spectrum, the question of assignment remains somewhat unsatisfactory. It is to be hoped that the complementary *i.r.* studies for which we are now equipped will help to resolve this problem.

Ammonium salts

We have amassed a large amount of data on the Raman spectra of ammonium salts in liquid ammonia. Just like the metal cation salts these exhibit complex spectra, often very similar to the spectra of the corresponding Na^+ salt solutions. Four sample spectra are illustrated in Fig. 12.

These spectra and the manner in which they vary with temperature and concentration appear to show all the characteristics found in, say, the Na^+ salt solutions, *i.e.* the species in equilibrium appear to be similar although their relative concentrations may differ.

Successive substitution of the hydrogens of the ammonium cation by $-\text{CH}_3$ groups has virtually no effect on the spectra until substitution is complete. At this stage the single sharp band of the free solvated anion indicates the absence of contact ion pairing. Thus the explanation of the NH_4CN spectra results in an assignment of band E to free CN^- anion, and bands B and C to the isomeric contact ion pairs $\text{NH}_4^+\dots\text{CN}^-$ and $\text{NH}_4^+\dots\text{NC}^-$. Band A is a dubious feature and, if present at all, it is of very low intensity. The assignment of band D to a solvent-shared ion pair is in accord with the proposal that the NH_4^+ ion in liquid ammonia behaves as a discrete thermodynamically stable entity in the solvent, much more so that the hydrated proton in aqueous

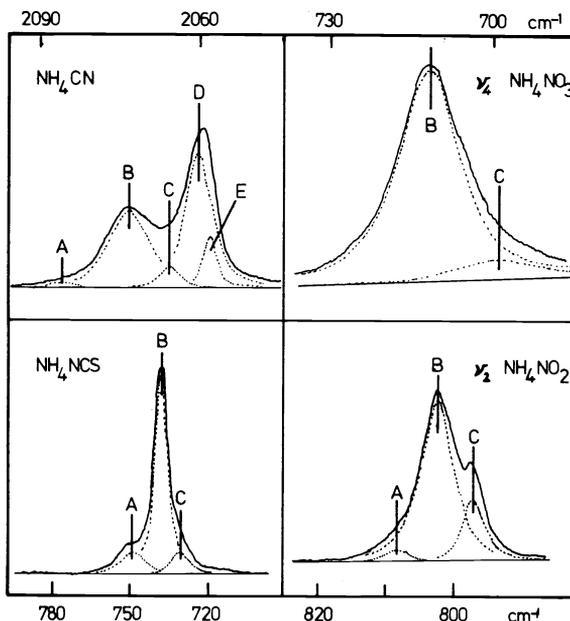


Fig. 12. Raman spectra of some NH_4^+ salt solutions in liquid ammonia at 293 K. NH_4CN , $R = 40$. NH_4NO_3 , $R = 22$. NH_4NCS , $R = 43$. NH_4NO_2 , $R = 40$.

solutions (56). This proposal is supported electrochemically by ion transference studies on ammonium salt solutions (57,58).

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