Use of vibrational spectroscopy to examine species in solution: ion-pairing and metal–ligand complexation in liquid ammonia

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Abstract – Vibrational spectroscopy is an excellent tool for
identification in solution of (i) electrostatic interactions
between anions and cations and (ii) covalent complexes of metal
cations and ligands. Unlike thermodynamic and transport
methods, each individual species of an equilibrium can be
identified in the vibrational spectrum by comparison of the
perturbation of the transition of an ion-pair or complex with
the vibration frequency due to the 'free' anion or ligand.
Liquid ammonia is an excellent medium for such studies because
its dielectric properties alter markedly over a relatively
small temperature interval to produce substantial shifts in the
equilibria between the species. Complementary use of Raman and
infrared spectra, together with modern spectrometer and data
handling techniques, provide evidence for equilibria between
contact ion-pairs (sometimes as isomers), solvent-shared ion-
pairs, and ion-aggregates; there is also evidence for 2:1
mixed contact/solvent-shared ion-pairs.

Illustrations of ion-pairing are possible from a large number
of vibrational spectra of solutions taken over wide
concentration and temperature ranges (salts or alkali, alkaline
earth, Be^{2+}, Al^{3+}, Zn^{2+}, Cd^{2+}, Hg^{2+}, Ag^+, Tl^+ cations with CN^-,
NCS^-, NCO^-, NO_3^-, NO_2^-, N_3^-, BF_4^-, ClO_4^- anions) but examples
have been restricted mainly to the CN^- and NCS^- salts of the
alkali and alkaline earth metal cations. Some examples of
ligation by CN^- and NCS^- ligands on Ag^+, Au^+, Hg^{2+}, Pd^{2+} and
Pt^{2+} in liquid ammonia are presented and differences in the
complexation behaviour of these systems in ammonia, and their
counterparts in water, are highlighted.

INTRODUCTION

Our examination of the profiles of Raman spectra of salts of multiatomic
anions in liquid ammonia began 10 years ago following observations made while
correlating cation-solvent vibration frequencies for liquid ammonia solutions
with those of the aqueous phase (ref. 1). Nitrate salts were used in this
cation solvation study mainly because of their relatively high solubilities in
ammonia. Although the low frequency $\nu(M-N)$ vibrations were our concern in
solvation number determinations the important observation was made that the
ν_3 and ν_4 vibration regions of the NO_3^- anion contain more underlying
component bands than symmetry requires. Also the band structure is cation-
dependent (ref. 2). The $\nu_1(NO_3)$ vibration is an extremely sharp band
$(w_{\frac{1}{2}} \approx 2\ cm^{-1})$ superimposed on the relatively weak and wide $\nu_2(NH_3)$ solvent
band at 1044 cm^{-1} (ref. 3). Its narrow bandwidth rendered it virtually
irresolvable, but even this sharp feature is structured like the $\nu_3(NO_3)$ and
$\nu_4(NO_3)$ vibrations.

Consequent upon these observations we embarked on a comprehensive systematic
survey of the Raman spectra of the CN^-, NCS^-, NO_3^-, NO_2^-, N_3^-, BF_4^- and ClO_4^-
salts of many cations in their liquid ammonia solutions over wide ranges of
concentration and temperature. Although a library containing over 3000 Raman
spectra of these solutions has now been established only a small proportion

of the total data collected has been published. From the outset it was clear
that the multicomponent spectra are due to different ion-paired species and
reflect the equilibria between them. It has always been our aim, before
publication of the detail, to explain the results in a comprehensive manner
with the overall ion-association picture presented in a self-consistent
framework applicable to all, or most of, the salt solutions studied. A series
of papers will shortly emerge to present this self-consistent picture of ion-
ion interaction behaviour and which will highlight specific differences
observed between salt and salt, and anion and anion.

Recently we designed and constructed a cell to enable the infrared spectra of
solutions in liquid ammonia to be obtained (ref. 4). As a result our collec-
tion of infrared spectra of liquid ammonia solutions is growing rapidly. With
only an Ar$^+$ laser in our Raman facility the work was limited to colourless
solutions, but the infrared cell now allows us to extend our studies to
include ion-pairing and complexation behaviour in coloured solutions (in
particular transition metal salts). The availability of infrared spectra, as
a complement to the Raman spectra, has greatly improved the experimental basis
of our understanding of electrolyte solutions in ammonia, particularly in the
area of complexation.

Observation of ion-pairing by vibrational spectroscopy is not new. Irish and
his coworkers have published a substantial·series of papers on the subject as
applied to aqueous solutions (ref. 5), and as to aprotic media such as
dimethylformamide (dmf) (ref. 6,7). As is to be expected, observations of
ion-pairs in 1:1 electrolyte solutions in water through vibrational
spectroscopy is limited because of their low degree of ion-association; for
NaNO$_3$, K_{ass} = 0.06 Kg^{-1} dm^3 (ref. 8). Irish's main successes were with 2:1
aqueous electrolyte solutions (ref. 9,10,11) where ion-association is
substantially increased due to the higher cation charge. The early use of
vibrational spectra in the study of ion-association in non-aqueous media was
also reviewed by Gardiner (ref. 12).

Work by Chabanel et al. in Nantes on thiocyanates and cyanates in dmf,
dimethylthioformamide ($dmtf$), dimethylsulphoxide ($dmso$), and other aprotic
solvents (refs. 13,14,15) produced thermodynamic data of ion-pair formation.
Our interpretations of the spectra observed for liquid ammonia solutions is
broadly in accord with that of these workers. Also in France, Corset et al.
studied cyanides, among other salts, in dmf and $dmso$ solutions (refs. 16,17,
18). While their spectra clearly indicate the existence of ion-pairing
between alkali metal cations and cyanide anions we differ in interpretation
because they assigned some of the features they observed to ion-triplets,
CN$^-$..M$^+$..CN$^-$. We find no evidence to support triplet ion formation in
ammonia solutions of cyanides, but the differences of opinion might be due to
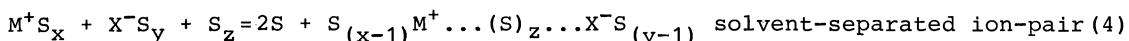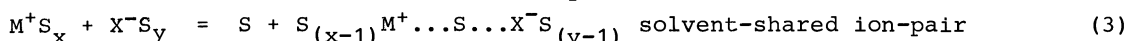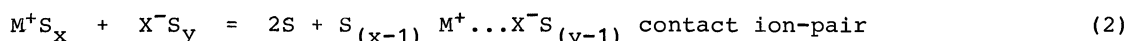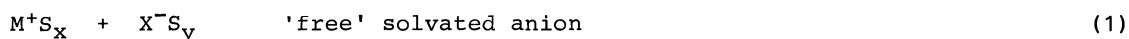the different solvents used in our respective research groups.

Relatively few reports of previous vibrational spectroscopic studies of ion
association in liquid ammonia have appeared. Perhaps this is because it is
thought that handling difficulties are a severe practical problem. As will
be shown, ammonia is probably the best medium available for the spectroscopic
examination of ion-pairing. Earlier publications on ammonia solutions
appeared separately from the groups led by Lagowski (refs. 19,20) and Tobias
(ref. 21). The Raman spectra of liquid ammonia solutions of LiSCN, NaSCN and
NH$_4$SCN were described by Lemley and Lagowski as containing only two
components in the ν(CS) stretching region. Without resorting to the use of
computer-aided band resolution techniques our early spectra of alkali metal
thiocyanates in ammonia could all be seen to contain at least three
components in this region at all concentrations and temperatures. These
previous workers attributed the two bands they observed to different forms
of SCN$^-$..NH$_3$ interaction and not to ion-association. Other studies with
nitrate solutions in liquid ammonia by Lagowski (ref. 20) and Tobias (ref. 21)
also led to substantially different interpretations from ours; that the
additional components found in the ν_3(NO$_3$) and ν_4(NO$_3$) regions of the Raman
spectra were attributed to degeneracy splitting resulting from interactions
between the anion and ammonia molecules. The work described by Lagowski et
al. was focussed specifically on the interactions between the solvent and its
solutes, and not on the interactions between the solute ions.

It must be asked why NMR spectroscopy has not been widely used to probe ion-
association. As a technique widely used in structural determination it might
be expected to be the main thrust of attack on ion-pair structures, but it
suffers from a major disadvantage. Because of their electrostatic origin

ion-ion interactions are ususaly short-lived (lifetimes could approach the diffusion limited value for the medium, *e.g.*, 10^{-9} s), much shorter than the timescale required in structural NMR work (10^{-3} to 10^{-5} s). One or two notable exceptions exist such as the ^{205}Tl NMR studies on $TlNO_3$ and $TlClO_4$ solutions in liquid ammonia, and a range of Tl salts in various other solvents (refs. 22,23,24). Association constants were calculated by separating the ^{205}Tl NMR signal into one component due to the 'free' Tl^+ cation, and another due to associated Tl^+ for various concentrations at three different temperatures. The analysed band appeared to consist of a single NMR signal whose chemical shift varied significantly as the salt concentration was increased from zero to 0.2M (interpreted as an increase in the degree of ion-pairing). ^{205}Tl is an excellent nucleus for such a study because of (i) its high receptivity and, (ii) the large chemical shifts observed.

Although shorter than the timescale of the NMR event the lifetime of an ion-pair is many times longer than the time of an electronic or a vibrational transition. Hence these spectroscopic techniques are applicable to the identification of short-lived ion-associates. Vibrational spectra possess distinct advantages over uv/visible spectra because the band profiles are generally much sharper and underlying components are more readily resolved. None the less uv/visible spectroscopy is showing some promise. The *d-d* transition of Ru^{3+} solutions of I^-, NCS^-, and NO_3^- in liquid ammonia (ref. 25) shifts its λ_{max} from 402nm (NO_3^-) to 388nm (NCS^-); with I^- the band intensity coefficient is increased x2. Considering the difficulties encountered in band analyses, we believe that future work lies with quantitative vibrational spectroscopy. Of the two methods the infrared technique is attractive because quantitative work with modern spectrometers offers a new and high level of photometric accuracy (ref. 4). On the other hand, whilst Raman spectroscopy is disadvantaged as a quantitative method because of its single beam nature, temperature surveying of ammonia solutions is relatively easy by this technique.

A set of simple step processes can define the interactions in a solution (the solvated cation is M^+S_x and the 'free' solvated anion is X^-S_y):

$$M^+S_x \;+\; X^-S_y \qquad \text{'free' solvated anion} \tag{1}$$

$$M^+S_x \;+\; X^-S_y \;=\; 2S + S_{(x-1)}\,M^+...X^-S_{(y-1)} \;\; \text{contact ion-pair} \tag{2}$$

$$M^+S_x + X^-S_y \;=\; S + S_{(x-1)}M^+...S...X^-S_{(y-1)} \;\; \text{solvent-shared ion-pair} \tag{3}$$

$$M^+S_x + X^-S_y + S_z = 2S + S_{(x-1)}M^+...(S)_z...X^-S_{(y-1)} \;\; \text{solvent-separated ion-pair} \tag{4}$$

Normally the perturbation of the frequency from that of the 'free' solvated anion, S_yX^-, is largest for the contact ion-pair (2), less for the solvent-shared ion-pair (3), and least for the solvent-separated ion-pair (4). Bands due to both contact and solvent-shared ion-pairs have been identified and unambiguously assigned (refs. 3,26). No identifiable feature attributable to a solvent-separated species has so far been observed in a spectrum, though changes in the half-widths and shapes of the band due to the 'free' solvated anion indicate their existence. The problem is that the band due to the solvent-shared species (3) is already so close to the 'free' anion band that resolution is either difficult or impossible; for the solvent-separated species the frequency separation from that due to the 'free' anion is only a fraction of a wavenumber and hence indistinguishable from it.

In solution chemistry the existence of ion-pairs, and the degree of association, has traditionally been sought through measurement of bulk thermodynamic properties such as solution enthalpies, ion activity co-efficients *etc.* and transport properties such as solution conductance. These measurements lead to ion-association constants which reflect the overall averaged values of all the events in (2), (3), and (4). Of course, it can reasonably be assumed that these three steps do not, by themselves, define all possible ion-association equilibria existent in a solution.

Bjerrum critical distances for some ion-pairs in water, ammonia, and acetonitrile at various temperatures are listed in Table 1. Within spheres defined by these radii ions must be regarded as associating. Accordingly, their contribution to conductance will alter significantly from that of isolated 'free' ions. In water, only 2:1, 2:2 and 3:3 systems will exhibit appreciable ion association at low to moderate concentrations, whereas

TABLE 1.   Bjerrum critical distances/pm

	T/K	ε	1:1	2:2	3:3
H_2O	298	78.3	357	1428	3213
Acetonitrile	298	36.7	761	3044	6849
Liquid Ammonia	203	26.3	1062	4248	9558
	230	22.4	1248	4992	11232
	298	16.9	1654	6616	14886
	350	13.5	2071	8284	18640

considerable association can be expected with 1:1 electrolytes in ammonia and acetonitrile. From these data it is to be expected that there will be similar behaviour between 1:1 salts in ammonia and 2:2 salts in water. Conductance constants for alkali halides in ammonia (refs. 27,28) and magnesium sulphate in water (ref. 29) have similar values, $ca.$ 10^{-3} M^{-1}. Ion transference numbers (ref. 30) and mean activity coefficients (ref. 31,32) can be similarly correlated.

An important comparison of association constants derived from vibrational spectra with those from conductances was made by Janz and Muller (ref. 33). They determined the association constant, K_{ass} = 84 ± 14 M^{-1} of pairing between Ag^+ and NO_3^- ions in acetonitrile by analysing the two components observed in the ν_1 (NO_3) region of the Raman spectrum at 1037 cm^{-1} (ion-pair) and 1042 cm^{-1} ('free' NO_3) over a range of concentrations. This result, compared with the association constant derived from conductance data (ref. 34) K_{ass} = 70 ± 1 M^{-1}, suggests that only contact ion-pairing (2) is important in acetonitrile. In contrast stoichiometric constants obtained from our vibrational spectra of ammonia solutions generally fall within K_{ass} = 1 to 30 depending on the ion-pairs considered, whereas values obtained from conductances (refs. 27,28) and ion activity coefficients (ref. 32) are much higher; $viz.$ K_{ass} = 5 x 10^2 to 2 x 10^3 M^{-1}.

Thus vibrational spectroscopy offers itself as a tool for the identification and measurement of the individual ion-associates which, hitherto, have been assessed collectively by the conductance method. It is clear that, with advances in spectroscopic technique, quantification of the steps in the equilibria between the species will greatly improve the scientist's understanding of the structure of electrolyte solutions.

LIQUID AMMONIA AS A SOLVENT FOR SPECTROSCOPIC STUDIES OF ION-ASSOCIATION

A comparison of some important physical properties of liquid ammonia and water is presented in Table 2.

TABLE 2.   Some physical properties of liquid ammonia and water.

		H_2O	NH_3
Boiling point	/K	373.16	293.8
Melting point	/K	273.16	195.5
Vapour pressure at 300K	/at	0.035	10.9
Critical pressure	/at	218.3	112.5
Critical temperature	/K	643.7	405.6
Dielectric constant at 203K		–	26.3[*]
	233K	–	22.1[*]
	298K	78.4	16.9[**]
	313K	73.2	15.8[**]
	373K	55.6	12.5[***]

[*] ref. 35   [**] ref. 36   [***] extrapolated

Experimentally liquid ammonia solutions are more easily handled than is commonly expected; either in the normal liquid temperature range between 196K and 240K, or at relatively low pressures at ambient temperatures and just above. Our infrared cell (ref. 4) is designed to work at ambient temperatures where the vapour pressure of liquid ammonia is between 6 and 10at By sealing samples of ammonia solutions in round glass tubes (capillary for temperatures above 300K) Raman spectra can be obtained between 196K and 350K. (An important advantage is that once a sample of a solution of known concentration is sealed it can be stored and used on any future occasion). Between these temperatures the dielectric constant changes by about x2, from that of a solvent of medium dielectric to that of one of low dielectric constant. Throughout its normal liquid temperature range the dielectric constant of water does not change sufficiently to remove it from the high dielectric range. It must be noted, however, that the dielectric constant of water falls rapidly into the low dielectric range when the temperature is taken through the sub-critical region, > 600K. Even in water, ion-pairing becomes dominant in 1:1 electrolytes at highly elevated temperatures, and important spectroscopic studies of aqueous solutions in this region have been undertaken by Franck (ref. 37) and Irish (ref. 38).
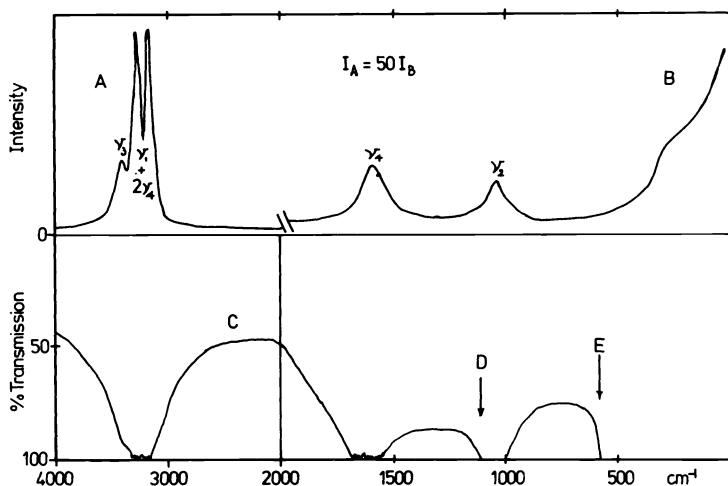
Fig. 1. Raman (A and B) and infrared (C, D and E) spectra of liquid NH_3. The infrared spectrum is for a pathlength of 50μm; C indicates the transmission window between 2600 and 1900 cm^{-1}; the 'window' below 1500 cm^{-1} is cut off at 1200 cm^{-1}(C) for CaF_2 plates, and at 600 cm^{-1}(E) for ZnSe plates.

From the spectroscopic standpoint both water and ammonia are both excellent solvents. These molecules, with a small number of atoms, have a low number of molecular vibrations. Most other ionising solvents such as *dmso*, *dmf*, acetonitrile (*an*) *etc.*have complicated spectra of their own which cause interferences in the analyses of the spectra of solutes. For example, a solvent band at 742 cm^{-1} seriously interferes with the examination of the ν(CS) stretching region of NCS⁻ in *dmf*. Raman and infrared spectra of pure liquid ammonia are displayed in Fig. 1. Both of these spectra contain large spectral 'windows' within which the vibrational spectra of solute ions can be examined without solvent interference. We are fortunate that many of the vibration frequencies of the anions we wish to study lie in these 'windows'.

ANALYTICAL METHODS

If equilibria between ion-pairs are to be established then the positions, widths, shapes and areas of the component bands in the spectra of the species must be ascertained. For this purpose we use TREAT, a computer-assisted derivative resolution enhancement technique (ref. 39), based on the smoothing procedure established by Savitsky and Golay (ref. 40), and a band resolution procedure VIPER developed by us (refs. 41,42). Used in conjunction with each other, these are very powerful tools. Inevitably problems occur when underlying bands are too closely spaced, and high correlation appears between the resolved band parameters. It is not feasible to contemplate curve-fitting when band separation is 0.5 $W_{\frac{1}{2}}$ or less (ref. 43).

When using computer-aided resolution it is important to adhere to firm ground
rules to avoid false interpretation by inclusion of 'computer bands' and other
artefacts independent of the system under examination. These can be broadly
generalised: (i) the existence of a band must be seen 'by eye' either as a
shoulder, or as an inflexion on the spectrum profile; (ii) a feature can be
identified in a derivative profile of the spectrum; (iii) the existence of a
band can be established as a result of a systemmatic survey in which
experimental conditions such as salt concentration, and/or solution
temperature are varied; (iv) the chemical interpretation demands inclusion of
a 'fitted' band under the profile, *etc*.

Since we began examining infrared spectra quantitatively we have obtained the
spectra of solutes by subtraction of the digitised spectra of the solution
and the solvent. Spectrum subtraction can be used to define the existence of
a band as in Fig. 2. Here the subtraction of the infrared spectra of
solutions of $(CH_3)_4NBr$ and $(CH_3)_4NNO_3$ at the same concentration in liquid
ammonia define the position, shape, and width, of the v_3 band due to 'free'
NO_3^-.
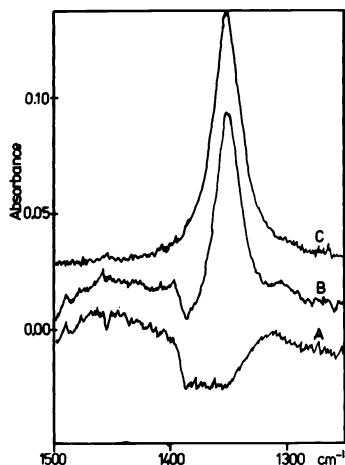
Fig. 2. The single band at
1350 cm^{-1} in the infrared
spectrum at 293K of 'free'
NO_3^- (C) in its v_3 (NO_3)
stretching region, obtained by
subtraction of spectrum (A) of
a solution of $(CH_3)_4N$ Br from
spectrum (B) of a solution of
$(CH_3)_4N$ NO_3. Pathlength = 50
µm; solution concentrations =

19.0 mM; absorbance scale
relates to spectrum (C).
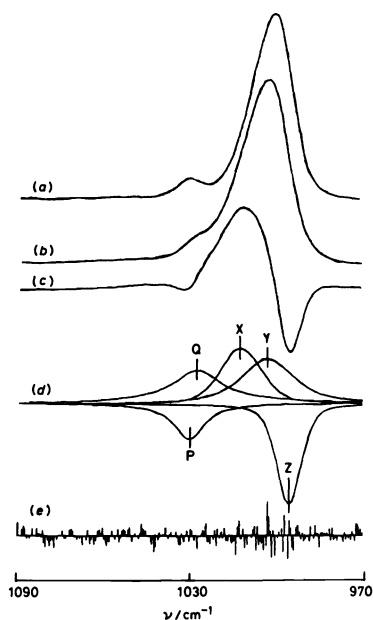
Fig. 3. VIPER fitting (d)
of a difference spectrum (c)
obtained by subtraction of
the $v(SO)_{dmso}$ region of the
Raman spectra of a $SO_2/dmso$
mixture of mole fraction
$SO_2 = 0.79$ at 170K (a) and
210K (b). The residuals
(x10) of the difference
between the calculated (d)
and the 'observed' (c) are
shown in (e). This
procedure confirms the
presence of band Z.

Another use of spectrum subtraction is shown in Fig. 3 for $SO_2/dmso$ mixtures.
Curve resolution by VIPER of the resultant subtracted spectrum obtained from
a subtraction of the spectra of the $v(SO)_{dmso}$ stretching region at two
temperatures (ref. 44) verified the existence of band Z at 997 cm^{-1} due to a
species with $2SO_2.dmso$ stoichiometry. This band cannot be identified in the
original spectrum and only shows in the 2nd derivative as an asymmetry in
another feature as the medium is cooled.

ION-PAIRING

In the following discussion of the use of vibrational spectroscopy to define
ion-pairing in liquid ammonia the examples are mainly of solutions of cyanide
and thiocyanate salts. Because of its single vibration frequency the CN^-
anion should produce the simplest possible spectra of all anions; the spectra
of SCN^- anions would also be expected to be comparatively simple. Figure 4
shows the Raman spectra at 293K of some alkali metal, Be, and Al cyanide
solutions in ammonia. These illustrate important and consistent
characteristics observed throughout all the spectra of the salt solutions we
have studied in ammonia.

(1) The band due to 'free' solvated anion occurs at its own characteristic
frequency irrespective of the cation; 2058 cm^{-1} for CN^-. The assignment is
established by examining the increase and decrease in relative intensity
observed for the free' anion band as solution concentrations and temperatures
are varied. Confirmation is given in the spectra of solutions containing a
cryptand (C222). This encloses the cation in an inclusion complex, to prevent
direct ion-pairing (ref. 45). A single symmetric feature at 2058 cm^{-1}
remains. Also the spectrum of a solution of $[(CH_3)_4]CN$ in ammonia appears as
a single sharp band at 2058 cm^{-1}.

(2) It is common to all series of salts of a given anion that the frequency
separation between the 'free' anion band and the bands due to its ion-
associates decreases in descent of a group. The band frequency perturbation
is always in the order: Li> Na> K> Rb> Cs; Be> Mg> Ca> Sr> Ba; and Al> Be>
Li.

(3) Most of the spectra are both concentration and temperature dependent
except those of Li salts, and perhaps Be. The dependency is such that the
band due to 'free', CN^-, at 2058 cm^{-1} (E) and observed in all spectra in Fig.
4, becomes increasingly dominant in the spectrum as the concentration is
reduced, and as the temperature is increased (*i.e.* as dielectric constant is
decreased). This behaviour is common to all salts irrespective of anion.
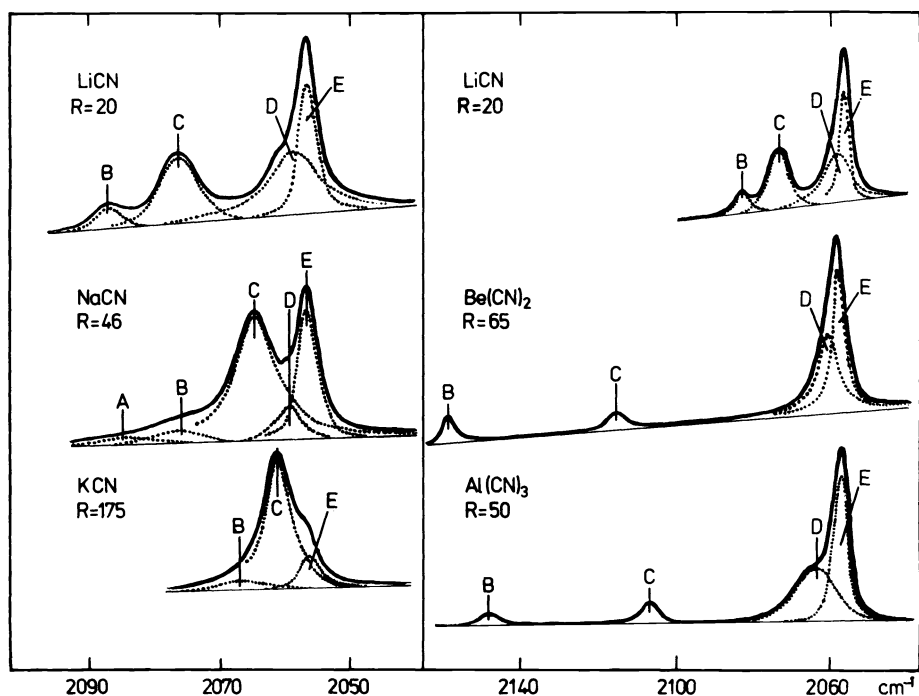

Fig. 4. The ν(CN) stretching region of the Raman spectra of some
cyanide salt solutions in liquid NH_3 at 293K.

(4)   The spectra of Na salt solutions are usually more complex, and contain more bands, than those of other salt solutions.

(5)   The bands marked B and C in Fig. 4 have been assigned to 1:1 contact ion-pairs. Both of these features increase in intensity relative to both the total spectrum area and to the area of band E, as the concentration and temperature are increased. However, if the temperature is changed the relative intensities of B and C change with respect to each other to reflect the equilibrium between the isomers.

To assist in the assignment of these bands we used a simple empirical approach. The ν(CS) stretching region of the spectra of alkali and alkaline earth thiocyanates is illustrated in Figs. 5 and 6. The bands at 736 cm^{-1} (B) and 729 cm^{-1}(C) are due to the 'free' NCS$^-$ anion, and the bands marked A to the 1:1 contact ion-pairs. A plot of the frequency shift, $\Delta\nu_A$ cm^{-1} versus $1/r_+{}^2$, where r_+ = crystallographic radius of the cation, is linear for a group of cations. This procedure is consistent for all the anions we have studied.
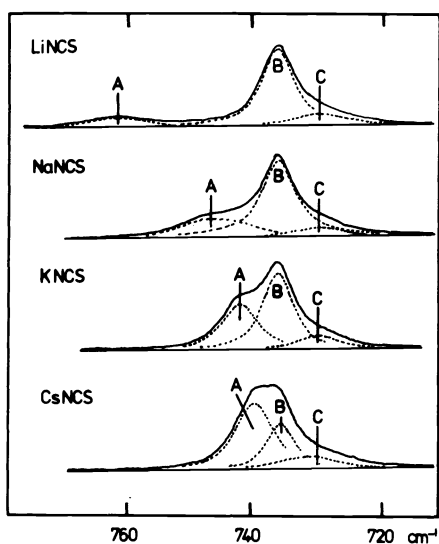
Fig. 5. The ν(CS) stretching region of the Raman spectra of alkali metal thiocyanate solutions in liquid NH$_3$ at 293K. R $\simeq$ 50.
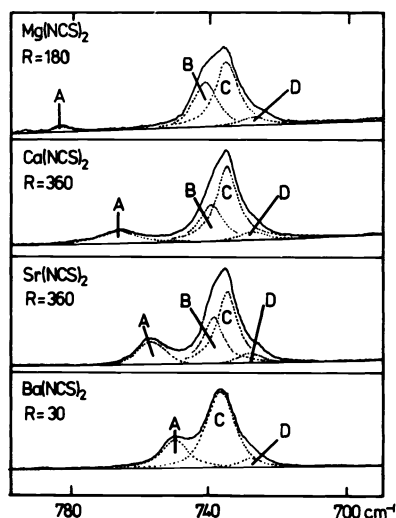
Fig. 6. The ν(CS) stretching region of the Raman spectra of alkaline earth metal thiocyanates in liquid NH$_3$ in 293K.

Both CN$^-$ and NCS$^-$ are ambidentate ligands. Although we have no evidence of isomers in ammonia solution in the case of NCS$^-$ in either its alkali or alkaline salts the existence of the two bands, B and C, in the CN$^-$ spectra demonstrates an equilibrium between M$^+$...CN$^-$ and a M$^+$...NC$^-$ contact ion-pairs. This attribution is qualitatively consistent with predictions based on the 'hard-soft' acid-base concept. Band C is more intense in the spectra because M$^+$...CN$^-$ is the favoured species of the equilibrium; the 'hard' alkali metal cation favours interaction with the 'hard'-atom ends of the NC$^-$ and NCS$^-$ anions. The ν(CN) frequency is higher when C-N is bonded to another atom at its N-atom end, and lower when bonded at its C-atom end (refs. 46,47,48). The spectra of the Ag(I)/CN$^-$ system in ammonia, for which bands due to the linkage isomers between Ag$^+$ and CN$^-$ have been identified (ref. 49), support this assignment.
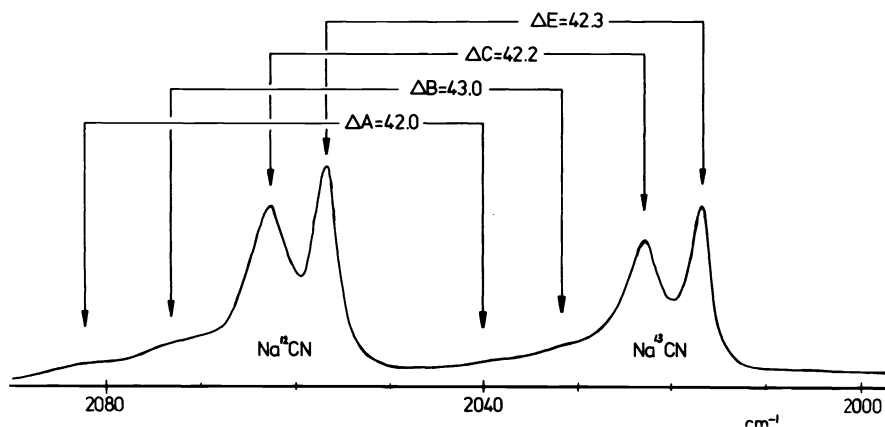
Fig. 7. The ν(CN) stretching region of the Raman spectrum (9 scans coadded) of a liquid NH_3 solution at 293K containing $Na^{12}CN$ and $Na^{13}CN$ at approximately equal concentrations. Total $[CN^-]$ is at R = 35.

Final confirmation comes from isotopic substitution studies (ref. 26). The spectrum of a solution containing similar concentrations of $Na^{13}CN$ and $Na^{12}CN$ (Fig. 7) shows that the relative band shift of the $Na^+..CN^-$ isomer is raised ($\Delta B = 43.0$ cm^{-1}), whilst that of the $Na^+..NC^-$ isomer is lowered ($\Delta C = 42.2$ cm^{-1}), with respect to that of the 'free' CN^- anion ($\Delta E = 42.3$ cm^{-1}). This assignment follows Nakamoto and Tevault (ref. 50) who established the isomers in $Zn(CN)_2$ complexes in water.

With alkali thiocyanates solutions three bands are observed in the ν(CS) region. The ν(CS) regions of the spectra of these solutions have been carefully examined but, contrary to most of the other spectra, the ν(CN) bands are broad and featureless changing little in shape as concentration and temperature are varied. Band resolution has proved virtually impossible in this region except for LiNCS and some NaNCS solutions in which there is correspondence with the three components of the ν(CS) region.

Initially it seemed reasonable to assign band A to a N-bonded contact ion-pair and band C at 729 cm^{-1} to its S-bonded isomer; because the frequency of A is higher, and that of C is lower, than that of the 'free' NCS^- anion at 736 cm^{-1} (ref. 51). This incorrect assignment arose from our work in the Ag^+/SCN^- complexation system where a substantial band due to the Ag-SCN bonded species occurs at 727 cm^{-1} (ref. 52). Bands C (Fig. 5), and D (Fig.6) are attributable to an upper stage vibrational transition ('hot' band) of the NCS^- ion. This transition in NCS^- is not unexpected; similar observations in other solvents have been made by Chabanel *et al*. (ref. 53). The two bands at 736 cm^{-1} can, with confidence, be assigned to the 'free' NCS^- anion, leaving band A to be attributed to an $M^+..NCS^-$ contact ion-pair. It should be noted that a recent analysis of the LiNCS solution spectrum with averaged S/N ratio (*ca*. 1000:1) also enabled the identification of a 'hot' band due to the $Li^+..NCS^-$ ion-pair.

(6) In the spectra of LiCN, $Be(CN)_2$ and $Al(CN)_3$ illustrated in Fig. 4 a shoulder close to, but at slightly higher frequency than, the 'free' ν(CN) band at 2056 cm^{-1} indicates the underlying band D. This feature, which also appears as band B in the spectra of the alkaline earth thiocyanate solutions (Fig. 6), is a manifestation of the solvent-shared ion-pair of (3).

In our first attempts to resolve the spectra of NaCN solutions we were unable to obtain satisfactory fits to the profiles without including band D (Fig. 4). At the time its inclusion merely to satisfy the fitting of the profile of the spectrum would have been contrary to our ground rules because it could have been claimed to be a computer-generated band with no chemical or physical significance. We listed it with a query in our preliminary publication on the spectra of cyanide solutions in ammonia (ref. 54). However, the development and use of spectrum differentiation has shown that band D was correctly
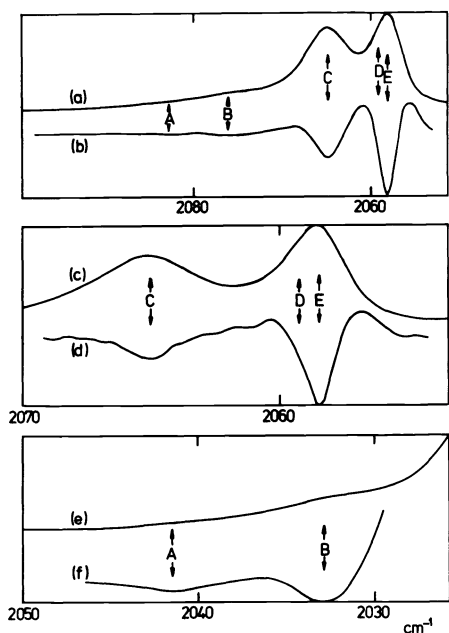
Fig. 8. The Raman spectrum (a) in the ν(CN) stretching region of a Na^{12}CN solution in liquid NH$_3$ at 293 K and its 2nd derivative (b). The section from 2070 to 2045 cm^{-1} is shown at (c); its 2nd derivative (d) indicates the existence of band D in the asymmetry of the feature at 2058 cm^{-1}. The 2nd derivative (f) of part of the spectrum (e) of Na^{13}CN identifies the positions ($\pm$ 0.125 cm^{-1}) of bands A and B.

included in the NaCN spectrum. Figure 8 shows a section of the ν(CN) region at high S/N ratio (148 coadded scans) of the Raman spectrum of a 1M NaCN solution in ammonia with its 2nd derivative. The asymmetry of the derivative at 2058 cm^{-1} points to the presence of at least one further band on its high frequency side; the separation from the 'free' CN^{-} band is < 1.0 cm^{-1}. Thus it is obvious that a band must be included in the NaCN solution spectrum to account for the presence of solvent-separated ion-pairs.

In the same way as for contact ion-pairs the band due to solvent-shared ion-pairs moves closer to that of the 'free' anion on descent of a group. Resolution of B from C (Fig. 6) is not difficult in the spectra of Mg(NCS)$_2$ and Ca(NCS)$_2$ solutions, but is a problem with Sr(NCS)$_2$ and, like NaCN, is impossible with Ba(NCS)$_2$. On reaching Ba(SCN)$_2$ it appears to have disappeared completely, but the observed feature is a composite band enclosing those due to both 'free' NCS^{-} and the 1:1 solvent-shared ion-pair (indicated by the increased half-width of the band at 736 cm^{-1}).

(7) Semiquantitative conclusions can be drawn. The spectra are cation-dependent in two ways. Not only does the perturbation of the anion frequency depend on the size and charge of the cation, the degree of association is also cation-specific (ref. 2). The spectra illustrate a competition between solvent molecules (solvation) and anions (ligation) for sites in both the inner-coordination (contact ion-pair) (2) and outer-coordination sphere (solvent-separated ion-pair) (3) of the cation.

The Li^{+} cation has a high solvation energy (manifest in the ability of most Li salts to form the concentrated Divers' solutions normally associated with NH$_4^{+}$ in ammonia. The low degree of ion-pairing in Li^{+} salt solutions is explained by this cation's desire to be solvated as Li(NH$_3$)$_4^{+}$, almost to the exclusion of ligation. Thus for Li^{+} process (2) lies well over to its left hand side.

Solvation enthalpies of the alkali metal cations in liquid ammonia decrease in the order Li > Na > K > Rb > Cs (ref. 55). On purely electrostatic reasoning ligation of these ions will follow the same order. Thus, on descending the group, the tendency to form covalent solvates decreases to a correspondingly greater extent than the ability of the same cations to form electrostatic ion-pairs. The stability orders for contact ion-pairing in liquid ammonia are: Cs > Rb > K > Na > Li, and Ba > Sr > Ca > Mg. Calculations based on the assumption that band areas are proportional to the concentrations of the constituent species and intensity coefficients remain the same for each of them within a spectrum, lead to stoichiometric association constants for the contact ion-pairs of the alkali thiocyanates: Cs(9.4 $\pm$ 0.6); K (6.4 $\pm$ 0.8); Na(1.5 $\pm$ 0.2); Cs(2.0 $\pm$ 0.7) Kg^{-1} dm^3.

Some approach can be made towards the determination of quantitative relationships for solvent-shared ion-pairing. Following the observation outlined above for the cyanide salts that the band due to a solvent-shared ion-pair is always close in frequency to that of the 'free' anion band, and that this band shifts closer in frequency to the 'free' anion band in the alkaline earth thiocyanate series, it is resonable to argue that the band at 736 cm^{-1} in the v(CS) region of the alkali thiocyanate spectra is a composite feature mainly composed of two contributions from bands due to the 'free' anion and the solvent-shared species. Calculations, based on this proposition for sets of spectra of each salt solution at different concentrations lead to values for equilibrium constants for (3) as follows: Li, 13.6 ± 0.7; Na, 2.0 ± 0.9; K, 5.0 ± 1.0; Cs, 2.2 ± 0.8 Kg^{-1} dm^3. Although these results are necessarily based on analyses which, in some cases, lead to correlations between band parameters the results indicate a definite stability trend for association constants of solvent-shared ion-pairs. This is broadly in the opposite direction to that for contact ion-pairing; namely Li > Na > K > Cs. There is every reason to believe that the order will be in the same direction for the alkaline earth metal cations.

(8) Ion-aggregation can best be examined by using the spectra of solutions (i) at higher concentrations, (ii) at higher temperatures (to reduce the dielectric constant), or (iii) which contain an excess of common ion. The spectra of Na^+ salts illustrate this phenomenon best; the additional band observed in these spectra, and not identified above (band A of Fig. 4), is attributable to ion-aggregation. Similarly, the high frequency ends of the spectra of NaN_3, $NaNO_2$ and $NaCN$ solutions all exhibit bands due to aggregates (Figs. 9,10).
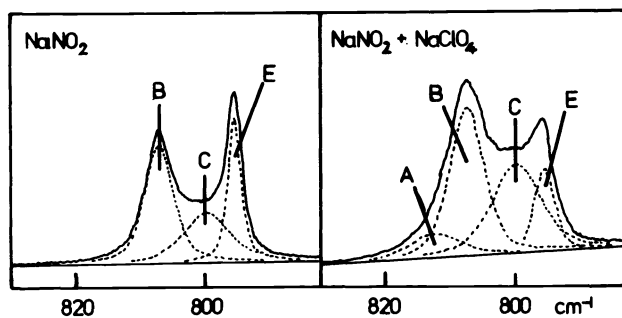

Fig. 9. The $v_2(NO_2)$ bending region of the Raman spectrum of $NaNO_2$ in liquid NH_3 at 293 at R = 40 : (i) without added Na^+ ion and, (ii) with Na^+ added as $NaClO_4$, $[ClO_4^-]/[NO_2^-]$ = 5. The appearance of band A in (ii) denotes increased ion-aggregation on addition of the common cation.

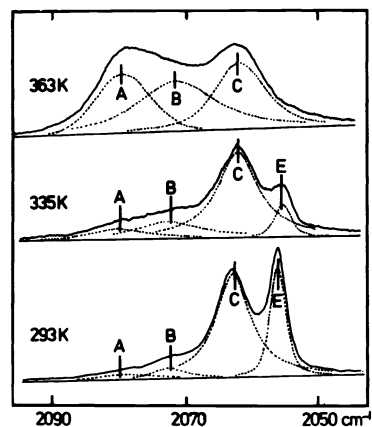Fig. 10. The Raman spectra of NaCN (R=45) in liquid NH_3 in the v(CN) stretching region at 293K, 335K and 363K.

The v_1 symmetric stretching region of NaN_3 solutions contains 3 bands at 1321, 1327, and 1338 cm^{-1}. The attribution of the middle band at 1327 cm^{-1} to a 1:1 contact ion-pair is in agreement with Chabanel's analysis of the Raman spectra of $NaN_3/dmso$ solutions (ref. 56). Because the band at 1321 cm^{-1} is due to 'free' N_3^-, the band at 1338 cm^{-1} could be attributed to either an ion-triplet or a larger aggregate (ref. 57).

The spectra of $NaNO_2$ solutions (Fig. 9) contain bands in the $v_2(NO_2)$ region at 808 (B), 800 (C) and 795 (D) cm^{-1}. As in the case of cyanide solutions the bands B and C are due to isomeric 1:1 contact ion pairs, whilst E is due to 'free' NO_2^- (ref. 2,57). Band A is a very weak feature and is not observed on the profile at 293 K. If the concentration is raised above, 1M, or common cation is added ($NaClO_4$), the relative intensity of A increases. Addition of common ion increases the relative intensities of B and C (in tandem) confirming their attributions to isomeric contact ion-pairs. The ion-aggregate which corresponds to the feature A at 814 cm^{-1} is probably an ion-triplet, $Na^+..NO_2^-..Na^+$; with this salt, the 'free' anion band always remains in evidence whatever the solution conditions.

The temperature variation of the spectra of the 2:1 alkaline earth metal nitrite solutions is more complicated. In the $v_2(NO_2)$ region the spectra of $Ca(NO_2)_2$ solutions contain a set of bands at 795 ('free' anion), 799 (either

solvent-shared ion-pair, or mixed inner- and outer-sphere ion-pair), 808 (1:1 contact ion-pair), 818 (1:1 contact ion-pair), 822 cm^{-1} (ion-aggregate) (ref. 58). The band at 799 cm^{-1} appears at high concentrations (>2M) where the band at 822 cm^{-1} dominates the spectrum. It is reasonable to assign one of these bands (822 cm^{-1}) to an ion-aggregate and the other (799 cm^{-1}) to a 'triplet' species in which one anion is directly in contact with the cation and the other anion is in a solvent shared configuration, *i.e.*, a mixed inner- and outer-sphere coordination structure, as in (5). At 335 K the spectra of Ba(NO$_2$)$_2$ solutions contain a band at 812 (A) cm^{-1}, not observed at 293 K. We can confidently ascribe this feature to ion-aggregation.

Irish and Brooker (ref. 59) found no evidence for ion-pairing in aqueous alkali nitrite solutions. However, they investigated the spectra of aqueous solutions if nitrates of divalent cations; Mg^{2+}, Ca^{2+}, Zn^{2+}, Ni^{2+}, and Cd^{2+}. These all contain bands due to both bound and 'free' NO$_2^-$ (refs. 59,60,61). Formation constants for the nitrito-complexes of Cd^{2+} were established: log β_1 = 1.7, log β_2 = 3.00, log β_3 = 3.38, and log β_4 = 3.28 (ref. 61).

By far the best evidence for ion-aggregation comes from the temperature variation of the spectra of NaCN solutions. (Figure 10). With increasing temperature and decreasing dielectric constant the relative intensity of band A (ion-aggregate) increases markedly, as it does also on addition of excess Na$^+$ ion (NaClO$_4$). At concentrations > 0.5M, at 293 K or lower, band A is absent from the spectrum. It cannot be assigned to a triplet ion, such as Na$^+$..CN$^-$..Na$^+$, because the mass balance demands the stoichiometry (NaCN)$_x$. Addition of excess Na$^+$ would cause an increase in the concentration of an aggregate whether it had 2:1 or 1:1 stoichiometry. The equilibrium concentrations of all the species seen in the spectra change markedly with temperature. At 363 K band A is a principal feature of the spectra and band E ('free' CN$^-$) has completely disappeared, whilst bands B and C, due to the 1:1 isometric contact ion-pairs, remain. For band A to be attributed to the triplet, Na$^+$..CN$^-$..Na$^+$, another feature due to either CN$^-$..Na$^+$..CN$^-$ or 'free' CN$^-$ should appear in the spectrum. As this is not the case all the evidence points to aggregation, perhaps as isomeric species of overall stoichiometry (NaCN)$_x$. This proposition is entirely consistent with the existence of (AgCN)$_2^-$ established in the Ag(I)/CN$^-$ system (ref. 49).

(9) Although we are at a comparatively early stage of analytical examination good evidence has appeared for the inclusion in the equilibria of ion-pairs of a mixed type. That is, a species with one anion in a contact- and another in a solvent-shared environment as in (5). The possibility that a band at 799 cm^{-1} in the spectra of Ca(NO$_3$)$_2$ solutions might relate to such a species has already been noted.

$$\{S_{(y-1)}X^-..M^+S_{(x-1)}\} + X^-S_z = \{S_{(y-1)}X^-..M^+S_{(x-1)}\}X^-S_z \qquad (5)$$
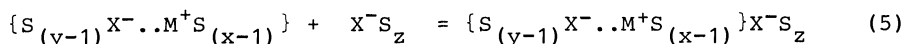
Equilibrium constants based on the band analysis of the three regions of the Raman and the infrared spectra of 2:1 nitrate solutions appear to need the inclusion of two bands (representing two species) at, or very close to, the position of the 'free' anion band.

COMPLEXATION OF PRECIOUS TRANSITION METAL CATIONS

The availability of infrared spectra of complexes in ammonia solutions has greatly assisted interpretations. We have found some significant differences in complexation properties between liquid ammonia and water. A major reason for this must be the differences in solvation energies of ions in the two solvents. For instance, the high solvation enthalpy of ions such as Ag$^+$, Hg^{2+}, Pt^{2+} *etc.* in ammonia explains why aquo-insoluble salts such as AgCN, AgI, HgI$_2$, Hg(CN)$_2$, Pd(CN)$_2$, Pt(CN)$_2$, AuCN *etc.* are all highly soluble in ammonia. Accordingly it is possible to examine the early ligation steps of these systems in ammonia, in sharp contrast to the aquo-phase in which such measurements are denied by insolubility.

Because of the exceptionally high donicity of ammonia, DN = 59 (ref. 62), it is expected that only the best donor ligands will be effective in the complexation of metal cations. It has already been stated that CN$^-$ and NCS$^-$ are both interesting because of their ambidentate character. Generally complexation by CN$^-$ in ammonia into an inner-coordination sphere is good. On the other hand inner-sphere coordination with NCS$^-$ in ammonia is somewhat ineffective, though the spectroscopic evidence suggests outer-sphere co-ordination involving NCS$^-$ to be more common.

Following its behaviour in the aqueous phase we initially expected NCS⁻ to complex well with Ag⁺ and Hg^{2+}. However, there is little spectroscopic evidence for this except with Ag⁺ and, even with this cation, there is little tendency for complexation to proceed beyond the 1:1 stage (ref. 63). The Raman spectroscopic titration (Fig. 11) shows a band at 2078 cm^{-1} in the v(CN) region due to the formation of monothiocyanato-Ag(I) complex. The band at 727 cm^{-1} in the v(CS) region due to this complex affirms the Ag–S bonding because of the shift to a lower frequency than the band due to 'free' NCS⁻ (ref. 51). The band at 727 cm^{-1} reduces in relative intensity with increasing ligand/metal ratio, but above [SCN⁻]/[Ag⁺] > 2.0, the spectrum is effectively that of a KNCS solution (Fig. 5). The stoichiometric stability constant calculated from these spectra, $K_1 \approx 5$ to 20 M^{-1}, has recently been confirmed by potentiometric titration; $K_1 = 5$ M^{-1} (ref. 64). Only when the [SCN⁻]/ [Ag⁺] ratio is > 20 is there any indication of the formation of [Ag(SCN)₂]⁻ with a minute feature (< 1%) appearing at 2094 cm^{-1}.
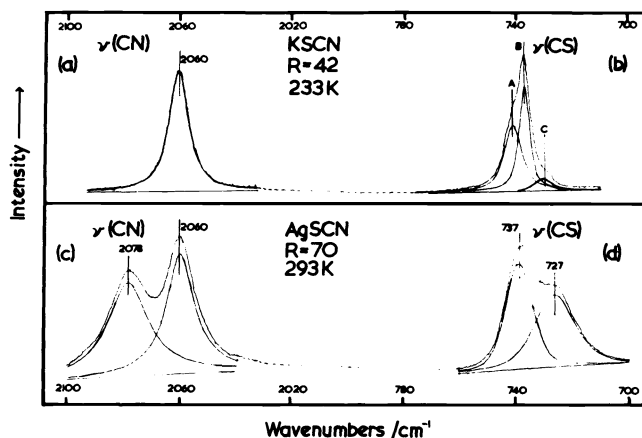

Fig. 11. The v(CN) (a and c) and v(CS) (b and d) stretching regions of the Raman spectra of a solution of KSCN AgSCN in liquid NH₃. Band A in (b) is due to K⁺..NCS⁻ contact ion pairs, and bands B and C are due to 'free' NCS⁻. The band at 737 cm^{-1} in (d) is due to 'free' SCN⁻ and the band at 727 cm^{-1} to AgSCN complex. The band at 2060 cm^{-1} in (a) and (c) is at the frequency of the band due to free SCN⁻ and the band at 2078 cm^{-1} in (c) is due to AgSCN complex.

Recently the infrared spectra of Ru^{3+} and Rh^{3+} thiocyanate solutions in ammonia revealed a broadening of the v(CN) stretching vibration band to indicate the existence of more than one species in solution. The infrared spectra of the thiocyanate and the nitrate solutions of both of these elements and also those of Pd^{2+} and Pt^{2+}, show that the anion does not enter the cation's inner-coordination sphere. Titration of Ru^{3+} with SCN⁻ cause broadening of the v(CN) band of the 'free' anion at 2060 cm^{-1} on its high frequency side. Inner-sphere complexation by SCN⁻ would be expected to give rise to a larger shift than that observed (> 5 cm^{-1}) in the v(CN) frequency of the complexed species (> 20 cm^{-1}), relative to 'free' SCN⁻ at 2060 cm^{-1}. We suggest that this broadening denotes the formation of an outer-sphere complex (solvent-shared ion-pair) of Ru^{3+}:

$$\{Ru(NH_3)_6^{3+}\} \;+\; SCN^- \;=\; \{Ru(NH_3)_6^{3+}\}SCN^- \tag{6}$$
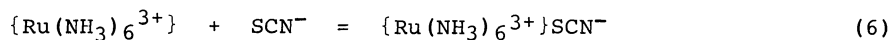
Similar observations on the spectra of other transition metal cations in SCN⁻ solutions suggest this form of interaction (6) with SCN⁻ anion to be normal in liquid ammonia. Some support comes from our recent uv/visible spectra of Ru^{3+} solutions: differences in frequency of the *d-d* transition occur from anion to anion often with substantial changes in band intensity with the anion (ref. 25).

Spectroscopic titration of Ag⁺ with CN⁻ provides a set of spectra containing vast changes in profile of the Raman spectrum of the v(CN) region between 2100 and 2150 cm^{-1} (ref. 49). By changing the [CN⁻]/[Ag⁺] ratio, the temperature,

and the $[Ag]_T$ concentration, the scheme shown below, containing 11 complexes and ion-pairs, has been established:
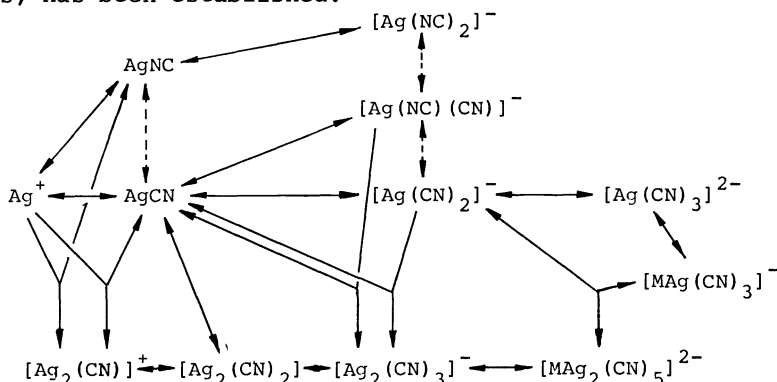
Resolution of spectrum of a solution of composition $[Ag^+]$ = $[CN^-]$ = 0.5 at 233 K into 6 underlying features is illustrated in Fig. 12(a). The 2nd derivative in Fig. 12(c) illustrates how differentiation aids the identification of band positions. Confirmation of the band analysis procedure is by comparison of the differentiation of the sum of the VIPER-resolved components Fig. 12(b) with the observed 2nd derivative of the spectrum (Fig. 12(c)).

The points which emerge are the following. (1) Complexation does *not* proceed from the 3:1 to the 4:1 stage. (2) Temperature variation establishes that equilibria exist between linkage isomeric M-NC and M-CN species for both the 1:1 (2 bands) and 2:1 (3 bands) complexes. (3) Temperature studies also highlight a large entropy change between the tetrahedral monocyano-Ag(I), $(NH_3)_3Ag(CN)$, and linear biscyano-Ag(I), $[Ag(CN)_2]^-$. This has been confirmed by potentiometric titration in the irregular stepwise stability constants obtained for the Ag(I)/CN^- system in ammonia; $\log K_1$ = 7, $\log K_2$ = 9, $\log K_3$ = 1.5 (ref. 64). (4) Changes in the species concentrations cause bands to appear in the spectra of more concentrated Ag^+ solutions. These are attributable to aggregation: $(AgCN)_2$, 2127 cm^{-1} (bridging), 2113 cm^{-1} (terminal); $[Ag_2(CN)]$, 2132 cm^{-1}. (5) Changes in the counter cation from Na to Li and K indicate ion-pairing between the counter cation and the 3:1 $[Ag(CN)_3]^{2-}$ complex: $M^+..[Ag(CN)_3]^{2-}$.

Whilst complexation of Ag(I) by CN^- in ammonia involves a large number and variety of species, a similar spectroscopic titration shows that complexation of Hg^{2+} by CN^- proceeds in 4 simple successive addition steps involving no change in the tetrahedral geometry around the central Hg^{2+} cation (ref. 65). It is worthy of note that $Hg(CN)_2$ is linear in the solid, and $[Ag(CN)_2]^-$ is linear-unsolvated in liquid ammonia, and that biscyano-Hg(II) has tetrahedral geometry in solution in ammonia.
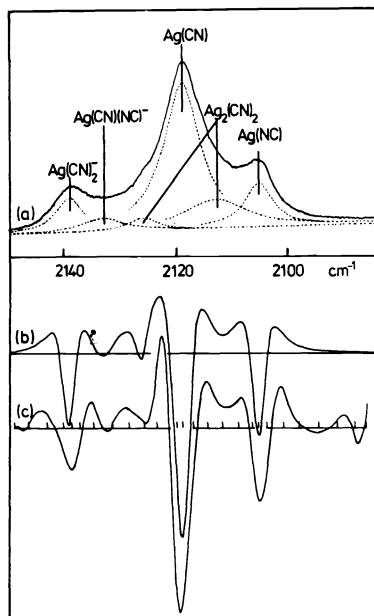

Fig. 12 The ν(CN) region of the Raman spectrum of a liquid NH_3 solution of composition AgCN (R=44) at 233K. (a) observed spectrum and its decomposition into 6 component bands, (b) calculated 2nd derivative spectrum obtained by summation of the 2nd derivatives of the component bands shown in (a), and (c) 2nd derivative of the observed spectrum. The similarity of (b) and (c) provides confidence in the analysis.

Complexation of Au(I) by CN^- in ammonia contrasts with that of Ag(I). Like the $[Ag(CN)_2]^-$ complex, $[Au(CN)_2]^-$ is linear as proved by the mutual exclusions of the infrared and Raman vibrations (ref. 66): the $\nu_1(CN)$ band at 2158 $cm^{-1}(p)$ in the Raman is absent from the infrared, and the $\nu_3(CN)$ at 2152 cm^{-1} in the infrared is absent from the Raman. Unlike the Ag(I)/CN^- system the Raman spectra of solutions in the range 2 > $[CN^-]/[Au^+]$ > 1 show no changes in relative band intensities between 220 K and 300 K. With no large entropy change between the 1:1 and 2:1 stages we conclude that no geometry changes occur in this step and that the 1:1 species exists in ammonia as linear $[(NH_3)Au(CN)]$; $\nu(CN)$ for this complex appears in both infrared and Raman (*dp*) at 2142 cm^{-1}.

Five cyano-complexes in stepwise equilibria on the square-plane around the Pd^{2+} cation have been identified. Successive square-planar addition to Pd^{2+} is to be expected but the vibrational spectra of solutions between 1 < $[CN^-]/[Pd^{2+}]$ < 3 are time dependent (ref. 67). With the complementary use of Raman and infrared spectra all 11 $\nu(CN)$ vibrations due to the 1:1, 2:1 (*cis-* and *trans-*), 3:1 and 4:1 complexes have been assigned in spite of the fact that they are all situated between 2152 and 2127 cm^{-1}. It was ascertained that the changes observed in the spectra with time were due to a slow interconversion from *trans-* to *cis-*$[(NH_3)_2Pd(CN)_2]$ at ambient temperature. A semi-quantitative infrared examination of solutions at $[CN^-]/[Pd^{2+}]$ = 2 gave $t_{\frac{1}{2}} \approx$ 6h at 298 K. The *trans-*isomer can be kinetically trapped in ammonia solution at 233 K.

Surprisingly, solutions of Pt(II)/CN^- mixtures are unlike their Pd(II) analogues. Complexation occurs as expected in square-planar geometry at the Pt(II) centre, but the bands in the spectra correspond to 2:1 and 4:1 complexes only (ref. 68): *trans-*$[(NH_3)_2Pt(CN)_2]$, 2117 cm^{-1} (ir), A_1, and 2143 cm^{-1} (R, p) A_g; $[Pt(CN)_4]^{2-}$, 2125 cm^{-1} (ir), E_u, 2158 cm^{-1} (R, p), A_{1g} and 2143 cm^{-1} (R, dp), B_{1g}. Hence the thermodynamically favoured processes are represented by,

$$[(NH_3)_4Pt]^{2+} + 2CN^- = trans-[(NH_3)_2Pt(CN)_2], \qquad (7)$$

$$trans-[(NH_3)_2Pt(CN)_2] + 2CN^- = [Pt(CN)_4]^{2-} \qquad (8)$$
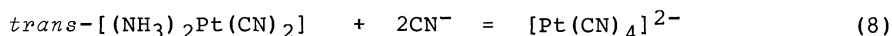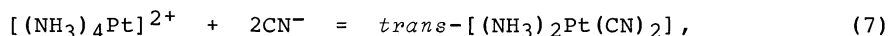
Unlike the Ag(I)/CN^- system there is no evidence for linkage isomerism in the cyano-complexes of Hg^{2+}, Au^+, Pd^{2+} and Pt^{2+} in liquid ammonia. The vibrational spectra also present some evidence for outer-sphere complexation (solvent-shared ion-pairs) between the anions NO_3^- and SCN^-, and Pd^{2+} and Pt^{2+} in ammonia.

Acknowledgements

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