Raman Spectra of Liquid Ammonia Solutions of Metal Salts

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Summary Liquid ammonia solutions of simple metal salts give good Raman spectra with little interference from solvent bands; the metal–nitrogen stretching vibrations indicate unusual co-ordination numbers with Zn^{2+}, Hg^{2+}, and Ag^{+}, and ion-association effects are smaller than in aqueous solutions.

RECENT reports[1,2] concerning the Raman spectra of liquid ammonia and its solutions prompt this communication. We have observed the Raman spectra of various nitrate, bromide, iodide, thiocyanate, and cyanide salts of monovalent, bivalent, and trivalent metal ions, in the concentration range 0·5—4M in liquid ammonia between −30 and −60 °C.

The pure ammonia spectrum contains strong N–H stretching bands[1,3] and weak H–N–H bending bands.[4] In addition there is a very weak band at *ca.* 1840 cm^{-1} and another at *ca.* 240 cm^{-1}. The Raman spectrum of water shows similar but more extensive features.[5]

All salts studied (except those of sodium and potassium) show a polarised low-frequency band which we attribute to a symmetric metal–nitrogen stretching vibration; frequencies are given in the Figure. The band for the lithium salts is much sharper than it is in the spectra of solutions at 20 °C,[1] and consequently it is a clearly resolved feature. The trend in Group IIB is irregular; comparison of these frequencies with i.r. frequencies of solid compounds and Raman frequencies of aqueous solutions suggests that zinc(II) is present in *ca.* 1M ammonia solution in 4- and 6-co-ordinated forms, whereas mercury(II) is only four-co-ordinate under the experimental conditions. The spectra of silver salts show only a very weak feature at *ca.* 270 cm^{-1}; the band observed[6] for the diammine silver ion at 370 cm^{-1} (which we confirm) is absent in the liquid ammonia solution. A tetrammine silver complex is possibly present.

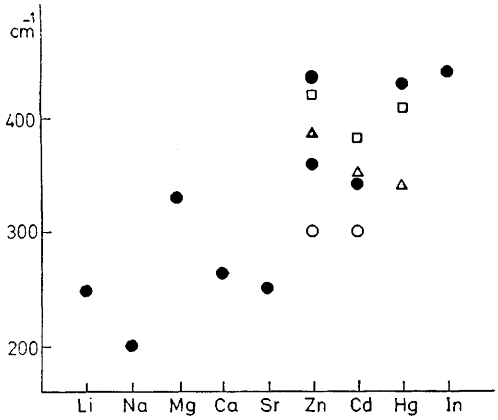

FIGURE. Raman frequencies of the polarised low-frequency bands assigned to the symmetric M–N stretching vibration in liquid ammonia solutions ●; i.r. values for solid tetrammine salts (G. M. Barrow, R. H. Krueger, and F. Basolo, *J. Inorg. Nuclear Chem.*, 1956, **2**, 340) □ and solid hexammine salts (L. Sacconi, A. Sabatini and P. Gans, *Inorg. Chem.*, 1964, **3**, 1772) ○. The point for Na$^+$ is taken from ref. 2. The points Δ represent the frequencies assigned to the M–O symmetric stretching vibrations in the Raman spectra of aqueous solutions.

Measurements of bulk quantities such as transference numbers,[7] ion activities,[8] and conductances[9] indicate that solutions of electrolytes in liquid ammonia (with its lower dielectric constant) possess much larger degrees of ion-association than similar solutions in water. By contrast, the effects of ion-association on the spectra are much smaller. For example, the splitting of the degenerate N–O stretching vibration of the nitrate ion is only *ca.* 20 cm^{-1} in the concentrated solutions of bivalent metal nitrates, as compared to 63 cm^{-1} in a dilute aqueous magnesium nitrate solution.[10] There is no clear evidence for 'contact ion-pairing' (anion co-ordination) in the O–N–O bending region, except with the trivalent indium ion. We suggest that the ligating ammonia molecules shield the anions more effectively from the cations than do water ligands and are also stronger donors.

Most anion bands are sharper in ammonia than in water, partly because of the lower temperature. For example, the symmetric N–O stretching band has a minimum half-width of *ca.* 7 cm^{-1} in water. In ammonia at room temperature it is 11 cm^{-1}, but at −40 °C it becomes *ca.* 2·5 cm^{-1}; consequently a peak associated with $(N^{18}O^{16}O_2)^-$ can easily be resolved in most spectra (isotopic shift 21 cm^{-1}, natural abundance 1/500), even at high solute concentrations.

We conclude that liquid ammonia is an excellent solvent for Raman spectroscopy, just as water is. The effects of ion-association are, unexpectedly, less noticeable and working at low temperature gives particularly well resolved spectra. Further study of these spectra should lead to new insights into solution processes and to a better understanding of solute–solvent interactions.

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[1] D. J. Gardiner, R. E. Hester, and W. E. L. Grossman, *J. Raman Spectroscopy*, 1973, **1**, 87; *J. Chem. Phys.*, 1973, **59**, 175; G. W. Leonard, E. R. Lippincott, R. E. Nelson, and D. E. Sellers, *J. Amer. Chem. Soc.*, 1955, **77**, 2029.

[2] J. H. Roberts, A. T. Lemley, and J. J. Lagowski, *Spectroscopy Letters*, 1972, **5**, 271.

[3] B. Bettignies and F. Wallart, *Compt. rend.*, 1970, **B271**, 640; **24A**, 1385, 2045.

[4] T. Birchall and I. Drummond, *J. Chem. Soc.* (*A*), 1970, 1859.

[5] G. E. Walrafen in 'Water. A Comprehensive Treatise,' ed. F. Franks, Plenum Press, New York, 1972.

[6] M. G. Miles, J. H. Patterson, C. L. Hobbs, M. J. Hopper, J. Overend, and R. S. Tobias, *Inorg. Chem.*, 1968, **7**, 1721.

[7] J. B. Gill, *J. Chem. Soc.*, **1965**, 5730.

[8] J. Baldwin, J. Evans, and J. B. Gill, *J. Chem. Soc.* (*A*), 1971, 3389; J. B. Gill and B. M. Lowe, *J.C.S. Dalton*, 1972, 1959.

[9] V. Hnizda and C. A. Kraus, *J. Amer. Chem. Soc.*, 1949, **71**, 1565.

[10] T. G. Chang and D. E. Irish, *J. Phys. Chem.*, 1973, **77**, 52.