

SHORT COMMUNICATIONS

OBSERVATION OF ION-PAIRS IN AQUEOUS SOLUTIONS BY VIBRATIONAL SPECTROSCOPY*

By H. LEE†‡ and J. K. WILMSHURST†

Mathieu and Lounsbury,¹ observing in strong aqueous solutions of both lithium and sodium nitrate that the doubly degenerate stretching mode of the anion was split into two components, interpreted this splitting in terms of ion-pair formation. We suggest that generally, for those strong electrolytes having a complex ion con-

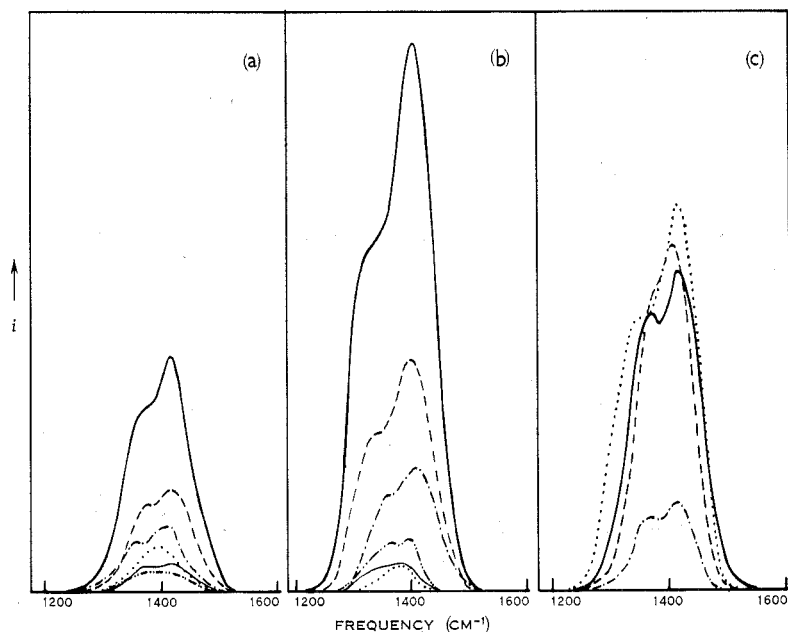


Fig. 1.—Raman spectra in the 1400 cm^{-1} region of:

- (a) LiNO_3 : ——— 3.0M; --- 1.5M; - - - 0.75M; ···· 0.6M; ····· 0.3M; ——— 0.6M LiNO_3 + 2.0M LiCl .
 (b) AgNO_3 : ——— 8.0M; --- 4.0M; - - - 1.6M; ····· 0.8M; ——— 0.4M; ···· 0.2M.
 (c) saturated aqueous solutions: ——— LiNO_3 ; --- NaNO_3 ; - - - KNO_3 ; ···· AgNO_3 .

taining at least a threefold rotation axis, the presence of ion-pairs may be established by observation of the removal of degeneracy of a vibration which is degenerate in dilute solution.

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† Division of Chemical Physics, CSIRO Chemical Research Laboratories, Melbourne.

‡ Present address: Department of Chemistry, Talan Sultan, Petaling Taya, Kuala Lumpur, Malaysia.

¹ Mathieu, J. P., and Lounsbury, M., *Disc. Faraday Soc.*, 1950, 9, 196.

Raman spectra of the 1400 cm^{-1} region are shown in Figure 1 for a number of concentrations of lithium and silver nitrate in water. In both cases it is apparent that only at very low concentrations (0.6M in LiNO_3 and 0.2M in AgNO_3) is the asymmetric stretching band $\nu_3(e')$ observed to be single and symmetric, being split into two components for concentrations of 0.75M or greater. Figure 1 also illustrates removal of the degeneracy of $\nu_3(e')$ in 0.6M lithium nitrate by the addition of lithium ions in the form of lithium chloride. In addition, the spectra of saturated solutions of lithium, sodium, potassium, and silver nitrates are shown for comparison. From these results it must therefore be concluded that the splitting of $\nu_3(e')$ at higher

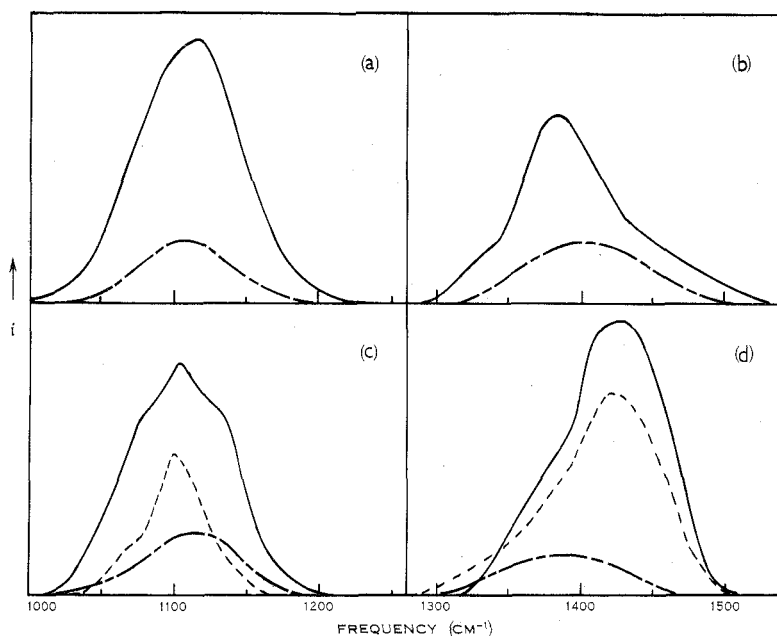


Fig. 2.—Raman spectra of dilute and concentrated aqueous solutions of strong electrolytes.

(a) LiClO_4 : ——— 5.0M ; - - - - - 0.5M .

(b) K_2CO_3 : ——— 5.0M ; - - - - - 0.5M .

(c) ——— $4.0\text{M } (\text{NH}_4)_2\text{SO}_4$; - - - - - $2.0\text{M } \text{Li}_2\text{SO}_4$; ····· $0.4\text{M } (\text{NH}_4)_2\text{SO}_4$.

(d) ——— $5.0\text{M } \text{NH}_4\text{Cl}$; - - - - - $4.0\text{M } (\text{NH}_4)_2\text{SO}_4$; ····· $0.4\text{M } (\text{NH}_4)_2\text{SO}_4$.

concentrations is due entirely to the effect of the cation. Similar results have also been obtained for the $\nu_3(f_2)$ sulphate band in lithium and ammonium sulphate, the $\nu_4(f_2)$ ammonium band in ammonium sulphate and ammonium chloride, the $\nu_3(e')$ carbonate band in potassium carbonate and the $\nu_3(f_2)$ perchlorate band in lithium perchlorate, the spectra of concentrated and dilute solutions of each of these systems being shown in Figure 2. We assert therefore that ion-pair formation occurs at the higher concentrations in all these solutions.

Obviously the present approach is purely operational in that we have defined and observed ion-pairs only in an operational manner and have nowhere determined anything of their real nature. In this respect, however, it is interesting to observe

that although the concept of an ion-pair is well accepted in the literature,^{2,3} the actual definition of an ion-pair varies among workers and in nearly all cases where experimental data have been interpreted in terms of ion-pair formation the real nature of the ion-pair has not been determined unambiguously.

If we consider lithium nitrate for discussion, then since $\nu_3(e')$ is degenerate in dilute solution, the anion in dilute solution must necessarily be in an environment having a common threefold rotation axis. Removal of this degeneracy in concentrated solution is therefore associated with the increased proximity of the cation, the effect of which is to define an axis of reference for the anion not coincident with its threefold axis. We can call this ion-pair formation.

The distinction between an ion-pair with ions in mutual contact and a molecular species is probably one of semantics. Nevertheless in both circumstances considerable mutual polarization will result and thus, besides removal of degeneracies, the frequencies of all bands should be markedly shifted from those of the unassociated ions as observed for instance in the nitric acid-water system.⁴ No such frequency shifts were observed in any of the systems investigated in the present work. In addition the observation of ion-pairs in such relatively dilute solutions (0.75M LiNO₃ for instance) is also a strong argument against considering them as ions in mutual contact. Separation of the ions by one or more water molecules should greatly decrease this polarization effect, but only in the former case would the anion-cation interaction be expected to be sufficient to define effectively an axis opposed to the rotation axis and thereby remove the degeneracy of the anion. Thus we believe the ion-pairs observed here to be of the type involving one water molecule common to the hydration sheaths of both ions. It is therefore not surprising that such ion-pairs have not been observed previously by their ion-ion stretching modes.

It should be noted in conclusion that ion-pairs observed by vibrational spectroscopy, where the time of observation is of the order of 10^{-12} sec, may not be the same as those determined by other methods involving a different order of lifetimes. This is probably the basic cause of the apparent discrepancy between the high concentrations of "spectroscopic" ion-pairs even in dilute solutions as compared to the very low concentrations of "kinetic" ion-pairs in the same solutions.⁵

Experimental

The Raman spectra of the aqueous electrolyte solutions were obtained with a Hilger Raman source and two-prism glass spectrograph having 21 Å/mm dispersion using mercury 4358 Å radiation for excitation, 4047 Å radiation being filtered out with a saturated solution of sodium nitrite. The spectra were photographed on Ilford R40 panchromatic plates and recorded graphically with a Joyce-Loebl microphotometer.

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² Robinson, R. A., and Stokes, R. H., "Electrolyte Solutions." (Butterworths: London 1955.)

³ Hamer, W. J. (Ed.), "The Structure of Electrolytic Solutions." (John Wiley: New York 1959.)

⁴ Young, T. F., in "The Structure of Electrolytic Solutions." (Ed. W. J. Hamer.) p. 39. (John Wiley: New York 1959.)

⁵ Davies, C. W., *Trans. Faraday Soc.*, 1927, **23**, 351.