were obtained in the carbonyl region on methylene chloride solutions. The P=O and P=S regions of the spectrum were obtained on Nujol mulls. The spectra were recorded on a Perkin-Elmer 521 spectrometer which had been calibrated with indene and polystyrene.

Acknowledgment.—This work was carried out under the sponsorship of the U. S. Army Missile Command, Redstone Arsenal, Ala., under Contract No. DAAH01-67-C-0655.

Correspondence

Proton Magnetic Resonance and Vibrational Spectra of Concentrated Aqueous Solutions of Aluminum(III) Nitrate. The Distinction between Intimate and Solvent-Separated Ion Pairs

Sir:

Recently much attention has been devoted to using the vibrational spectroscopy of concentrated aqueous solutions containing the nitrate ion as a probe to detect the formation of ion pairs.[1-8] The basis of the application is that if there occurs a "strong" specific association of a cation with the NO_3^- ion along the C_2 axis of the latter, the "site" symmetry of NO_3^- is lowered from D_{3h} to C_{2v} (or C_s). This lowering of the symmetry is usually manifested in the splitting of the band for the doubly degenerate stretching mode (ν_3) into two components in the ir and Raman spectra and in the appearance in the ir spectrum of the ν_1 band which is forbidden for the free NO_3^- ion.[1-8]

These effects have been observed for a variety of nitrates of the representative elements (*e.g.*, $Ca(NO_3)_2$ and $Al(NO_3)_3$[2-8]), and it is generally agreed that they are due to a specific association of NO_3^- with a cation. However, with the use of vibrational spectroscopy alone, it has not been possible to distinguish unequivocally whether NO_3^- in these "ion pairs" resides in the first or second hydration sphere of the cation, that is, to distinguish whether an intimate or solvent-separated ion pair is formed. By using proton magnetic resonance (pmr) spectroscopy we have been able to show that the primary hydration number of the Al(III) ion is 6 in concentrated aqueous aluminum nitrate solutions and from this result we infer that the Al^{3+}–NO_3^- ion pair, detected in vibrational spectroscopy, is a solvent-separated one.

A typical 60-MHz pmr spectrum of a concentrated aqueous solution of $Al(NO_3)_3$ at a low temperature is represented in Figure 1. From the dependence of the relative signal intensities upon the solution composition, the low-field resonance is assigned to water within and the high-field one to water outside the first hydration sphere of the Al(III) ion. The large area of the coordinated water signal relative to that of the "bulk" water permits the determination of the very precise hydration numbers listed in Table I which also includes signal line widths and relative chemical shifts. It is apparent that the hydration number of the Al(III) ion in the concentrated solutions of $Al(NO_3)_3$ is not significantly different from 6 and it exhibits no apparent trend with the temperature or composition of the solution. In the 100-MHz pmr spectra of solutions having the compositions listed in Table I, the bulk and coordinated water signals are well resolved at −14° and provide a hydration number for Al(III) of 6.01 ± 0.02.[9] The hydration number of 6 is consistent with the values obtained from: (a) isotope dilution studies of $Al(ClO_4)_3$ aqueous solutions;[10] (b) O^{17} nmr studies of $Al(ClO_4)_3$ aqueous solutions;[11] and (c) pmr studies of $AlCl_3$ aqueous solutions.[12]

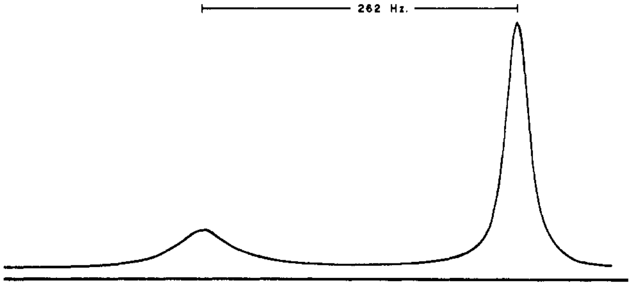

Figure 1. Pmr spectrum of a 2.1 *m* aqueous solution of $Al(NO_3)_3$ at −40°. The magnetic field increases from left to right.

Unless a coordination number of 7 for Al(III) is invoked, our pmr data demonstrate that only trace quantities of NO_3^- can reside in the primary hydration sphere of the Al(III) ion in concentrated aqueous nitrate solutions. Nonetheless, Raman and ir data indicate that significant quantities of NO_3^- ion are in some way associated to Al(III). Hester and Plane[2]

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(1) J. R. Ferraro, *J. Mol. Spectry.*, **4**, 99 (1960).

(2) R. E. Hester and R. A. Plane, *Inorg. Chem.*, **3**, 769 (1964).

(3) H. Lee and J. K. Wilmshurst, *Australian J. Chem.*, **17**, 943 (1964).

(4) R. E. Hester and R. A. Plane, *J. Chem. Phys.*, **40**, 411 (1964).

(5) R. E. Hester and R. A. Plane, *ibid.*, **45**, 4588 (1966).

(6) D. E. Irish and G. E. Walrafen, *ibid.*, **46**, 378 (1967), and references therein.

(7) D. E. Irish and A. R. Davis, *Can. J. Chem.*, **46**, 943 (1968).

(8) R. E. Hester and K. Krishman, *J. Chem. Phys.*, **46**, 3405 (1967).

(9) A referee has expressed concern that the systems discussed here might be solids. It should be emphasized that they are *solutions*. At the temperatures listed in Table I, the solutions, though viscous, flow freely, do *not* exhibit a Tyndall effect, and do *not* deposit precipitates even when stored over powdered glass at −55° for 8 hr. In addition, the pmr signal shapes for solutions having the compositions listed in Table I are characteristic of those for liquids, not glasses or solids. When the solutions were cooled below the freezing point (< −65°), a copious amount of precipitate developed in the nmr tube and the pmr signals could be detected no longer with the high-resolution Varian A-60A spectrometer which was used.

(10) H. W. Baldwin and H. Taube, *J. Chem. Phys.*, **33**, 206 (1960).

(11) R. E. Connick and D. N. Fiat, *ibid.*, **39**, 1349 (1963).

(12) R. E. Schuster and A. Fratiello, *ibid.*, **47**, 1554 (1967).

TABLE I

HYDRATION NUMBER OF THE Al(III) ION IN AQUEOUS SOLUTIONS OF $Al(NO_3)_3$

Solution compn, mol		Temp, °C	Hydration no.[a] (±0.02)	Chem shift (±0.5),[b] Hz	Line width (±0.5),[c] Hz	
$Al(NO_3)_3$	H_2O				$\Delta\nu_c$	$\Delta\nu_f$
1	25.8	−30	5.97	240	97	37
		−40	6.02	262	40	13
		−45	5.97	262	36	12
		−50	5.95	261	36	13
		−55	6.02	261	37	14
1	22.15	−30	6.02	243	113	44
		−40	6.02	262	54	22
		−50	5.01	260	52	22
1	35.0	−40	6.02	260	34	12

[a] Hydration numbers were calculated using the relative areas of the coordinated and bulk water pmr signals, and the known solution composition: N. A. Matwiyoff, *Inorg. Chem.*, **5**, 788 (1966); N. A. Matwiyoff and W. G. Movius, *J. Am. Chem. Soc.*, **89**, 6077 (1967). Relative areas were obtained by planimetry and manual integration. [b] Shift of the coordinated water pmr signal downfield relative to the free-water signal. [c] Width of the line at half the maximum height: $\Delta\nu_c$ refers to the coordinated- and $\Delta\nu_f$ to the free-water signal.

have reported that the asymmetric stretching vibration of the NO_3^- ion (the degenerate ν_3 vibration of the free ion) in $Al(NO_3)_3$ aqueous solutions gives rise to Raman lines at 1420 and 1340 cm^{-1}. Our own Raman spectra of solutions having the compositions listed in Table I consist in this region of two lines which are centered at 1410 and 1320 cm^{-1} and which have approximately equal integrated intensities. At 24°, the ir spectra in this region also consist of two broad bands of approximately equal intensity centered at 1320 and 1400 cm^{-1}. Low-temperature ir spectra consist of narrow bands of equal intensity at 1320, 1380, and 1436 cm^{-1}.[13] Although the quantitative distribution of species cannot be extracted from the data we obtained, the relative intensity of the bands near 1400 and 1300 cm^{-1} requires that a large fraction of the NO_3^- ion be coordinated. Consequently, considering the pmr data and accepting a coordination number of 6 for Al(III), we conclude that the coordination of the NO_3^- ion detected in a vibrational spectroscopy experiment can occur, in this case, only *via* the second coordination sphere of the cation.

In a larger context, the results considered here demonstrate that the lifting of the degeneracy of the vibrational modes of an anion in the presence of a cation is, of itself, not a sufficient condition for concluding that the anion has entered the first coordination sphere of the cation. Anticipating advances in ir and Raman instrumentation, we would also suggest that, for the systems discussed here, the detection of anion–cation stretching vibrations in the ir or Raman spectrum should not be taken as proof of a first coordination sphere interaction. Taube[14] has discussed the possibility that cations of high charge might exhibit an ability to bind ligands specifically in their second coordination spheres. This possibilty of a residual specific binding power, which may be manifested in the ir and Raman spectra, appears especially attractive in view of the large solvation numbers obtained from isotope dilution studies of the Fe(III) ion in solutions of $Fe(ClO_4)_3$ in methanol.[15]

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(13) Unfortunately, we do not have the equipment necessary to record ir spectra at a constant low temperature. The low-temperature spectra were obtained by packing the sample cell in Dry Ice for 10 min, removing it, and then scanning through the region of interest until the cell had warmed to 0°. The effects were reversible with temperature and the sample remained a liquid throughout the temperature range. The spectrum of polycrystalline $Al(NO_3)_3 \cdot 9H_2O$ and $Al(NO_3)_3 \cdot 9H_2O$ dispersed in ice in this region consists of a relatively weak narrow band centered at 1384 cm^{-1}.

(14) H. Taube, *Progr. Stereochem.*, **3**, 95 (1962) (see especially p 110); see also J. H. Swinehart, T. E. Rogers, and H. Taube, *J. Chem. Phys.*, **38**, 398 (1963).

(15) T. E. Rogers, J. H. Swinehart, and H. Taube, *J. Phys. Chem.*, **69**, 134 (1965).

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RECEIVED NOVEMBER 15, 1967

Vibrational Spectra of Hexafluoroiodate Salts

Sir:

The recent note by Christe, Guertin, and Sawodny[1] on the Raman and infrared spectra of $CsIF_6$ prompts this communication reporting work of a similar nature at the University of Glasgow and Argonne National Laboratory. Additional results obtained by Christe, Guertin, and Sawodny are also included. For comparison purposes the data on the vibrational spectra are given in Table I.

All quoted Raman spectra were run on Cary Model 81 spectrometers using Hg 4358-Å excitation (Argonne; Christe, *et al.*) or the 6328-Å line of a Spectrophysics He–Ne 50-MW laser (Glasgow). Christe, Guertin, and Sawodny, as well as Sharp and Beaton, transferred their samples to Pyrex Raman tubes in a drybox. At Argonne National Laboratory, a solution of the salt in IF_5 was transferred to a sapphire tube using Kel-F tubing attached to a vacuum line and the excess solvent was pumped off.

The Raman spectra previously reported by Christe, Guertin, and Sawodny are in essential agreement with those obtained at Argonne National Laboratory.

The Raman spectrum of an earlier sample (listed as sample 2) prepared by Christe, *et al.*, is more like that of the Glasgow work, whereas its infrared spectrum is more like that of their own later preparation.

The sample preparation for the infrared measurements was different in each case. Christe, *et al.*, ran the material as a dry powder between AgCl plates or polyethylene disks using Beckman IR9, IR-12, and IR-11 instruments. At Glasgow, infrared spectra over the range of 4000–400 cm^{-1} were obtained from Nujol mulls using a Perkin-Elmer Model 225 spectro-

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(1) K. O. Christe, J. P. Guertin, and W. Sawodny, *Inorg. Chem.*, **7**, 626 (1968).