TABLE I

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

Solution compn, mol $Al(NO_3)_3$	H_2O	Temp, °C	Hydration no.[a] (±0.02)	Chem shift (±0.5),[b] Hz	Line width (±0.5),[c] Hz $\Delta\nu_c$	$\Delta\nu_f$
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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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).

TABLE I

VIBRATIONAL SPECTRA OF HEXAFLUOROIODATE SALTS

Christe, *et al.*				Glasgow				Argonne National Laboratory[a]	
Ref 1		Sample 2		KIF_6		$CsIF_6$		$CsIF_6$, $RbIF_6$, KIF_6	$CsIF_6$
Raman	Ir	Raman	Ir	Raman	Ir	Raman	Ir	Raman	Ir
							64		
					135		136		
					223				
							210		
(274)								275 vvw	
	285			285 vw	285		280		
(322)	322				323		316		
					340 m				
							364		375 m
			468						
	485								
			495						
					526				
	534 m		535 m			536 ms	535 b, vs		
546 m		545 w, b		540 m, b	543 } vs			545 m	
					567				565 vs
591 m	592 m		589					595 m	590 vs
							599 s		
			605 m						
						616			
		620 m							
				625 s	623 } s				
					631				
				644 ms					
							649 m		
	653 m		652 w			655 m			
677 m			678 m					677 s	677 s
	754 vw		754 w						
	828 w								
	853 w								
	888 m		891 m						

[a] Work performed under the auspices of the United States Atomic Energy Commission.

photometer and over the range 400–40 cm^{-1} from polyethylene disks using an RIIC FS-720 interferometer with a Fourier transform computer (FTC 100) working in the double-beam mode. Samples were allowed to hydrolyze and spectra rerun. Bands obviously due to hydrolysis products are not recorded in Table I. At Argonne National Laboratory, CsF disks were prepared in an He-atmosphere drybox and mounted in the center of a Kel-F gas cell of 5-mm path length fitted with AgCl windows. Spectra of the CsF disk before and after treatment with IF_5 vapor were run on a Beckman IR-12 spectrophotometer. The bands listed are only those which appeared after the IF_5 treatment. The strongest band mentioned by Christe, *et al.*, at 485 cm^{-1}, is possibly due to hydrolysis products, which show a strong band in the 490–400-cm^{-1} region. It is a strong band and appears as a band of medium intensity in the Argonne spectra of the untreated CsF disk. Also, the bands in the 800-cm^{-1} region of the spectra of Christe, *et al.*, must be due to hydrolysis products since they do not appear in either of the other spectra and are in the region characteristic of I=O stretching vibrations.[2]

The infrared spectra recorded by the three groups agree fairly well except that a strong band is not observed near to 677 cm^{-1} by the Glasgow group. The detailed spectra depend upon the counter ion as might be expected.[3] None of the sets of data can be reconciled with the presence of a discrete octahedral IF_6^- anion, which would require two ir bands and three Raman bands without ir–Raman coincidence. In the isoelectronic xenon compound, XeF_6, three solid phases have been isolated.[4] There seems to be strong evidence that polymeric structures are present in xenon hexafluoride.[5] Similarities in Raman spectra between some preparations and solid (rather than gaseous) xenon hexafluoride suggest equally complex anions in $CsIF_6$ and KIF_6.

It is evident that in the hexafluoroiodates(V) also several different solid phases must occur depending on rather subtle differences in the method of preparation. We cannot suggest possible structures for any of the preparations at this time. We cannot even unequivocally assign all vibrational bands to unique identifiable

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(2) D. F. Smith and G. M. Begun, *J. Chem. Phys.*, **43**, 2001 (1963); W. E. Dasent and T. C. Waddington, *J. Chem. Soc.*, 2429 (1960); 3350 (1960).

(3) D. H. Brown, K. R. Dixon, C. M. Livingston, R. H. Nuttall, and D. W. A. Sharp, *ibid.*, 100 (1967).

(4) P. A. Agron, C. K. Johnson, and H. A. Levy, *Inorg. Nucl. Chem. Letters*, **1**, 145 (1965).

(5) F. Schreiner, D. W. Osborne, and J. G. Malm, to be published.

phases of established chemical composition. The alkali hexafluoroiodates are reactive and very hygroscopic materials, difficult to purify and maintain as pure materials.

The Raman spectrum of $CsBrF_6$ has also been obtained at Argonne National Laboratory on a sample prepared by the method used for $CsIF_6$. Its bands are at 452, 505, 528, and 565 cm^{-1}. The 452-cm^{-1} band is the more intense one and the sharpest. The 505-cm^{-1} band is weak. Reliable infrared spectra for this material have not yet been obtained. Again it is apparent that the pattern of the Raman bands is not that expected for an octahedral species and that it differs from the pattern of the $CsIF_6$ bands.

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