often severe overlap of the weak new bands with either this water band or an oxyanion line made quantitative measurements of their intensities, and hence of their degrees of depolarization, impractical in most cases. Depolarization ratios of $\rho = 0.2$ and $\rho = 0.11$ were obtained for the new lines from solutions of cupric and mercuric ions, respectively.[3]

The absence of a low frequency polarized line from the spectrum of liquid water, the lack of dependence of the new lines on the nature of the oxyanion in solution, and the constant frequency obtained from solutions containing the same metal ion lead to the conclusion that the origins of these new lines are in some symmetric forms of vibration within the hydration sheaths of the dissolved metal ions. Evidence in support of this assignment is found in the work of Mathieu[5] and Lafont[6] on solid hydrates containing the ions $Mg(H_2O)_6^{2+}$ and $Zn(H_2O)_6^{2+}$. The polarized nature of the new lines suggests their assignment to metal–water-oxygen symmetric stretching modes, and the smallness of the frequency dependence on the mass of the metal ion then follows from the necessity for the metal to remain stationary in such vibrational modes. Thus all divalent ions except copper listed in Table I give lines in the narrow region 360–400 cm.$^{-1}$, consistent with the formation of hexacoordinated aquo complexes in each case. Jahn–Teller modifications in the case of the copper complex may account for its nonconformity. The line intensities, as well as the frequencies, were higher for the gallium and indium aquo complexes than for the other metals studied. These are clearly related to the stronger bonding of the hydration sheaths brought about by the increased ionic charges. The gallium and indium solutions were also found to be exceptionally viscous—a property fully consistent with a high degree of hydration.[7,8]

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A Raman Spectrophotometric Comparison of Interionic Association in Aqueous Solutions of Metal Nitrates, Sulfates, and Perchlorates[1]

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Recent reports from our laboratory have dealt in detail with complex formation in aqueous solutions of calcium nitrate[2] and indium sulfate.[3] These earlier results arose from the more general study of metal–oxyanion associations in aqueous solutions which we briefly report on here.

The complete Raman spectra of the uncomplexed oxyanions nitrate, sulfate, and perchlorate are well known, that of the nitrate ion being consistent with its D_{3h} symmetry, those of sulfate and perchlorate ions being consistent with T_d symmetries.[4] In concentrated aqueous solutions it is known from a variety of physical measurements that many metal nitrates[5,6] and sulfates[7,8] form associated species, and though the evidence is much less abundant, it appears that in concentrated perchloric acid even the perchlorate ion forms a complex.[9]

We have used a Cary Model 81 Raman spectrophotometer to obtain Raman spectra of a wide range of metal nitrates, sulfates, and perchlorates, taking the usual precautions to ensure precise frequency, intensity, and depolarization values.[2,3] The spectra reported were all obtained from near-saturated solutions at room temperature, in order to force as much ion association as possible. Tables I, II, and III summarize our spectral frequency data and demonstrate that using the criterion that strong association between an oxyanion and a metal ion will distort the symmetry of the oxyanion, it is evident that nitrate complexes are much more common than are sulfate complexes, while there is no evidence here for perchlorate complexes. However, conductivity and solubility measurements show that most metal sulfates are very highly associated even in dilute aqueous solution.[7,8] The Raman frequencies suggest that, with the single exception of indium, these metal sulfate complexes are solvent separated; at least one water molecule being trapped between the metal ion and the sulfate ion. This interpretation is consistent with Eigen's findings from chemical relaxation spectra.[10] The new frequencies arising from nitrate complexes can all be accommodated by a C_{2v} point group assignment, indicative of complexing through oxygen atoms of the NO_3^- ions rather than through the nitrogen atoms, but in no case can a line characterizing the metal–oxygen bonds be assigned. The extreme distortions of nitrate ion symmetry make it probable that the association with metal ions is at least through intimate ion pairing, but some small degree of covalent bond formation cannot be ruled out. The magnitude of the splitting of the $\nu_2(E')$ line of D_{3h} nitrate into ν_4 (B_1) and $\nu_1(A_1)$ lines characteristic of the distorted C_{2v} ion has been used as a measure of the dissymmetry arising in the nitrate group as a result of interaction

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TABLE I

RAMAN FREQUENCIES, IN CM.$^{-1}$, FROM CONCENTRATED AQUEOUS SOLUTIONS OF METAL NITRATES

	C_{2v}, bound nitrate					D_{3h}, free nitrate		
Nitrate	$\nu_4(B_1)$	$\nu_1(A_1)$	$\nu_2(A_1)$	$\nu_3(B_2)$ or $\nu_5(B_1)$	$\nu_3(A_1)$	$\nu_3(E')$	$\nu_1(A_1')$	$\nu_4(E')$
Na^+						1410	1052	720
K^+						1400	1055	725
NH_4^+						1400	1052	725
Ag^+		1340				1420	1040	720
Cu^{2+}	1490	1325	1040	810	760	1425	1060	725
Zn^{2+}		1340				1425	1052	720
Hg^{2+}	1465	1320		810	735	1400	1040	720
Ca^{2+}	1450	1360			744	1400	1053	720
Al^{3+}		1340				1420	1048	720
In^{3+}	1510	1315	1040		750	1425	1050	720
Ce^{3+}	1470	1360		830	745	1400	1050	720
Th^{4+}	1536	1322	1039	810	745	1428	1052	717
Polarization	dp	p	p	dp	p/dp	dp	p	dp

TABLE II

RAMAN FREQUENCIES, IN CM.$^{-1}$, FROM CONCENTRATED AQUEOUS SOLUTIONS OF METAL SULFATES

	C_{3v}, bound sulfate				T_d, free sulfate			
Sulfate	$\nu_1(A_1)$	$\nu_2(A_1)$	$\nu_3(A_1)$	ν(M–O)	$\nu_3(F_2)$	$\nu_1(A_1)$	$\nu_4(F_2)$	$\nu_2(E)$
Na^+					1105	980	625	450
NH_4^+					1120	985	620	460
Tl^+					1100	985	625	452
Cu^{2+}					1100	980	620	450
Zn^{2+}					1112	985	618	455
Cd^{2+}					1105	985	615	451
Mg^{2+}					1120	985	618	455
Al^{3+}					1100	985	625	455
Ga^{3+}					1200	985	600	475
In^{3+}	1125	1000	650	225	1105	980	620	~450[a]

[a] Overlap with an aquo–indium complex line prevented precise determination of the $\nu_2(E)$ frequency from the In^{3+} salt.[3]

TABLE III

RAMAN FREQUENCIES, IN CM.$^{-1}$, FROM CONCENTRATED AQUEOUS SOLUTIONS OF METAL PERCHLORATES

	Point group T_d assignment			
Perchlorate	$\nu_3(F_2)$	$\nu_1(A_1)$	$\nu_4(F_2)$	$\nu_2(E)$
Na^+	1112	942	634	465
Li^+	1120	941	636	468
H^+ (70% $HClO_4$)	1125	933	630	460
Ag^+	1105	929	625	462
Be^{2+}	1130	937	631	464
Mg^{2+}	1130	940	634	467
Ca^{2+}	...	942	634	465
Cu^{2+}	1120	940	635	470
Hg^{2+}	1110	938	633	467
Pb^{2+}	1105	937	632	465
Al^{3+}	1120	937	632	465
In^{3+}	1125	935	630	465
La^{3+}	1130	939	634	467
Ce^{3+}	...	933	630	462
Th^{4+}	1110	940	633	465

with the various metal ions.[11] The Raman results given in Table I reveal the following order of nitrate deformations: $Th^{4+} > In^{3+} > Cu^{2+} > Hg^{2+} > Ce^{3+} > Ca^{2+} > Zn^{2+}, Al^{3+}, Ag^+ > Na^+, K^+, NH_4^+$.

A more sensitive test of the invariance of the spectra of the sulfate and perchlorate ions is the intercomparison of line intensities. Accordingly, measurements of the molar intensities of the $\nu_1(A_1)$ lines from solutions listed in Tables II and III have been made, but were found to be constant within the possible 6% limit of experimental error.[12] Likewise, no significant change in the relative intensities of the four fundamentals was discovered by intercomparisons in the perchlorate series.[12] Our measurements justify the use of the $\nu_1(A_1)$ line of the perchlorate ion as an internal standard for Raman line intensity measurements under usual aqueous conditions. It is clear that the tetrahedral symmetry of the anion is not appreciably diminished for any of the perchlorates or any of the sulfates with the exception of In^{3+}.

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Metal Carbonyls. VIII. Kinetics of Carbon Monoxide Exchange with Trichlorobis(triphenylphosphine)carbonylrhodium(III)

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Compounds of the types $[Rh(PR_3)_2COCl]$ and $[Rh(PR_3)_2COCl_3]$ were first prepared by Vallarino[1] and described as being very stable because the compounds do

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