Ion–Ion–Solvent Interactions in Solution. XI*
Spectroscopic Studies of Group 2
Perchlorates in Acetone

David W. James and Paul G. Cutler

Chemistry Department, University of Queensland,
St. Lucia, Qld. 4067.

Abstract

Solutions of $Mg(ClO_4)_2$ and $Sr(ClO_4)_2$ in acetone have been studied at various concentrations up to saturation by using infrared absorption, Raman scattering and multinuclear n.m.r. (^1H, ^{13}C, ^{17}O, ^{25}Mg, ^{35}Cl). Solvation numbers of *c.* 4·5 (Mg^{2+}) and *c.* 5·5 (Sr^{2+}) were determined from component band analysis of the *c.* 800 cm^{-1} acetone band in the Raman spectra. The solvent shell about the Mg^{2+} had a high level of steric crowding. There was a small amount of solvent-shared ion-pair formation at all concentrations in solutions of $Mg(ClO_4)_2$ which showed little concentration dependence. In solutions of $Sr(ClO_4)_2$ there was evidence for the formation of both solvent-shared associated-ion species and ion-contact species. The solvent-shared species appeared to have two alternative configurations in one of which the anion was both polarized and highly hindered. There was a salt-promoted reaction in which the perchlorate was reduced to chloride and the solution darkened. This reaction prevented the use of Raman spectra to quantify the association equilibria.

There have been few studies of solution interactions in solutions of the perchlorates of divalent metal ions in non-aqueous solvents. The reactivity of acetone in aldol condensation reaction was found to be enhanced by the presence of the cations Mg^{2+}, Sr^{2+} and Ba^{2+}.[1] A study of the infrared spectrum suggested that the cations resulted in weakening of the C=O bond, a drift of electrons from the methyl groups and a favouring of the reaction between C=O and the methyl group of adjacent molecules. A series of papers[2,3] reported the infrared spectra of solutions of the perchlorates of Li^+, Na^+ and Mg^{2+} in non-aqueous solvents. The C–C–C stretching vibration of acetone was found to split into two concentration-dependent bands the separation of which was independent of concentration but varied with the cation.[2] A measurement of the ^{25}Mg n.m.r. spectrum in acetone[4] showed that the signals broadened much more than in aqueous solution indicating the formation of associated species. The

* Part X, *Aust. J. Chem.*, 1986, **39**, 137.

[1] Bukowska, J., and Kecki, Z., *J. Mol. Struct.*, 1975, **26**, 289.

[2] Perelygin, I. S., and Klimchuk, M. A., *Russ. J. Phys. Chem.*, 1974, **48**, 1466; 1975, **49**, 76.

[3] Perelygin, I. S., and Osipov, V. S., *Russ. J. Phys. Chem.*, 1979, **53**, 1036; Perelygin, I. S., and Klimchuk, M. A., *Russ. J. Phys. Chem.*, 1973, **47**, 1354, 1402; Perelygin, I. S., and Yamidanov, S. Y., *Russ. J. Phys. Chem.*, 1979, **53**, 1354.

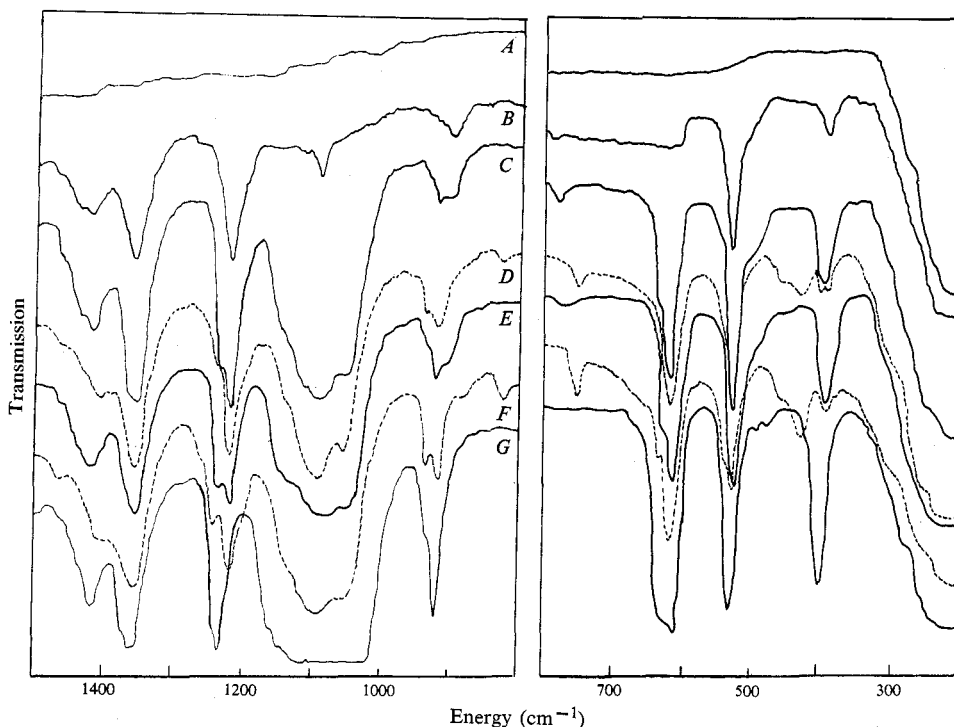[4] Heubel, P. H., and Popov, A. I., *Inorg. Nucl. Chem. Lett.*, 1979, **8**, 283.

Fig. 1. Infrared spectra of acetone solutions of $Mg(ClO_4)_2$ and $Sr(ClO_4)_2$: *A*, baseline; *B*, pure acetone; *C*, $Sr(ClO_4)_2$, 0.5 M; *D*, $Mg(ClO_4)_2$, 0.5 M; *E*, $Sr(ClO_4)_2$, 1.0 M; *F*, $Mg(ClO_4)_2$, 1.0 M; *G*, $Sr(ClO_4)_2$, 2.5 M.

Table 1.   N.m.r. spectra for acetone solutions of $Sr(ClO_4)_2$ and $Mg(ClO_4)_2$

δ are chemical shifts in ppm relative to acetone; $\nu_{1/2}$ are band full widths at half-height in Hz

Ion	Concn (mol dm^{-3})	^{1}H δ	^{13}C $\delta_{C=O}$	δ_{Me}	^{17}O $\delta_{C=O}$	$\nu_{1/2}$	^{35}Cl $\nu_{1/2}$	^{25}Mg $\nu_{1/2}$
Sr^{2+}	0.5	0.12	2.8	0.25	-15.3	95.1	39.2	
	1.0	0.23	5.5	0.62	-23.9	151.1	67.2	
	1.5	0.31	7.8	0.88	-34.8	307.8	140.1	
	2.0	0.39	9.5	1.09	-52.5	526	308.1	
	2.5	0.49	11.8	1.32			1557	
Mg^{2+}	0.25	0.008	2.1	0.23	-5.9		58.7	21
	0.5	0.15	5.0	0.68	-18.2		70.2	
	0.75	0.23	5.8	0.80	-26.1		80.7	35.1
	1.0	0.30	7.9	0.90	-41.5		105.4	44.9
	1.25	0.37	8.9	0.96	-52.5		145.0	70.2
	1.5	0.50	9.1	1.03			217.7	112.4

breadth of the ^{35}Cl resonance has also been examined for solutions of $Mg(ClO_4)_2$ in acetone[5] and at 1 M concentration widths of over 200 Hz indicated ion association. Studies of $LiClO_4$ in acetone[6,7] have shown that changes in the solvent spectrum may be used to estimate the solvation number of the cation.

Experimental

The preparation of the anhydrous salts and the details of spectroscopic measurements are the same as described previously.[7] Acetone was initially dried over $CaCl_2$ then distilled from P_2O_5 under atmospheric pressure and stored in dark bottles over freshly activated molecular sieve. The anhydrous salt was weighed under dry nitrogen and solutions made up in the usual way. There was no evidence of water in the OH stretching region of the infrared spectrum. Concentrations were determined by atomic absorption.

Results and Discussion

Solvation Processes

The infrared spectra shown in Fig. 1 illustrate that for both solutes the acetone bands at 1200 cm^{-1} and 500 cm^{-1} give rise to a second higher energy component as the concentration of salt increases. As reported previously,[7] this indicates the presence of perturbed acetone molecules involved in solvating the electrolyte. With both electrolytes there is movement of the band due to C=O stretching to lower energy: this is more pronounced for solutions of $Mg(ClO_4)_2$ and indicates solvation through the carbonyl oxygen. The appearance of broad low-energy bands [420 cm^{-1} and 290 cm^{-1} for $Mg(ClO_4)_2$ solutions and 390 cm^{-1} for solutions of $Sr(ClO_4)_2$ with the suggestion of a second band at 260 cm^{-1}] for all solutions may be associated with the presence of solvated cations in solution.

The involvement of the carbonyl group in the solvation interaction is supported by the observation of the ^{13}C n.m.r. spectrum the results for which are included in Table 1. The change with concentration of the signal for the carbonyl carbon is reasonably large with the concentration gradient of the change being slightly greater for Mg^{2+}
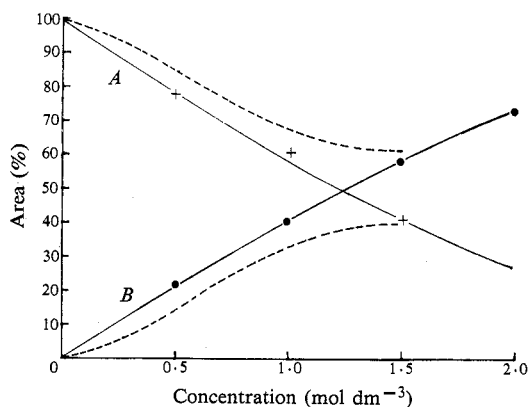
Fig. 2. Component band intensities for the 800 cm^{-1} band of acetone in presence of ClO_4^-:
A, fee acetone
--- $Mg(ClO_4)_2$,
— $Sr(ClO_4)_2$;
B, bound acetone
--- $Mg(ClO_4)_2$,
— $Sr(ClO_4)_2$.

[5] Berman, H. A., and Stengle, T. R., *J. Phys. Chem.*, 1975, **79**, 1001.
[6] Wong, M. K., McKinney, W. J., and Popov, A. I., *J. Solution Chem.*, 1975, **4**, 441.
[7] James, D. W., and Mayes, R. E., *Aust. J. Chem.*, 1982, **35**, 1775.

than for Sr^{2+}. The change is towards less shielding indicating a loss of electron density about the carbon. This is consistent with a polarization of the carbonyl oxygen by the cation with consequent drift of electrons away from the carbonyl carbon. The methyl carbon resonance shows a small deshielding change with added salt which is larger than the expected bulk susceptibility corrections.[8] This may reflect an induced change caused by the polarization of the oxygen. The ^1H signal for solutions of both salts shows a small linear deshielding shift with added salt. Both salts produce similar shifts which are appreciably smaller than for the ^{13}C signals.

Some quantitative measure of solvation may be obtained from the Raman spectra of the acetone. The band due to the C–C symmetric stretching vibration occurs in pure acetone at 789 cm^{-1} and as salt is added the band becomes split into two components with the new component occurring at higher energy. The total molar intensity of the band complex does not change when the new band appears. Component band analysis of the band shows that the two components have a similar shape and half-width. We associate the new band component with acetone molecules solvating the cations and the change in this component intensity is shown in Fig. 2. Because the total molar intensity of the band complex does not change as the salt is added the component band intensities may be used to give the ratio of free molecules to solvating molecules. Knowing the densities of the solutions the solvation number of the cation was calculated with the results shown in Table 2. For Sr^{2+} a solvation number between 5 and 6 is indicated whereas for Mg^{2+} a solvation number between 4 and 5 is likely.

Table 2.   Cation solvation numbers in acetone

Per-chlorate	Concn (mol dm^{-3})	Free (%)	Bound (%)	Density (g/ml)	Mole ratio acetone/salt	Solvation number
	0	100		0·79		
$Mg(ClO_4)_2$	0·25	96	4	0·84	54·6	2·3
	0·50	84	16	0·88	27·6	4·4
	1·00	66	34	0·98	14·1	4·8
	1·25	61	39	1·03	11·3	4·5
	1·50	62	38	1·08	9·6	3·6
$Sr(ClO_4)_2$	0·5	78	22	0·90	27·0	6·0
	1·0	60	40	1·01	13·5	5·4
	1·5	42	58	1·13	9·0	5·2
	2·0	27	73	1·24	6·8	4·9

The energy of the component due to solvating acetone gives some further information on the solvation interaction. For solutions of $Sr(ClO_4)_2$ the second component appears at 802 cm^{-1} which is similar to solutions of $LiClO_4$ while for $Mg(ClO_4)_2$ solutions it is at 813 cm^{-1}. Although the Mg^{2+} ion is similar in size to the Li^+ ion, the greater charge leads to a stronger solvation interaction. This is reflected in the greater solvation number for Mg^{2+} (4·5) than for Li^+ (3·5) which causes greater crowding about the Mg^{2+} ion. The steric hindrance produced by this crowding is reflected in greater constraint to movement in the methyl groups and a movement to higher energy of the vibration. This crowding would also be expected to influence the rotational

[8] James, D. W., and Mayes, R. E., *J. Phys. Chem.*, 1984, **88**, 637.

relaxation time of the methyl groups which could be probed by n.m.r. techniques. There is, however, no available experimental information on this proposal.

Association in Mg(ClO₄)₂ Solutions

The infrared spectra shown in Fig. 1 indicate that even at low concentrations of salt (0·5 M) the degenerate antisymmetrical stretching vibrational band is split into three components: this indicates a significant symmetry distortion of the perchlorate anion. The complete loss of degeneracy indicates a symmetry reduction to at least C_{2v} which implies that the perchlorate is polarized through two oxygen atoms. The triply degenerate bending vibration also gives evidence for loss of degeneracy which is, however, less obvious than for the stretching vibration. It is frequently found that degenerate bending vibrations are less sensitive to symmetry disturbance than are stretching vibrations. The appearance of the symmetric stretching vibration, forbidden in the infrared under T_d selection rules, at all concentrations provides a third piece of evidence for the symmetry distortion of the perchlorate anion which would usually be attributed to the formation of ion pairs.

The measurement of n.m.r. spectra for different nuclei yields further information on the association process. In addition to the information on ^{13}C and ^{1}H already discussed, measurements of the resonances for [35]Cl, [17]O of the carbonyl and [25]Mg are listed in Table 1. The [35]Cl, being a quadrupolar nucleus, has a half-width which reflects electrical field gradients at its nucleus. The half-width of almost 60 Hz measured in the most dilute solution indicates that a sizable field gradient is already present. This half-width is greater than that measured in saturated aqueous solutions of the perchlorates of Li^+, Na^+, Mg^{2+} or Ca^{2+}. It may be expected that this breadth indicates extensive ion association even at low concentration of salt. As the concentration of salt increases the half-width gradually increases indicating a progressively stronger field gradient. The value, however, never reaches the breadth measured for contact ion pairs of $LiClO_4$ in acetone. The linewidth which we measure in saturated solution (105 Hz) is narrower than that previously reported.

The [17]O is also a quadrupolar nucleus, and so will give indication of ion association through the ClO_4^- signal and the solvation through the C=O signal. The [17]O of the perchlorate does not give clear evidence of coupling to the [35]Cl at any temperature which in accord with the rapid relaxation implied by the width of the [35]Cl signal. The width of the [17]O signal did not show a marked increase as the concentration increased which implies that the extent of ion association may not increase appreciably with concentration. The [17]O signal of the carbonyl oxygen shows a significant shift to greater shielding (52 ppm) as the concentration of salt increases but the width of the resonance did not show an appreciable increase. This is unexpected in view of the strong solvation interaction between the C=O and Mg^{2+}. From the Raman analysis it is evident that at saturation less than 40% of the acetone is bound to the cation. The [17]O half-width for these bound molecules is expected to be very large. The measured half-width, on the other hand, probably reflects the unbound acetone molecules which are still the largest fraction. This will be re-examined for the Sr^{2+} case below. The chemical shift for the two [17]O nuclei indicate that C=O is ~ 270 ppm more shielded than ClO_4^- which is ~ 300 ppm more shielded than D_2O. The position of the resonance for ClO_4^- showed little change with concentration.

The [25]Mg nucleus is also a quadrupolar nucleus and in the most dilute solution is already relatively broad (21 Hz). It shows a relatively smooth increase in half-width

as the concentration increases; this indicates that the electric field gradient shows a small regular increase with concentration. The width found in saturated solution, 112 Hz, is not in good agreement with the previously reported value of 310 Hz. The value we report was quite reproducible and we cannot offer an explanation for the difference.

Fig. 3. Component band analysis of $ClO_4{}^-$ symmetrical stretching vibration for $Mg(ClO_4)_2/Me_2CO$ solutions. (a) At 0·25 M; (b) at 1·5 M.
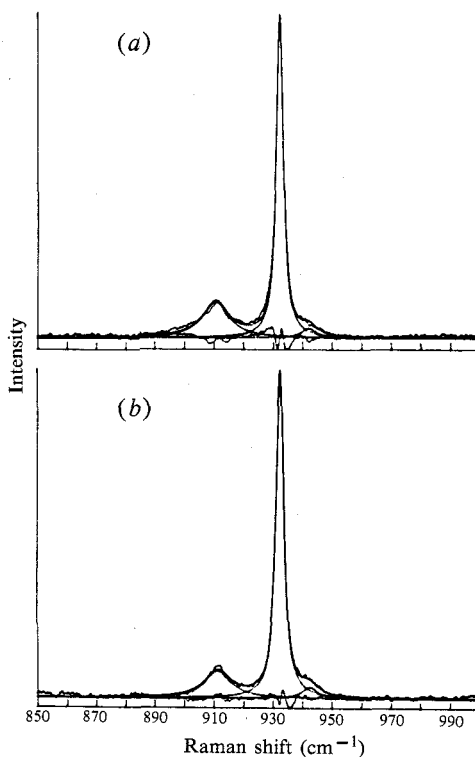
The infrared and n.m.r. measurements all indicate a strong distortion of the $ClO_4{}^-$ ion, and the Mg^{2+} ion and strong solvation of the Mg^{2+} ion. They are not, however, capable of yielding quantitative estimates of the extent or nature of the ion association. Analysis of the non-degenerate, Raman-active symmetrical stretching vibrational band provides such quantitative information. The bands which are shown for two concentrations in Fig. 3 consist clearly of three components. The lowest of these occurring at ~ 911 cm^{-1} is assigned as an overtone of the double degenerate bending mode at 460 cm^{-1} in accord with the arguments previously presented.[9] The remainder of the spectrum consists of a dominant feature at ~ 932 cm^{-1} which has a half-width of $\sim 1 \cdot 5$ cm^{-1} and a weak high-energy component at a 942 cm^{-1} which is broader ($\omega_{h/2}$ 3·0 cm^{-1}) and constitutes about 6% of the band area at all concentrations. This weaker component corresponds in position to that associated with solvent-shared ion pairs in non-aqueous systems[7,8]. The narrow width of the stronger component is consistent with very slow vibrational relaxation which implies that the perchlorate ions are not solvated and are not undergoing a time-dependent

[9] James, D. W., and Cutler, P. G., *Aust. J. Chem.*, 1986, **39**, 137.

symmetry perturbation which would lead to enhanced dephasing. This finding is in apparent contradiction with the infrared and n.m.r. evidence presented earlier which indicated that the perchlorate anion was perturbed at all concentrations.

The Raman spectra indicate a steady small concentration of solvent-shared ion pairs while the ^{17}O n.m.r. signal does not change appreciably with concentration which is consistent with the major proportion of the perchlorate anions being unperturbed. The infrared spectra can be explained as the superposition of a triplet (due to the solvent-shared ion pairs) and a singlet representing the major part of the perchlorate anions. The width of the ^{35}Cl signal at all concentrations can be considered to arise from a time averaging of the electric field gradient in the solvent-shared ion pair. In this regard the different time frame of the n.m.r. and Raman measurements needs to be remembered.

Association in Sr(ClO₄)₂/Acetone Solutions

It was found that all solutions of $Sr(ClO_4)_2$ in acetone decomposed with time. The solutions slowly turned yellow in colour and a fine white precipitate formed. At long time the colour becomes so intense that the solutions appeared black. The decomposition was more rapid in concentrated solutions and appeared to be photochemically promoted. It has previously been reported that aldol condensation reactions involving acetone are promoted by the presence of Sr^{2+}.[1] The white precipitate was filtered from the solution, was found to be soluble in water and to give positive tests for Sr^{2+} and Cl^-. It is thus probable that the Sr^{2+} is promoting a condensation reaction which is accompanied by oxidation by the perchlorate to yield chloride. Mass spectrometric analysis of the product indicated that it was an aldol polymer of acetone.
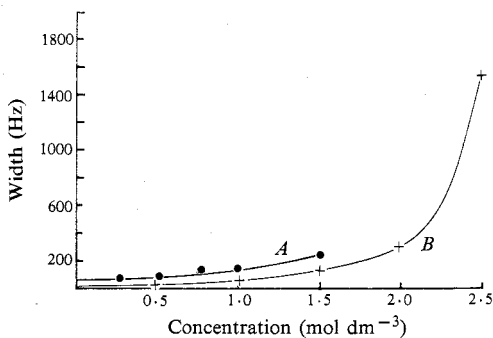

Fig. 4. Variation with concentration for the half-width (FWHH) of the ^{35}Cl resonance in acetone solutions: A, $Mg(ClO_4)_2$; B, $Sr(ClO_4)_2$.

The infrared spectra which are represented in Fig. 1 show similar behaviour to those for $Mg(ClO_4)_2$ solutions. The acetone band at ~ 1210 cm^{-1} is progressively replaced by a band at higher energy; the antisymmetric stretching vibrational band of ClO_4^- shows evidence for loss of degeneracy at all concentrations; the infrared-forbidden symmetric stretch of ClO_4^- appears at all concentrations; the triply degenerate bending mode shows evidence for loss of degeneracy at all concentrations and a band due to solvated cations grows with concentration at ~ 400 cm^{-1}. The product of the reaction did not appear to be formed in sufficient concentration during the spectral observation to influence the results. The results indicate that, as for $Mg(ClO_4)_2$, there is distortion of the perchlorate ion which would be consistent with the presence of ion association.

Fig. 5. Component band analysis
of ClO_4^- symmetrical stretching
vibrational band for $Sr(ClO_4)_2$
in acetone solutions:
(a) 0·5 M;
(b) 2·0 M.
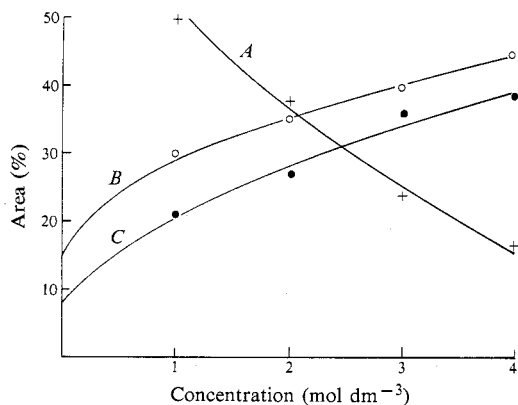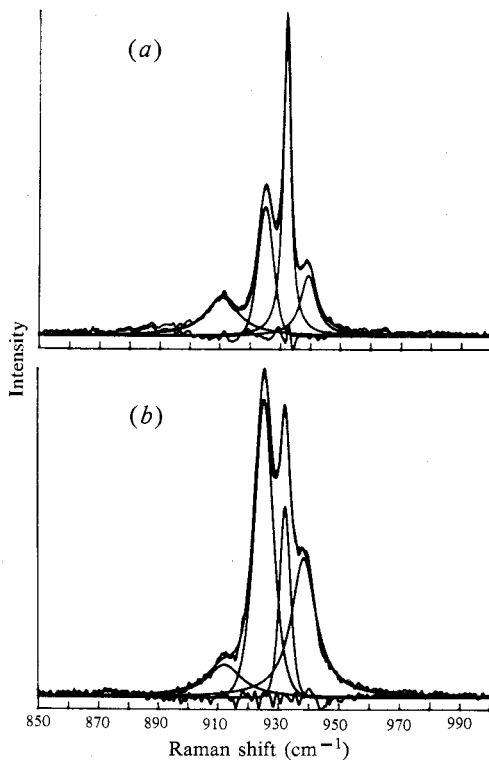

Fig. 6. Variation with
concentration of component
bands of the symmetrical
stretching vibrational band in
$Sr(ClO_4)_2$/acetone solutions:
A, isolated perchlorate;
B, C, solvent-shared
ion-associated species.

Table 3. $Sr(ClO_4)_2$ in acetone: band analysis parameters for ClO_4^- symmetric stretch

X_2, band maximum (cm^{-1}); R_s, shape ratio $X_3/(X_3 + X_4)$; $\omega_{h/2}$, band half-width at half-height (cm^{-1})

Concn (M)	Composite band			Associated band			Free ClO_4^- band			Associated band II		
	X_2	R_s	$\omega_{h/2}$	X_2	R_s	$\omega_{h/2}$	X_2	R_s	$\omega_{h/2}$	X_2	R_s	$\omega_{h/2}$
0·50	910·82	0·99	6·53	925·01	0·51	2·99	932·01	0·99	1·48	939·25	0·99	3·21
1·0	910·86	0·99	6·70	925·06	0·58	3·16	932·01	0·84	1·60	938·98	0·99	3·79
1·50	911·88	0·99	6·90	925·23	0·61	3·41	932·17	0·72	3·41	932·17	0·99	4·34
2·00	912·37	0·99	7·10	925·28	0·64	3·61	932·30	0·61	2·11	938·60	0·99	4·47

The n.m.r. spectra for the quadrupolar nuclei [35]Cl and [17]O (C=O) are collected in Table 1. The variation in the width of the [35]Cl signal for the two solutes is compared in Fig. 4. It is evident that both show a slow regular increase up to $1 \cdot 5$ M concentration but at higher concentrations the broadening in the case of the $Sr(ClO_4)_2$ solutions accelerates dramatically to yield widths consistent with the presence of ion-contact species in these solutions. It may be noted that at the highest concentration where the half-width indicates considerable concentrations of ion contact the chemical reaction was much more rapid than at lower concentrations. The combination of the yellow coloration and the white precipitate prevented Raman spectra being obtained for this concentration.

The [17]O signal (C=O) shows distinctly different behaviour from that in $Mg(ClO_4)_2$ solutions. There is an initial slow increase in bandwidth but above $1 \cdot 5$ M concentration the breadth increases rapidly. It may be noted that below $1 \cdot 5$ M concentration the acetone solvating the cation is the minor acetone component while above $1 \cdot 5$ M it becomes the major component. If the [17]O half-width is plotted against the ratio of bound/free acetone it is found to increase in an approximately linear fashion.

When the Raman band corresponding to the symmetric stretching motion of the ClO_4^- anion is examined it is found to be different from any previously reported. As shown in Fig. 5 it consists of the weak low-energy band which has been assigned to an overtone together with three clearly resolved components. The sharpest of these which is strongest in low concentration corresponds closely with the band previously assigned to the unassociated (solvated) ClO_4^- anion (932 cm^{-1}). There are now two additional bands, one at lower energy and one at higher energy than the 932 cm^{-1} band. These two bands maintain the same relative intensity ratio and grow as the concentration increases at the expense of the 932 cm^{-1} band. We associate both of these Raman components with solvent-shared ion-associated species in solution. The results of band component analysis are given in Table 3 with the variation in intensity for the three components being given in Fig. 6.

The presence of two components assigned to the solvent-shared associated species indicates that there are two different modes of interaction present. The first, producing a component at 939 cm^{-1}, is similar to that previously observed when the ClO_4^- anion is polarized by a cation in the second solvation shell.[7,8,10] The second type of perturbation producing a band component having lower energy than the isolated ClO_4^- has not been previously observed. For solutions of metal nitrates an interaction which is not averaged over the anion by rotational place exchange yields component bands lower than the isolated anion band.[11] It is possible that for the $Sr(ClO_4)_2$ solutions there are two configurations for the approach of the anion to the solvated cation. In one of these the anion has reasonably free rotation which allows the polarization to be averaged over time. In the other configuration the anion is constrained and rotational place exchange is hindered producing a directional polarization. In this hindered configuration the oxygen atoms of the anion remain in a position relative to the acetone molecules for an extended time while at the same time the Cl–O bonds are destabilized by polarization. This would enhance the possibility of an oxidation reaction involving the anion and such an oxidation does occur.

[10] Frost, R. L., James, D. W., Appleby, R., and Mayes, R. E., *J. Phys. Chem.*, 1982, **86**, 3840.

[11] Frost, R. L., and James, D. W., *J. Chem. Soc., Faraday Trans. 1*, 1982, **78**, 3263; James, D. W., and Frost, R. L., *Aust. J. Chem.*, 1982, 1793.

The appearance of the lower energy component for solutions of $Sr(ClO_4)_2$ but not for any of the other perchlorate solutes studied can be understood in terms of the strength of the solvation interaction and the crowding in the solvation shell. For $Mg(ClO_4)_2$ the solvation of the Mg^{2+} is very strong and the perchlorate only enters the second solvation sphere in low concentrations. For Li^+, which is comparable in charge/size ratio to Sr^{2+}, the solvation number is lower and in the formation of solvent-shared ion pairs the anion does not encounter such a crowded environment. The reaction noted for solutions of Sr^{2+} does, however, take place in solutions of $LiClO_4$ but has a very long half-life and solutions must be left for several weeks for any observable darkening to occur. For the $Sr(ClO_4)_2$ the weaker solvation forces and the high degree of crowding produce conditions in which the anion can enter the second solvation sphere but is then in a highly crowded hindered environment. In this regard the ability of the alkaline earth cations to promote aldol condensations in acetone[1] ($Ca^{2+} < Sr^{2+} < Ba^{2+}$) follows an expected increase in the ease with which the anion can enter the solvation shell of the cation.