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Matrix Spectra, Force Constants, and Structures for $M^+ClO_4^-$ and Hydrated Alkali Metal Perchlorate Ion Pairs

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Received September 16, 1977

The effect of hydration on the ion pairs $Li^+ClO_4^-$ and $K^+ClO_4^-$ isolated in argon matrices has been followed by observing the progressive reduction in the magnitude of the splitting between components of the ν_3(f) antisymmetric stretching mode. Though this splitting is strongly reduced (by a factor of 3) for the hydrated ion pairs, $MClO_4{\cdot}H_2O$, relative to the simple ion pairs, $M^+ClO_4^-$, the splitting pattern remains that calculated for a bidentate coordination of the metal with the anion. This frequency splitting pattern has been predicted by decreasing the two coordinated Cl–O bond force constants while increasing the F_{ClO} values for the noncoordinated bonds. This procedure generates a frequency vs. ΔF_{ClO} plot for each ClO_4^- mode of a $M^+ClO_4^-$ bidentate complex. Besides reflecting the fact that the observed frequency pattern indicates a bidentate structure for all cases, this procedure has also permitted stretching force constants to be estimated for the various hydrates, $M^+ClO_4^-{\cdot}nH_2O$, where n varies from 0 to 4. The new data are consistent with the idea that the ClO_4^- ion is only very weakly distorted through interactions with either a water or an ammonia solvent medium and, together with similar results for $M^+NO_3^-$ ion pairs, establish the general nature of the marked reduction in the strength of contact cation–anion interactions that accompanies Lewis base solvation of the cation.

Introduction

The vibrational spectra of the argon matrix isolated alkali metal perchlorate ion pairs are known to be characterized by large degeneracy splittings, particularly for the ν_3(f) mode,[1] which are comparable in magnitude with $\Delta\nu_3$ values for the alkali metal nitrates.[2,3] The triply degenerate stretching mode is split into three components as a result of the cation distortion of the anion with approximate values for ν_{3_a}, ν_{3_b}, and ν_{3_c} of 1000, 1130 and 1200 cm^{-1}. These splittings require a bidentate or bidentate-like association of the cation with the anion and, since recent molecular orbital results indicate that the bidentate form is the minimum energy structure for the $M^+NO_3^-$ ion pairs,[4] it will be assumed throughout this paper that the perchlorate structures are bidentate in nature. A similar bidentate arrangement occurs for the M^+AlF^{4-} ion pairs.[5] Consistent with the C_{2v} symmetry classes of the bidentate structure, the split components of the ν_3(f) mode will be labeled $\nu_{3_{b1}}$, $\nu_{3_{a1}}$, and $\nu_{3_{b2}}$.

When the argon matrix was replaced by a glassy water or glassy ammonia matrix, the isolated $M^+ClO_4^-$ $\Delta\nu_3$ values collapsed to approximately a third of the original values.[1] This behavior also mirrors the $M^+NO_3^-$ response to solvation by Lewis base solvents,[6] a response that has recently been analyzed in detail by using an ab initio SCF molecular orbital approach.[4] The collapse can be understood in terms of the reduced polarizing power of the solvated cation together with the transfer of electrons, via the cation, from the Lewis base to the π-bonding MO's of the anion.

Insights to the bonding of the solvated $M^+NO_3^-$ ion pairs have been enhanced by matrix experiments wherein, by adjusting the amount of Lewis base in the argon matrices, $\Delta\nu_3$ for the ion pairs, solvated to varying degrees, has been observed to decrease in a stepwise manner from the simple ion pair values of $\sim$200 cm^{-1} to the completely solvated values, <65 cm^{-1}.[3] Since the perchlorate $\Delta\nu_3$ behavior for the extreme cases (argon and pure glassy H_2O matrices) is similar to that of the nitrates, observation of the stepwise changes between the two extremes was expected to be informative.

This paper is devoted primarily to an analysis of the response of the $M^+ClO_4^-$ matrix spectra to the hydration of the ion pair as the number of water molecules coordinated with the cation is increased from zero to the limiting numbers for a pure H_2O matrix, probably four or five. It is understood throughout that, as for the nitrates, the cation–anion contact pairing is preserved for all matrices, a fact that is affirmed by the strong cation dependence of perchlorate $\Delta\nu_3$ values for a pure H_2O matrix (see Table III of ref 1). This contact pairing must reduce the maximum hydration number for the cation.

Table I. Valence Force Constants (mdyn/Å) Transferred for the Free Perchlorate Anion (Column 2)[b] Which Set Is the Basis for the Curves in Figure 1[d]

valence coordinate	valence force constant values			
	ClO_4^-	$Li^+ClO_4^-$	$Na^+ClO_4^-$	$K^+ClO_4^-$
Cl–O*	6.60[c]	5.05 (5.0)	5.32 (5.3)	5.54 (5.5)
Cl–O	6.60[c]	8.12 (8.2)	7.75 (7.8)	7.71 (7.7)
M–O		0.60	0.45	0.30
O*ClO* bend	2.55[a]	1.67	1.38	1.27
OClO* bend	2.55[a]	2.51	2.51	2.39
OClO bend	2.55[a]	3.28	3.33	3.21
ΔF_{OCl}	0.0	3.06 (3.2)	2.43 (2.5)	2.17 (2.2)

[a] Units of 10^{11} ergs/rad^2. [b] Force constants transferred from A. Miller and B. Krebs, *J. Mol. Spectrosc.*, **24**, 180 (1967). Values of 0.46 and 0.59 were also transferred for the Cl–O bond–bond interaction constant and bend–bend interaction constant, respectively. These constants, along with the bending constants O*–M–O* (0.12) and M–O*–Cl (0.1), were constrained during the least-squares fitting of the $M^+ClO_4^-$ data. [c] Reduced by 0.09 mdyn/Å to bring the absolute ν_3 component frequencies more in line with experimental results. [d] Columns 3–5 contain the least-squares fitted force constants using the frequency data of ref 1. Parenthetic values are taken from curves of Figure 1.

In many studies of oxyanion ion pairing, the plots of ν_3 component values vs. $\Delta F_{X\text{-}O}$, prepared by Hester et al. for various oxyanions and for both mono- and bidentate coordination, have been a significant aid.[7] However, the bidentate perchlorate case is not covered by the published plots so one has been prepared and will be used for analysis of the $M^+ClO_4^-$ results for various matrix media.

$M^+ClO_4^-$ Force Constants

Stretching force constants, $F_{Cl\text{-}O}$, have been estimated for the bidentate $M^+ClO_4^-$ simple ion pairs by two methods. In the first approach the procedures of Hester et al.[7] were followed: namely the free anion valence force constants were obtained (literature values, Table I) and that force field was systematically adjusted by increasing the $F_{Cl\text{-}O}$ values for noncoordinated Cl–O bonds while reducing $F_{Cl\text{-}O*}$ for the coordinated Cl–O* bonds by the same magnitude. The resulting plot (Figure 1), obtained without regard to the M–O bond, was then used, along with the experimental $\nu_{3_{b1}}$, $\nu_{3_{a1}}$, and $\nu_{3_{b2}}$ values to estimate $F_{Cl\text{-}O}$ and $F_{Cl\text{-}O*}$ for a particular ion pair. The values deduced through this approximate, but systematic, approach are given in parentheses in Table I.

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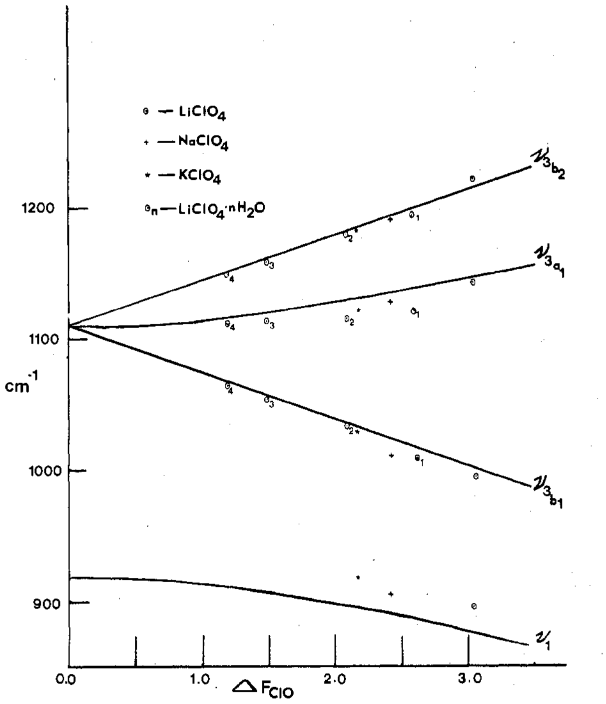

Figure 1. Plot of ClO_4^- stretching mode frequencies for a C_{2v} (bidentate) configuration beginning with $F_{ClO} = 6.60$ mdyn/Å. ΔF_{Cl-O} measures the difference between the noncoordinated and metal coordinated Cl–O bonds. Frequencies for the simple ion pairs, $M^+ClO_4^-$, are positioned in this figure on the basis of ΔF_{ClO} values determined by a least-squares analysis.

In the second approach the initial force constant set was least-squares adjusted to give the best fit to the observed frequencies. For the best case, $Li^+ClO_4^-$, eight experimental frequencies were used to fit six principal force constants with the interaction constants constrained to the free anion values and the bending constants of the four-membered ring assigned small, but basically arbitrary, values. The F_{MO} value determined for $Li^+ClO_4^-$ in this manner was used to gauge F_{MO} values chosen for the subsequent fitting of the $Na^+ClO_4^-$ and $K^+ClO_4^-$ data. The resultant complete force constant sets for the $M^+ClO_4^-$ species are presented in Table I.

The main interest was in the difference $F_{Cl-O} - F_{Cl-O*}$ (or ΔF_{Cl-O}) estimated by these two methods. It is comforting that the values deduced are very similar. This implies that, provided bidentate coordination is retained during cation solvation, the plots of Figure 1 can be used to convert experimental frequencies to reliable anion stretching constants. This application will be considered after reviewing the matrix isolation data for hydrated $M^+ClO_4^-$ ion pairs.

Though potential energy distributions are not presented in this paper it is interesting to note that the C_{2v} symmetry of the bidentate coordinated $M^+ClO_4^-$ ion pair separates the Cl–O and Cl–O* stretching internal coordinates in the $\nu_{3_{b1}}$ and $\nu_{3_{b2}}$ normal modes. Because of the plane of symmetry which included the four-membered ring, the Cl–O* coordinates, but not the Cl–O coordinates, dominate the $\nu_{3_{b1}}$ (~1000 cm^{-1}) vibration, while the $\nu_{3_{b2}}$ (~1200 cm^{-1}) mode is a nearly pure (90%) Cl–O stretch. Thus, the frequency difference, $\Delta\nu_{3_{b1,b2}}$, between the high- and low-frequency ν_3 components, reflects directly the strengthening of the Cl–O and the weakening of the Cl–O* bonds that accompanies M^+ coordination.

Finally, it is judged that the excellent fit of the experimental $M^+ClO_4^-$ frequencies to the splitting pattern predicted in Figure 1 is confirmation that the metal–perchlorate coordination is true bidentate and, henceforth, need not be characterized as "bidentate or bidentate-like". This fit is emphasized in Figure 1 through indication of the observed frequencies for ν_1, $\nu_{3_{a1}}$, $\nu_{3_{b1}}$, and $\nu_{3_{b2}}$.

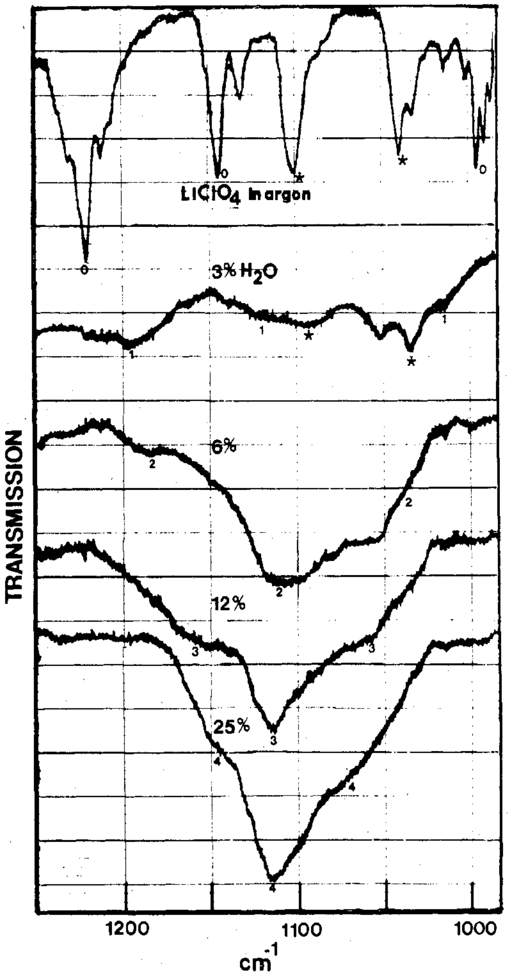

Figure 2. Infrared bands for the ν_3 mode of $Li^+ClO_4^-$ ion pairs isolated in matrices containing varying amounts of water. The percentages refer to the H_2O in the matrices, on a mole basis. Bands are labeled according to the hydration number of the ion pair. Asterisks denote dimer bands.

Experimental Section

The experimental procedures that have been previously described[1,3] have been used in this study without need for any modification. Premixed argon–Lewis acid matrix gases have been codeposited with molecular beams containing primarily $M^+ClO_4^-$ ion pairs. The H_2O (or NH_3) content was varied from ~0 to 100% with the percentage doubled in successive experiments beginning at 3%, 6%, ... The ion-pair molecular beams were generated from resistance heated Pyrex glass Knudsen cells at ~450 °C and deposited at ~10 K onto a CsBr substrate cooled by an Air Products CS-202 closed-cycle helium refrigerator. The $M^+ClO_4^-$ concentrations in the matrix were chosen so that, for the pure argon case, the monomer spectra dominated, a situation which suggests matrix to ion-pair ratios of 500 or greater. Spectra were measured with a Beckman IR-7 spectrometer.

Hydration Effects on $\Delta\nu_3$

The stepwise effect on the ν_3 components of the ClO_4^- ion from the hydration of $Li^+ClO_4^-$ is clear from Figure 2. As expected, on the basis of limited earlier perchlorate data[1] and the known behavior of $M^+NO_3^-$ ion pairs,[3] the $\Delta\nu_3$ splittings decrease in magnitude in a regular fashion as additional waters of hydration coordinate with the Li^+ cation. Four steps, apparently associated with successively greater hydration numbers that range from 0 to 4, have been identified in Figure 2. The corresponding frequencies are listed in Table II along with the stretching force constants obtained by application of the curves in Figure 1. The $Li^+ClO_4^-\cdot nH_2O$ frequencies are

Table II. ν_3 Component Frequencies (cm^{-1}) and Cl–O Stretch Force Constants (mdyn/Å) for $Li^+ClO_4^-$ and the Hydrates of $Li^+ClO_4^-$ [a]

	$Li^+ClO_4^-$	$Li^+ClO_4^-\cdot H_2O$ (3% H_2O)	$Li^+ClO_4^-\cdot 2H_2O$ (6% H_2O)	$Li^+ClO_4^-\cdot 3H_2O$ (12% H_2O)	$Li^+ClO_4^-\cdot 4H_2O$ (24% H_2O)
$\nu_{3_{b_1}}$	994	1015	1035	1055	1065
$\nu_{3_{a_1}}$	1143	1122	1115	1115	1113
$\nu_{3_{b_2}}$	1220	1196	1183	1160	1150
F_{ClO}	8.12	7.9	7.65	7.35	7.2
F_{ClO^*}	5.05	5.3	5.55	5.85	6.0
ΔF_{ClO}	3.06	2.6	2.1	1.5	1.2
$\Delta\nu_{3_{b_1},b_2}$	226	181	148	105	85

[a] The frequency and coordination number for the hydrates are estimates (see text). Percentages refer to H_2O concentrations for the matrices which best display the set of bands.

Table III. ν_3 Component Frequencies (cm^{-1}) and Cl–O Stretch Force Constants (mdyn/Å) for $K^+ClO_4^-$ and the Hydrates of $K^+ClO_4^-$ [a]

	$K^+ClO_4^-$	$K^+ClO_4^-\cdot H_2O$ (3% H_2O)	$K^+ClO_4^-\cdot 2H_2O$ (6% H_2O)	$K^+ClO_4^-\cdot 3H_2O$ (12% H_2O)	$K^+ClO_4^-\cdot 4H_2O$ (24% H_2O)
$\nu_{3_{b_1}}$	1028	1035	1055	1070	1085
$\nu_{3_{a_1}}$	1122	1110	1110	1108	1107
$\nu_{3_{b_2}}$	1184	1177	1160	1140	1130
F_{ClO}	7.71	7.6	7.35	7.15	6.9
F_{ClO^*}	5.54	5.6	5.85	6.05	6.3
ΔF_{ClO}	2.17	2.0	1.5	1.1	0.6
$\Delta\nu_{3_{b_1},b_2}$	156	142	105	70	45

[a] The frequency and coordination numbers for the hydrates are estimates (see text). Percentages refer to the water concentrations in the matrices which best display the particular set of bands.

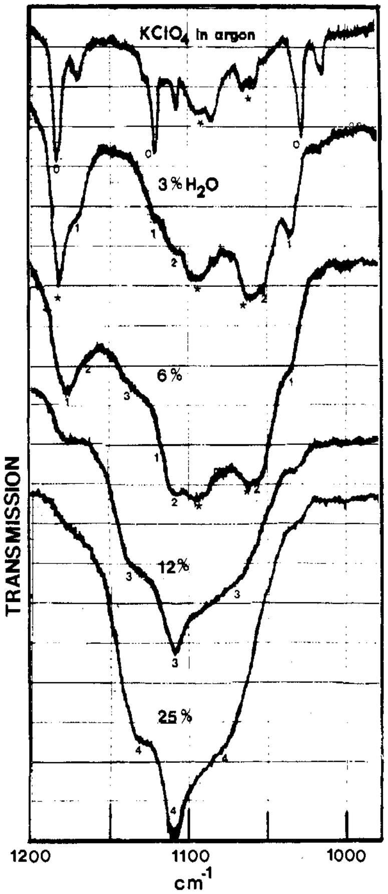

Figure 3. Infrared bands for the ν_3 mode of $K^+ClO_4^-$ ion pairs isolated in matrices containing varying amounts of water. The percentages refer to the H_2O in the matrices, on a mole basis. Bands are labeled according to the hydration number of the ion pair. Asterisks denote dimer bands.

also indicated in Figure 1, positioned on the ν_3 curves so as to reflect the appropriate ΔF_{Cl-O} value and, thereby, the values of F_{Cl-O*} and F_{Cl-O}. As for nitrates,[3b] the frequencies assigned to the $M^+ClO_4^-\cdot H_2O$ and $M^+ClO_4\cdot 2H_2O$ species are fairly well determined but at the higher matrix water concentrations required for the higher hydrates the ν_3 bands broaden and coalesce making definite frequency assignments impossible. The situation, relative to the nitrates, is also complicated by the presence of the intermediate $\nu_{3_{a_1}}$ band.

The stepwise hydration of $K^+ClO_4^-$ ion pair proceeds in much the same manner as noted above for $Li^+ClO_4^-$ with the major difference in the $K^+ClO_4^-$ spectra of Figure 3 being the presence of stronger dimer bands (asterisk). These bands have previously been identified and described for the $(M^+ClO_4^-)_2$ species (Table II of ref 1). The ν_3 band positions chosen for the hydrates of $K^+ClO_4^-$ are listed in Table III along with the F_{Cl-O} values estimated from Figure 1. These assignments are less reliable than for the $Li^+ClO_4^-$ study for two reasons: (1) the spacing of the ν_3 components is less for the pure argon matrix, and for all other cases as well, and (2) the dimer contribution to the spectra tended to be somewhat greater.

Ammoniation Effect on $\Delta\nu_3$

More limited data have also been obtained that show the parallelism of the ammoniation effect to that observed for hydration. The results for $K^+ClO_4^-$ in argon matrices with ND_3 percentages ranging from 8 to 100% are presented in Figure 4. Because of interfering solvent bands the data for the lower percentage ammonia matrices are not included.

Conclusions

Though one can argue with the specific assignments made for the ν_3 components in Tables II and III, several definite conclusions can be drawn from the data in Figures 2–4. Perhaps most obvious is the progressive reduction in the splitting of the ν_3 components with both increasing hydration and increasing ammoniation of the $M^+ClO_4^-$ ion pairs. Together with similar published results for the $M^+NO_3^-$ species, this establishes the generality of the strong reduction in the contact cation–anion interaction that is associated with Lewis base solvation of the cation. Also obvious, from these data together with published $M^+ClO_4^-$ results,[1] is the retention of the contact cation–anion interaction through the entire matrix series including the pure glassy H_2O and pure glassy

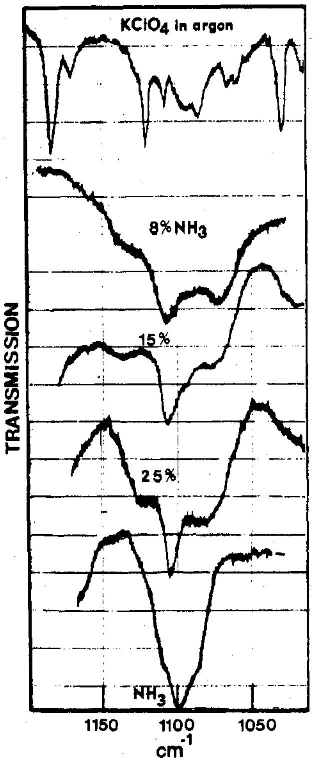

Figure 4. Infrared bands for the ν_3 mode of $K^+ClO_4^-$ ion pairs isolated in matrices containing varying amounts of ammonia. The percentages refer to the NH_3 in the matrices, on a mole basis.

NH_3 matrix samples. This is reflected in both the stepwise nature of the decrease in the $\Delta\nu_3$ values during solvation and the retention of a cation effect in the pure glassy H_2O matrices. Thus the $\Delta\nu_3$ values for $Li^+ClO_4^-$ in glassy H_2O are nearly twice those for $K^+ClO_4^-$. This is clear from comparison of the 25% H_2O matrix curves for Figures 2 and 3 (there is no measurable change in band positions between the 25% H_2O and pure H_2O matrix cases).

Another interesting implication of these data is that the bidentate nature of the metal–anion coordination is retained regardless of the extent of hydration or ammoniation of the $M^+ClO_4^-$ ion pairs. Thus, a definite ν_3 triplet is apparent throughout these studies, with a splitting pattern consistent with that predicted for a strict bidentate interaction (Figure 1). Recent ab initio SCF MO results for hydrated $Li^+NO_3^-$ also indicate that the bidentate interaction is most stable for $Li^+NO_3^-$ through $Li^+NO_3^-{\cdot}4H_2O$.[4]

Finally, there is some indication that the NH_3 molecule is slightly more effective than H_2O in reducing the cation–anion interaction, as measured by the distortion of the ClO_4^- anion, which is reflected in the magnitude of the $\Delta\nu_3$ values. Findlay and Symons have argued that, unlike the known distortion induced in the NO_3^- ion by association with H_2O,[8] there is no significant distortion of the ClO_4^- ion by water of solvation so that a single ν_3 band is observed for dilute $M^+ClO_4^-$ solutions in H_2O.[9] If we assume this to be correct, then all of the distortion of the ClO_4^- ion indicated by the curves in Figures 2 and 3 must arise from cation–anion interactions and the values for the pure H_2O (and NH_3) matrices (Table III, ref 1) must reflect the anion distortion produced by a cation that is completely solvated except for that coordination site at which it contacts the anion. It follows that, since the $\Delta\nu_3$ values are greater for the glassy H_2O than for the glassy NH_3 matrices, NH_3 more effectively cancels the ability of the M^+ ions to distort a coordinated ClO_4^- anion.

Further, it can be noted that, to a degree, the matrix data support the viewpoint of Findlay and Symons[9] referred to above. The glassy water $\Delta\nu_{3_{b1,b2}}$ value for the perchlorates decreases from ~85 to ~45 cm^{-1} in the series $Li^+ClO_4^-$, $Na^+ClO_4^-$, and $K^+ClO_4^-$. This cation effect is several times more pronounced than for the same nitrate series, using a water matrix, and suggests that any $\Delta\nu_{3_{b1,b2}}$ splitting produced by the solvent (water) alone is significantly less than 45 cm^{-1}, the value for $K^+ClO_4^-$ in glassy H_2O. Since the ν_3 anion bands in water solutions tend to be quite broad, it follows that any solvent splitting that may exist will probably not be observable. By the same token, any ammonia–ClO_4^- interaction must be very weak since the $K^+ClO_4^-$-in-glassy-ND_3 data sets the upper limit on the solvent induced distortion splitting at 20 cm^{-1} for $\Delta\nu_{3_{b1,b2}}$.

Acknowledgment. This research has been sponsored by the National Science Foundation under Grant CHE-7709653.

Registry No. $Li^+ClO_4^-$, 7791-03-9; $Li^+ClO_4^-{\cdot}H_2O$, 18716-61-5; $Li^+ClO_4^-{\cdot}2H_2O$, 17829-71-9; $Li^+ClO_4^-{\cdot}3H_2O$, 13453-78-6; $Li^+ClO_4^-{\cdot}4H_2O$, 17829-71-9; $K^+ClO_4^-$, 7778-74-7; $K^+ClO_4^-{\cdot}H_2O$, 70196-95-1; $K^+ClO_4^-{\cdot}2H_2O$, 70196-96-2; $K^+ClO_4^-{\cdot}3H_2O$, 70196-97-3; $K^+ClO_4^-{\cdot}4H_2O$, 70196-98-4; $K^+ClO_4^-{\cdot}NH_3$, 70196-99-5; $K^+ClO_4^-{\cdot}2NH_3$, 70197-00-1; $K^+ClO_4^-{\cdot}3NH_3$, 70197-01-2; $K^+ClO_4^-{\cdot}4NH_3$, 70197-02-3; $Na^+ClO_4^-$, 7601-89-0.

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