

Structural Studies of Matrix-isolated Alkali-metal Perchlorates: Proof of a Bidentate Interaction

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The vapours from heated alkali-metal perchlorates isolated in nitrogen matrices have been studied by i.r. spectroscopy. The use of $^{18}\text{O}/^{16}\text{O}$ isotopic substitution demonstrates the presence of two distinct pairs of oxygen atoms for the RbClO_4 molecule isolated in a nitrogen matrix. Similar results were obtained for the caesium salt. This bidentate interaction between the 'tetrahedral' ClO_4^- ion and the Rb^- (or Cs^-) ion contrasts sharply with the tridentate interaction found previously between the pyramidal ClO_3^- ion and Cs^+ .

Detailed studies of the effect of $^{16}\text{O}/^{18}\text{O}$ substitution on the i.r. spectra of a variety of alkali-metal salts of oxo-anions have shown that the most commonly found interaction between the anion and the cation is bidentate in nature. However, we have recently shown that the chlorate ion in CsClO_3 isolated in argon matrices retains C_{3v} symmetry implying a tridentate interaction.¹ Previous literature studies suggest that the alkali-metal perchlorates isolated in inert matrices undergo an interaction such that the degeneracy of ν_3 (the antisymmetric stretching vibration of the ClO_4^- 'tetrahedron') is completely removed.² However this does not *prove* that the interaction is bidentate. Bearing in mind that the interaction in CsClO_3 is tridentate we felt it essential to determine the mode of interaction of ClO_4^- with alkali-metal ions.

Results and Discussion

Preliminary i.r. experiments on a number of alkali-metal perchlorates isolated in argon or nitrogen matrices gave bands in the regions expected for the ClO_4^- ion.³ For the lighter alkali metals relatively large amounts of decomposition products such as chlorine dioxide were observed. Figure (a) shows the i.r. spectrum of RbClO_4 isolated in a nitrogen matrix in the region of ν_3 of the ClO_4^- ion. If the triplet of doublets (intensity ratio 3 : 1 for $^{35}\text{Cl} : ^{37}\text{Cl}$) is due to complete lifting of the three-fold degeneracy of ν_3 , the *highest* rotation axis must be C_2 . The highest symmetry is thus C_{2v} , but a lower symmetry would not alter the number of bands observed. (A band at approximately 930 cm^{-1} is assigned as ν_1 rendered i.r. active because of the lower symmetry.) If we assume that the symmetry of RbClO_4 isolated in a nitrogen matrix is C_{2v} , then the lifting of the degeneracy of ν_3 (t_2 in T_d symmetry) leads to b_2 at 1170.0 , a_1 at 1122.1 , and b_1 at 1051.7 cm^{-1} for the ^{35}Cl molecules. Here we assume that the lower-frequency component (1051.7 cm^{-1}) derives from the antisymmetric stretching vibration of the bridge oxygens, which also define the xz plane. Correspondingly the higher-frequency component (1170.0 cm^{-1}) is assumed to involve the terminal oxygens (yz plane). The a_1 component deriving from ν_3 (1122.1 cm^{-1}) may be loosely described as the out-of-phase symmetric stretching of the two ClO_2 units. (The weakly i.r.-active ν_1 is then the in-phase symmetric stretch.)

Because of the high quality of the RbClO_4 and CsClO_4 spectra these compounds were chosen for the crucial $^{16}\text{O}/^{18}\text{O}$ studies. Figure (b) shows the i.r. spectrum of ^{18}O (ca. 40 atom %) and ^{35}Cl (ca. 90 atom %) enriched RbClO_4 isolated in a nitrogen matrix. We assign the lower-frequency triplet (1051.7 , 1037.2 , 1020.7 cm^{-1}) to the antisymmetric stretching vibration of the bridging ClO_2 unit (16,16; 16,18; 18,18) and the higher-frequency triplet (1169.5 , 1157.0 , 1134.5 cm^{-1}) to the corres-

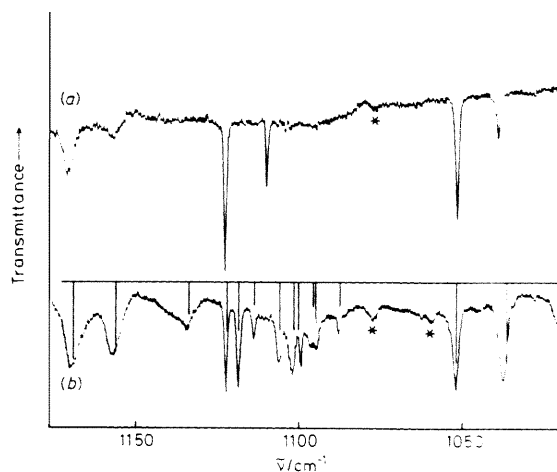


Figure. The i.r. spectrum of rubidium perchlorate in nitrogen matrices: (a) $\text{Rb}^{35/37}\text{Cl}^{16}\text{O}_4$; (b) $\text{Rb}^{35}\text{Cl}^{16/18}\text{O}_4$. Vertical lines show the calculated spectrum for $\text{Rb}^{35}\text{Cl}^{16/18}\text{O}_4$ using intensities based on isotopomer abundance. An asterisk indicates an impurity

ponding terminal ClO_2 unit isotopomers. Each component of a triplet formally contains three lines arising from the isotopomer distribution of the other ClO_2 unit. The evidence at this stage is thus in agreement with the presence of two pairs of equivalent oxygen atoms.

The key pattern in proving C_{2v} symmetry is however that obtained from the out-of-phase a_1 components deriving from ν_3 (1122.2 — 1088.0 cm^{-1}). Inspection of Figure (b) shows the presence of nine bands as required for the nine possible isotopomers under C_{2v} symmetry. The nine bands consist of a triplet of triplets. The high-frequency triplet (1122.2 , 1118.5 , 1114.0 cm^{-1}) shows a similar intensity distribution to that of the b_1 and b_2 components of ν_3 . This triplet corresponds to the isotopomers $\text{Rb}^{16}\text{O}_2\text{Cl}^{16}\text{O}_2$, $\text{Rb}^{16}\text{O}^{18}\text{OCl}^{16}\text{O}_2$, and $\text{Rb}^{18}\text{O}_2\text{Cl}^{16}\text{O}_2$, where the oxygen sequence is bridge, bridge (Cl) terminal, terminal as in Table 1. This triplet thus derives from the all- ^{16}O terminal split into a triplet by the three possible substitutions on the bridge oxygens. Closer inspection reveals two other triplets with a near coincidence of two of the bands.

In this particular case the entire spectrum can be assigned without the need for calculation, and demonstrates that in the RbClO_4 molecule isolated in a nitrogen matrix there are two sets of oxygen atoms (two equivalent bridge atoms, two equivalent terminal atoms). A normal-co-ordinate calculation based on a stretch-only force field with tetrahedral angles and using the four observed all- ^{16}O frequencies led to too large a

Table 1. Observed and calculated ^a Cl-O stretching modes (cm⁻¹) for Rb³⁵Cl^{16/18}O₄ in a nitrogen matrix

Observed	Calculated ^a		Assignment (bridge, bridge, terminal, terminal)					
1 169.5	1 169.0	(ν ₃ b ₂) ^b	b ₂	16	16	16	16	C _{2v}
	1 169.0		a''	16	18	16	16	C _s
	1 169.0		b ₂	18	18	16	16	C _{2v}
	1 156.3		a'	16	16	16	18	C _s
1 157.0	1 156.1		a	16	18	16	18	C ₁
	1 156.0		a'	18	18	16	18	C _s
1 134.5	1 133.4		b ₂	16	16	18	18	C _{2v}
	1 133.4		a''	16	18	18	18	C _s
	1 133.4		b ₂	18	18	18	18	C _{2v}
1 122.2	1 122.0	(ν ₃ a ₁) ^b	a ₁	16	16	16	16	C _{2v}
	1 118.5		a'	16	18	16	16	C _s
1 114.0	1 113.1		a ₁	18	18	16	16	C _{2v}
1 106.0	1 106.0		a'	16	16	16	18	C _s
1 102.0	1 102.0		a ₁	16	18	16	18	C _{2v}
1 099.5	1 100.4		a	16	16	18	18	C ₁
1 096.6	1 095.7		a'	16	18	16	18	C _s
1 094.7	1 095.2		a'	16	18	18	18	C _s
1 088.0	1 087.5		a ₁	18	18	18	18	C _{2v}
1 051.7	1 051.7		(ν ₃ b ₁) ^b	b ₁	16	16	16	16
1 037.2	1 051.7		a''	16	16	16	18	C _s
	1 051.7		b ₁	16	16	18	18	C _{2v}
	1 036.9		a'	16	18	16	16	C _s
	1 036.1		a	16	18	16	18	C ₁
1 020.7	1 035.1		a'	16	18	18	18	C _s
	1 019.7		b ₁	18	18	16	16	C _{2v}
	1 019.7		a''	18	18	16	18	C _s
	1 019.7		b ₁	18	18	18	18	C _{2v}

^a Effective mass of Cl ≡ 25; *f*_i 7.31, *f*_b 6.25, *f*_{t1} 0.37, *f*_{bb} 0.62, and *f*_{bt} 0.46 mdyn Å⁻¹ (1 dyn = 10⁻⁵ N). ^b Parent.

separation between the all-¹⁶O and all-¹⁸O frequencies. However the general frequency and intensity pattern followed those of the observed spectra. Further, the *observed* splittings between the all-¹⁶O and all-¹⁸O components compared favourably with that observed for ν₃ of ClO₄⁻ doped into a potassium iodide matrix.⁴ A normal-co-ordinate analysis of ClO₄⁻ in C_{2v} symmetry would require 21 general valence force field (GVFF) force constants, which is a formidable task and unlikely to yield significant results even if the geometry were known. Instead of introducing deformation and stretch-deformation constants⁵ into the analysis it is possible to assign an 'effective mass' to the chlorine atom. The results of Klee⁴ were used to calculate an 'effective mass' which when used as the basis of a stretch-only cation with tetrahedral angles yielded a very close fit between observed and calculated frequencies for RbCl^{16/18}O₄ isolated in a nitrogen matrix (see Table 1). Further, all of the crucial (ν₃) a₁ frequencies are predicted to better than one wavenumber. Similar results were obtained for Cs³⁵Cl^{16/18}O₄.

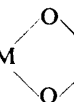
It is interesting to observe that, for the all-¹⁶O molecules, (i) the arithmetic mean of the three components of ν₃ and (ii) the frequency of ν₁ are almost independent of the cation (Table 2). By contrast the *separation* of the b₁ and b₂ components deriving from ν₃ changes from 149.1 cm⁻¹ at sodium to 116.4 cm⁻¹ at caesium. A simple point-charge model based on the change in ionic radius of the alkali-metal ion would lead to prediction of the trends observed. Further, for the b₂ component the change in frequency from sodium to caesium is a *decrease* of 18.8 cm⁻¹. By contrast, for the b₁ component there is an increase of 13.9 cm⁻¹. Again this is intuitively satisfying in that for the assumed 'bridge' modes the frequency is greatest for caesium. The converse is true for the assumed 'terminal' modes.

Table 2. Infrared stretching frequencies (cm⁻¹) of alkali-metal perchlorates isolated in nitrogen matrices (³⁵Cl components only)

	Na ⁺	K ⁺	Rb ⁺	Cs ⁺
ν ₁	—	927.2	928.2	928.6
ν ₃ b ₂	1 187.5	1 173.5	1 170.0	1 168.7
a ₁	1 131.5	1 124.8	1 122.1	1 120.0
b ₁	1 038.4	1 048.5	1 051.7	1 052.3
ν ₃ mean	1 119.1	1 115.6	1 114.6	1 113.7
ν ₃ (b ₂ - b ₁)	149.1	125.0	118.3	116.4

Finally we comment on the half-widths of the bands. In all the spectra of M⁺ClO₄⁻ (M = Na, K, Rb, or Cs) the b₂ component of ν₃ is broad. Initially we took this to indicate that the M⁺ ion could rotate on the bidentate oxygen 'hinge' (effective-

ly varying the M—O—Cl dihedral angle at the oxygens). The



principal effect of this would be to remove the equivalence of the two *terminal* oxygens. However the narrowness of the lines in the a₁ component suggests that this explanation is incorrect. Nonetheless it is of interest that the bending of the dihedral angle is of the same symmetry as the terminal anti-symmetric stretching vibration (b₂). The deformation ν₄ (like the antisymmetric stretching vibration ν₃) is of t₂ symmetry in the T_d point group, leading to three components in the (lowered) C_{2v} symmetry of RbClO₄. Two sharp bands showing chlorine-isotope effects are observed at 635.6 and 623.5 cm⁻¹ for RbClO₄ isolated in nitrogen. As these bands are of equal intensity they may be the a₁ and b₁ components of ν₄. There is also a broad feature around 629 cm⁻¹ which may be the b₂ component. This is difficult to prove because of the complexity of the Rb³⁵Cl^{16/18}O₄ spectra in this region.

Conclusions

These results demonstrate the C_{2v} structure of RbClO₄. The ion ClO₄⁻ is isoelectronic with AlF₄⁻. Calculations on LiAlF₄ suggest a C_{2v} interaction similar to the one found, here.⁶ Similarly the i.r. spectra of vapours from equimolar mixtures of MF (M = Li, Na, K, Rb, or Cs) and AlF₃ condensed with nitrogen or argon at cryogenic temperatures have been interpreted in terms of a C_{2v} model.⁷ However in the case of fluorine only one stable isotope is available so that the occurrence of two sets of fluorine atoms cannot be proved.

Experimental

Sodium perchlorate (Aldrich) and potassium perchlorate (BDH) were used as supplied, apart from preliminary out-gassing under vacuum. Samples of isotopically enriched (and unenriched) rubidium and caesium perchlorate were prepared by extended electrolysis¹ of the corresponding chlorides in aqueous solution using platinum electrodes. Enriched samples of Rb³⁵ClO₄ and Cs³⁵ClO₄ were prepared by the foregoing method using ¹⁸O-enriched water (40 atom % ¹⁸O) and enriched Rb³⁵Cl or Cs³⁵Cl (90 atom % ³⁵Cl-enriched NaCl exchanged with rubidium- or caesium-enriched Dowex 50-X8 cation resin). High-purity nitrogen was supplied by BOC. Vaporisation was accomplished from borosilicate or silica sample holders heated resistively. Deposition times were typically 1 h and during this period the CsI window of the cryostat was held at ca. 12 K. Spectra (200—4 000 cm⁻¹) were recorded on a Perkin-Elmer 225 spectrometer calibrated in the normal way.

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