

## 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  $\text{RbClO}_4$  molecule isolated in a nitrogen matrix. Similar results were obtained for the caesium salt. This bidentate interaction between the 'tetrahedral'  $\text{ClO}_4^-$  ion and the  $\text{Rb}^+$  (or  $\text{Cs}^+$ ) ion contrasts sharply with the tridentate interaction found previously between the pyramidal  $\text{ClO}_3^-$  ion and  $\text{Cs}^+$ .

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  $\text{CsClO}_3$  isolated in argon matrices retains  $C_{3v}$  symmetry implying a tridentate interaction.<sup>1</sup> Previous literature studies suggest that the alkali-metal perchlorates isolated in inert matrices undergo an interaction such that the degeneracy of  $\nu_3$  (the antisymmetric stretching vibration of the  $\text{ClO}_4^-$  'tetrahedron') is completely removed.<sup>2</sup> However this does not *prove* that the interaction is bidentate. Bearing in mind that the interaction in  $\text{CsClO}_3$  is tridentate we felt it essential to determine the mode of interaction of  $\text{ClO}_4^-$  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  $\text{ClO}_4^-$  ion.<sup>3</sup> 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  $\text{RbClO}_4$  isolated in a nitrogen matrix in the region of  $\nu_3$  of the  $\text{ClO}_4^-$  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  $\nu_3$ , 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  $930\text{ cm}^{-1}$  is assigned as  $\nu_1$  rendered i.r. active because of the lower symmetry.) If we assume that the symmetry of  $\text{RbClO}_4$  isolated in a nitrogen matrix is  $C_{2v}$ , then the lifting of the degeneracy of  $\nu_3$  ( $t_2$  in  $T_d$  symmetry) leads to  $b_2$  at  $1170.0$ ,  $a_1$  at  $1122.1$ , and  $b_1$  at  $1051.7\text{ cm}^{-1}$  for the  $^{35}\text{Cl}$  molecules. Here we assume that the lower-frequency component ( $1051.7\text{ cm}^{-1}$ ) derives from the antisymmetric stretching vibration of the bridge oxygens, which also define the  $xz$  plane. Correspondingly the higher-frequency component ( $1170.0\text{ cm}^{-1}$ ) is assumed to involve the terminal oxygens ( $yz$  plane). The  $a_1$  component deriving from  $\nu_3$  ( $1122.1\text{ cm}^{-1}$ ) may be loosely described as the out-of-phase symmetric stretching of the two  $\text{ClO}_2$  units. (The weakly i.r.-active  $\nu_1$  is then the in-phase symmetric stretch.)

Because of the high quality of the  $\text{RbClO}_4$  and  $\text{CsClO}_4$  spectra these compounds were chosen for the crucial  $^{16}\text{O}/^{18}\text{O}$  studies. Figure (b) shows the i.r. spectrum of  $^{18}\text{O}$  (ca. 40 atom %) and  $^{35}\text{Cl}$  (ca. 90 atom %) enriched  $\text{RbClO}_4$  isolated in a nitrogen matrix. We assign the lower-frequency triplet ( $1051.7$ ,  $1037.2$ ,  $1020.7\text{ cm}^{-1}$ ) to the antisymmetric stretching vibration of the bridging  $\text{ClO}_2$  unit (16,16; 16,18; 18,18) and the higher-frequency triplet ( $1169.5$ ,  $1157.0$ ,  $1134.5\text{ cm}^{-1}$ ) to the corres-

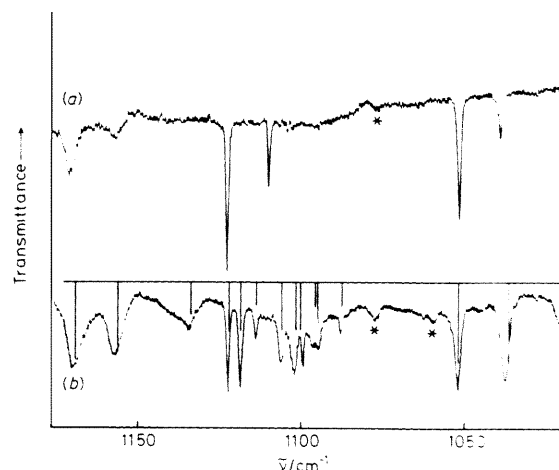


Figure. The i.r. spectrum of rubidium perchlorate in nitrogen matrices: (a)  $\text{Rb}^{35/37}\text{Cl}^{16}\text{O}_4$ ; (b)  $\text{Rb}^{35}\text{Cl}^{16/18}\text{O}_4$ . Vertical lines show the calculated spectrum for  $\text{Rb}^{35}\text{Cl}^{16/18}\text{O}_4$  using intensities based on isotomer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

ponding terminal  $\text{ClO}_2$  unit isotomers. Each component of a triplet formally contains three lines arising from the isotomer distribution of the other  $\text{ClO}_2$  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  $\nu_3$  ( $1122.2$ – $1088.0\text{ cm}^{-1}$ ). Inspection of Figure (b) shows the presence of nine bands as required for the nine possible isotomers under  $C_{2v}$  symmetry. The nine bands consist of a triplet of triplets. The high-frequency triplet ( $1122.2$ ,  $1118.5$ ,  $1114.0\text{ cm}^{-1}$ ) shows a similar intensity distribution to that of the  $b_1$  and  $b_2$  components of  $\nu_3$ . This triplet corresponds to the isotomers  $\text{Rb}^{16}\text{O}_2\text{Cl}^{16}\text{O}_2$ ,  $\text{Rb}^{16}\text{O}^{18}\text{OCl}^{16}\text{O}_2$ , 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- $^{16}\text{O}$  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  $\text{RbClO}_4$  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- $^{16}\text{O}$  frequencies led to too large a

**Table 1.** Observed and calculated <sup>a</sup> Cl-O stretching modes (cm<sup>-1</sup>) for Rb<sup>35</sup>Cl<sup>16/18</sup>O<sub>4</sub> in a nitrogen matrix

Observed	Calculated <sup>a</sup>		Assignment (bridge, bridge, terminal, terminal)
1 169.5	1 169.0	( <i>v</i> <sub>3</sub> <i>b</i> <sub>2</sub> ) <sup>b</sup>	<i>b</i> <sub>2</sub> 16 16 16 16 C <sub>2v</sub>
	1 169.0		<i>a</i> <sub>1</sub> 16 18 16 16 C <sub>s</sub>
	1 169.0		<i>b</i> <sub>2</sub> 18 18 16 16 C <sub>2v</sub>
	1 156.3		<i>a</i> <sub>1</sub> 16 16 16 18 C <sub>s</sub>
1 157.0	1 156.1		<i>a</i> 16 18 16 18 C <sub>1</sub>
	1 156.0		<i>a</i> <sub>1</sub> 18 18 16 18 C <sub>s</sub>
1 134.5	1 133.4		<i>b</i> <sub>2</sub> 16 16 18 18 C <sub>2v</sub>
	1 133.4		<i>a</i> <sub>1</sub> 16 18 18 18 C <sub>s</sub>
	1 133.4		<i>b</i> <sub>2</sub> 18 18 18 18 C <sub>2v</sub>
1 122.2	1 122.0	( <i>v</i> <sub>3</sub> <i>a</i> <sub>1</sub> ) <sup>b</sup>	<i>a</i> <sub>1</sub> 16 16 16 16 C <sub>2v</sub>
1 118.5	1 118.2		<i>a</i> <sub>1</sub> 16 18 16 16 C <sub>s</sub>
1 114.0	1 113.1		<i>a</i> <sub>1</sub> 18 18 16 16 C <sub>2v</sub>
1 106.0	1 106.0		<i>a</i> <sub>1</sub> 16 16 16 18 C <sub>s</sub>
1 102.0	1 102.0		<i>a</i> <sub>1</sub> 16 18 16 18 C <sub>2v</sub>
1 099.5	1 100.4		<i>a</i> 16 16 18 18 C <sub>1</sub>
1 096.6	1 095.7		<i>a</i> <sub>1</sub> 16 18 16 18 C <sub>s</sub>
1 094.7	1 095.2		<i>a</i> <sub>1</sub> 16 18 18 18 C <sub>s</sub>
1 088.0	1 087.5		<i>a</i> <sub>1</sub> 18 18 18 18 C <sub>2v</sub>
1 051.7	1 051.7	( <i>v</i> <sub>3</sub> <i>b</i> <sub>1</sub> ) <sup>b</sup>	<i>b</i> <sub>1</sub> 16 16 16 16 C <sub>2v</sub>
	1 051.7		<i>a</i> <sub>1</sub> 16 16 16 18 C <sub>s</sub>
	1 051.7		<i>b</i> <sub>1</sub> 16 16 18 18 C <sub>2v</sub>
1 037.2	1 036.9		<i>a</i> <sub>1</sub> 16 18 16 16 C <sub>s</sub>
	1 036.1		<i>a</i> 16 18 16 18 C <sub>1</sub>
	1 035.1		<i>a</i> <sub>1</sub> 16 18 18 18 C <sub>s</sub>
1 020.7	1 019.7		<i>b</i> <sub>1</sub> 18 18 16 16 C <sub>2v</sub>
	1 019.7		<i>a</i> <sub>1</sub> 18 18 16 18 C <sub>s</sub>
	1 019.7		<i>b</i> <sub>1</sub> 18 18 18 18 C <sub>2v</sub>

<sup>a</sup> Effective mass of Cl ≡ 25; *f*<sub>i</sub> 7.31, *f*<sub>b</sub> 6.25, *f*<sub>t</sub> 0.37, *f*<sub>bb</sub> 0.62, and *f*<sub>bt</sub> 0.46 mdyn Å<sup>-1</sup> (1 dyn = 10<sup>-5</sup> N). <sup>b</sup> Parent.

separation between the all-<sup>16</sup>O and all-<sup>18</sup>O frequencies. However the general frequency and intensity pattern followed those of the observed spectra. Further, the *observed* splittings between the all-<sup>16</sup>O and all-<sup>18</sup>O components compared favourably with that observed for *v*<sub>3</sub> of ClO<sub>4</sub><sup>-</sup> doped into a potassium iodide matrix.<sup>4</sup> A normal-co-ordinate analysis of ClO<sub>4</sub><sup>-</sup> in C<sub>2v</sub> 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 constants<sup>5</sup> into the analysis it is possible to assign an 'effective mass' to the chlorine atom. The results of Klee<sup>4</sup> 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<sup>16/18</sup>O<sub>4</sub> isolated in a nitrogen matrix (see Table 1). Further, all of the crucial (*v*<sub>3</sub>) *a*<sub>1</sub> frequencies are predicted to better than one wavenumber. Similar results were obtained for Cs<sup>35</sup>Cl<sup>16/18</sup>O<sub>4</sub>.

It is interesting to observe that, for the all-<sup>16</sup>O molecules, (i) the arithmetic mean of the three components of *v*<sub>3</sub> and (ii) the frequency of *v*<sub>1</sub> are almost independent of the cation (Table 2). By contrast the *separation* of the *b*<sub>1</sub> and *b*<sub>2</sub> components deriving from *v*<sub>3</sub> changes from 149.1 cm<sup>-1</sup> at sodium to 116.4 cm<sup>-1</sup> 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 *b*<sub>2</sub> component the change in frequency from sodium to caesium is a *decrease* of 18.8 cm<sup>-1</sup>. By contrast, for the *b*<sub>1</sub> component there is an increase of 13.9 cm<sup>-1</sup>. 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<sup>-1</sup>) of alkali-metal perchlorates isolated in nitrogen matrices (<sup>35</sup>Cl components only)

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

Finally we comment on the half-widths of the bands. In all the spectra of M<sup>+</sup>ClO<sub>4</sub><sup>-</sup> (M = Na, K, Rb, or Cs) the *b*<sub>2</sub> component of *v*<sub>3</sub> is broad. Initially we took this to indicate that the M<sup>+</sup> 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 *a*<sub>1</sub> 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 (*b*<sub>2</sub>). The deformation *v*<sub>4</sub> (like the antisymmetric stretching vibration *v*<sub>3</sub>) is of *t*<sub>2</sub> symmetry in the T<sub>d</sub> point group, leading to three components in the (lowered) C<sub>2v</sub> symmetry of RbClO<sub>4</sub>. Two sharp bands showing chlorine-isotope effects are observed at 635.6 and 623.5 cm<sup>-1</sup> for RbClO<sub>4</sub> isolated in nitrogen. As these bands are of equal intensity they may be the *a*<sub>1</sub> and *b*<sub>1</sub> components of *v*<sub>4</sub>. There is also a broad feature around 629 cm<sup>-1</sup> which may be the *b*<sub>2</sub> component. This is difficult to prove because of the complexity of the Rb<sup>35</sup>Cl<sup>16/18</sup>O<sub>4</sub> spectra in this region.

## Conclusions

These results demonstrate the C<sub>2v</sub> structure of RbClO<sub>4</sub>. The ion ClO<sub>4</sub><sup>-</sup> is isoelectronic with AlF<sub>4</sub><sup>-</sup>. Calculations on LiAlF<sub>4</sub> suggest a C<sub>2v</sub> interaction similar to the one found, here.<sup>6</sup> Similarly the i.r. spectra of vapours from equimolar mixtures of MF (M = Li, Na, K, Rb, or Cs) and AlF<sub>3</sub> co-condensed with nitrogen or argon at cryogenic temperatures have been interpreted in terms of a C<sub>2v</sub> model.<sup>7</sup> 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 outgassing under vacuum. Samples of isotopically enriched (and unenriched) rubidium and caesium perchlorate were prepared by extended electrolysis<sup>1</sup> of the corresponding chlorides in aqueous solution using platinum electrodes. Enriched samples of Rb<sup>35</sup>ClO<sub>4</sub> and Cs<sup>35</sup>ClO<sub>4</sub> were prepared by the foregoing method using <sup>18</sup>O-enriched water (40 atom % <sup>18</sup>O) and enriched Rb<sup>35</sup>Cl or Cs<sup>35</sup>Cl (90 atom % <sup>35</sup>Cl-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<sup>-1</sup>) were recorded on a Perkin-Elmer 225 spectrometer calibrated in the normal way.

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