The Structural Parameters of $FClO_3$ and $HClO_4$

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PERCHLORYL FLUORIDE, $FClO_3$, has been studied previously by infrared[1] and microwave spectroscopy.[2] No definite structural parameters were obtained in these investigations. The infrared study[1] showed that the three oxygen atoms are equivalent and a model with C_{3v} symmetry and tetrahedral co-ordination around chlorine was suggested. The microwave investigation confirmed this and established that the centre of mass of the ^{35}Cl species of the molecule is situated 0·154 Å from chlorine. It was assumed to lie between the chlorine and fluorine atoms although this was not actually proved.

We have recently carried out an electron diffraction study of $FClO_3$ in the vapour phase using a sample of the compound given to us by the Pennsalt Chemical Corporation, Pennsylvania, U.S.A. A Balzers electron diffraction instrument was used. Least-squares refinement of the structural parameters of the C_{3v} model using molecular intensity data gave the dimensions shown in the Figure. The centre of mass for this model is situated 0·151 Å from the chlorine atom in the ^{35}Cl species, and lies between chlorine and fluorine, thus confirming the microwave result.[2]

The related molecule of perchloric acid, $HOClO_3$, has been studied previously by electron diffraction[3] and by infrared spectroscopy.[4] The i.r. study suggested a model with C_s symmetry and the electron diffraction study obtained approximate dimensions for the ClO_4 fragment of C_{3v} symmetry, although it did not establish the position of the hydrogen atom.

We have reinvestigated perchloric acid by gas-phase electron diffraction, with a sample prepared by dehydration of a 68% aqueous solution of the acid and have obtained parameters for the ClO_4 skeleton. These are shown in the Figure. It has again proved difficult to determine the situation of the hydrogen atom.

From these results it is evident that the peripheral Cl–O bonds in both molecules have a similar geometry and hence should have a similar electron environment; their π-bond orders should be approximately the same. It seems likely that the Cl–O(H) and Cl–F bonds also have similar π-bond orders. The Cl–O(H) bond in perchloric acid is shorter than the 1·70 Å of the Cl–O bridge bonds in Cl_2O_7 and Cl_2O, which may be regarded as very nearly single bonds.[5,6] The Cl–F distance of 1·610 Å in perchloryl fluoride is also shorter than the value of 1·64 Å expected for a Cl–F single bond.[7]

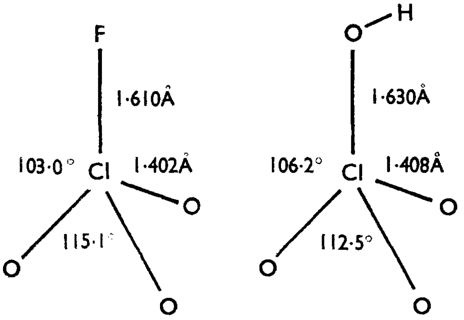

FIGURE. *The dimensions of* $FClO_3$ *and* $HClO_4$. *E.s.d.'s are* 0·002 Å *in* Cl–O; 0·008 Å *in* Cl–O(H) *and* Cl–F; *and* 1·0° *in angles.*

In crystals of sulphates or phosphates the differences between S–O and S–O(H) bonds, or P–O and P–O(H) bonds, are typically much smaller than the difference reported here for the Cl–O and Cl–O(H) bonds in isolated $HClO_4$ molecules. These comparisons strengthen the arguments[8,9] that X–O and X–O(H) bond lengths in crystals are appreciably affected by the formation of hydrogen bonds.

Reductions in the e.s.d.'s of the dimensions of the two molecules should be possible when we have calculated mean amplitudes of vibration from spectroscopic data and have used them as constants in the least-squares refinement. This procedure should improve the resolution of the rather similar tetrahedron-edge distances which occur.

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