THE STRUCTURE OF HALOGEN DIMERS: MICROWAVE SPECTRUM OF $(ClF)_2$

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The rotational spectrum of $(ClF)_2$ is reported. The molecule is a slightly asymmetric prolate rotor. A number of transitions have been observed for the four isotopomers. A very detailed study of the $J = 1 \leftarrow 0$ transitions provides precise values for the rotational constants $\frac{B+C}{2}$ as well as hyperfine structure constants $eqQ_{aa}(Cl)$. A series of a-type transitions up to J = 7 are observed under somewhat lower resolution. We also observe several b-type transitions with $K = 1 \leftarrow 0$.

Preliminary values of the rotational constants for the $(^{35}ClF)_2$) isotopomer are $A = 21722, B = 1111.7, C = 1055.7$ MHz. These values may be compared to the rotational constants calculated from the minimum energy geometry obtained at the MP2 level: $A = 21654, B = 1121, C = 1066$ MHz. The geometry is planar with the center of mass separation 3.89 Å . The array FCl$\cdots$F is almost linear and the angle between the two FCl units is 111°. The complex appears to be quite rigid. The experimental hyperfine structure constants for the $(^{35}ClF)_2$ isotopomer are $eqQ_{aa}(Cl_1)$ = -123.9 MHz and $eqQ_{aa}(Cl_2)$ = -6.72 MHz. Constants calculated from the MP2 geometry by projecting the monomer eqQ(Cl) values to the inertial axes are in good agreement with experiment.

The crystal structure of ClF appears to be presently undetermined. A comparison of $(Cl_2)_2$ calculated at a level similar to $(ClF)_2$ is compared with the crystal structure of Cl_2.