Vibrational Spectrum and Structure of Fluorine Peroxide O_2F_2

By K. R. LOOS,* C. T. GOETSCHEL, and V. A. CAMPANILE
(*Shell Development Company, Emeryville, California* 94608)

THE structure of O_2F_2 has been known for some time from microwave studies,[1] and several of the vibrational frequencies have been either estimated[1] or observed;[2–4] however, no complete i.r. spectrum of this molecule has yet appeared. Although the molecule has the same symmetry as H_2O_2, namely C_2, the O–O bond is much shorter than that in H_2O_2 (1·217 Å *vs.* 1·48 Å), being about the same as that of O_2, while the O–F bonds are considerably longer than those in OF_2 (1·575 Å *vs.* 1·409 Å). Thus the O–O bond seems to retain double bond character, while the O–F bonds are weaker than regular OF single bonds.

We have observed and analyzed the i.r. spectra of solid $^{16}O_2F_2$ and $^{18}O_2F_2$. Spectra were recorded at 77°K over the range 3000—350 cm.$^{-1}$ with the sample suspended between two AgCl plates; below 350 cm.$^{-1}$ it proved possible to obtain the spectrum with the sample suspended between two high-density polyethylene slabs. Although some reaction with the polyethylene was noted, it did not prove a serious problem at these low temperatures.

The O_2F_2 was prepared by radiolysis of liquid mixtures of O_2 and F_2 at 77° K followed by thermal decomposition of the superoxides of fluorine.[5] At low temperatures O_2F_2 is a pale yellow solid which melts sharply at 119° K.

It appeared surprising that the O–O stretching vibration does not appear in the vicinity of 1500 cm.$^{-1}$, where it has been located for the O_2F radical,[3,4] whose bonding is believed to be analogous to that in O_2F_2. Instead, it appears that the O–O stretching mode occurs at 1306 cm.$^{-1}$ for O_2F_2. This has been confirmed by the results of studies with oxygen-18. For $^{18}O_2F_2$ the band at 1306 cm.$^{-1}$ disappears and is replaced by one at 1239 cm.$^{-1}$.

The fundamental frequencies of $^{16}O_2F_2$ and $^{18}O_2F_2$ are listed in the Table along with their tentative assignment based upon a normal co-ordinate analysis. The torsional fundamental was not observed for $^{18}O_2F_2$ since insufficient oxygen-18 was available for a sample large enough to enable this weak transition to be located. From the normal co-ordinate analysis it appears that there is no normal vibration composed of a purely torsional motion. This complicates the calculation of the internal rotation barrier and makes a comparison with H_2O_2 difficult.

Fundamental vibrations of O_2F_2

ν (cm.$^{-1}$)		
$^{16}O_2F_2$	$^{18}O_2F_2$	Assignment
1306	1239	O–O str.
621	595	O–F sym. str.
615	586	O–F anti-sym. str.
457	444	O–O–F anti-sym. bend
369	362	O–O–F sym. bend
205	—	Torsion

The results of a molecular-orbital calculation carried out by us, using the extended Hückel approximation, confirm the earlier description of the bonding in O_2F_2[1,3] in which the strength of the O–O bond is explained by the interaction of the electronegative fluorine atoms with the unpaired π^* orbitals on the oxygens to form a three-centre (O–O–F) molecular orbital, which is anti-bonding with respect to O–O, but bonding with respect to O–F. Thus, the overall O–O bond order remains virtually the same, but the O–F bonds are weakened because they are part of a three-centre bonding system instead of being regular two-centre, two-electron bonds.

This work was supported in part by a contract from the Advanced Research Projects Agency, through the U.S. Army Research Office, Durham, North Carolina.

(*Received, October 29th,* 1968; *Com.* 1470.)

---

[1] R. M. Jackson, *J. Chem. Soc.*, 1962, 4585.

[2] H. W. Brown, unpublished work.

[3] R. D. Spratley, J. J. Turner, and G. C. Pimentel, *J. Chem. Phys.*, 1966, **44**, 2063.

[4] A. Arkell, *J. Amer. Chem. Soc.*, 1965, **87**, 4057.

[5] C. T. Goetschel, V. A. Campanile, C. D. Wagner, and J. N. Wilson, publication in preparation.