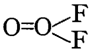
884. *The Microwave Spectrum, Structure, and Dipole Moment of Dioxygen Difluoride.*

By Robert H. Jackson.

The rotational spectra of $F_2{}^{16}O_2$, $F_2{}^{16}O^{18}O$, and $F_2{}^{18}O_2$ in the microwave region have been examined. From detailed assignments for the ground vibrational states, effective moments of inertia have been evaluated. These demonstrate that the structure is a chain, F–O–O–F, with the structural parameters: r(O–O) = 1·217 ± 0·003 Å, r(F–O) = 1·575 ± 0·003 Å, ∠OOF = 109° 30′ ± 30′, and dihedral angle = 87° 30′ ± 30′. The O–O distance is particularly short and the O–F distance particularly long.

A value of 1·44 ± 0·04 D was obtained for the dipole moment of the molecule from measurements of the Stark effect.

Rotational spectra associated with two vibrational modes of the molecule have been observed. For the lowest-frequency mode, effective moments have been determined for the first three excited vibrational states. Approximate intensity measurements indicate that this vibrational mode has a frequency of 160 ± 10 cm.$^{-1}$, so that the barrier to internal rotation must be fairly high.

There are at present four known oxygen–fluorine compounds, namely, F_2O, F_2O_2, F_2O_3,[1] and F_2O_4.[2] The structure and dipole moment of the monoxide were determined recently by microwave spectroscopy.[3] The structures of F_2O_2 and F_2O_4 are unknown, but the precise details obtained for F_2O_2 may provide valuable information for any investigation of these compounds. In a recent review [4] it was pointed out that, although no direct evidence was available for the structure of F_2O_2, kinetic evidence seemed to indicate a structure  $O{=}O{<}^{F}_{F}$ rather than an F–O–O–F arrangement. Owing to this lack of initial structural information it was not possible to predict the features of the spectrum, as is usual in microwave investigations. For a F–O–O–F chain, moments were calculated by using various sets of structural parameters. This structure has a C_2 axis of symmetry, and calculations showed that it would have a *b*- or a *c*-type selection-rule spectrum. Calculations for the $O{=}OF_2$ model showed that both *b*- and *c*-type spectra should occur. This model does not have a C_2 symmetry axis unless the molecule is planar.

Experimental and Results

Preparation of Samples.—Dioxygen difluoride $F_2{}^{16}O_2$ was prepared by the method of Ruff and Menzel [5] who first obtained the compound. The fluorine and oxygen were commercial supplies. The species enriched in ^{18}O were prepared by using a pre-mixed sample of $^{18}O_2$ and $^{16}O_2$ for the reaction.

Observation of the Spectrum.—The spectrum was observed by using Stark modulated spectrometers;[6] the frequency coverage available was 8—37·5 and 49—60 KMc./sec. from klystrons and two backward wave oscillators. Frequencies were measured against a conventional frequency standard, and also a Gertsch FM-4A locked to a Gertsch FM6 frequency meter; both standards were checked against Radio Station W.W.V. Relative peaks heights of absorption signals were measured by a technique developed by Mr. A. Esbitt in these laboratories.[7]

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[1] Kirschenbaum and Grosse, *J. Amer. Chem. Soc.*, 1959, **81**, 1277.

[2] Grosse, Streng, and Kirschenbaum, *J. Amer. Chem. Soc.*, 1961, **83**, 1004.

[3] Pierce, Jackson, and DiCianni, *J. Chem. Phys.*, 1961, **35**, 2240.

[4] George, " Progress in Inorganic Chemistry," Interscience Publ., Inc., New York, 1960, Vol. II, p. 68.

[5] Ruff and Menzel, *Z. anorg. Chem.*, 1933, **211**, *B*, 204.

[6] McAfee, Hughes, and Wilson, *Rev. Sci. Instr.*, 1949, **20**, 821.

[7] Esbitt, Symposium on Molecular Structure and Spectroscopy, Columbus, Ohio, June 1961.

F_2O_2 is said [8] to decompose into fluorine and oxygen with a half-life at −50° of 3 hr. for the homogeneous unimolecular decomposition. In order to maintain a sample in the absorption cell, the gas was passed continuously through the cell, which was cooled with solid carbon dioxide. The necessity for continuous passage was easily demonstrated; if, while a line was being observed, a given amount of sample was trapped in the cell, the line disappeared within 30 sec. However, the disappearance of the spectrum assigned to F_2O_2 was accompanied by appearance of a spectrum of another molecule which is very stable under the conditions of the experiment. The latter spectrum was found, by the use of microwave and mass-spectrum techniques, to arise from carbonyl fluoride, produced presumably when F_2O_2 attacks the " Teflon " in the absorption cell.[9]

TABLE 1.

The rotational assignment of the three species of F_2O_2.

	$F_2{}^{16}O_2$		$F_2{}^{16}O^{18}O$		$F_2{}^{18}O_2$	
	Frequency [a]		Frequency [a]		Frequency [a]	
Transition	obs.	calc.	obs.	calc.	obs.	calc.
$1_{01} \longrightarrow 1_{10}$	15,906·04	15,906·04	15,213·30	15,213·30	14,579·88	14,579·88
$2_{02} \longrightarrow 2_{11}$	16,577·38	16,577·38	15,892·15	15,892·15	15,261·76	15,261·78
$3_{03} \longrightarrow 3_{12}$	17,622·05	17,622·28	16,950·37	16,950·81	16,327·46	16,326·98
$4_{04} \longrightarrow 4_{13}$	19,084·40	19,084·87				
$5_{05} \longrightarrow 5_{14}$	21,019·40	21,020·64				
$6_{06} \longrightarrow 6_{15}$	23,488·36	23,491·50				
$7_{07} \longrightarrow 7_{16}$	26,552·38	26,558·07				
$8_{08} \longrightarrow 8_{17}$	30,258·95	30,269·61				
$9_{09} \longrightarrow 9_{18}$	34,636·60	34,653·54				
$0_{00} \longrightarrow 1_{11}$	24,626·32	24,626·32	23,850·65	23,850·65	23,138·5	23,138·50
$1_{01} \longrightarrow 2_{12}$	33,346·88	33,346·60	32,488·1	32,488·00	31,697·0 [b]	31,697·12
$3_{03} \longrightarrow 2_{12}$	13,406·8	13,407·71				
$3_{12} \longrightarrow 2_{21}$	16,690·0	16,688·14				
$3_{13} \longrightarrow 4_{04}$	23,563·25	23,565·19	23,951·57	23,953·08		
$3_{03} \longrightarrow 4_{14}$	49,860·8	49,860·41				
$4_{14} \longrightarrow 5_{05}$	33,871·6	33,876·03	34,171·9	34,175·97	34,395·9	34,401·52

[a] Mc./sec. Accuracy ±0·1 Mc. where quoted to 0·01 Mc.; ∓0·5 Mc. where quoted to 0·1 Mc.
This line falls near another strong line.

The Spectrum.—The rotational transitions assigned to each species of the molecule are listed in Table 1. The assignments are based on observed Stark patterns for each line. The fact that each line has associated with it a series of satellite lines spaced regularly from the main line helped considerably in the initial assignments. Comparison between observed and calculated frequencies indicates how the effects of centrifugal distortion become increasingly important for the higher rotational energy states. The rotational constants used in computing the calculated frequencies were obtained from the frequencies of the $1_{11} \longleftarrow 0_{00}$, $1_{10} \longleftarrow 1_{01}$, and $2_{11} \longleftarrow 2_{02}$ transitions. The rotational constants together with the corresponding moments of inertia are given in Table 2.

TABLE 2.

Ground-state rotational constants and moments of inertia of F_2O_2.

	$F_2{}^{16}O_2$	$F_2{}^{16}O^{18}O$	$F_2{}^{18}O_2$		$F_2{}^{16}O_2$	$F_2{}^{16}O^{18}O$	$F_2{}^{18}O_2$
A (Mc./sec.) ...	20,266·18	19,531·98	18,859·19	I_A (amu Å^2) ...	24·94456	25·88222	26·80555
B	5,011·09	4,975·78	4,938·34	I_B	100·8824	101·5981	102·3686
C	4,360·14	4,318·68	4,279·31	I_C	115·9438	117·0570	118·1338
κ	−0·91815	−0·91362	−0·90960				

The spectra of the $F_2{}^{16}O_2$ and $F_2{}^{18}O_2$ species showed very clearly the effect of nuclear-spin statistics on the line intensities, demonstrating that the intermediate axis of inertia of the molecule is a C_2 axis of symmetry. Though no precise intensity measurements were carried out, examination of the spectrum indicated that for an initial $^{18}O_2 : {}^{16}O_2$ ratio of 1 : 9 the observed product ratio of $F_2{}^{16}O_2 : F_2{}^{16}O^{18}O : F_2{}^{18}O_2$ was compatible with the theoretical ratio of 81 : 18 : 1. This is the ratio to be expected if the mechanism of the reaction forming F_2O_2 involves an initial dissociation of the O_2 molecule.

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[8] Frisch and Schumacker, *Z. phys. Chem.*, 1937, *B*, **37**, 1.

[9] Laurie and Jackson, unpublished work.

Dipole Moment.—Analysis of the Stark effect for the four transitions, $1_{10} \longleftarrow 1_{01}$, $2_{11} \longleftarrow 2_{02}$, $1_{11} \longleftarrow 0_{00}$, and $2_{12} \longleftarrow 1_{01}$, yields a value of 1·44 ± 0·04 D for the dipole moment of the molecule. The theory developed by Golden and Wilson [10] was used in the evaluation of the dipole moment. The Stark effect of the $1 \longleftarrow 0$ transition for carbonyl sulphide was used in calibrating the field in the Stark cell, with a value of 0·7124 D for the dipole moment of the sulphide.[11] From a precise investigation of the Stark effects it was possible to show that μ_a and μ_c (the components of dipole among the *a*- and the *c*-inertial axis) are both zero within the accuracy of the determination. This finding is substantiated by the fact that a search failed to reveal an *a*- or *c*-type transition.

Molecular Structure.—The aim of this section is to present arguments which lead to the final structural parameters, and at the same time to show that these conclusions can be reached without having to assume a particular molecular model at any stage in the calculation.

(*a*) Table 2 shows that $I_A + I_B - I_C >>> 0$ and hence the molecule is non-planar.

(*b*) From the observed alternation in intensities it is deduced that the molecule has an axis of symmetry C_n, where *n* must be two since the spectrum observed is due to an asymmetric rotor molecule and values of *n* greater than two would give a symmetric rotor spectrum.

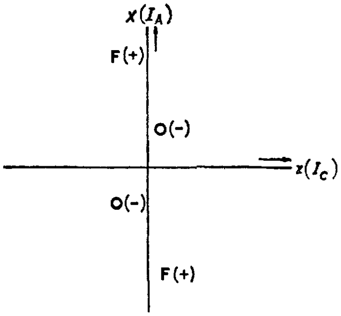

FIG. 1. Distribution of the atoms of F_2O_2 with respect to the *a*- and the *c*-inertial axis.

TABLE 3.

Atomic co-ordinates and structural parameters of F_2O_2.

(*a*) Oxygen-atom co-ordinates.

	Parent molecule $F_2{}^{16}O_2$	Substd. molecule $F_2{}^{18}O{}^{16}O$	Parent molecule $F_2{}^{18}O_2$	Substd. molecule $F_2{}^{18}O{}^{16}O$
x_O	0·4754		0·4761	
y_O	0·5816		0·5499	
z_O	0·3814		0·3783	
r(O–O)	1·2190		1·2162	

(*b*) Fluorine-atom co-ordinates.

Choice of moments:	(1) I_A and I_B;	(2) I_C and I_B;	(3) I_A and I_B;	(4) I_C and I_B.
	$F_2{}^{16}O_2$	$F_2{}^{16}O_2$	$F_2{}^{18}O_2$	$F_2{}^{18}O_2$
x_F	1·527	1·528	1·526	1·528
y_F	0·4896	0·4896	0·5210	0·5210
z_F	0·098	0·077	0·109	0·087

(*c*) Structural parameters.

Choice of moments	(1)	(2)	(3)	(4)
r(O–O)	1·219	1·219	1·216	1·216
r(F–O)	1·575	1·572	1·577	1·574
∠FOO	109° 20′	109° 50′	109° 15′	109° 46′
Dihedral angle	87° 48′	87° 4′	88° 2′	87° 20′

(*c*) Analysis of the Stark effect shows that the dipole is along the *b*-axis and that therefore the C_2 axis is along *b*.

(*d*) The spectra of the ^{18}O species give two further pieces of information. In the first place

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[10] Golden and Wilson, *J. Chem. Phys.*, 1948, **16**, 669.

[11] Marshall and Weber, *Phys. Rev.*, 1957, **105**, 1502.

the $F_2{}^{16}O^{18}O$ spectrum does not exhibit the effect of nuclear-spin statistics. Secondly, only one spectrum for the $F_2{}^{16}O^{18}O$ species was observed.

Hence it can be concluded that the two fluorine atoms must be exchanged by a rotation of 180° about the *b*-axis. The two oxygen atoms must also be exchanged by the same operation. The possibility that the two oxygen atoms both lie on the C_2 axis is excluded by a combination of arguments (*a*) and (*b*).

Fig. 1 illustrates how the atoms must be distributed within the quadrants defined by the *a*- and the *c*-inertial axis.

The C_2 axis is perpendicular to the plane of the paper; this is the *b*-inertial axis. The two oxygen atoms lie in a plane perpendicular to the C_2 axis; in the convention shown, they are below the plane of the paper. By the centre-of-mass condition the two fluorine atoms lie in a similar plane above the plane of the paper.

Kraitchman [12] has shown how changes in the moments of inertia on isotopic substitution can be used to determine the co-ordinates, with respect to the inertial axes, of the atom substituted. Since three isotopic species have been studied, two independent sets of oxygen co-ordinates can be determined. The results are tabulated in Table 3. The oxygen–oxygen bond length comes directly from this analysis [equal to $2(x_0{}^2 + z_0{}^2)^{\frac{1}{2}}$]; this bond length is very short and the two values show the expected degree of agreement. The centre-of-mass condition is then applied to determine y_F. The two remaining co-ordinates x_F and z_F can be determined from the information already obtained and any two of the observed moments of inertia. Four

TABLE 4.

Rotational assignment of vibrational satellite spectra.

Vibrational state	$\nu' = 1$, $F_2{}^{16}O_2$		$\nu' = 2$, $F_2{}^{16}O_2$		$\nu' = 3$, $F_2{}^{16}O_2$	
Transition	Obs. freq.[a]	Calc. freq.	Obs. freq.	Calc. freq.	Obs. freq.	Calc. freq.
$1_{01} \longrightarrow 1_{10}$	16,016·74	16,016·74	16,127·52	16,127·52	16,239·55	16,239·55
$2_{02} \longrightarrow 2_{11}$	16,700·24	16,700·23	16,822·03	16,822·02	16,944·86	16,944·96
$3_{03} \longrightarrow 3_{12}$	17,764·15	17,764·47	17,903·30	17,903·74	18,042·39	18,042·99
$4_{04} \longrightarrow 4_{13}$	19,253·5	19,254·81	19,418·45	19,419·15	19,581·70	19,584·23
$5_{05} \longrightarrow 5_{14}$	21,225·3	21,228·25	21,424·8	21,426·58	21,620·05	21,625·31
$6_{06} \longrightarrow 6_{15}$	23,743·20	23,748·23	23,986·65	23,990·81	24,224·09	24,233·39
$0_{00} \longrightarrow 1_{11}$	24,715·57	24,715·57	24,804·00	24,804·00	—	24,889·46
$1_{01} \longrightarrow 2_{12}$	33,414·80	33,414·40	33,480·62	33,480·48	33,539·31	33,539·31
$3_{13} \longrightarrow 4_{04}$	23,443·76	23,447·06	23,314·70	23,318·03	—	23,170·19
$3_{03} \longrightarrow 4_{14}$	49,870·9	49·869·38	49,880·2	49,876·34	—	49,867·79
$4_{14} \longrightarrow 5_{05}$	33,765·25	33,769·79	33,625·6	33,631·66	33,484·7	33,497·27
A (Mc./sec.) ...	20,366·16		20,465·76		20,564·51	
B	5011·93		5011·24		5008·34	
C	4349·42		4338·24		4324·96	
κ	−0·91727		−0·91654		−0·91584	

Mc./sec.

Vibrational state	$\nu'' = 1$, $F_2{}^{16}O_2$		$\nu' = 4$, $F_2{}^{16}O_2$		$\nu' = 1$, $F_2{}^{16}O^{18}O$	
Transition	Obs. freq.	Calc. freq.	Obs. freq.	Calc. freq.	Obs. freq.	Calc. freq.
$1_{01} \longrightarrow 1_{10}$	15,817·85	15,817·85	16,353·	16,353·00	15,319·85	15,319·85
$2_{02} \longrightarrow 2_{11}$	16,491·51	16,491·71	—	17,068·01	—	—
$3_{03} \longrightarrow 3_{12}$	17,540·88	17,540·86	18,182·24	18,182·24	17,089·0	17,089·00
$4_{04} \longrightarrow 4_{13}$	—	19,009·98				
$5_{05} \longrightarrow 5_{14}$	—	20,955·16				
$6_{06} \longrightarrow 6_{15}$	23,433·29	23,438·90				
$0_{00} \longrightarrow 1_{11}$	24,484·06	24,484·06				
$1_{01} \longrightarrow 2_{12}$	—	—				
$3_{13} \longrightarrow 4_{04}$	23,436·63	23,441·79				
$3_{03} \longrightarrow 4_{14}$	—	—				
$4_{14} \longrightarrow 5_{05}$	33,700·7	33,703·97				
A (Mc./sec.) ...	20,150·96		$A—C = 16{,}353{\cdot}0$		$A—C = 15{,}319{\cdot}85$	
B	4986·31					
C	4333·11					
κ	−0·91741		−0·91530		−0·9127	

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[12] Kraitchman, *Amer. J. Phys.*, 1953, **21**, 17.

choices are shown in Table 3. z_F is determined less precisely than x_F because the fluorine-atom lies very close to the a-axis. Application of the condition $\sum_i m_i x_i z_i = 0$ confirms the distribution of the atoms shown in Fig. 1. Thus it is possible to determine unambiguously both the relative signs and the magnitudes of the co-ordinates of each atom in the molecule. Also in Table 3 the four structural parameters of chemical interest have been determined from the co-ordinates obtained above. The calculation has been performed for the four choices of the moments used to locate the fluorine atoms. As a final check on the calculation, rotational constants for the molecule were recalculated by using the first two sets of co-ordinate obtained in Table 3; the agreement between observed and the calculated constants was within 0·1% for each set of co-ordinates taken.

Vibrational Satellite Spectra.—Table 4 lists assignments obtained for rotational transitions associated with excited vibrational states of the molecule. In making the assignments both the Stark effects and the regular displacements of the lines from the ground-state lines were used. The states labelled $\nu' = 1, 2, 3, 4$ correspond to different excited states of one vibrational mode; the state labelled $\nu'' = 1$ is a different vibrational mode for which the spectrum has been observed only for the first excited state. Relative-intensity measurements have been used to determine the vibrational frequencies associated with the ν' and ν'' modes. This has been done by comparing the relative peak heights of the $1_{10} \longleftarrow 1_{01}$ transition for the ground state with that of the same transition for the $\nu' = 1$ and the $\nu'' = 1$ state. By assuming that the ratio of peak heights is equal to exp $(\mathbf{h}\nu/\mathbf{k}t)$, a value of ν (the vibrational frequency) of 160 ∓ 10 cm.$^{-1}$ is obtained for the ν' mode of vibration. All the lines in the ν' series have the same nuclear spin weight for a particular rotational transition, as was demonstrated by approximate intensity measurements on higher members in the series. Since for the ν'' mode lines in higher excited states than $\nu'' = 1$ were not observed, it is not possible to determine what is the spin-weight factor for the excited state. If it has the same spin weight as the main line, *i.e.*, 3, the ratio of observed peak heights corresponds to a vibrational frequency of 250 ± 20 cm.$^{-1}$. If the excited state has a spin weight of unity, then the vibrational frequency is 100 ± 10 cm.$^{-1}$. Since a search did not reveal lines which could be associated with the second excited state of this vibration, it is almost certain that the frequency of this mode is 250 ± 20 cm.$^{-1}$.

TABLE 5.

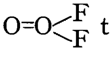
Moments of inertia and dipole moments of excited vibrational states.

	I_A	I_B	I_C	μ
$\nu = 0$	24·94456	100·8824	115·9438	1·44
$\nu' = 1$	24·82211	100·8655	116·2296	1·43
$\nu' = 2$	24·70131	100·8794	116·5291	1·47
$\nu' = 3$	24·58269	100·9378	116·8870	1·48
$\nu'' = 1$	25·08720	101·3839	116·6671	—

By comparing the Stark effects of the $1_{10} \longleftarrow 1_{01}$ line in the $\nu' = 1, 2$, and 3 states with that for the same transition in the ground state, a value for the dipole moment in these states was obtained. Table 5 lists the observed values, together with the observed moments of inertia.

The molecular model found must have two equivalent equilibrium configurations differing by an internal rotation about the oxygen–oxygen bond, reversing the sign of the dihedral angle. No evidence for splitting of the levels by tunnelling was observed. The vibrational levels $\nu' = 1, 2, 3, 4$ are probably due to excitation of the torsional oscillation; hence the barrier between the two conformations must be higher than 4×169 cm.$^{-1}$ and presumably is considerably higher because these states are still approximately equally spaced in the moments of inertia and diminish approximately regularly in intensity (as judged qualitatively). If a single term in cos 2θ is used to approximate the potential barrier, a barrier of 30 kcal./mole is obtained from the estimated vibrational frequency of 160 cm.$^{-1}$, but this is of course a very crude approximation.

DISCUSSION

A representation of the molecule is given in Fig. 2, together with the molecular parameters determined from this investigation. The results show that the molecule has the F–O–O–F structure rather than the  $O{=}O{<}^{F}_{F}$ type of structure. The structure is at least formally analogous to that of hydrogen peroxide, but a comparison of the two molecules shows that there are important differences in detail. The other basis of comparison is between F_2O and F_2O_2, on the one hand, and H_2O and H_2O_2 on the other. To facilitate this comparison various structural items obtained from the literature have been grouped together in Table 6. After allowance for some uncertainty in the structure of hydrogen peroxide, it seems fairly certain that r(O–O) in this compound is similar to that found in other peroxides and that r(O–H) is like that in H_2O. In contrast, r(O–O) in F_2O_2 is much shorter than in H_2O_2 and r(O–F) is much longer than in F_2O. Whereas the H_2O_2 structure can be understood in terms of a singly-bonded covalent chain it seems certain that this is not sufficient to describe F_2O_2. The fact that r(O–O) in F_2O_2 is very similar to that found for the oxygen molecule indicates that there must be some multiple bonding between the two atoms.

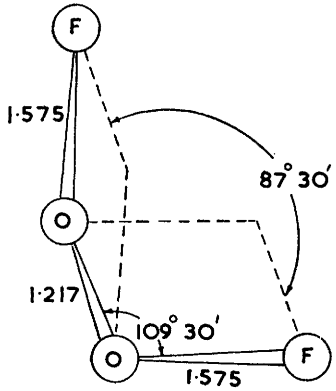


FIG. 2. Structure of F_2O_2.

TABLE 6.

Structural parameters relevant to the discussion of F_2O_2.

Compound	r(O–O)	r(X–O)			Ref.
F_2O_2	1·22	1·58	∠FOO 109° 30′	Dihedral <87° 30′	
H_2O_2	1·48	0·95	∠HOO 94·8°	Dihedral <119·8°	13 (I.R.)
H_2O_2	1·49	0·97 (ass.)	∠HOO 96·9°	Dihedral <93·6°	14 (*X*)
F_2O	—	1·41	∠FOF 103° 18′		3 (M)
H_2O	—	0·96	∠HOH 104·45°		15 (M)
O_3..................	1·28		∠OOO 116° 58°		16 (M)
O_2..................	1·21				17 (U.V.)
O_2^+	1·12				18 (U.V.)
O_2^-	1·28 (KO_2)				19 (*X*)
O_2^{2-}...............	1·49 (BaO_2)				20 (*X*)

I.R. = Infrared spectroscopy. M = Microwave spectroscopy. U.V. = Ultraviolet spectroscopy. *X* = *X*-Ray crystallography.

In a valence-bond approach to the problem considerable contributions from ionic structures of the type F^- $O{=}^+OF$ would lead to a shortening of r(O–O) and a lengthening of r(O–F). The electronegative character of fluorine would tend to make these ionic contributions energetically favourable. In F_2O contributions from structures of the form F^- O^+F might be expected to be small because here two fluorine atoms are competing

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[13] Redington, Olsen, and Cross, unpublished work.

[14] Abrahams, Collin, and Lipscomb, *Acta Cryst.*, 1951, **4**, 15.

[15] Posener and Strandberg, *Phys. Rev.*, 1954, **95**, 374.

[16] Pierce, *J. Chem. Phys.*, 1956, **24**, 139.

[17] Babcock and Herzberg, *Astrophys. J.*, 1948, **180**, 167.

[18] Herzberg, " Molecular Spectra and Molecular Structure: Infrared Spectra of Diatomic Molecules," van Nostrand Co., New York, 2nd edn.

[19] Abrahams and Kalnajs, *Acta Cryst.*, 1954, **7**, 838.

[20] Abrahams and Kalnajs, *Acta Cryst.*, 1955, **8**, 503.

for electrons from only one oxygen. In H_2O_2, on the other hand, the ionic contributions are of the form H^+ ^-OOH and there is no tendency to double-bond formation between the two oxygen atoms. Also there is no reason why structures of the type H^+ ^-OH should not contribute to the overall structure of water. In this context it can be noted that the dipole moments indicate that the F–O bond moment in F_2O_2 is four times as large as in F_2O whereas the bond moments in H_2O and H_2O_2 are very nearly equal. The large contributions from the doubly-bonded resonance structures would also account for the high barrier to internal rotation.

There are in the literature two pieces of evidence where a similar effect may be occurring. By electron diffraction Hirota[21] observed that for S_2Cl_2 and S_2Br_2 the S–S distance is shorter than is usually found for a single bonded S–S link and that the S–Cl bond in S_2Cl_2 is longer than that found in SCl_2. Bauer,[22] in studying N_2F_2 by the same technique, found the N–F bond to be longer than expected for a normal single bond.

Professor Lipscomb in these laboratories has put forward an alternative explanation. The molecular orbitals for the O_2 molecule are shown in Fig. 3. On this basis it is possible to account for many of the properties of oxygen, *e.g.*, its paramagnetic character and bond length. In Fig. 4, an attempt has been made to show that the $2py$-orbital on O_1 can overlap with the $2py$-orbital on O_2 to form the πy^*2p-molecular orbital which has one electron in it. A fluorine atom could bond to this π^*2p-orbital, adding an electron, to give a resultant electron pair in a three-centre orbital.* A similar situation obtains with the $2pz$-orbitals, and the second fluorine atom (Fig. 4). This description would certainly account in a qualitative way for the observed molecular parameters in F_2O_2. The dissociation energy of F_2 (36 kcal./mole) is much lower than for the other halogens; this abnormality is usually ascribed to repulsions between pairs of non-bonding electrons on the fluorine atoms. A similar effect here may favour the bonding scheme described in preference to the normal covalent bonding as in H_2O_2. Now, F_2O cannot form the three-centre orbital bonds and it is found that the F–O bond in F_2O is weaker than the H–O bond in H_2O (64 compared with 117 kcal./mole), which supports the argument. The three-centre bond would also account qualitatively for the fact that the barrier to internal

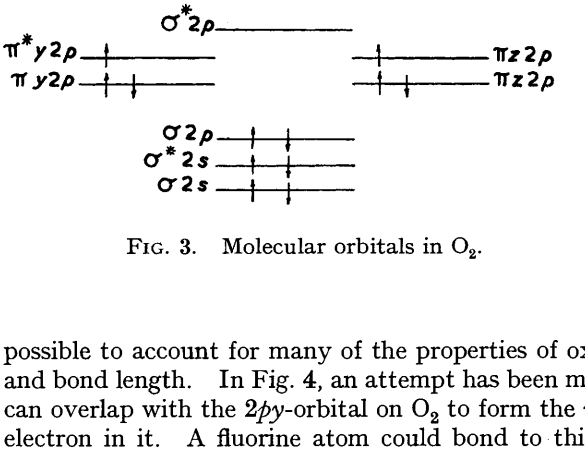

Fig. 3. Molecular orbitals in O_2.

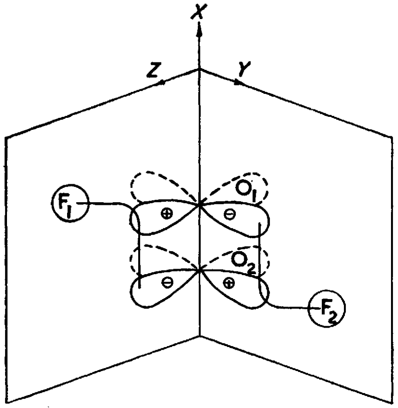

Fig. 4. Diagrammatic representation of the bonding molecular orbitals in F_2O_2.

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* As pointed out by one of the Referees. these three-centre orbitals do not have the full symmetry of the whole molecule. However, from the point of view of transferability to other similar molecules, it is more convenient to consider them in this way rather than to consider the appropriate linear combination which would have the full symmetry of the molecule.

[21] Hirota, *Bull. Chem. Soc. Japan*, 1958, **31**, 130.

[22] Bauer, *J. Amer. Chem. Soc.*, 1947, **69**, 3104.

rotation in F_2O_2 appears to be considerably higher than that reported[13] for H_2O_2 (300 cm.$^{-1}$).

The variation of dipole moment with vibrational state (presumably the torsional vibration) is small but might be expected to be speculatively interpreted in terms of a lower *cis*- than *trans*-barrier.

The author thanks Professor E. Bright Wilson, Jr., for suggesting the problem and for his constant help and advice; also Mr. S. Butcher for help in the preparative work. This research was made possible by a contract with Harvard University from the Office of Naval Research of the United States of America.

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[*Received, February 26th,* 1962.]