The Vibrational Spectra and Structure of Inorganic Molecules. I. The InfraRed Spectrum of F2O from 2.5 to 25μ

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TABLE I.

Infra-red spectrum of F_2O Hettner et al.	Interpretation I. Hettner	Interpretation II. Hettner	Interpretation Sutherland and Penney
2544			$2\nu_1+2\nu_2$
2190			$2\nu_3$
1740		fundamental	$\nu_1+2\nu_2$
1280	fundamental	fundamental	$\nu_1+\nu_2$
1110			ν_3 fundamental
926	fundamental		$2\nu_2$
	fundamental } 870	fundamental	
833	fundamental		ν_1 fundamental
625			$\nu_3-\nu_2$
492			ν_2 fundamental

TABLE II. F_2O 170 mm Hg.

K	Obs. cm^{-1}
10	963.0
9	959.5
8	956.4
7	952.8
6	949.0
5	945.4
4	942.6
3	(939.5)
2	(935.0)
1	(931.2)
0	
−1	(927.7)
−2	(923.6)
−3	(921.0)
−4	917.0
−5	913.6
−6	910.5
−7	907.5
−8	904.5
−9	902.5
−10	899.0
−11	895.5
−12	893.2
−13	891.0

CF_4 it is apparent that the complexity of Hettner's spectrum was due to CF_4 as impurity (see Table IV).

FINE STRUCTURE OF THE BAND AT 10.8μ AND A REFINEMENT OF THE MOLECULAR DIMENSIONS OBTAINED BY ELECTRON DIFFRACTION

Since the F_2O molecule is an approximate symmetric top the frequency of the Q branches is given by[7]

$$\nu = \nu_0 + (A'-B') \pm 2K(A'-B') + [(A'-B')-(A''-B'')]K^2. \quad (1)$$

The differences between the rotational constants of the upper and lower states are obtained from

$$^RQ_K - {}^PQ_K = 4K(A'-B') \quad (2)$$

and

$$^RQ_{K-1} - {}^PQ_{K+1} = 4K(A''-B'') \quad (3)$$

respectively. The band center may be obtained from

$$^RQ_K + {}^PQ_{K+1} = 2\nu_0 + [(A'-B')-(A''-B'')] \times [K^2+(K+1)^2]. \quad (4)$$

One might expect relations (2) and (3) to be valid for higher K values for an approximate symmetric top since the effects of K-type doubling are minimized. Also, the spectrum near the band origin may be complicated by weak overlapping with $2\nu_2 = 922$ cm^{-1}. Since ν_2 is so very much weaker than ν_1 it is extremely unlikely that $2\nu_2$ will contribute much to the band ν_1, especially at higher K values. Table V gives values of $A''-B''$ and $A'-B'$ obtained from relations (2) and (3) for higher K values. The mean values obtained are

$$A''-B'' = 1.60 \pm 0.02 \text{ cm}^{-1},$$
$$A'-B' = 1.60 \pm 0.02 \text{ cm}^{-1}.$$
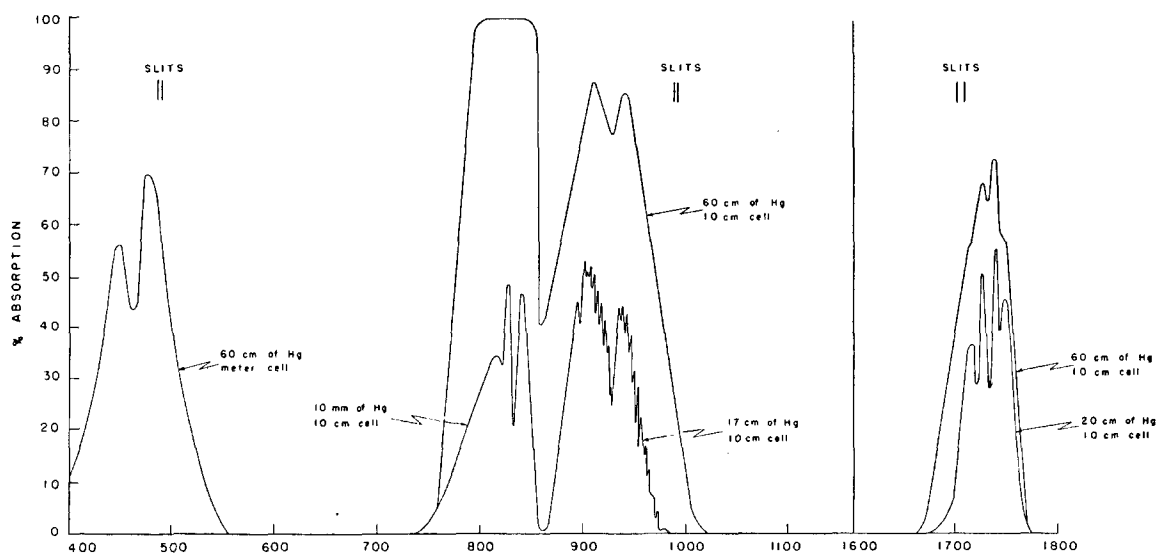
FIG. 1. Frequency in cm^{-1}.

[7] G. Herzberg, *Infrared and Raman Spectra of Polyatomic Molecules* (D. Van Nostrand Company, Inc., New York, 1945), p. 483.

TABLE III.

Infra-red band cm^{-1}	Structure	Separation cm^{-1}	Assignment
1700–1764 (m)	PQR and doublet		$\nu_1+\nu_3(B_1)$ and $2\nu_1(A_1)$ [a]
929 (s)	Doublet	30	$\nu_1(A_1)$
826 (v.s.)	PQR	28	$\nu_3(B_1)$
461 (w)	Doublet	27	$\nu_2(A_1)$

[a] The band at ∼1740 cm^{-1} is primarily due to the combination tone $\nu_1+\nu_3$ with $2\nu_1$ probably contributing some intensity. $2\nu_2$ would have to have a very large anharmonicity with opposite sign to appear in this region.

Since $(A'-B')-(A''-B'')=0\pm0.04$ cm^{-1} it is not possible to obtain an accurate value of ν_0 from Eq. (4). In the above formula B'' is actually $(B''+C'')/2$ so that

$$A''-B''=1.60\pm0.02 \text{ cm}^{-1}$$

$$=28.00\left[\frac{1}{I_A}-\frac{1}{2}\left(\frac{1}{I_B}+\frac{1}{I_C}\right)\right]\text{cm}^{-1}$$

where the I's are in units of 10^{-40}. Letting r be the O–F distance in A, and 2θ the apex angle, substitution for I_A, I_B, and I_C in terms of r and 2θ gives the relation

$$r^2=17.5\pm0.20\left[\frac{1}{18.7\cos^2\theta}\right.$$

$$\left.-\frac{1}{2}\left(\frac{1}{18.7\cos^2\theta+63.05\sin^2\theta}+\frac{1}{63.05\sin^2\theta}\right)\right].$$

In Table VI the OF bond distances have been calculated from this equation for one degree changes in 2θ from $2\theta=97°$ to $2\theta=103°$.

TABLE IV.

F$_2$O this work	F$_2$O Hettner et al.[a]	CF$_4$[b]
	2544	2541
	2190	2180
1740	1740	
	1280	1265
	1110	1112
929	926	
826	833	
	625	630
	492	
461		

[a] See reference 1.
[b] Bailey, Hale, and Thompson, Proc. Roy. Soc. London A167, 555 (1938) These authors did not investigate the spectrum as far down as 492 cm^{-1}.

These limiting values for 2θ are indicated by the error of the electron diffraction measurement,[4] namely, $2\theta=100\pm3°$. Since the electron diffraction result for the OF bond distance is 1.41 ± 0.05A, the first three values of r_{OF} in Table VI are excluded, leaving the only possible range of values for 2θ and r consistent with the moment of inertia obtained from the spacing of the fine structure. In this way the electron diffraction results may be refined to

$$r_{OF}=1.38\pm0.03\text{A},$$
$$2\theta=101.5\pm1.5°.$$

POTENTIAL FUNCTION OF F$_2$O

A suitable quadratic potential function for F$_2$O is given by

$$2V=K[(\delta r_1)^2+(\delta r_2)^2]+K_{2\theta}(r\delta_{2\theta})^2$$
$$+2K_1\delta r_1\delta r_2+2K_2(\delta r_1+\delta r_2)r\delta_{2\theta}$$

where δr_1, δr_2, $\delta_{2\theta}$ are the displacements of bond 1, bond 2, and the apex angle, respectively, from the equilibrium configuration. K, $K_{2\theta}$, K_1, and K_2 are the bond stretch-

FIG. 2. FREQUENCY IN cm^{-1} (BAND AT 10.8 μ).

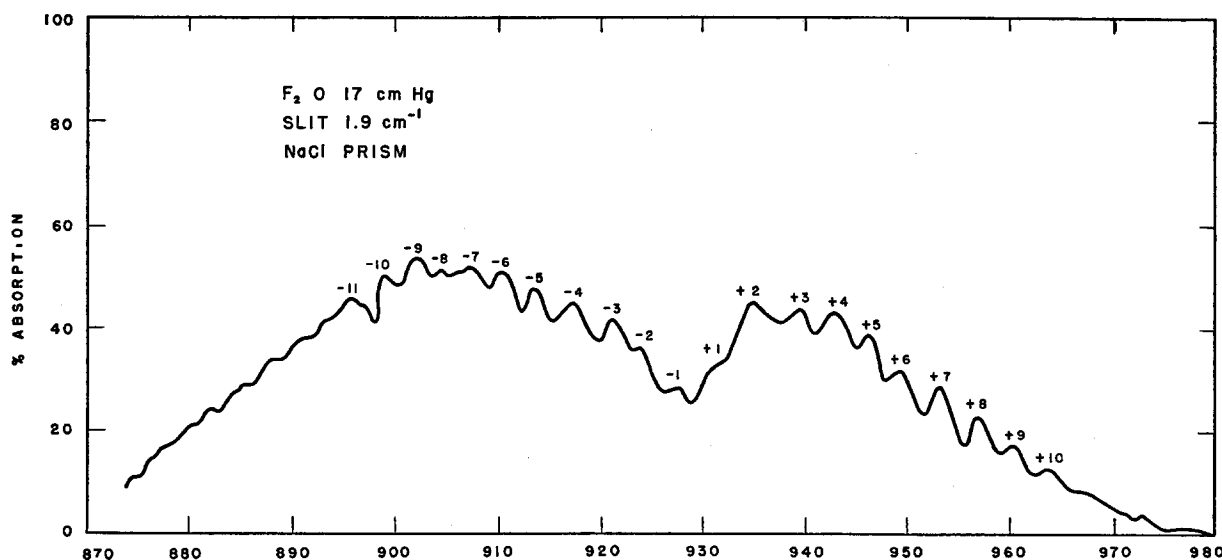TABLE V. F_2O 170 mm Hg.

K	$^RQ_{K-1}$	$^PQ_{K+1}$	$4K(A''-B'')$	$A''-B''$
11	963.0	893.2	69.8	1.585
10	959.5	895.5	64.0	1.600
9	956.4	899.0	57.4	1.603
8	952.8	902.5	50.3	1.575
7	949.0	904.5	44.5	1.590
6	945.4	907.5	37.9	1.580
5	942.6	910.5	32.1	1.605
4	(939.5)	913.6	25.9	(1.622)
			Mean	1.60±0.02 cm^{-1}

K	^RQ_K	^PQ_K	$4K(A'-B')$	$A'-B'$
10	963.0	899.0	64.0	1.600
9	959.5	902.5	57.0	1.585
8	956.4	904.5	51.9	1.621
7	952.8	907.5	45.3	1.619
6	949.0	910.5	38.5	1.605
5	945.4	913.6	31.8	1.590
4	942.6	917.0	25.6	1.600
			Mean	1.60±0.02 cm^{-1}

TABLE VI.

2θ	$r_{OF}A$
97	1.298±0.007
98	1.317±0.008
99	1.336±0.007
100	1.355±0.008
101	1.373±0.008
102	1.396±0.008
103	1.415±0.008

TABLE VII. Force constants of the F_2O molecule in units of 10^5 dynes per cm for various potential functions.

	Four-constant potential function	Potential function with $K_2=0$		Potential function with $K_1=0$		K from Badger's rule[a]
K	3.21 to 5.23	3.63,	2.62	3.17		5.4±0.8
$K_{2\theta}$	0.05 to 1.67	0.84,	1.66	0.46,	3.43	
K_1	0.04 to 2.06	0.46,	−0.56	0.0		
K_2	0.00 to 0.98	0.0	0.0	−0.78,	2.31	

[a] Substituting for the OF bond distance (1.38 ±0.03A) into Badger's relation $K(r-0.68)^3 = 1.86 \times 10^5$ dynes per cm gives $K=5.4 \pm 0.8 \times 10^5$ dynes per cm [J. Chem. Phys. 2, 128 (1934).]

ing, bond deformation, and interaction constants, respectively.

If M is the mass of the oxygen atom and m the mass of the fluorine atom in atomic units, the determinantal equation gives[8]

$$\lambda_1+\lambda_2=(K+K_1)\left(\frac{1}{\mu}+\frac{\cos 2\theta}{M}\right)$$
$$+2K_{2\theta}\left(\frac{1}{\mu}-\frac{\cos 2\theta}{M}\right)-\frac{4K_2}{M}\sin 2\theta, \quad (5)$$

$$\lambda_1\lambda_2=\frac{M+2m}{Mm^2}[2K_{2\theta}(K+K_1)-4K_2^2], \quad (6)$$

$$\lambda_3=(K-K_1)\left(\frac{1}{\mu}-\frac{\cos 2\theta}{M}\right), \quad (7)$$

where $\mu = Mm/(M+m)$ and $\lambda_i=0.590\times10^{-6}\nu_i^2$ for ν_i in cm^{-1}.

It has been shown that a four-constant potential function is necessary to describe the dynamics of symmetrical non-linear triatomic molecules and that the interaction constants K_1 and K_2 are equally important.[9]

The three frequencies are not sufficient to evaluate the four force constants of these equations but considerable information may be obtained as to the upper and lower limits that these constants may have.

With the values $\nu_1=929$ cm^{-1}, $\nu_2=461$ cm^{-1}, $\nu_3=828$ cm^{-1}, and $2\theta=101.5°$ elimination of K_1 and K_2 from Eqs. (5)–(7) gives a quadratic relation between K and $K_{2\theta}$. For K to have real roots it is found that 0.05×10^5 dynes per cm $\leqslant K_{2\theta}\leqslant 1.67\times10^5$ dynes per cm. The

[8] Ta-You Wu, *Vibrational Spectra and Structure of Polyatomic Molecules* (J. W. Edwards, Ann Arbor, Michigan, 1946), p. 163.
[9] Coulson, Duchesne, and Manneback, Vol. comm. Victor Henri, Maison Desoer, Liège (1947–48), p. 33.

maximum and minimum values that K can take are given by the condition $\partial K/\partial K_{2\theta}=0$. Numerically, this condition is satisfied for $K_{2\theta}=0.514$ and 1.20×10^5 dynes per cm. Substituting these values for $K_{2\theta}$ in the quadratic expression for K as a function of $K_{2\theta}$ gives the upper limit of K as 5.23×10^5 dynes per cm and the lower limit of K as 3.21×10^5 dynes per cm.

From Eq. (7) the upper limit and lower limit of K_1 is found to be 2.06 and 0.04×10^5 dynes per cm, respectively.

From Eq. (5) the upper and lower limits of K_2 are found to be 0.98 and 0.0×10^5 dynes per cm, respectively.

In Table VII the force constants are given for the complete four-constant potential function; when $K_2=0$; and for $K_1=0$.

When $K_2=0$, two sets of force constants are obtained whereas when $K_1=0$, K is obtained directly from Eq. (7) and substitution in (5) and (6) gives two sets of values for $K_{2\theta}$ and K_2. The columns give corresponding sets of the constants.

An approximation to the ratio $(\nu_1/\nu_3)^2$ is given by

$$(\nu_1/\nu_3)^2=[(K+K_1)/(K-K_1)]$$
$$\times[(M+\mu\cos 2\theta)/(M-\mu\cos 2\theta)].$$

In a linear molecule such as CO_2 or CS_2 the value of $\mu\cos 2\theta$ is of the same order of magnitude as M so that the ratio $(M+\mu\cos 2\theta)/(M-\mu\cos 2\theta)$ is small (since $\cos 2\theta=-1$). This ratio is so small that the R.H.S. of the above equation remains <1 even after multiplied by the force constant ratio. For F_2O, however, since 2θ is closer to 90° than to 180° the $\mu\cos 2\theta$ term is very much less than the M so that $(M+\mu\cos 2\theta)/(M-\mu\cos 2\theta)$ is only slightly less than one. As a result the force constant ratio is responsible for making the R.H.S. greater than one and thus $\nu_3<\nu_1$.

It is apparent then why ν_3 is less than ν_1 for F_2O whereas in other symmetric triatomic molecules ν_3 is usually greater than ν_1.

Magnetic Evidence for d^3s Bond Hybridization in Chromium (II) Acetate. The Oxidation State of Chromium in a Reported Tris(8-Hydroxyquinoline) Chromium (II)

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Magnetic susceptibilities of solid $Cr(OOCCH_3)_2$ and its monohydrate were measured, and these compounds were shown to contain no unpaired electrons. This fact indicates that the four unpaired $3d$ electrons of the normal Cr^{++} ion are paired in these compounds, the three $3d$ orbitals thus made available being utilized in the formation of covalent bonds. The fourth covalent bond probably involves use of the $4s$ orbital of chromium. This evidence may constitute the first example of d^3s bond hybridization postulated by Pauling. Susceptibility measurements were also carried out on tris(8-hydroxyquinoline) chromium (III) and a reported tris(8-hydroxyquinoline) chromium (II). The evidence indicates both to be the same compound, with the chromium having a tripositive oxidation state.

INTRODUCTION

IN the course of other work on chromium compounds we have investigated the magnetic susceptibilities of chromium (II) acetate and its monohydrate. The orange-tan and red colors, respectively, of these compounds and their moderately low (<1 percent) solubility in water suggest a different type of bonding of the chromium from that in the typical blue and very soluble salts of dipositive chromium, such as the perchlorate and chloride. The magnetic results presented in this paper bear out this idea and indicate d^3s (or possibly d^3p) bond hybridization for chromium in the acetate. Pauling[1] has pointed out that three d eigenfunctions may be used together with some s and p character to give equivalent tetrahedrally directed bond eigenfunctions of "strength" 2.950, nearly equal to the maximum "strength" of 3, and he has concluded that examples of such bonds should be provided by $CrO_4^=$, $MoO_4^=$, and related oxy-ions. Although the magnetic criterion[1,2] for bond type cannot be applied to these latter ions, it may be applied to divalent chromium compounds.

Hume and Stone[3] prepared by the action of an excess of 5 percent 8-hydroxyquinoline in 2f. CH_3COOH on chromium (II) chloride solution an orange-yellow compound which they assumed to be an 8-hydroxyquinoline chromium (II), i.e., "chromous 8-hydroxyquinolate." On the basis of his analyses of the purified

compound, indicating three 8-hydroxyquinolate addenda per chromium atom, Hume[4] suggested the possibility of d^2sp^3 bonding of the chromium in this compound. In order to investigate this point we prepared this compound by the method of Hume and Stone,[3] and also prepared tris(8-hydroxyquinoline) chromium (III), and measured the magnetic susceptibility of each. The results indicate that these two compounds are identical, with the chromium in the tripositive oxidation state. In the case of the presumed chromium (II) compound, the Cr (II) is apparently oxidized to Cr (III) by the 8-hydroxyquinoline during the preparation.

PREPARATION AND ANALYSIS OF COMPOUNDS

Chromium (II) Acetate Monohydrate

Freshly prepared solutions of dichlorotetraquo chromium (III) chloride (c.p. green $CrCl_3 \cdot 2H_2O$) were reduced with amalgamated zinc in an upflow-type Jones reductor.[3] The resulting chromium (II) solution was run directly into an excess of saturated $NaOOCCH_3$ solution covered by a layer of petroleum ether in order to exclude air. The precipitated $Cr(OOCCH_3)_2 \cdot H_2O$ was washed free of excess $NaOOCCH_3$ and Zn^{++} with O_2-free water. The resultant water slurry was used for magnetic measurements. For analyses the precipitate was washed with C_2H_5OH and then with $(C_2H_5)_2O$ and dried in a stream of O_2-free N_2. The analyses (27.6 percent Cr, C/Cr=3.94) indicate the formula $Cr(OOCCH_3)_2 \cdot H_2O$ (27.6 percent Cr, C/Cr=4.00). The compound had a red color.

[1] L. Pauling, J. Am. Chem. Soc. **53**, 1367 (1931).
[2] L. Pauling, *The Nature of the Chemical Bond* (Cornell University Press, Ithaca, New York, 1945), second edition, p. 112.
[3] D. N. Hume and H. W. Stone, J. Am. Chem. Soc. **63**, 1200 (1941).
[4] D. N. Hume, Master's Thesis, U.C.L.A. (1941).