

Microwave Absorption Spectra of  $\text{MnO}_3\text{F}$  and  $\text{ReO}_3\text{Cl}^*\dagger$ ALI JAVAN, *Department of Physics, Columbia University, New York, New York*

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The microwave spectra of  $\text{MnO}_3\text{F}$  and  $\text{ReO}_3\text{Cl}$  near 1-cm wavelength have been studied. From the spectra of the first molecule and its isotopic species  $\text{Mn}(\text{O}^{16})_2\text{O}^{18}\text{F}$ , the structural parameters were determined as:

$$\text{Mn}-\text{O}=1.586 \text{ \AA}, \quad \text{Mn}-\text{F}=1.724 \text{ \AA}, \quad \angle(\text{O}, \text{Mn}, \text{F})=108^\circ 27'.$$

The nuclear quadrupole coupling constant of  $\text{Mn}^{55}$  was measured as  $eqQ=16.8$  Mc/sec. Because of the spin and statistics of  $\text{O}^{16}$  nuclei not all of the rotational states are allowed. It was found that, whereas in the ground vibrational states only states with  $K$  a multiple of three are permissible, in the excited vibrational states of the perpendicular normal modes the states with  $K-l$  a multiple of three can occur. For  $K=l=\pm 1$  appreciable  $l$ -type doubling was observed. The amounts of  $l$  doubling and their corresponding values of  $\alpha_e$  were determined for  $\text{MnO}_3\text{F}$ . The molecular dipole moment of this molecule was found to be  $\mu=1.5$  Debye units. The hyperfine structure of  $\text{ReO}_3\text{Cl}$  gives for the ratio of quadrupole moments of the two abundant isotopes of Re a value of  $Q_{\text{Re}^{187}}/Q_{\text{Re}^{185}}=1.067\pm 0.045$  and for the quadrupole coupling constant of  $\text{Re}^{187}$ ,  $eqQ=253$  Mc/sec. This coupling constant and the known optical value of the quadrupole moment of  $\text{Re}^{187}$  give some information about the electronic structure of the molecular bonds, from which an approximate value of the nuclear quadrupole moment of  $\text{Mn}^{55}$  was obtained as  $Q=0.55\times 10^{-24}$  cm<sup>2</sup>.

MOLECULES containing the elements Mn and Re are not easily obtainable in the gaseous state for microwave or electron diffraction study. Partly for this reason experimental data on the covalent radii of these elements has previously been limited to certain anomalously large radii measured for Mn in crystalline  $\text{MnS}_2$  and similar compounds. Isolation<sup>1</sup> in 1950 of the molecule  $\text{MnO}_3\text{F}$  allowed the microwave measurement of its rotational spectrum reported below. This plus the microwave spectrum<sup>2</sup> of  $\text{ReO}_3\text{Cl}$  give the first accurate determinations of the geometry of bonds of Mn and Re.

The single stable isotope  $\text{Mn}^{55}$  has a spin of 5/2 and hence a quadrupole moment which produces a hyperfine structure in the rotational spectrum giving some information about the value of the quadrupole moment. The two isotopes  $\text{Re}^{187}$  and  $\text{Re}^{185}$  which occur in nature in relative abundance, 61.8 percent and 38.2 percent, respectively, also have spin 5/2 and give quadrupole hyperfine structure from which a fairly accurate measure of the ratio of their two quadrupole moments is obtained.

The spectrometer used for the measurements was a Stark modulation type of more or less conventional design except for the absorption cell and gas handling system. Both molecules  $\text{MnO}_3\text{F}$  and  $\text{ReO}_3\text{Cl}$  are highly reactive and rather unstable. Their handling required special care which will be described in a subsequent paper.<sup>3</sup>

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<sup>1</sup> A. Engelbrecht and A. V. Grosse, *J. Am. Chem. Soc.* **76**, 2042 (1954).

<sup>2</sup> Amble, Miller, Schawlow, and Townes, *J. Chem. Phys.* **20**, 192 (1952).

<sup>3</sup> J. Lotspeich and A. Javan (to be published).

## ROTATIONAL SPECTRUM

The observed spectrum of  $\text{MnO}_3\text{F}$  and  $\text{ReO}_3\text{Cl}$  show clearly that the molecules are symmetric tops. The three oxygen atoms are located at the corners of an equilateral triangle forming the base of a pyramid with the metal at its apex. The halogen is on the symmetry axis.

The allowed rotational transitions of such a molecule involve a change of total angular momentum  $\Delta J=\pm 1$  with no change of  $K$ , the projection of  $J$  on the symmetry axis. In the absence of hyperfine structure, the frequency of a transition of this kind is independent of quantum number  $K$  except for a small factor due to centrifugal stretching of the molecule, and given by  $\nu=2B(J+1)$ , where  $B=h/(8\pi^2 I_B)$ .  $I_B$  is the moment of inertia of the molecule about a direction perpendicular to the symmetry axis.

When  $J$  is greater than zero, lines due to molecules having several different values of  $K$  are superimposed. The quadrupole interaction mentioned above causes a splitting of the rotational lines which depends on the absolute value of  $K$ .<sup>4</sup> Hence the hyperfine structure may be complicated due to the superposition of patterns belonging to different  $K$  states. However, in the cases of  $\text{Mn}(\text{O}^{16})_3\text{F}$  and  $\text{Re}(\text{O}^{16})_3\text{Cl}$  not all values of  $K$  are permissible because of the statistics and spin of  $\text{O}^{16}$ .  $\text{O}^{16}$  nuclei have zero spin and follows Bose-Einstein statistics so that only those states occur which remain symmetric under any permutation of the three oxygen nuclei.

These molecules belong to point group  $C_{3v}$ . Since permutations of the three oxygen nuclei is isomorphous with operations of the point group  $C_{3v}$ , totally symmetric wave functions belong to irreducible represen-

<sup>4</sup> J. Bardeen and C. H. Townes, *Phys. Rev.* **73**, 97 (1948).

tation of class  $A$ . It can be shown<sup>6</sup> that, when  $K$  is a multiple of three, the rotational wave function can be reduced to belong to classes  $A$  or  $B$  of the point group  $C_{3v}$ . Rotational wave functions with  $K$  other than a multiple of three are doubly degenerate and belong to the irreducible representation of class  $E$ . In the ground vibrational state, the total vibrational wave function belongs to class  $A$  or  $B$  according to whether the molecule is in the symmetric or antisymmetric inversion state. Hence only states with  $K$  a multiple of three can form total symmetric wave functions and, therefore, are allowed.

In contrast to the ground state, values of  $K$  not a multiple of three can occur in some excited vibrational states. Molecules such as  $\text{MnO}_3\text{F}$  have six different normal frequencies of oscillation. Three of these correspond to three pairs of doubly degenerate modes and when excited can give rise to internal angular momentum. These modes are known as perpendicular modes and the other three are nondegenerate and known as parallel modes. The internal angular momentum for the

$v$ th excited state of a degenerate mode can take values corresponding to the quantum number  $l$ , where  $l$  is a positive or negative integer running by steps of two from  $+v$  to  $-v$ .

Vibrational wave functions of a pair of degenerate normal modes transform in a way which is fairly similar to that of the rotational wave function under permutations of the three oxygen nuclei. When  $|l|$  is a multiple of three, this wave function can hence be put in a form to belong to classes  $A$  or  $B$ , but for  $|l|$  other than a multiple of three it belongs to class  $E$ .<sup>5</sup> In the latter case, this wave function when combined with rotational wave function of  $E$  symmetry can furnish wave functions of classes  $A$  and  $B$  because the result would have symmetry of  $E \times E = A + B + E$ . Thus values of  $K$  not a multiple of three become permissible when a doubly degenerate mode of class  $E$  is excited. An explicit form of the transformations of the total rotation-vibrational wave functions shows that the criterion for the permissible states is that  $|K-l|$  be a multiple of three.

In the presence of internal angular momentum, the rotational energy levels undergo a first-order Coriolis splitting,<sup>6</sup> ( $K$ -type doubling), which in the absence of centrifugal stretching is independent of  $J$ . The contribution to the energy levels due to this term is  $2C_v \zeta K l$ , where  $C_v = h/8\pi^2 I_{zz} c$ ,  $\zeta$  is the Coriolis coupling constant. The two members of this doublet correspond to positive or negative signs of the product  $Kl$ . The frequency of the rotational transition is unaffected by the presence of this splitting due to the lack of dependence on  $J$ . However, the levels corresponding to  $|K-l|$  a multiple of three which are the only permissible values as discussed above, undergo further an  $l$ -doublet splitting. When  $K=l=\pm 1$ , the amount of splitting<sup>5,6</sup> is given by  $q_l J(J+1)$ , and rotational transitions are manifested as doublets with separations  $\Delta\nu = 2q_l(J+1)$  in a transition  $J+1 \leftarrow J$ . For higher values of  $K$  and  $l$ , the  $l$  doubling is very small, and the splitting of the corresponding rotational lines are undetectable.

#### SPECTRUM OF $\text{MnO}_3\text{F}$

The rotational transition  $J=3 \leftarrow 2$  of this molecule is particularly suitable for study of hyperfine structure. According to the above discussions, in the ground vibrational state only  $K=0$  can occur. The first excited states of degenerate modes provide transitions with  $K=\pm 1$  and  $K=\pm 2$  displaced from the position of the ground state transition according to their corresponding values of  $\alpha_v$ . Because of  $l$ -type doubling the  $K=\pm 1$  transitions are manifested as doublets. The two components of each doublet are symmetrically located on either side of  $K=\pm 2$  transition for the same excited vibrational state. The values of  $\alpha_v$  and the amounts of  $l$ -type doublings are large enough to prevent any

TABLE I. Hyperfine structure of  $\text{MnO}_3\text{F}$  for the ground vibrational state and first excited state  $v_6=1$ . The experimental errors where not indicated are less than 50 kc/sec.

Transition	Measured frequency Mc/sec	Calculated frequency Mc/sec
$v=0, K=0$		
$9/2 \leftarrow 9/2$	24 777.526	24 777.517
$5/2 \leftarrow 3/2$	24 775.949	24 775.949
$7/2 \leftarrow 5/2$	24 775.125	24 775.117
$11/2 \leftarrow 9/2$	24 774.445	24 774.437
$9/2 \leftarrow 7/2$	24 774.250	24 774.277
$7/2 \leftarrow 5/2$		
$5/2 \leftarrow 3/2$	24 773.85 $\pm$ 0.15	24 773.984
$5/2 \leftarrow 5/2$	24 773.505	24 773.549
$1/2 \leftarrow 3/2$	24 772.39 $\pm$ 0.1	24 772.477
$3/2 \leftarrow 5/2$	24 771.56 $\pm$ 0.1	24 771.589
$v_6=1, K=2$		
$3/2 \leftarrow \begin{cases} 1/2 \\ 1/2 \end{cases}$	24 755.95 $\pm$ 0.15	24 736.06
$11/2 \leftarrow \begin{cases} 9/2; 5/2 \\ 9/2; 3/2 \end{cases}$	24 738.20	24 738.22
$7/2 \leftarrow \begin{cases} 5/2 \\ 1/2 \end{cases}$		
$7/2 \leftarrow 5/2$	24 740.60	24 740.62
$5/2 \leftarrow 3/2$		
$9/2 \leftarrow 7/2$	24 741.49	24 741.46
$7/2 \leftarrow 5/2$		
$v_6=1, l_2, K=1$		
$3/2 \leftarrow 3/2$	24 768.00	24 768.03
$1/2 \leftarrow 1/2$		
$11/2 \leftarrow 9/2$	24 768.38	24 768.40
$9/2 \leftarrow 7/2$		
$7/2 \leftarrow 5/2$	24 769.14	24 769.10
$3/2 \leftarrow 1/2$		
$7/2 \leftarrow 5/2$	24 769.55	24 769.52
$5/2 \leftarrow 3/2$		
$9/2 \leftarrow 9/2$	24 770.68	24 770.71

<sup>5</sup> G. Herzberg, *Infrared and Raman Spectra of Polyatomic Molecules* (D. Van Nostrand Company, Inc., New York, 1945).

<sup>6</sup> M. Johnston and D. M. Dennison, *Phys. Rev.* **48**, 868 (1935). See also reference 12.

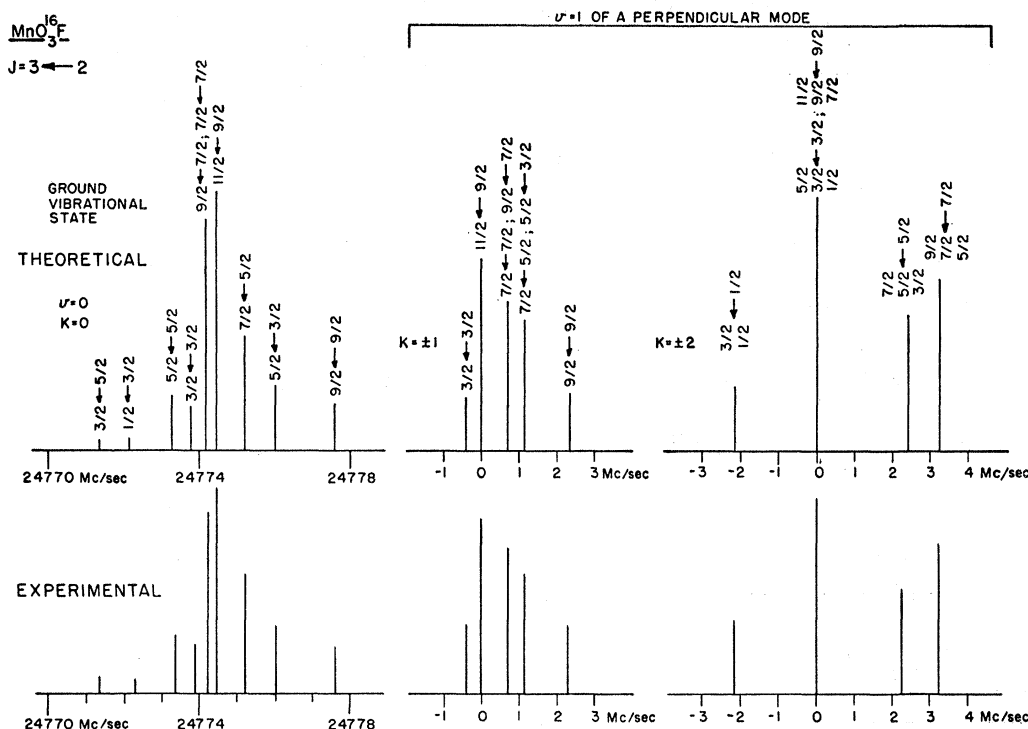


FIG. 1. The quadrupole hyperfine structure of  $\text{MnO}_3\text{F}$  in the rotational transition  $J=3 \leftarrow 2$ .

superposition of hyperfine structures arising from different values of  $K$ .

The hyperfine structure verifies a spin  $5/2$  for  $\text{Mn}^{55}$  and gives  $eqQ=16.8$  Mc/sec and  $B_0=4129.106 \pm 0.004$  Mc/sec. In Table I the measured lines for the ground vibrational state and the first excited state of one of the degenerate modes are listed. In Fig. 1 observed hyperfine structures are compared with the theoretical patterns. The hyperfine patterns of the first excited vibrational states of the three perpendicular normal modes are identical. This indicates that there is no detectable change of the coupling constant  $eqQ$  in these excited states. Table II contains the list of values of  $\alpha_v$  and  $l$ -type doubling constants  $q_l$  for the three degenerate normal modes and  $\alpha_v$  of one of the nondegenerate modes. Also a rough estimate of the normal frequencies of oscillation is given on the basis of the observed relative intensities.

The second excited states of the perpendicular modes and the excited state  $v_6=1$ ,  $v_5=1$  were also observed. Since in these cases, the total angular momentum due to vibration corresponds to  $l=\pm 2$  or  $l=0$ , the allowed values of  $K$  are  $K=\pm 2$ ,  $K=\pm 1$ , and  $K=0$ .

A recorder tracing of over-all spectra of the excited vibrational states of the perpendicular modes discussed above appears in Fig. 2. This tracing was taken under a low Stark modulation field, hence only lines corresponding to  $K=\pm 1$  and  $K=\pm 2$  which can show a first-order Stark splitting are detected. Since the tracing was taken under relatively low resolution conditions,

only the hyperfine splittings of the  $K=\pm 2$  lines could be seen, these being larger than the splittings of the  $K=\pm 1$  transitions.

#### SPECTRA OF $\text{Mn}(\text{O}^{16})_2\text{O}^{18}\text{F}$ AND STRUCTURAL PARAMETERS

The size and geometry of  $\text{MnO}_3\text{F}$  depends on three independent parameters. They can be taken as the distances  $\text{Mn}-\text{O}$ ,  $\text{Mn}-\text{F}$  and the angle  $\angle(\text{O}, \text{Mn}, \text{F})$ . The moment of inertial  $I_B$ , obtained from the  $B$  value of  $\text{Mn}(\text{O}^{16})_3\text{F}$  is not alone sufficient to yield values for these parameters. In order to obtain enough experimental data for determining completely the structure of the molecule, the rotational spectrum of the isotopic species  $\text{Mn}(\text{O}^{16})_2\text{O}^{18}\text{F}$  was examined. Due to the presence of  $\text{O}^{18}$ , the  $C_{3v}$  symmetry of this molecule is destroyed, and hence all of the asymmetric rotor energy levels are permissible.

The rotational transition  $J=3 \leftarrow 2$  was observed and the stronger hyperfine components of the transitions which in the limiting case of a symmetric prolate rotor

TABLE II. Vibrational and  $l$ -type doubling constants and approximate normal vibration frequencies of  $\text{MnO}_3\text{F}$ .

Normal mode	$\alpha_v$ (Mc/sec)	$q_l$ (Mc/sec)	$\omega$ ( $\text{cm}^{-1}$ )
6	5.87	9.81	350
5	-12.80	16.20	470
4	14.38	5.90	600
3	7.77		400

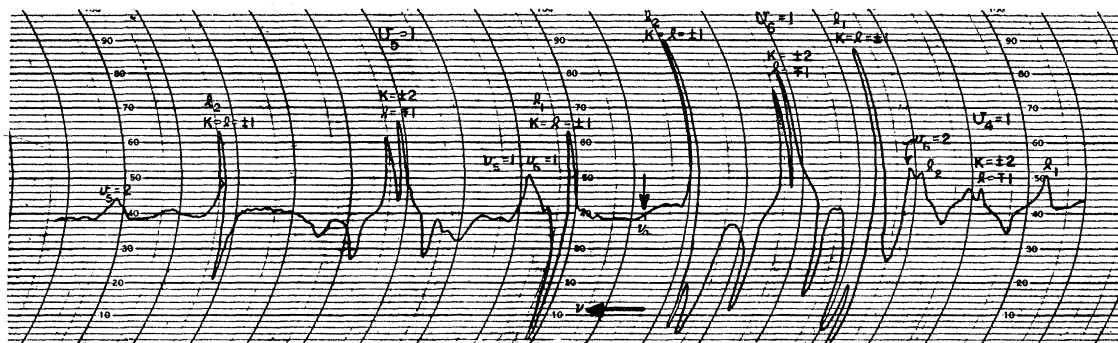


FIG. 2. Recorder tracing of the  $J=3 \leftarrow 2$  transition of  $\text{MnO}_3\text{F}$  under low Stark modulation field. The lines are due to transitions in the excited vibrational states of the perpendicular normal modes of oscillation. The frequency  $\nu_0$  is the center of the hyperfine transitions in the ground vibrational state which, because of the high modulation field requirements for their detection, do not show on this tracing.

correspond to  $K$  values of 0, 1 and 2 show patterns similar to those obtained for the molecule  $\text{Mn}(\text{O}^{16})_3\text{F}$  with the same values of  $K$ . The difference is mainly in a reduction of the spread of these hyperfine patterns due to the effect of the asymmetry of the molecule on the average gradient of the molecular electric field  $q_J$ , in the direction of  $J$ . The molecule is a nearly prolate rotor, and the quantity  $q_J$  can conveniently be expanded<sup>7,8</sup> in terms of the asymmetry parameter  $b_p = (C-B)/(2A-C-B)$ , where  $A$ ,  $B$ , and  $C$  are the three rotational constants in decreasing order of magnitude. For  $K=1$  and  $K=2$  this expansion to the second power of  $b$  is given by

$$K=1, \quad q_J = \frac{q_m}{(J+1)(2J+3)} \left\{ 3 - J(J+1) \mp \frac{J(J+1)}{2} \eta + \left( \frac{3}{2}b^2 - b\eta \right) \frac{f(J,2)}{4} \pm \frac{3}{128} \eta b^2 f(J,2) J(J+1) \right\};$$

$$K=2, \quad q_J = \frac{q_m}{(J+1)(2J+3)} \left\{ 12 - J(J+1) + \left( \frac{3}{2}b^2 - b\eta \right) \times \left[ \frac{f(J,3)}{6} - \frac{f(J,1)}{2} \right] \mp \left( \frac{3}{2}b^2 - b\eta \right) \frac{f(J,1)}{2} \right\},$$

where, in the case of a nearly prolate rotor, the upper and lower signs correspond to the upper and lower asymmetric rotor energy levels, respectively, and

$$f(J,n) = \frac{1}{4} [J^2 - n^2] [(J+1)^2 - n^2], \quad q_m = \partial^2 V / \partial Z_m^2, \\ \eta = \left( \frac{\partial^2 V}{\partial X_m^2} - \frac{\partial^2 V}{\partial Y_m^2} \right) / q_m.$$

$Z_m$  is the principal axis of the least moment of inertia and  $Y_m$  is that of the largest.

<sup>7</sup> G. Knight and B. T. Feld, Report No. 123, Massachusetts Institute of Technology Research Laboratory of Electronics, 1949), (unpublished).

<sup>8</sup> J. Kratchman, J. Chem. Phys. (to be published).

Since the  $Z_m$  direction is rotated somewhat from the direction of the F—Mn bond due to the asymmetry of  $\text{Mn}(\text{O}^{16})_3\text{O}^{18}\text{F}$ , this quantity is consequently smaller than that of the  $\text{Mn}(\text{O}^{16})_3\text{F}$ , hence the splittings of the hyperfine components are smaller for the asymmetric molecule. The effect of the terms in  $(\frac{3}{2}b^2 - b\eta)$  is a slight shift and removal of some accidental degeneracies which exist especially in the hyperfine splittings of  $K=2$  levels. This removal of degeneracy produces only a small splitting and shows only as a broadening of the absorption lines.

Table III contains a list of the measured lines, from which the three rotational constants can be obtained as

$$A = 4488.81 \pm 0.3 \text{ Mc/sec}, \\ B = 4098.088 \pm 0.01 \text{ Mc/sec}, \\ C = 3963.552 \pm 0.01 \text{ Mc/sec}.$$

On the basis of these constants, values of  $eqQ$  and  $\eta$  can be calculated from the coupling constant  $eqQ$  of  $\text{Mn}(\text{O}^{16})_3\text{F}$  by expressing the electric field gradient tensor in the coordinate system coinciding with the principal axes of the asymmetric molecule. The values obtained are  $eq_m Q = 16.4 \text{ Mc/sec}$ ,  $\eta = 0.044$ . These values fit the observed hyperfine patterns, indicating that there is no detectable change of the electronic structure resulting from a substitution of  $\text{O}^{18}$  in the molecule.

The centrifugal stretching of the molecule is small and less than experimental error. In terms of the limiting case of a symmetric prolate rotor an upper limit to the centrifugal distortion coefficient  $D_{JK}$  can be given as 10 kc/sec from the relative position of different rotational transitions in the spectrum.

The three rotational constants are inversely proportional to the principal moments of inertia of the molecule from which three structural parameters can be evaluated. The main source of uncertainty on this determination is due to the zero-point vibrations.<sup>9</sup> These cause slight change in the  $\angle (\text{O}^{18} - \text{Mn} - \text{F})$  angle

<sup>9</sup> Townes, Holden, and Merritt, Phys. Rev. 74, 1113 (1948).

and Mn—O<sup>18</sup> distance compared to  $\angle(\text{O}^{16}\text{—Mn—F})$  and Mn—O<sup>16</sup>. The available data on the two isotopic species can not be used for separately evaluating all parameters involving O<sup>18</sup> and O<sup>16</sup>. However, if it is assumed that isotopic substitution affects only the bond angle, a fit of the spectrum can be obtained with the  $\angle(\text{O}^{18}\text{,Mn,F})$  angle 2' smaller than that for O<sup>16</sup>. On the other hand, if Mn—O bond is assumed to be shortened by one part in one thousand due to the substitution of O<sup>18</sup> for O<sup>16</sup>, then the O—Mn—F angle must change by 10' for the isotopic substitution.

The best values of structural parameters and errors expected from zero-point vibrations are

$$\text{Mn—O} = 1.586 \pm 0.005 \text{ \AA},$$

$$\text{Mn—F} = 1.724 \pm 0.005 \text{ \AA},$$

$$\angle(\text{O,Mn,F}) = 108^\circ 27' \pm 7'.$$

These parameters are rather sensitive to slight changes in the angle and the distance due to the substitution of O<sup>18</sup>. However, the projection of the Mn—O distance on a plane perpendicular to Mn—F axis is quite insensitive to these changes and can be determined more accurately as  $1.5020 \text{ \AA} \pm 0.0001 \text{ \AA}$ .

We can obtain a value for the covalent radius of doubly bonded Mn by subtracting the covalent radius of doubly bonded oxygen from our measured bond lengths Mn—O. The ionic character of this bond is not expected to have a large effect on the bond length; thus one obtains the double bond radius for Mn as 1.04 \AA.

Since the amount of ionic character of Mn—F bond is not known, the single-bond radius of Mn can not be determined precisely. However, ignoring ionicity of this bond, a radius of 1.08 \AA is obtained for the single-bond radius of Mn. The presence of ionic character in the bond shortens the bond length; hence, this value should be considered as a lower limit.

The anomalously large bond radius of about 1.50 \AA<sup>10</sup> reported for the octahedral radius of bivalent Mn in MnS<sub>2</sub>, MnSe<sub>2</sub>, and MnTe<sub>2</sub> is in striking contrast with our observed bond radii.

It should be noted that the angle  $\angle(\text{O,Mn,O})$  is very close to a tetrahedral angle obtained ordinarily for structurally similar molecules formed by tetravalent atoms.

The degeneracy of a pair of degenerate normal modes of oscillation in the molecule Mn(O<sup>16</sup>)<sub>3</sub>F is removed when one of the oxygens is replaced by O<sup>18</sup>. However, it is expected that the separation of vibrational levels corresponding to such a pair in the molecule Mn(O<sup>16</sup>)<sub>2</sub>O<sup>18</sup>F is small and of the same order as the rotational frequencies, so that appreciable perturbation will occur. Hence modified Coriolis interactions and *l*-doubling effects<sup>11</sup> may be observable. Unfortunately, the absorption lines due to the molecule Mn(O<sup>16</sup>)<sub>2</sub>O<sup>18</sup>F in the

excited vibrational states were so weak that these effects could not be clearly observed.

### DIPOLE MOMENT

The molecular electric dipole moment  $\mu$  of MnO<sub>3</sub>F is measured by a study of the Stark effect in the transition  $J=3 \leftarrow 2$ . Because of the large Stark splitting of the lines corresponding to  $K=\pm 1$  and  $K=\pm 2$ , it was preferred to make the measurements on the transitions in an excited perpendicular vibrational mode. The *l*-type doublet with  $v_6=1$  was chosen for this purpose. The change in energy due to Stark effect for each rotational level of such a doublet is given by<sup>12</sup>

$$\Delta E = [(\Delta W/2)^2 + \mu^2 E^2 \phi^2]^{\frac{1}{2}} - \Delta W/2,$$

where  $\phi$  is the matrix element of the direction cosine, and  $\Delta W$  is the separation of the doublet.

In the absence of hyperfine interaction, there are two well-defined Stark components for each member of the observed doublet corresponding to  $M_J=1$  and  $M_J=2$

TABLE III. Measured lines of Mn(O<sup>16</sup>)<sub>2</sub>O<sup>18</sup>F.  $\nu_0$  is the frequency of the rotational transition after correction for the hyperfine splitting.

$J'_{K'-1'K1'} \rightarrow$ $J_{K-1K1}$	Transition		Measured frequency (Mc/sec)	$\nu_0$ (Mc/sec)
	$F' \leftarrow F$			
$3_{13} \leftarrow 2_{12}$	$11/2 \leftarrow 9/2$		$23\,966.310 \pm 0.040$	
	$9/2 \leftarrow 7/2$			$23\,966.710$
	$7/2 \leftarrow 7/2$			
	$7/2 \leftarrow 5/2$		$23\,967.106 \pm 0.040$	
	$5/2 \leftarrow 3/2$			
$3_{03} \leftarrow 2_{02}$				$24\,076.35 \pm 0.3$
$3_{22} \leftarrow 2_{21}$	$3/2 \leftarrow \left\{ \begin{array}{l} 1/2 \end{array} \right.$		$24\,181.70 \pm 0.150$	
	$5/2 \leftarrow \left\{ \begin{array}{l} 3/2 \end{array} \right.$			
	$3/2 \leftarrow \left\{ \begin{array}{l} 3/2 \end{array} \right.$			
	$11/2 \leftarrow \left\{ \begin{array}{l} 9/2 \end{array} \right.$		$24\,183.70 \pm 0.05$	$24\,184.90$
	$9/2 \leftarrow \left\{ \begin{array}{l} 9/2 \end{array} \right.$			
	$7/2 \leftarrow \left\{ \begin{array}{l} 9/2 \end{array} \right.$			
	$9/2 \leftarrow \left\{ \begin{array}{l} 7/2 \end{array} \right.$		$24\,186.85 \pm 0.1$	
	$7/2 \leftarrow \left\{ \begin{array}{l} 7/2 \end{array} \right.$			
	$5/2 \leftarrow \left\{ \begin{array}{l} 7/2 \end{array} \right.$			
	$5/2 \leftarrow \left\{ \begin{array}{l} 3/2 \end{array} \right.$			
	$3/2 \leftarrow \left\{ \begin{array}{l} 3/2 \end{array} \right.$			
	$11/2 \leftarrow \left\{ \begin{array}{l} 9/2 \end{array} \right.$		$24\,292.35 \pm 0.08$	$24\,293.45$
$3_{21} \leftarrow 2_{20}$	$9/2 \leftarrow \left\{ \begin{array}{l} 9/2 \end{array} \right.$			
	$7/2 \leftarrow \left\{ \begin{array}{l} 9/2 \end{array} \right.$			
	$9/2 \leftarrow \left\{ \begin{array}{l} 7/2 \end{array} \right.$		$24\,295.45 \pm 0.1$	
	$7/2 \leftarrow \left\{ \begin{array}{l} 7/2 \end{array} \right.$			
	$5/2 \leftarrow \left\{ \begin{array}{l} 7/2 \end{array} \right.$			
	$5/2 \leftarrow \left\{ \begin{array}{l} 3/2 \end{array} \right.$			
	$3/2 \leftarrow \left\{ \begin{array}{l} 3/2 \end{array} \right.$			
	$11/2 \leftarrow \left\{ \begin{array}{l} 9/2 \end{array} \right.$			
$3_{12} \leftarrow 2_{11}$	$11/2 \leftarrow 9/2$		$24\,365.64 \pm 0.030$	
	$9/2 \leftarrow 7/2$		$24\,366.331 \pm 0.060$	$24\,366.05$
	$7/2 \leftarrow 7/2$			
	$7/2 \leftarrow 5/2$		$24\,366.80 \pm 0.050$	
	$5/2 \leftarrow 3/2$		$24\,367.89 \pm 0.030$	
	$9/2 \leftarrow 9/2$			

<sup>10</sup> L. Pauling, *Nature of the Chemical Bond* (Cornell University Press, Ithaca, 1948).

<sup>11</sup> H. H. Nielsen, *Revs. Modern Phys.* **23**, 90 (1951).

<sup>12</sup> R. G. Shulman and C. H. Townes, *Phys. Rev.* **77**, 500 (1950).

which under a reasonable amount of electric field can be separated appreciably from their allied zero-field lines. For fields of this order of magnitude, the nuclear quadrupole interaction can be considered approximately as a small perturbation and causes a hyperfine pattern for each of the Stark components. The main sources of error in this measurement were due to an incomplete resolution of the hyperfine structure of these components which, owing to the inhomogeneity of the electric field, are ordinarily broader than the zero-field lines. However, the line shapes could clearly be recognized as those caused by the expected structures and their centers measured. The magnitude of the electric field was chosen such that the Stark components were completely removed from the total range of the hyperfine structure of the zero-field transitions.

The measurements of the electric field were made by a study of the Stark effect in the molecule OCS which has a known dipole moment. It was found that, in spite of the high instability of  $\text{MnO}_3\text{F}$ , it can coexist together with the molecule OCS for a reasonable length of time. Both samples were admitted simultaneously into the wave guide and their Stark splittings studied under the same field.

Table IV contains a list of the measured splittings. The values given for each setting of the electric field is an average for the Stark splittings of the two members of the doublet. From this table we obtain  $\mu = 1.5 \pm 0.2$  for the dipole moment of  $\text{MnO}_3\text{F}$ .

All of the measurements on  $\text{MnO}_3\text{F}$  were made at a temperature of about  $-60^\circ$  centigrade.

#### CHEMICAL PREPARATION OF $\text{Mn}(\text{O}^{18})_2\text{O}^{18}\text{F}$

The details of the preparation of  $\text{MnO}_3\text{F}$  appears elsewhere.<sup>1</sup> The  $\text{O}^{18}$  was introduced in the following way. One gram of  $\text{KMn}(\text{O}^{16})_4$  was refluxed for 42 hours with 4 cc of  $\text{H}_2\text{O}^{18}$  (5 percent  $\text{O}^{18}$ ). Then the water was distilled off, and the enriched  $\text{KMnO}_4$  was used for the preparation of  $\text{Mn}(\text{O}^{16})_2\text{O}^{18}\text{F}$ . For this purpose it was reacted with about 1 cc of  $\text{SO}_3\text{HF}$ , and the effluent  $\text{MnO}_3$  collected in Kel-F traps. Purification was carried out by repeated distillation with an excess of enriched  $\text{KMnO}_4$  to remove the last traces of  $\text{SO}_3\text{HF}$  and HF.

#### SPECTRUM OF $\text{ReO}_3\text{Cl}$

The rotational transitions  $J=5 \leftarrow 4$  and  $6 \leftarrow 5$  of this molecule are studied for hyperfine structure. There are two nuclei in this molecule with sizable contributions to the quadrupole interaction energy, namely Re and Cl. Due to these interactions, spins of both Re and

Cl nuclei are coupled to the rotational angular momentum  $J$ . Our observation shows that the energy of interaction of the Re nucleus is considerably larger than that of the Cl nucleus. Hence to a good approximation the energy levels can be designated with quantum numbers corresponding to  $F_1$  and  $F$ , where  $F_1$  is the resultant angular momentum obtained by addition of the spin of the Re nucleus to the rotational angular momentum  $J$  and  $F$  is that obtained by further addition of the spin of the Cl nucleus. The selection rules for allowed transitions are  $\Delta F_1 = 0$  or  $\pm 1$  and  $\Delta F = 0$  or  $\pm 1$ .

The hyperfine pattern is complicated by the presence of a large number of hyperfine components. Furthermore, there is an overlap of hyperfine structures due to either of the two Re isotopes in both of our observed rotational transitions. For example, the isotopic shift of the lines corresponding to  $J=6 \leftarrow 5$  is 7.4 Mc/sec while the spread due to hyperfine structure is about 15 Mc/sec. The presence of two Cl isotopes does not cause any complication since isotopic shift due to Cl is large, and the hyperfine patterns are well separated.

In order to differentiate decisively between components belonging to either of the two isotopic species in Re, spectroscopy was done on a small quantity of  $\text{ReO}_3\text{Cl}$  prepared with Re metal enriched almost to 100 percent in  $\text{Re}^{187}$ . The observed spectrum of this sample for the transition  $J=6 \leftarrow 5$  provided a clear identification of those components of the spectrum which were due to the  $\text{Re}^{187}$  isotope. Most of the final measurements were performed on normal isotopic material.

From analysis of observed lines a spin 5/2 for both Re isotopes is verified and the following constants are obtained:

$$eqQ_{\text{Re}^{187}} = 253 \pm 6 \text{ Mc/sec},$$

$$eqQ_{\text{Re}^{185}} = 270 \pm 6 \text{ Mc/sec},$$

$$eqQ_{\text{Cl}^{35}} = -34 \text{ Mc/sec},$$

$$B_0 \text{ for } \text{Re}^{185}\text{O}_3^{16}\text{Cl}^{35} = 2094.20 \text{ Mc/sec},$$

$$B_0 \text{ for } \text{Re}^{187}\text{O}_3^{16}\text{Cl}^{35} = 2093.58 \text{ Mc/sec}.$$

In Fig. 3 the observed structure for  $K=\pm 3$  and  $K=0$  are compared separately with the theoretical patterns. The  $K=0$  lines show Stark effect only to the second order. Their presence could conveniently be suppressed for the measurements on the  $K=\pm 3$  transitions, by using relatively low Stark modulation field. However, under such a field, often there was unfavorable interference from the Stark components of different absorption lines in the pattern. It was necessary to adjust separately the amplitude of the Stark modulation field for each specific line. This difficulty prevented acceptably accurate measurements of some of the components. For example, the  $K=\pm 3$  transitions at about 25 123 Mc/sec (refer to Fig. 3) were so badly masked by the Stark components of the various nearby lines that in order to free these transitions from such interferences a larger modulation field seemed to be required. However, under higher fields, the transition  $K=0$ ,  $17/2 \leftarrow$

TABLE IV. Stark splitting of the  $l$  doublet,  $v_6=1$ .

$E(\text{volts/cm})$	(Mc/sec), $M_J=1$	(Mc/sec), $M_J=2$
57.5		3.2
80	1.5	5.55
86	1.9	

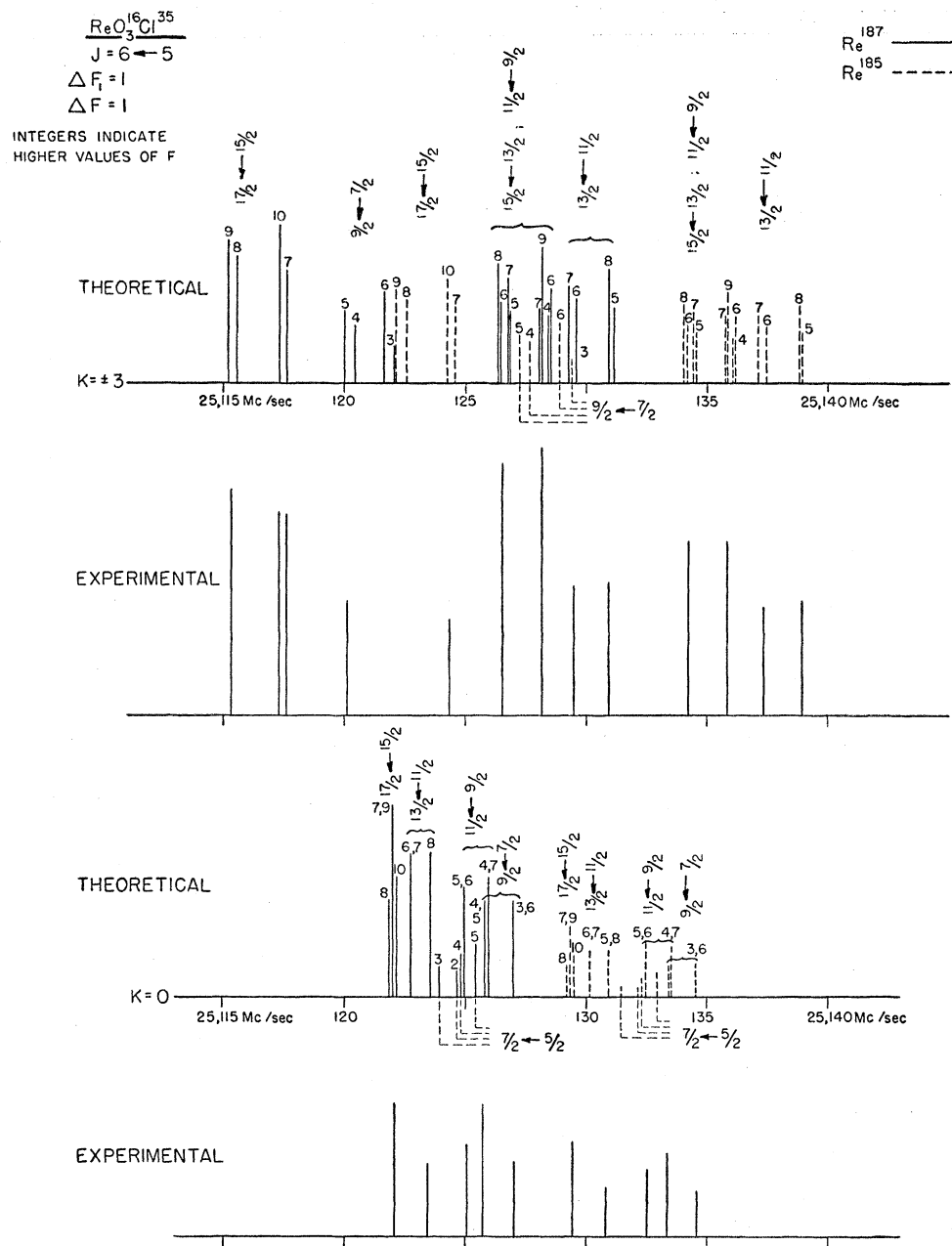


FIG. 3. The quadrupole hyperfine structure of  $\text{ReO}_3\text{Cl}$  in the  $J=6 \leftarrow 5$  transition arising from quadrupole couplings of Re and Cl nuclei. The spectrum is a superposition of the transitions originating from the two isotopic species in Re.

$15/2$  began to show appreciable microwave absorption, and thus no accurate measurements of these lines were possible.

For the measurements on the  $K=0$  lines, advantage was taken of the extreme Stark sensitivity of  $K=\pm 3$  transitions. By subjecting the molecules to a dc electric field, it was possible to split these lines into Stark components considerably removed from their zero-field

positions and make measurements on the  $K=0$  transitions which undergo virtually no splitting.

As can be seen from Fig. 3, there are frequently several lines superimposed within a range of about 500 kc/sec. In such cases, although a complete resolution was not achieved, the line shapes were observed to be in agreement with those predicted from the theoretical hyperfine pattern.

TABLE V. The measured lines of  $\text{ReO}_3\text{Cl}$ , in Mc/sec. The experimental error where not indicated is about 0.1 Mc/sec.

$\text{Re}^{187}$		$\text{Re}^{186}$		Transition	$J=6 \leftarrow 5$
Experimental frequency	Theoretical frequency	Experimental frequency	Theoretical frequency	$F' \leftarrow F$	$F_1' \leftarrow F_1$
$K=\pm 3$					
25 115.33	25 115.37			$\left\{ \begin{smallmatrix} 9 \leftarrow 8 \\ 8 \leftarrow 7 \end{smallmatrix} \right\}$	$17/2 \leftarrow 15/2$
25 117.36 $\pm$ 0.06	25 117.37			$10 \leftarrow 9$	$17/2 \leftarrow 15/2$
25 117.66 $\pm$ 0.04	25 117.59			$7 \leftarrow 6$	$17/2 \leftarrow 15/2$
		25 124.35 $\pm$ 0.06	25 124.37	$\left\{ \begin{smallmatrix} 10 \leftarrow 9 \\ 7 \leftarrow 6 \end{smallmatrix} \right\}$	$17/2 \leftarrow 15/2$
25 120.10	25 120.10			$\left\{ \begin{smallmatrix} 5 \leftarrow 4 \\ 4 \leftarrow 3 \end{smallmatrix} \right\}$	$9/2 \leftarrow 7/2$
				$\left\{ \begin{smallmatrix} 8 \leftarrow 7 \\ 7 \leftarrow 6 \end{smallmatrix} \right\}$	$15/2 \leftarrow 13/2$
25 126.52	25 126.54	25 134.24	25 134.23	$\left\{ \begin{smallmatrix} 6 \leftarrow 5 \\ 5 \leftarrow 4 \end{smallmatrix} \right\}$	$11/2 \leftarrow 9/2$
				$\left\{ \begin{smallmatrix} 9 \leftarrow 8 \\ 6 \leftarrow 5 \end{smallmatrix} \right\}$	$15/2 \leftarrow 13/2$
25 128.15 $\pm$ 0.05	25 128.24	25 135.82 $\pm$ 0.06	25 135.93	$\left\{ \begin{smallmatrix} 7 \leftarrow 6 \\ 6 \leftarrow 5 \end{smallmatrix} \right\}$	$11/2 \leftarrow 9/2$
25 129.47	25 129.40	25 137.40	25 137.29	$\left\{ \begin{smallmatrix} 7 \leftarrow 6 \\ 6 \leftarrow 5 \end{smallmatrix} \right\}$	$13/2 \leftarrow 11/2$
25 130.93 $\pm$ 0.06	25 131.06	25 138.80 $\pm$ 0.07	25 138.95	$\left\{ \begin{smallmatrix} 8 \leftarrow 7 \\ 5 \leftarrow 4 \end{smallmatrix} \right\}$	$13/2 \leftarrow 11/2$
$K=0$					
25 122.08 $\pm$ 0.05	25 122.03	25 129.42 $\pm$ 0.08	25 129.36	$17/2 \leftarrow 15/2$	
25 123.45 $\pm$ 0.20	25 123.54	25 130.80 $\pm$ 0.2	25 130.97	$\left\{ \begin{smallmatrix} 5 \leftarrow 4 \\ 8 \leftarrow 6 \end{smallmatrix} \right\}$	$13/2 \leftarrow 11/2$
25 125.00	25 124.90	25 132.56	25 132.47	$\left\{ \begin{smallmatrix} 5 \leftarrow 4 \\ 6 \leftarrow 5 \end{smallmatrix} \right\}$	$11/2 \leftarrow 9/2$
				$\left\{ \begin{smallmatrix} 5 \leftarrow 4 \\ 4 \leftarrow 3 \end{smallmatrix} \right\}$	$7/2 \leftarrow 5/2$
25 125.75	25 124.90	25 133.38	25 133.45	$\left\{ \begin{smallmatrix} 4 \leftarrow 3 \\ 5 \leftarrow 2 \end{smallmatrix} \right\}$	$9/2 \leftarrow 7/2$
				$\left\{ \begin{smallmatrix} 4 \leftarrow 3 \\ 7 \leftarrow 6 \end{smallmatrix} \right\}$	$11/2 \leftarrow 9/2$
25 127.03 $\pm$ 0.06	25 126.96	25 134.59 $\pm$ 0.07	25 134.59	$\left\{ \begin{smallmatrix} 3 \leftarrow 2 \\ 6 \leftarrow 5 \end{smallmatrix} \right\}$	$9/2 \leftarrow 7/2$

The excited vibrational states of the perpendicular normal modes appear at frequencies below 25 110 and above 25 140 Mc/sec. A complete resolution of these lines was not possible due to additional complications of the  $l$ -type doublings. However, there were indications that the amount of  $l$  doubling is considerably smaller than that observed in the molecule  $\text{MnO}_3\text{F}$ .

Table V contains a list of the measured lines and their theoretical fit. The quadrupole coupling of the Cl nucleus is treated as small compared to that of the Re.

It is expected that a higher-order calculation in the treatment of the quadrupole coupling of Cl nucleus would improve the error in the evaluation of the Re coupling constant from our measured data. This requires a complete solution of the secular determinants obtained in the Hamiltonian of the quadrupole interaction for the case of two nuclei.<sup>4</sup> However, the effect of the Cl quadrupole coupling can be eliminated in a calculation of the difference of the quadrupole coupling constants of the two Re isotopes. One obtains for this difference a value of  $17 \pm 1.5$  Mc/sec, with the coupling constant for  $\text{Re}^{186}$  larger than that for  $\text{Re}^{187}$ .

Although complete measurements were not carried out on the  $J=5 \leftarrow 4$  transition, the relative position of components of hyperfine pattern of this transition

appears to agree well with the above constants and its study gave a helpful check on their values.

Amble *et al.*<sup>2</sup> have measured the  $B$  values of  $\text{ReO}_3\text{Cl}$  for different isotopic species without a complete solution of the hyperfine structure. Our measured values are consistent with their results, although their approximate evaluation of the Re quadrupole coupling constant appears to be incorrect.

From the interatomic distances given by Amble *et al.* for  $\text{ReO}_3\text{Cl}$ , the bond radii for Re can be obtained as was done above for Mn. One obtains for the Re double-bond radius 1.21 Å and for the single-bond radius a lower limit of 1.25 Å.

The angle  $\angle(\text{O}, \text{Re}, \text{O})$  is very close to the angle  $\angle(\text{O}, \text{Mn}, \text{O})$  observed in  $\text{MnO}_3\text{F}$  indicating structural similarity of these two molecules.

The ratio of the nuclear quadrupole moments of  $\text{Re}^{186}$  and  $\text{Re}^{187}$  can be gotten by dividing the values of their quadrupole coupling constants giving

$$Q_{\text{Re}^{187}}/Q_{\text{Re}^{186}} = 1.067 \pm 0.045.$$

While the quadrupole moment of  $\text{Re}^{187}$  is known satisfactorily from optical data,<sup>13</sup> there is apparently an uncertainty in the value of quadrupole moment of the

<sup>13</sup> H. Schuler and H. Korsching, Z. Physik **105**, 168 (1937).



Re<sup>185</sup>.<sup>14</sup> The above value of the ratio of these two moments fixes a value of  $2.8 \times 10^{-24}$  cm<sup>2</sup> for Re<sup>185</sup> from that of the Re<sup>187</sup>.

Kopfermann<sup>15</sup> has suggested an approximate proportionality of the deviation,  $\delta\mu$ , of magnetic dipole moments from the Schmidt limits and the electric quadrupole moments in pairs of isotopes of the same spin differing by two neutrons. In the case of Re the magnetic moments are known for both isotopes and their ratio of  $\delta\mu$  is 1.05 which is close to our observed ratio of their quadrupole moments and hence in agreement with Kopfermann's relation. The existence of a correlation between these two moments can be understood qualitatively in most cases on the basis of approach to strong coupling approximation.<sup>16</sup> However, such close agreement in this proportionality for the case of Re may be purely coincidental.

#### MOLECULAR ELECTRONIC STRUCTURE AND NUCLEAR QUADRUPOLE MOMENT OF Mn<sup>55</sup>

Ordinarily the coupling constant  $eqQ$  is used for estimating  $Q$  through an evaluation of  $q$  from a reasonable assignment of valence electrons to the atomic orbitals.<sup>17</sup> However, in these molecules the state of the bonding electrons is complex and not well known. The valence electrons of heptavalent Mn and Re contain  $s$ ,  $p$ , and  $d$  orbitals. The possibility of obtaining an electronic wave function for the molecular bonds in terms of these orbitals is rather unfeasible since little is known about the manner in which  $d$  orbitals are involved, particularly in the formation of double bonds.

Fortunately, the nuclear quadrupole moments of both Re isotopes are known. Hence, knowledge of the coupling constants  $eqQ$  for Re isotopes in the molecule ReO<sub>3</sub>Cl can be used for experimentally determining  $q$  at the nucleus of Re in this molecule, which in turn gives some information about the bonding electrons. The value of  $q$  obtained in this way is  $q = 1.4 \times 10^{15}$  esu.

The gradient of electric field at the nucleus of Re can be calculated for a pure  $p$  electron by studying fine structure of the optical spectra of ReI.<sup>18</sup> Under an assumption of an approximate  $LS$  coupling, the splitting of  $Z^3p^0$  multiplet together with  $Z^5p^0$  can be solved for the spin-orbit coupling constant,<sup>19</sup> which subsequently furnishes the quantity  $\langle 1/r^3 \rangle$  for the  $6p$  electron of Re necessary for an evaluation of its  $q$ . In this way one obtains  $\langle 1/r^3 \rangle = 21.6 \times 10^{24}$  cm<sup>-3</sup>, giving  $q(p_\sigma) = 8.13 \times 10^{15}$  esu for a  $p_\sigma$  orbital ( $\sigma$  standing for  $m=0$ ). In this calculation it is necessary to know the effective value

of  $Z$  near the nucleus. The value used for  $Z_{\text{effective}}$  is 69 as suggested by Barnes and Smith.<sup>20</sup>

The value of  $q$  for a pure  $d$  electron can also be obtained approximately from optical data, which show that  $q$  due to a  $d$  electron is about 25 times smaller than that for a  $p$  electron (see also reference 17). Although the presence of  $d$  electrons may effect  $q$  through their bearings on the population of  $p$  orbitals, the direct contribution of  $d$  electrons to the observed  $q$  is, from the above, small enough to be ignored.

The amount of unbalanced  $p$  electrons  $u_p$ ,<sup>17</sup> defined by  $q = u_p q(p_\sigma)$ , can be evaluated by using above values of  $q(p_\sigma)$ . One obtains a value of about 20 percent for this quantity which is a measure of the deviation of the  $p$  electrons from an equal population of all  $p$  orbitals. The sign of  $u_p$  indicates that there is an excess of perpendicular  $p$  orbitals,  $p_\pi$ , over the  $p$  orbitals along the symmetry axis  $p_\sigma$ . The value of  $u_p$  obtained for ReO<sub>3</sub>Cl can be used to deduce an estimate of the gradient of the electric field at the nucleus of Mn in the molecule MnO<sub>3</sub>F.

The chemical and structural similarity of ReO<sub>3</sub>Cl and MnO<sub>3</sub>F discussed earlier, indicate a close similarity between their chemical bonds. Hence it is reasonable to assume that the atomic orbitals involved in the bond formations have more or less the same relative populations in both cases so that the same amount of unbalanced  $p$  electrons  $u_p$  may be assumed for both molecules.

The gradient of electric field at the nucleus of Mn for a pure  $p$  electron can be evaluated, as was done in the case of Re, from optical fine structure of MnI. One obtains  $\langle 1/r^3 \rangle = 0.9 \times 10^{24}$  cm<sup>-3</sup> for the  $4p$  electrons of Mn leading to  $q(p_\sigma) = 2.4 \times 10^{15}$  esu. The value of this quantity for a  $d$  electron is estimated as about 25 times smaller than that for a  $p$  electron indicating that the arguments used in this connection in the case of Re holds also for Mn. This value of  $q(p_\sigma)$  together with an assumption of 20 percent unbalanced  $p$  electron gives  $q = 0.45 \times 10^{15}$  esu as an estimate of the gradient of the molecular electric field at the nucleus of Mn.

Using the above value of  $q$  and the observed coupling constant  $eqQ = 16.8$  Mc/sec, one obtains a value of  $Q = 0.55 \times 10^{-24}$  cm<sup>2</sup> for the nuclear quadrupole moment of Mn<sup>55</sup>. The probable error in this result is difficult to assess because it depends primarily on the differences between Mn and Re bonding orbitals. However, there seems to be little reason to doubt the correctness of the sign of  $Q$ , and probably the value is correct to within a factor of two. This value was reported in a short abstract several months ago.<sup>21</sup> Since then Murakawa and Kamei<sup>22</sup> have measured this quantity from optical hyperfine structure of MnI. Their value is  $0.4 \pm 0.2$ , which agrees with our result and indicates the validity of the approximate calculation used here.

<sup>14</sup> J. E. Mack, Revs. Modern Phys. **22**, 64 (1950).

<sup>15</sup> H. Kopfermann, Naturwiss. **38**, 29 (1951).

<sup>16</sup> A. Bohr and B. R. Mottelson, Kgl. Danske Videnskab. Selskab. Mat.-fys. Medd. **27**, No. 16 (1953).

<sup>17</sup> C. H. Townes and B. P. Dailey, J. Chem. Phys. **17**, 782 (1949).

<sup>18</sup> W. F. Meggers, Bur. Standards J. Research **6**, 1027 (1931).

<sup>19</sup> H. E. White, *Introduction to Atomic Spectra* (McGraw-Hill Book Company, Inc., New York, 1934).

<sup>20</sup> R. G. Barnes and W. V. Smith, Phys. Rev. **93**, 95 (1954).

<sup>21</sup> Javan, Silvey, Townes, and Grosse, Phys. Rev. **91**, 222 (1953).

<sup>22</sup> K. Murakawa and T. Kamei, Phys. Rev. **92**, 325 (1953).

The nucleus of  $\text{Mn}^{55}$  is one of the exceptions to Meyer's rules for nuclear spin.<sup>23</sup> This nucleus is thought to have 5 protons in  $f_{7/2}$  orbits outside of a closed shell which are coupled to a total spin 5/2. The observed sign and the exceptionally large quadrupole moment of this nucleus is consistent with the expected value of such a state. In fact, for all possible spins consistent with Pauli's exclusion principle which one can expect from a  $(f_{7/2})^5$  configuration, the state of total spin 5/2 gives the largest positive quadrupole moment. It is remarkable that all nuclei which are exceptions to the normal shell structure rules for spin have a ground

state with an exceptionally large positive quadrupole moment,<sup>24</sup> as is found here for  $\text{Mn}^{55}$ .

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We should like to take this opportunity to express our appreciation to Professor C. H. Townes for his guidance throughout the course of this research.

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## Electric Excitation of $\text{Au}^{197}\dagger$

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The gamma radiation emitted from  $\text{Au}^{197}$  following the electric excitation of the nucleus by protons of from 2 to 5 Mev has been studied. The angular distributions and absolute yields of the two intense gamma rays of the spectrum at 279 and 555 kev have been measured. The angular distributions of these two gamma rays were found to agree well with those calculated for  $5/2 \rightarrow 3/2$  ( $M1+E2$ ) and  $7/2 \rightarrow 3/2$  ( $E2$ ) transitions, respectively, the excitation being  $E2$  in both cases. The yield from the 279-kev state was observed to increase with beam energy in the manner predicted by theory for electric quadrupole excitation. On the basis of the Bohr-Mottelson unified model of the nucleus the results indicate a larger than expected cross section for the formation of the 555-kev state. Values for the quadrupole moment and magnetic moment of the ground state of gold calculated from the cross section for the formation of the 279-kev state agree with spectroscopic values.

### INTRODUCTION

THE low-lying states of  $\text{Au}^{197}$  have been accessible heretofore through the beta decay of  $\text{Hg}^{197}$  and  $\text{Pt}^{197}$ , and through the decay from the metastable state excited by the inelastic scattering of neutrons.<sup>1,2</sup> On the basis of the  $\text{Hg}^{197}\text{-Au}^{197}$  decay, Mihelich and de-Shalit have proposed a level scheme for gold having excited states at 77, 268, 279, and 409 kev, as shown in Fig. 1, which is compatible with the observed gamma ray and internal conversion electron spectra. The results from inelastic neutron scattering indicate that the 409-kev state is metastable. Spin assignments of  $1/2^+$  or  $3/2^+$  have been made to both the 77- and 268-kev levels. Both values are consistent with the available data,

although the  $1/2^+$  assignment is preferred for the 77-kev state. Some evidence also supports the prediction of the shell model that the 279-kev and 409-kev levels are  $d_{5/2}$  and  $h_{11/2}$  states, respectively.

Recent work has shown that the low-energy states of gold can also be reached by electric (or Coulomb) excitation of the nucleus. Using a beam of 3-Mev alpha particles Heydenburg and Temmer<sup>3</sup> have observed gamma rays emitted subsequent to excitation having energies of 77, 191, and 279 kev, which can be identified as due to transitions between the known levels listed. The 191- and 279-kev gamma rays have also been found with proton bombardment,<sup>4,5</sup> and in addition, a gamma ray of 555 kev has been reported which is now assigned to a new level of that energy.<sup>6</sup>

Further study of the gamma radiation due to the Coulomb excitation of gold has been undertaken in the

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