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## The Molecular Structure, Dipole Moment, and $g$ Factor of Ozone from Its Microwave Spectrum\*

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(Received December 8, 1952)

Four low- $J$  rotational transitions of  $O_3^{16}$  have been measured in the region from 42 to 118 kmc. The rotational spectroscopic constants found are  $A = 106,530.0 \pm 1.1$  Mc,  $B = 13,349.06 \pm 0.06$  Mc,  $C = 11,834.3 \pm 1.1$  Mc. The oxygen nuclei form an isosceles triangle with an apex angle of  $116^\circ 49' \pm 30'$ , and the two equal internuclear distances are  $1.278 \pm 0.003$  Å. From the Stark splitting of the  $2_{0,2} \rightarrow 1_{1,1}$  transition the dipole moment is  $0.53 \pm 0.02$  debye. Zeeman splittings of this transition show that ozone is not significantly paramagnetic.

### INTRODUCTION

ALTHOUGH the structure of ozone has been the subject of many investigations, no consistent and definitive assignment of the molecular dimensions has been accomplished until the recent microwave investigations made by Hughes<sup>1</sup> of Westinghouse, and those made concurrently in this laboratory<sup>2</sup> and reported here.

By the electron diffraction method Shand and Spurr<sup>3</sup> assigned an apex angle of  $127^\circ \pm 3^\circ$  and the two similar 0-0 distances as  $1.26 \pm 0.02$  Å. Although their assignment of the bond lengths is within the upper limit of their estimated error the apex angle which they assigned is  $10^\circ$  too large.

Difficulties have been encountered in assigning the fundamental vibrational frequencies from the infrared spectrum,<sup>4,5</sup> and it would appear from the fine structure of the vibrational bands examined by Adel and Dennison<sup>4</sup> that the apex angle is acute. However, the recent discovery of a new fundamental band by Wilson and Badger<sup>6</sup> favors a model with an obtuse apex angle.

In the microwave region from 9 to 44 kmc Hughes<sup>1</sup> identified eighteen rotational transitions of ozone for which two lines involved values of  $J$  lower than nine. From these results Hughes obtained an angle of  $116.5^\circ$ – $117^\circ$  and two like distances of 1.276–1.279 Å. In the present work three additional lines involving  $J = 4$  or lower were found and identified in the region from 96 to 118 kmc. These lines, along with the low- $J$  transition at 42 kmc, allow the parameters of the molecule to be unquestionably assigned. Although only one transition,

that at 42 kmc, included in our study was measured also by Hughes, his assignment of the structural parameters from the lower frequency lines which he measured are in essential agreement with our assignment from the high frequency low- $J$  transitions. There is some discrepancy, however, in the two electric dipole moment determinations.

### EXPERIMENTAL PROCEDURE

A Stark-modulation spectrograph<sup>7</sup> with 4 kc square wave modulation was employed. The cell was 94.5 cm long from window to window and was made of gold-plated  $K$ -band wave guide with a silver Stark electrode supported by Teflon spacers. Sources of energy were crystal harmonic generators<sup>8</sup> driven by Ratheon klystrons. Second, third, fourth, and fifth harmonics were utilized. At the higher frequencies the cell loss was about 10 db. To increase the strength of the lines the cell was cooled with dry ice. The absorption lines were detected by a Sylvania type 1N53 crystal and were displayed on a recorder preceded by a lock-in amplifier. Frequencies were measured with harmonics from a crystal controlled oscillator<sup>9</sup> which was monitored by comparison with station WWV.

Ozone was prepared in the small quantities required by passing a silent discharge through electrolytic oxygen which had been dried with sulfuric acid and phosphorus pentoxide. Oxygen was admitted to the discharge chamber to a pressure of about half an atmosphere. As ozone was formed, it was condensed with liquid air; and after the discharge had taken place for about 20 minutes, unconverted oxygen was pumped off. The ozone was admitted to the cell to pressures of about  $10^{-1}$  mm of Hg from the discharge chamber which was cooled with liquid air. In preliminary experiments formaldehyde lines were found. The formaldehyde was apparently produced by reaction of the ozone with stopcock grease in the vacuum system.

<sup>7</sup> R. H. Hughes and E. B. Wilson, Jr., *Phys. Rev.* **71**, 562 (1947).

<sup>8</sup> The multipliers used in most measurements were modified forms suggested by C. M. Johnson of crossed wave-guide designs already described. For references to the earlier designs see Johnson, Trambarulo and Gordy, *Phys. Rev.* **84**, 1178 (1951).

<sup>9</sup> R. R. Unterberger and W. V. Smith, *Rev. Sci. Instr.* **19**, 580 (1948).

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<sup>1</sup> R. H. Hughes, *Phys. Rev.* **85**, 717 (1952); *Symposium on Molecular Structure and Spectroscopy*, Ohio State University, June 1952.

<sup>2</sup> Preliminary results given in Quarterly Progress Reports, Air Force Contract No. W19-122-ac-35, November, 1950, February, 1951, March, 1952.

<sup>3</sup> W. Shand and R. A. Spurr, *J. Am. Chem. Soc.* **65**, 179 (1943).

<sup>4</sup> A. Adel and D. M. Dennison, *J. Chem. Phys.* **14**, 379 (1946).

<sup>5</sup> D. M. Simpson, *Trans. Faraday Soc.* **41**, 209 (1945); *J. Chem. Phys.* **15**, 846 (1947).

<sup>6</sup> M. K. Wilson and R. M. Badger, *J. Chem. Phys.* **16**, 741 (1948).

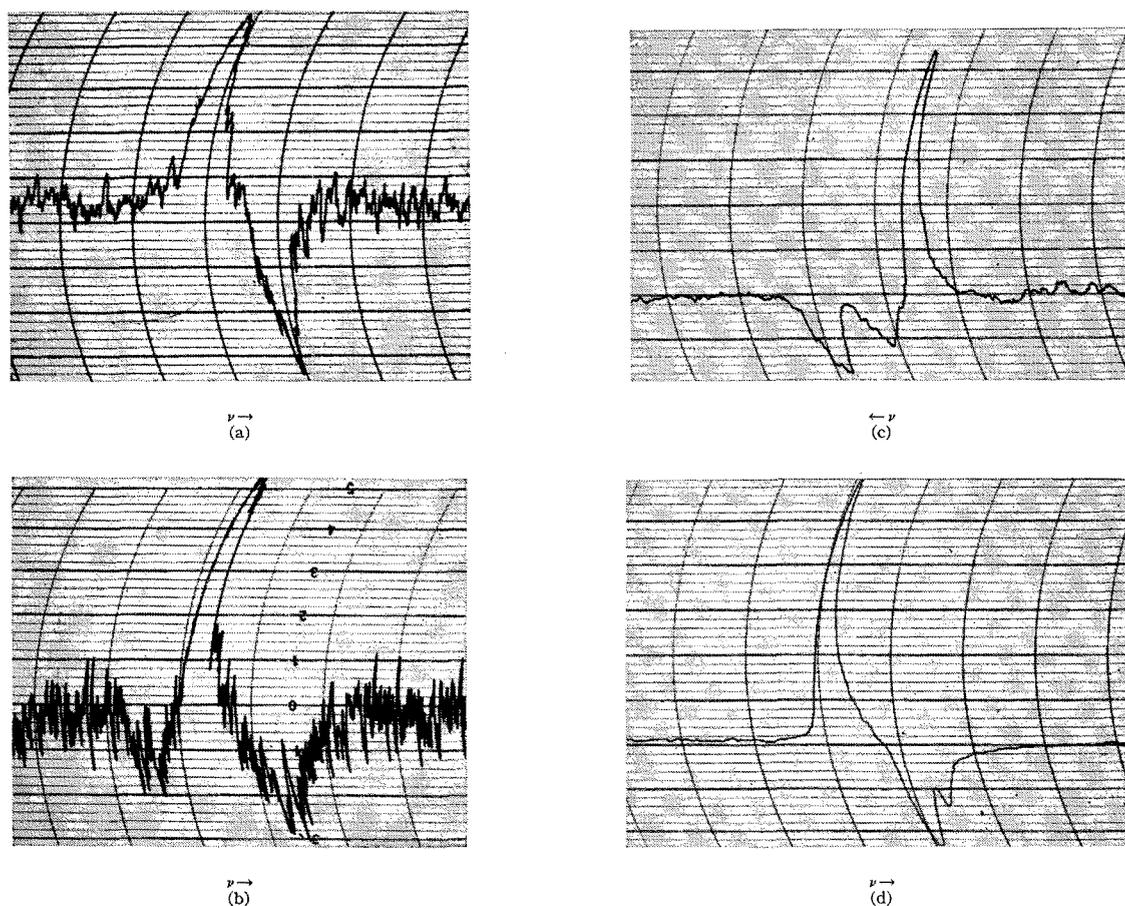


FIG. 1. Recordings of four low- $J$  ozone lines and their Stark components. (a) The  $0_{0,0} \rightarrow 1_{1,1}$  transition at 118 364 Mc. (b) The  $4_{0,3} \rightarrow 4_{1,3}$  transition at 101 736 Mc. (c) The  $2_{0,2} \rightarrow 2_{1,1}$  transition at 96 229 Mc. (d) The  $2_{0,2} \rightarrow 1_{1,1}$  transition at 42 833 Mc. Stark components point downward, undisplaced line upward.

Ozone lines appeared immediately upon introduction of the gas to the cell, and they gradually became weaker, whereas formaldehyde lines did not appear until after several minutes and grew stronger. This behavior served as a convenient means of distinguishing new ozone lines from those of formaldehyde.

The  $2_{0,2} \rightarrow 1_{1,1}$  transition near 43 kmc was split by a magnetic field of about 3000 oersteds which was formed by placing nine similar magnetron magnets side by side with soft iron strips linking the similar pole pieces of each individual magnet. By arranging the magnetron magnets and by placing shims between their pole pieces and the iron strips, it was possible to attain a field which varied by less than 5 percent over a distance of 60 centimeters. This magnet could be oriented along the wave-guide cell with the field parallel to either the wide or narrow dimension of the guide.

#### THE OZONE SPECTRUM

Recordings of the four low- $J$  lines are shown in Fig. 1. Frequencies of the lines and identifications are given in Table I. Also listed in Table I is the harmonic

of the klystron frequency used to obtain each line. The transitions were identified as to the values of  $J$  involved from the Stark patterns and as to the particular sub-levels from a comparison with the energy level scheme. Since the  $O^{16}$  nucleus has a spin of zero and ozone has a  $C_{2v}$  symmetry, with the dipole moment along the axis of intermediate moment of inertia, only  $++$  and  $--$  levels are possible. This restriction prevents ozone from having more lines of low  $J$  in the microwave region.

Table II lists the spectroscopic constants  $A$ ,  $B$ ,  $C$  and the asymmetry parameter,  $\delta = (B - C)/(A - C)$ , which were obtained from the three transitions,  $0_{0,0} \rightarrow 1_{1,1}$ ,  $2_{0,2} \rightarrow 1_{1,1}$ , and  $2_{0,2} \rightarrow 2_{1,1}$ , with centrifugal distortions neglected. Errors listed result from uncertainties in the

TABLE I. Observed transitions of ozone.

Transition	Frequency (Mc)	Klystron harmonic used
$2_{0,2} \rightarrow 1_{1,1}$	$42\,832.62 \pm 0.07$	2
$2_{0,2} \rightarrow 2_{1,1}$	$96\,228.84 \pm 0.18$	4
$4_{0,3} \rightarrow 4_{1,3}$	$101\,736.83 \pm 0.14$	3
$0_{0,0} \rightarrow 1_{1,1}$	$118\,364.3 \pm 0.5$	5

line frequency measurements. From the constants so obtained, the  $4_{0,4} \rightarrow 4_{1,3}$  transition is calculated to occur at 101,738.63 Mc as compared with the measured frequency of 101,736.83 Mc. This small discrepancy results partly from centrifugal distortions.

#### MAGNETIC SPLITTINGS OF THE $2_{0,2} \rightarrow 1_{1,1}$ TRANSITION

It is difficult to measure accurately the paramagnetic susceptibility of liquid ozone because of the presence of small amounts of dissolved oxygen which is strongly paramagnetic. Nevertheless from susceptibility measurements Laine<sup>10</sup> obtained evidence which he interpreted to indicate that ozone is slightly paramagnetic. A sensitive indicator of paramagnetism, one which is not influenced by paramagnetic impurities, is the Zeeman splitting of microwave absorption lines. As is seen from Fig. 2, the Zeeman splitting of the  $2_{0,2} \rightarrow 1_{1,1}$  rotational line of ozone is not very large at a field strength of about 3 kilo-oersteds, and consequently ozone is at most only weakly paramagnetic. The analysis of this splitting given below indicates that the magnetism of ozone arises principally from its molecular rotation. Evidently the electronic ground state of ozone is  $^1\Sigma$ .

For the alternating electric field vector parallel to the stationary magnetic field  $\Delta M=0$  transitions ( $\pi$ -type) are induced while  $\Delta M=\pm 1$  transitions ( $\sigma$ -type) occur for the electric field vector perpendicular to the imposed magnetic field. The shifts,  $\Delta\nu$ , in the transition frequency for the two magnetic field orientations are

$$\Delta\nu(\pi) = -M(g' - g)\beta_I H/h$$

and

$$\Delta\nu(\sigma) = -(M'g' - Mg)\beta_I H/h,$$

where the primes correspond to the upper rotational state of the transition and  $\beta_I$  is the nuclear magneton. Other symbols have the usual significance. Thus, if the  $g$  factors of the two rotational states are sensibly different, and neither is equal to zero, three lines are expected for the  $\pi$ -transition and six for the  $\sigma$ -transition from the  $2_{0,2}$  to the  $1_{1,1}$  levels. However, only three resolved lines are observed for the  $\sigma$ -transition [Fig. 2(a)]. This can be explained if the  $g$  factor for the  $2_{0,2}$  state is much smaller than that for the  $1_{1,1}$  state. The

TABLE II. Molecular constants of ozone.

$A = 106\,530.0 \pm 1.1$ Mc	$I_a = 7.8749 \times 10^{-40}$ g cm <sup>2</sup>
$B = 13\,349.06 \pm 0.06$ Mc	$I_b = 62.844 \times 10^{-40}$ g cm <sup>2</sup>
$C = 11\,834.3 \pm 1.1$ Mc	$I_c = 70.888 \times 10^{-40}$ g cm <sup>2</sup>
$\delta = 0.015996 \pm 0.000012$	
Electric dipole moment $\mu = 0.53 \pm 0.02$ debye	
$g$ factor = $1.54 \pm 0.09$ n.m. for $1_{1,1}$ state	
= $0.15 \pm 0.03$ n.m., for $2_{0,2}$ state	
Structure: isosceles triangle	
Two equal OO bond lengths = $1.278 \pm 0.003$ Å	
Angle between bonds = $116^\circ 49' \pm 30'$	

<sup>10</sup> P. Laine, Ann. phys. 3, 461 (1935).

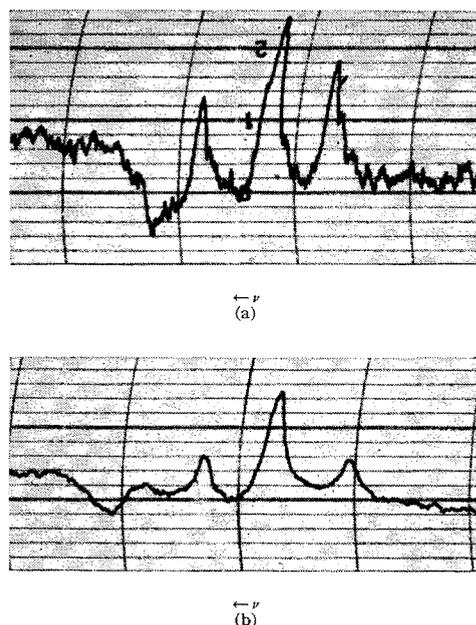


FIG. 2. Zeeman splittings of the  $2_{0,2} \rightarrow 1_{1,1}$  transition of ozone. Stark components have been pulled out far enough not to interfere with the magnetic splitting of the lines. (a) Magnetic field perpendicular to the electric component of the radiation. (b) Magnetic field parallel to the electric component of the radiation.

center line on each tracing of Fig. 2 is more intense than would be expected since the magnetic field included only 65 percent of the absorbing path of the radiation. For a field of  $2.93 \pm 0.07$  kilo-oersteds the component spacing for the  $\sigma$ -transitions is  $2.78 \pm 0.05$  Mc and for the  $\pi$ -transitions is  $3.12 \pm 0.05$  Mc. If it is assumed that the  $g$  factors of both rotational states have the same sign, then the factors are  $1.54 \pm 0.09$  for the  $1_{1,1}$  state and  $0.15 \pm 0.03$  for the  $2_{0,2}$  state. The large dependence of  $g$  factors upon the rotational state is interesting. The  $g$  factor for the  $1_{1,1}$  state of ozone is considerably larger than those found by Jen<sup>11</sup> for other molecules in singlet sigma-states. If the ozone magnetism arises from contributions of excited electronic states, then the electronic structure of the molecule depends to a surprising extent upon rotation. From the formal charges on the atoms in the most probable electronic ground state (see structures I and II below) one would expect a significant magnetic moment to be generated by rotation about the symmetry axes.

#### ELECTRIC DIPOLE MOMENT

Stark splitting of the  $2_{0,2} \rightarrow 1_{1,1}$  transition yield a value of the dipole moment of  $0.53 \pm 0.02$  debye which is in agreement with the values 0.49 debye found by Lewis and Smyth<sup>12</sup> and 0.52 debye reported by Epprecht,<sup>13</sup> but not with the value  $0.65 \pm 0.05$  debye given by Hughes.<sup>1</sup>

<sup>11</sup> C. K. Jen, Phys. Rev. 81, 197 (1951).

<sup>12</sup> G. L. Lewis and C. P. Smyth, J. Am. Chem. Soc. 61, 3063 (1939).

<sup>13</sup> G. W. Epprecht, Z. angew. Math. Physik 1, 138 (1950).

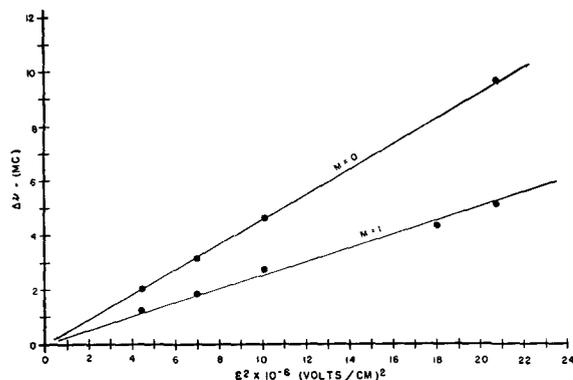


FIG. 3. A plot of the Stark splitting versus  $\mathcal{E}^2$  for the  $2_{0,2} \rightarrow 1_{1,1}$  transition from which the dipole moment of  $O_3$  was obtained.

The theory of Golden and Wilson<sup>14</sup> with the intensity tables of Cross, Hainer, and King<sup>15</sup> was used in evaluating the electric dipole moment. For calibration of the Stark spectrometer, OCS with known dipole moment<sup>16</sup>  $0.7085 \pm 0.004$  debye was employed. Since the observed Stark effect is second order, the plot of the component displacements against the field strength squared,  $\mathcal{E}^2$ , is a straight line. With the imposed field parallel to the electric vector of the microwave radiation only  $\Delta M = 0$  components are observed. Figure 3 shows a plot of the line splitting versus  $\mathcal{E}^2$  for the  $2_{0,2} \rightarrow 1_{1,1}$  transition from which the dipole moment was obtained.

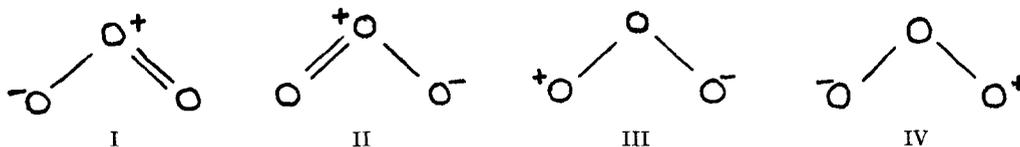
#### THE MOLECULAR DIMENSIONS

The three principal moments of inertia and other properties are given in Table II. For a rigid planar molecule the moment of inertia  $I_c$  should be the sum of the moments  $I_a$  and  $I_b$ ; however, in the ground vibrational state this relationship breaks down because of zero-point vibrations. A measure of this departure is the quantum defect,  $I_c - (I_a + I_b)$  which for ozone is  $0.169 \times 10^{-40}$  g cm<sup>2</sup>.

The molecular structure obtained from our results is an isosceles triangle with  $1.278 \pm 0.003$  Å for the two similar sides and an apex angle of  $116^\circ 49' \pm 30'$ . These values represent the mean of the structures calculated from the three moments of inertia taken two at a time, and the errors quoted are the maximum deviation from the mean.

#### ELECTRONIC STRUCTURE

The molecular dimensions and dipole moment of ozone throw light on the complex electronic structure



<sup>14</sup> S. Golden and E. B. Wilson, Jr., *J. Chem. Phys.* **16**, 669 (1948).

<sup>15</sup> Cross, Hainer, and King, *J. Chem. Phys.* **12**, 210 (1944).

<sup>16</sup> R. G. Shulman and C. H. Townes, *Phys. Rev.* **77**, 500 (1950).

<sup>17</sup> L. Pauling, *The Nature of the Chemical Bond* (Cornell University Press, 1945), pp. 164, 195.

of the molecule. Qualitatively, the electronic structure can be discussed most conveniently in terms of the valence bond resonance concepts of Pauling. The most reasonable contributing structures are I and II with perhaps small contributions from III and IV. The observed bond angle is near the  $120^\circ$  trigonal bonds formed by  $sp^2$  hybrid orbitals. This and other facts suggest that to a first approximation the four valence orbitals of the apex oxygen consist of three  $sp^2$  hybrids which lie in a plane and a pure  $p$  orbital which is normal to this plane. Two of the  $sp^2$  orbitals presumably form bonds to the two end oxygens in all forms I-IV, and the  $p$  orbital forms the second component of the double bond in forms I and II. The third  $sp^2$  hybrid of the apex oxygen is directed upward along the symmetry axis and has an unshared electron pair in all forms I-IV.

It is significant that the bond length in ozone, 1.278 Å, is intermediate between the double bond length in oxygen, 1.21 Å, and the single bond length in hydrogen peroxide, 1.47 Å. It is somewhat nearer, however, to the double bond than to the single bond value. The observed lengths with the Pauling rule<sup>17</sup> indicate that the bonds have almost 50 percent double bond character. Thus the two equivalent resonating forms I and II essentially represent the electronic structure of ozone. The fact that the apex angle is slightly less than  $120^\circ$  may, however, indicate some contributions from forms III and IV because the unlike charge on the end oxygens in these forms would tend to decrease the apex angle.

In molecular orbitals terminology, each of the bonding  $sp^2$  orbitals would form a localized  $\sigma$ -molecular orbital by combination with a bonding orbital of an end oxygen, while the  $p$  orbital would be combined with orbitals of both end oxygens to form  $\pi$ -molecular orbitals. The electrons in the  $\pi$ -orbitals are not then considered as localized in a pair bond, as in the hypothetical forms I and II, but as moving throughout the molecule. If the  $\pi$ -molecular orbital is represented by the linear combination,

$$\psi = a\psi_1 + b\psi_2 + c\psi_3,$$

of the atomic orbital where  $\psi_1$  refers to the apex oxygen, then from the previous structural considerations it is evident that  $b^2 = c^2 \approx a^2/2$ .

If it is assumed that the positive and negative charges in I and II are separated by the bond length, the primary dipole moment resulting from these forms

would be about 3.0 debye. This primary component evidently is mostly canceled by the large, oppositely-directed atomic hybridization moment of the apex oxygen. If we subtract the observed moment from the primary moment, an approximate value for the atomic

moment, 2.5 debye, is obtained. This value is not unreasonable, considering the one unbalanced electron in the  $sp^2$  orbital directed along the symmetry axis. However, hybridization in the end oxygens, which is neglected, may be important.

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## The Vibration Frequencies of the Halogenated Methanes and the Substitution Product Rule\*

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(Received January 16, 1953)

The extension of the Teller-Redlich product rule to the substitution of different atoms or groups, which was previously applied to the methyl benzenes, is here applied to the halogenated methanes. The rule is found to hold accurately enough to be useful in assigning fundamental frequencies or in computing unobserved fundamentals.

SEVERAL years ago Pitzer and Scott extended the Teller-Redlich product rule to the substitution of methyl groups for hydrogen atoms in certain hydrocarbons.<sup>1</sup> Similar extensions of the isotopic product rule have been made by others.<sup>2</sup> The present paper presents the results of applying the substitution product rule to the halogen derivatives of methane.

The recent force constant-frequency calculations of Stepanov,<sup>3</sup> Decius,<sup>4</sup> Pace,<sup>5</sup> and others<sup>6-8</sup> yield more detailed information on these simple compounds. The application of these force constants to more complex molecules would give, in principle, the desired guidance to spectral assignments. However, normal coordinate calculations become very laborious for larger molecules of low symmetry. Consequently, while the product rule yields less information, its ease of application makes it particularly valuable. This will be illustrated with some methane derivatives of low symmetry in the present paper.

In the earlier paper the product ratio  $\tau$  was defined as

$$\tau = \prod_i \left( \frac{\nu_i'}{\nu_i} \right) \left[ \prod_j \left( \frac{I_j}{I_j'} \right) \prod_k \left( \frac{M_k}{M_k'} \right) \right]^{\frac{1}{2}}, \quad (1)$$

where the prime mark indicates the substituted mole-

cule and where the indices  $i$ ,  $j$ , and  $k$  cover all the vibrations, rotations, and translations, respectively, of a given symmetry type. The other symbols  $\nu$ ,  $I$ , and  $M$  refer to vibration frequencies, moments of inertia, and molecular masses, respectively.

An examination of normal coordinate theory shows that in every case  $\tau$  will be given by a product of mass and bond distance ratios and a ratio of force constants. In isotopic substitution one assumes no change in bond distances or force constants, hence the factors depending on these quantities are unity. Then it is customary to combine the mass ratio with the terms in square brackets in Eq. (1) so as to yield a theoretical value for the ratio of frequencies.

However, the substitution of new atoms changes bond distances and force constants as well as masses. Thus, a reliable theoretical value of  $\tau$  is not available. It seems best to combine all of the observable quantities in the form of Eq. (1), so that the  $\tau$ -values for similar substitutions will be comparable. Furthermore, the theory does not indicate exactly the same  $\tau$ -value for all examples of a given substitution. The cross terms in the potential expression enter in different ways. Also the distances and principal force constants for a given bond may vary slightly from one molecule to another. Consequently, we do not expect exact constancy of these substitution product ratios but rather will wish to see whether the variation is small enough to make them useful. The vibration frequency assignments for  $\text{CH}_4$ ,  $\text{CH}_3\text{F}$ ,  $\text{CH}_3\text{Cl}$ ,  $\text{CH}_3\text{Br}$ ,  $\text{CH}_2\text{F}_2$ ,  $\text{CH}_2\text{Cl}_2$ ,  $\text{CH}_2\text{Br}_2$ ,  $\text{CHF}_3$ ,  $\text{CHCl}_3$ ,  $\text{CHBr}_3$ ,  $\text{CF}_4$ ,  $\text{CCl}_4$ ,  $\text{CBr}_4$ ,  $\text{CF}_3\text{Cl}$ ,  $\text{CF}_2\text{Cl}_2$ ,  $\text{CFCl}_3$ ,  $\text{CF}_3\text{Br}$ ,  $\text{CF}_2\text{Br}_2$ ,  $\text{CFBr}_3$ ,  $\text{CCl}_3\text{Br}$ ,  $\text{CCl}_2\text{Br}_2$ , and  $\text{CClBr}_3$  seem sufficiently reliable to be used in the determination of the  $\tau$ -values and their constancy.

The experimental frequency values adopted in the

\* This research was a part of the program of Research Project 50 of the American Petroleum Institute.

<sup>1</sup> K. S. Pitzer and D. W. Scott, *J. Am. Chem. Soc.* **65**, 803 (1943).

<sup>2</sup> See, for example, Mizushima, Morino, and Shimanouchi, *Sci. Papers Inst. Phys. Chem. Research (Tokyo)* **40**, 87 (1942).

<sup>3</sup> B. Stepanov, *Acta Physicochim. U.R.S.S.* **20**, 174 (1945).

<sup>4</sup> J. C. Decius, *J. Chem. Phys.* **16**, 214 (1948).

<sup>5</sup> E. L. Pace, *J. Chem. Phys.* **18**, 881 (1950).

<sup>6</sup> Meister, Rosser, and Cleveland, *J. Chem. Phys.* **18**, 346 (1950).

<sup>7</sup> Zietlow, Cleveland, and Meister, *J. Chem. Phys.* **18**, 1076 (1950).

<sup>8</sup> E. K. Plyler and W. S. Benedict, *J. Research Natl. Bur. Standards* **47**, 202 (1951).