Microwave Investigations of Methyl Fluoride, Fluoroform, and Phosphorus Trifluoride

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From measurements on pure rotational transitions in the microwave region the moments of inertia, I_B in g cm$^2\times10^{-40}$, have been determined as follows: 32.8544 for $C^{12}H_3F$, 33.7444 for $C^{13}H_3F$, 81.0693 for $C^{12}HF_3$, and 107.286 for $P^{31}F_3$. The molecular dimensions determined are: for CH_3F, $d_{CH}=1.109$A, $d_{CF}=1.385$A, and $\angle HCH=110°\,0'$; for CHF_3, $d_{CF}=1.326$A, with $d_{CH}=1.111$A (assumed) and $\angle FCF=110°$ (assumed); for PF_3, $d_{PF}=1.546\pm0.008$A with $\angle FPF=104\pm3°$ (assumed). The line breadth parameters, $\Delta\nu$, normalized to 1 mm of Hg pressure are for CH_3F 20 mc, for CHF_3 18 mc, and for PF_3 16 mc. Confirming evidences for the nuclear spin values, $\frac{1}{2}$ for P^{31} and F^{19} have been obtained.

MEASUREMENTS have been made on pure rotational transitions of methyl fluoride, fluoroform, and phosphorus trifluoride occurring in the millimeter wave region. The experimental methods used have been described in previous publications.[1] The frequencies were measured by harmonics of a 10-mc signal monitored by radio station W W V, of the Bureau of Standards.

Table I lists the measured frequencies, B values, and moments of inertia. Each of these molecules has a strictly symmetric-top structure. For the low rotational states which are involved here the effects of centrifugal distortion are not very significant, and the rotational frequencies are given quite accurately by the simple formula,

$$\nu(\text{cm}^{-1})=2B(J+1)=[2h(J+1)/8\pi^2cI_B],$$

where J is the rotational quantum number for the lower state involved. However, for the $J=2\rightarrow3$ transition of PF_3, the $K=2$ line was resolved, and the centrifugal distortion constants D_J and D_{JK} in the more general equation,[2]

$$\nu(\text{cm}^{-1})=2B(J+1)-2D_{KJ}K^2(J+1)-4D_J(J+1)^3,$$

were evaluated as +7 Kc/sec. and −8 Kc/sec., respectively. The moment of inertia for CHF_3 recently determined from optical spectra,[3] $I_B=81.08\times10^{-40}$ g cm^2, is in remarkably good agreement with the present results. The I_B value obtained for $C^{12}H_3F$ lies between 32.95 and 32.21, the two values[4,5] previously obtained from infra-red spectroscopy. No previous spectral evaluation of the PF_3 moment of inertia has been made.

TABLE I. Pure rotational frequencies and molecular constants for ground vibrational state.

Molecule	Transition	Observed frequencies in mc/sec.	Absorption coefficients (cm^{-1})	B_0	$I_B^{(0)}$*
$C^{12}H_3F$	0→1	51071.69±0.18	1.4×10^{-4}	25535.85	32.8544
$C^{13}H_3F$	0→1	49724.73±0.18		24862.37	33.7444
HCF_3	1→2	41394.95±0.18	2.2×10^{-5}	10348.74	81.0693
PF_3	1→2	31279.60±0.10		7819.900	107.286
	2→3	46918.82±0.18 (K=0 or 1) 46919.02±0.18 (K=2)			
PF_3	2→3	46940±10 47010±10 47033±10 47040±10	excited vibration states		

* The value of h is taken as 6.624×10^{-27} erg-sec.

Table II gives the molecular dimensions calculated from the data. In determining the complete structure of methyl fluoride the I_A value which depends on infra-red data was employed. The I_A value 5.52 g cm$^2\times10^{-40}$ was calculated from the Johnston-Dennison formula[6]

$$\sum\Delta\nu=[(6/I_A)-(7/I_B)](h/8\pi^2c),$$

with the I_B for $C^{12}H_3F$ determined in the present measurement and with $\sum\Delta\nu=24.44$ cm^{-1} obtained by re-averaging the data of Bennett and Meyer[4] on the three perpendicular type infra-red vibration-rotation bands. Bennett and Meyer give $\sum\Delta\nu=24.30$. This would require that $I_A=5.49$. In our re-averaging, we have omitted lines of high J at the ends of the observed bands. Possible error in the I_A makes uncertain the last figure quoted for d_{CH} and the bond angle, but it is not probable that the value given for d_{CF} will be significantly affected by this error since the determination of this dimension depends only slightly on I_A.

The surprisingly short d_{CF} distance in fluoroform

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[1] (a) W. Gordy and M. Kessler, Phys. Rev. **72**, 644 (1947); (b) R. Unterberger and W. V. Smith, Rev. Sci. Inst. **19**, 580 (1948); (c) W. Gordy, Rev. Mod. Phys. **20**, 668 (1948).

[2] Z. I. Slawsky and D. M. Dennison, J. Chem. Phys. **7**, 509 (1939); G. Herzberg, *Infrared and Raman Spectra of Polyatomic Molecules* (D. Van Nostrand Company, Inc., New York, 1945), p. 400.

[3] H. J. Bernstein and G. Herzberg, J. Chem. Phys. **16**, 30 (1948).

[4] W. H. Bennett and C. F. Meyer, Phys. Rev. **32**, 888 (1928).

[5] K. P. Yates and H. H. Nielsen, Phys. Rev. **71**, 349 (1947).

[6] M. Johnston and D. M. Dennison, Phys. Rev. **48**, 868 (1935).

found by Bernstein and Herzberg[3] is confirmed. Fortunately, the moments of inertia of CHF_3 and PF_3 are not very sensitive to small variations in the parameters which must be assumed. Though the limits of error cannot be established definitely, the probable errors in d_{CF} and d_{PF} are indicated by the changes produced when the assumed angle is changed by ±3°. The electron diffraction values[6a] for PF_3 are $d_{PF} = 1.52 \pm 0.04$A and $\angle FPF = 104° \pm 4°$. To our knowledge, no electron diffraction studies of fluoroform have been made.

Table III compares the CF and PF distances measured here with the added single bond covalent radii and with this sum corrected by the Schomaker-Stevenson rule[7] for the shortening caused by resonance with ionic structures. Bond lengths in some similar molecules recently measured with microwaves are listed for comparison. The Pauling[8] radii are here employed with the revised radius for carbon, 0.79A, suggested by Gordy,[9] and the fluorine radius, 0.72A, proposed by Schomaker and Stevenson.[7] For methyl fluoride, the Schomaker-Stevenson correction for resonance caused by ionic character provides a reasonably good explanation for the observed bond shortening, though for methyl chloride, bromide, and iodide this correction makes agreement with observation slightly worse. Pauling[10] has suggested resonance with double bonded structures as well as with ionic structures as a possible cause of the anomalously short bonds in molecules of the PF_3 type.

Unfortunately the determinations of the molecular structures are still not sufficiently accurate to establish the relative differences of the bond angles and CH lengths in the methyl halides. The latest values are: for the HCH angles, 110° 0′, 110° 0′, 109° 22′, and 110° 58′; for the CH lengths 1.109A, 1.109A, 1.111A, and 1.100A, for methyl fluoride, chloride, bromide, and iodide, respectively. The values for the last three are taken from the paper by Gordy, Simmons, and Smith.[11] In this paper an arithmetical error was made in the calculations for methyl bromide.* The corrected value is given here. It seems unlikely that the methyl bromide would fall out of sequence. Microwave studies on the methyl halides containing other isotopes are being undertaken by James W. Simmons. Thus these difficulties should soon be cleared up.

TABLE II. Molecular dimensions.

Molecule	Bond	Internuclear distance*	Bond angles
CH_3F**	CF	1.385A	
	CH	1.109	$\angle HCH = 110° 0'$
CHF_3	CF	1.326 ± 0.013	$\angle FCF = 110° \pm 3°$ (assumed)
	CH	1.111 (assumed)	
PF_3	PF	1.546 ± 0.008	$\angle FPF = 104° \pm 3°$ (assumed)

* Values of constants used are: $h = 6.624 \times 10^{-27}$ erg-sec., $M_H = 1.00813$ a.m.u., $M_{C^{12}} = 12.00386$ a.m.u., and $M_1 = 1.6599$ g, all from R. T. Birge, Rev. Mod. Phys. **13**, 233 (1941); $M_{C^{13}} = 13.00761$ a.m.u. from M. S. Livingston and H. A. Bethe, Rev. Mod. Phys. **9**, 373 (1937); $M_F = 19.0045$ and $M_{P^{31}} = 30.9836$ from F. W. Aston, Proc. Roy. Soc. **A163, 391** (1937).

** The values 1.106A for d_{CH} and 109° 42′ for $\angle HCH$ are obtained if $I_A = 5.49$ g cm^{-40} is used for CH_3F. However, d_{CF} remains 1.385A. With $I_A = 5.55$ the values $d_{CH} = 1.111$A, $d_{CF} = 1.385$A, and $\angle HCH = 110° 6'$, are obtained.

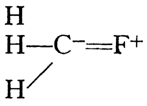
It is of interest to compare the HCH bond angle found for CH_3F, 110° 0′, with that for SiH_3Cl, 103° 57′, recently determined from microwave spectroscopy by Sharbaugh.[12] The CH_3F angle, also that for the other methyl halides, is slightly greater than the tetrahedral angle 109° 28′, while that for SiH_3Cl is significantly less. In most of these molecules, particularly in SiH_3Cl, there is appreciable ionic character of the bond linking the halogen. This ionic character would tend to make the bond angle larger than tetrahedral because of sp^2 hybridization in C^+H_3 or Si^+H_3. On the other hand, contributions from double-bonded structures of the type  $\overset{H}{\underset{H\diagup}{H—C^-}}=F^+$ would presumably decrease $\angle HCH$. The latter structure would probably not be very important in the methyl halides because, in addition to putting a plus charge on the electronegative halogen, it also requires one of the CH bonds to be broken. The latter effect would be partly offset by the Coulomb attraction between the H^- and the F^+. This attraction would again

TABLE III. Comparison of some calculated and observed interatomic bond lengths.

Molecule	Bond	Observed bond length	Added covalent radii	Added radii corrected for ionic character*
CH_3F	CF	1.385[a]	1.51	1.38
CHF_3	CF	1.326[a]	1.51	1.38
PF_3	PF	1.546[a]	1.82	1.65
AsF_3	AsF	1.712[b]	1.93	1.75
CH_3Cl	CCl	1.779[c]	1.78	1.75
CH_3Br	CBr	1.932[c]	1.93	1.91
CH_3I	CI	2.139[c]	2.12	2.12
SiH_3Cl	SiCl	2.035[d]	2.16	2.05

[a] Present work.

[b] Dailey, Rusinow, Shulman and Townes, Bull. Am. Phys. Soc. **23**, No. 3, 53 (1948).

[c] W. Gordy, J. W. Simmons, and A. G. Smith, Phys. Rev. **74**, 243 (1948).

[d] A. H. Sharbaugh, Phys. Rev. **74**, 1870 (1948).

* Calculated with the Schomaker-Stevenson rule,

$$d_{AB} = r_A + r_B - 0.09 |X_A - X_B|.$$

J. Am. Chem. Soc. **63**, 37 (1941).

[6a] L. Pauling and L. O. Brockway, J. Am. Chem. Soc. **57**, 2684 (1935).

[7] V. Schomaker and D. P. Stevenson, J. Am. Chem. Soc. **63**, 37 (1941).

[8] L. Pauling, *The Nature of the Chemical Bond* (Cornell University Press, Ithaca, New York, 1940), p. 164.

[9] Walter Gordy, J. Chem. Phys. **15**, 81 (1947).

[10] L. Pauling, reference 8, p. 216.

[11] W. Gordy, J. W. Simmons, and A. G. Smith, Phys. Rev. **74**, 243 (1948).

* We are indebted to Mr. A. H. Sharbaugh for calling our attention to this error.

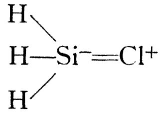
[12] A. Harry Sharbaugh, Phys. Rev. **74**, 1870 (1948).

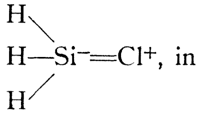
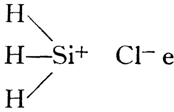
TABLE IV. Line breadth parameters.*

Molecule	$2\Delta\nu$ measured	Pressure mm of Hg	Temp.	$\Delta\nu$ for 1 mm Hg**
CH_3F	3.0 mc	7.5×10^{-2}	27°C	20 mc
CHF_3	0.82	2.3×10^{-2}	27°C	18
PF_3	1.1	3.4×10^{-2}	27°C	16

* Line breadth, $\Delta\nu$, here is half the width of the line measured between half-intensity points.

** Conversion of the data to 1-mm Hg pressure assumes a linear variation of $\Delta\nu$ with pressure.

tend to make the HCH angle large. Because of the *d* orbitals available in the valence shell of Si, contributions from structures of the type  $\mathrm{H_2(H{-})Si^-{=}Cl^+}$ are possible in chlorosilane. Significant contributions from the latter structure could account for the abnormally small H Si H bond angle and the short Si—Cl distance in SiH_3Cl as contrasted with the corresponding dimensions in CH_3Cl. This explanation is in harmony with the fact that the dipole moment of SiH_3Cl is appreciably lower than that for any of the methyl halides, whereas purely electronegativity considerations would imply a greater dipole moment for H_3SiCl than for CH_3Cl.

Significant contributions of  $\mathrm{H_2(H{-})Si^-{=}Cl^+}$, in addition to the larger amount of  $\mathrm{H_2(H{-})Si^+\ Cl^-}$ expected, could account for the fact that the nuclear quadrupole coupling of Cl in SiH_3Cl is only 53 percent of its value in CH_3Cl.

Line breadths obtained for CH_3F and CHF_3 are listed in Table IV. These are comparable in value to those of other molecules with similar dipole moments.

The observed line breadth parameters have been used with the dipole moments 1.83 and 1.59 for CH_3F and CHF_3 to calculate the peak absorption coefficients listed in Table I. No dipole moment value is available for PF_3. The procedure for the calculations is outlined in reference 1(c). For symmetric molecules of the type considered here (three identical corner atoms with nuclear spin $\frac{1}{2}$) the formula giving the resonant frequency absorption coefficient can be reduced to the form,

$$\alpha(\mathrm{cm^{-1}})=0.140\frac{BA^{\frac{1}{2}}F_v\nu^2\mu^2g}{(\Delta\nu)_1T^3}\times\left[\frac{(J+1)^2-K^2}{J+1}\right]\exp\left(\frac{-E_r}{kT}\right),$$

where F_v = fraction of molecules in the vibration state considered; μ = molecular dipole moment in Debye units; $g=1$ for $K=0$, 1, 2, 4, 5, 7 etc., $=2$ for $K=3$, 6, 9, etc.; $(\Delta\nu_1)$ = line breadth in cm^{-1} for 1 mm of Hg pressure and for $T=300$; ν = resonant frequency in cm^{-1}; T = temperature in degree Kelvin; k = Boltzmann's constant; $B=(h/8\pi^2cI_B)$, $A=(h/8\pi^2cI_A)$; and $E_r=hc[BJ(J+1)+(A-B)K^2]$. Here A and B are in cm^{-1} and E_r is in ergs. J is the rotational quantum number for the lower state of the transition.

Nuclear spins of $\frac{1}{2}$ for P^{31} and for F^{19} are supported by the fact that no nuclear quadrupole hyperfine structure was detected in the molecules containing these atoms. From the rather large nuclear coupling observed[13] for As in AsF_3, one would expect to detect quadrupole coupling in PF_3 if the quadrupole moment of the P nucleus were not zero or very nearly zero. The spin $\frac{1}{2}$ for P^{31} is also indicated by the relative intensities of the lines of different K in the $J=2\rightarrow3$ transition of PF_3, which are separated by centrifugal distortions.

Theoretical considerations indicate that a nucleus of spin $\frac{1}{2}$ would have spherical symmetry and hence no electrical quadrupole moment. Since $(\partial^2V)/(\partial z^2)$ is large for the F in CH_3F and can be evaluated approximately from the Townes[14] theory, it follows from the present measurement that the quadrupole moment of F must indeed be very small. The doublet separation, $\Delta\nu=407$ cm^{-1}, with $Z_i=7.2$ yields with the formula,[14]

$$\partial^2V/\partial z^2=(8e\Delta\nu/15Z_iR\alpha^2a_0^3),$$

a value for $(\partial^2V)/(\partial z^2)$ of 17×10^{15} e.s.u. Our observations with $I=\frac{3}{2}$ indicate $|eQ(\partial^2V/\partial z^2)|<0.5$ mc. Hence, $|Q|<0.0003\times10^{-24}$ cm^2. This upper limit shows that the quadrupole moment, if not zero, must be less than about 1/10 of that of the small deuterium nucleus, and less than 1/200 that of the Cl^{35}.

We are attempting to obtain samples of $P^{32}F_3$, DCF_3, and $HC^{13}F_3$ for similar studies so that the structures of phosphorus trifluoride and fluoroform can be completely determined and the nuclear spin and quadrupole coupling of P^{32} can be evaluated.

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[13] B. P. Dailey, K. Rusinow, R. G. Shulman, and C. H. Townes, Bull. Am. Phys. Soc. **23**, No. 3, 53 (1948).

[14] Charles Hard Townes, Phys. Rev. **71**, 909 (1947).