gadolinium is positron emission from mass 153, and the short-lived samarium is due to electron emission from samarium of mass 153, both transitions ending in the same excited levels of europium 153. The impurities revealed by this method may be present in only slight traces, yet by virtue of their large capture cross section for neutrons, they introduce a disturbingly large radioactivity with certainty, but a half-life of 110 days is indicated.

Two electron groups of energy 39.0 and 56.1 kev, when interpreted as K-conversion lines in gadolinium, indicate gamma-rays of energy 91.0 and 108.1 kev. Because of the interference of impurities such as europium with a six-year half-life, it is impossible to fix the periods of the gadolinium activities.

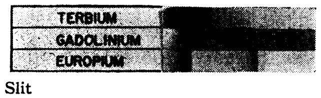

FIG. 6. Spectrograms showing the presence of terbium and europium as impurities in gadolinium.

The new information pertaining to this group of elements is assembled together in Table II.

The beta-spectrum of terbium was observed on the spectrometer by Mr. E. Salmi and that of europium by Mr. F. Shull. This investigation was made possible by the support of the Office of Naval Research.

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Microwave Determination of the Molecular Structures and Nuclear Couplings of the Methyl Halides*

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Accurate measurements on the pure rotation spectra of methyl chloride, bromide and iodide have been made with multiples of a 10 mc/sec. frequency monitored by station WWV. The measurements, with existing infra-red data, allow a complete determination of the structures of these molecules. The I_B values in $\mathrm{g/cm^2} \times 10^{-40}$ are: 63.11_{38} for $C^{12}H_3Cl^{35}$, 64.10_{09} for $C^{12}H_3Cl^{37}$, 87.68_{35} for $C^{12}H_3Br^{79}$, 88.01_{80} for $C^{12}H_3Br^{81}$, 111.8_{48} for $C^{12}H_3I^{127}$ and 117.8_{48} for $C^{13}H_3I^{127}$. The molecular dimensions obtained are: for methyl chloride, $d_{\mathrm{CH}} = 1.109\mathrm{A}$, $d_{\mathrm{CCl}} = 1.779\mathrm{A}$, $<\mathrm{HCH} = 110°\,0'$; for methyl bromide, $d_{\mathrm{CH}} = 1.104\mathrm{A}$, $d_{\mathrm{CBr}} = 1.936\mathrm{A}$, $<\mathrm{HCH} = 110°\,15'$; for methyl iodide, $d_{\mathrm{CH}} = 1.100\mathrm{A}$, $d_{\mathrm{CI}} = 2.139\mathrm{A}$, $<\mathrm{HCH} = 110°\,58'$. The nuclear quadrupole couplings, $eQ(\partial^2 V/\partial z^2)$, are: for Cl^{35}, -75.13 mc/sec.; for Cl^{37}, -59.03 mc/sec.; for Br^{79}, 577.0 mc/sec.; for Br^{81}, 482.0 mc/sec.; and for I^{127}, -1934 mc/sec. Second-order effects in the hyperfine structure were observed for methyl bromide and methyl iodide.

I. INTRODUCTION

PRELIMINARY results on the microwave absorption of CH_3Cl, CH_3Br, and CH_3I have been reported.[1] In the earlier work the measurements were made with cavity wave meters and were accurate to four places only. Since that time an instrument has been constructed in our laboratory for multiplying to the millimeter region 10 mc/sec. frequencies monitored by WWV, the station of the Bureau of Standards. With it the lines of methyl chloride, bromide, and iodide occurring in the region of 8 to 11.5 mm have been measured to seven significant figures. Some improvement has also been made in the measurements of relative intensities, although we are not yet able to measure these with a high degree of accuracy.

As pointed out in the previous notes, the rotational levels of the above molecules have

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[1] W. Gordy, J. W. Simmons, and A. G. Smith, Phys. Rev. 72, 249, 344 (1947).

TABLE I. Hyperfine structure of the $J=0$ to $J=1$, $K=0$ to $K=0$ rotational transition of CH_3Cl in the ground vibrational state.

F transition	Frequency Observed	Frequency Calculated*	Relative intensity Observed	Relative intensity Theoretical
		For $C^{12}H_3Cl^{35}$		
$3/2\rightarrow 1/2$	26604.57 mc/sec.	26604.55 mc/sec.	25	33.3
$3/2\rightarrow 3/2$	26570.77	26570.74	78	66.7
$3/2\rightarrow 5/2$	26589.49	26589.53	100	100.0
		For $C^{12}H_3Cl^{37}$		
$3/2\rightarrow 1/2$	26191.13	26191.13	6	11.1
$3/2\rightarrow 3/2$	26164.57	26164.56	22	22.2
$3/2\rightarrow 5/2$	26179.30	26179.32	34	33.3
		Probable error ±0.07 mc/sec.		

* Using $eQ(\partial^2V/\partial z^2)=-75.13$ mc/sec. for CH_3Cl^{35} and -59.03 mc/sec. for CH_3Cl^{37}.

hyperfine structure caused by the interaction of the nuclear quadrupole moment of the halogen. More recently anomalies have been reported[2] in this hyperfine structure for the $J=2\rightarrow 3$ transition of methyl iodide. The more accurate measurements have revealed second-order effects in the hyperfine spectra of CH_3Br and CH_3I reported here. Prior to our detection of the rotational spectra and its hyperfine structure for these molecules Hershberger[3] has made microwave measurements of the attenuation at high pressures in non-resonant regions of methyl chloride and methyl bromide.

TABLE II Hyperfine structure of the $J=1$ to $J=2$ rotational transition of CH_3Br in the ground vibrational state.

F transition	Frequency Observed	Frequency Calculated*	Relative intensity Observed	Relative intensity Theoretical**
		For $C^{12}H_3Br^{79}$		
		$K=0\rightarrow K=0$		
$1/2\rightarrow 1/2$	38272.40 mc/sec.	38272.38 mc/sec.	14	13.6
$1/2\rightarrow 3/2$	38417.09	38417.01	14	13.6
$3/2\rightarrow 3/2$	38157.30	38157.34	21	17.5
$3/2\rightarrow 5/2$	38260.10	38260.05	100	100.0
$5/2\rightarrow 7/2$	38260.10	38260.10		
$5/2\rightarrow 5/2$	38404.49	38404.43	21	14.8
		$K=1\rightarrow K=1$		
$1/2\rightarrow 1/2$	38128.40	38128.38	7	10.2
$1/2\rightarrow 3/2$	38200.52	38200.50	7	10.2
$3/2\rightarrow 3/2$	38330.25	38330.30	10	13.2
$3/2\rightarrow 5/2$	38381.70	38381.73	27	25.8
$5/2\rightarrow 5/2$	38309.45	38309.55	10	11.1
$5/2\rightarrow 7/2$	38237.14	38237.15	51	49.2
		For $C^{12}H_3Br^{81}$		
		$K=0\rightarrow K=0$		
$1/2\rightarrow 1/2$	38126.97	38126.98	14	13.6
$1/2\rightarrow 3/2$	38247.77	38247.68	27	13.6
$3/2\rightarrow 3/2$	38030.77	38030.84	14	17.5
$3/2\rightarrow 5/2$	38116.65	38116.61	100	100.0
$5/2\rightarrow 7/2$	38116.65	38116.65		
$5/2\rightarrow 5/2$	38237.14	38237.20	25	14.8
		$K=1\rightarrow K=1$		
$1/2\rightarrow 1/2$	38006.47	38006.48	10	10.2
$1/2\rightarrow 3/2$	38066.72	38066.73	7	10.2
$3/2\rightarrow 3/2$	38175.08	38175.16	14	13.2
$3/2\rightarrow 5/2$	38218.21	38218.13	27	25.8
$5/2\rightarrow 5/2$	38157.70	38157.85	10	11.1
$5/2\rightarrow 7/2$	38097.45	38097.50	55	49.2
		Probable error ±0.08 mc/sec.		

* This calculation includes both first- and second-order nuclear effects and a centrifugal stretching term $-D_{J,K}J(J+1)K^2$. The values of $eQ(\partial^2V/\partial z^2)$ used are 577.0 mc/sec. and 482.0 mc/sec. for CH_3Br^{79} and CH_3Br^{81}, respectively. The value of $D_{J,K}$ is 90 kc/sec. The $F\rightarrow F-1$ transitions are omitted because of their low intensity.

** The factor $\nu e^{-(E_r/kT)}$ is neglected in the calculations.

The first rotational transition of methyl fluoride has been observed at 5.87-mm wave-length by Edwards, Gilliam, and Gordy.[3a] No nuclear quadrupole splitting of the line was observed. This is in agreement with the value of 1/2 for the nuclear spin of fluorine.

II. EXPERIMENTAL PROCEDURE

The observations were made with the gas at low pressure, $\approx 10^{-3}$ mm of Hg, in a silver wave guide cell 60 feet in length. The single crystal detecting system[4] was used, employing video filtering to eliminate the r-f reflections and mode contour. The system for frequency measurement was constructed in this laboratory by Mr. R. Unterberger. It employs a conventional electronic multiplier to convert the signal of a 10-mc/sec. crystal oscillator monitored by the standard 10-mc/sec. broadcast by WWV to a frequency of 270 mc/sec., then a klystron multiplier and a crystal converter to obtain standard markers in the desired region. A tuneable receiver, also calibrated with WWV, is used to interpolate between the standard markers, which are 90 mc/sec. apart. Relative intensities of the components of the hyperfine structure were observed by comparing the heights of the different lines on the oscilloscope with the detector crystal tuned to each line and with the power adjusted as nearly as possible to the same level. The millimeter wave oscillators used as sources, QK-140, QK-141, and QK-142, were obtained from the Raytheon Manufacturing Company.

III. THEORY

Frequencies

The pure rotational energy levels of the non-rigid symmetric top molecules as derived

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[2] O. R. Gilliam, H. D. Edwards, and W. Gordy, Phys. Rev. **73**, 635 (1948).

[3] W. D. Hershberger, J. App. Phys. **17**, 495 (1946).

[3a] H. D. Edwards, O. R. Gilliam, and W. Gordy, to be published.

[4] W. Gordy and M. Kessler, Phys. Rev. **71**, 640 (1947); **72**, 664 (1947).

by Slawsky and Dennison are given by the formula:[5, 6]

$$E_r=\frac{h}{8\pi^2 c}\left[\frac{J(J+1)}{I_B}+\left(\frac{1}{I_A}-\frac{1}{I_B}\right)K^2\right]$$
$$-D_J J^2(J+1)^2-D_{J,K}J(J+1)K^2-D_K K^4, \quad (1)$$

where the selection rules for the pure rotation absorption spectra are:

$$\Delta J=+1, \quad \Delta K=0.$$

Here I_A is the moment of inertia about the axis of symmetry and I_B that about the axis perpendicular to the symmetry axis. The last three terms in this expression are corrections for nonrigidity. The constants D_J, $D_{J,K}$, and D_K are extremely small, and the last terms do not contribute significantly to the energy when J and K are small. The present work indicates that $D_{J,K}$ for the methyl halides is ≈ 90 kc/sec. or 3×01^{-6} cm^{-1}. No evaluation of D_J and D_K can be made from the present data.

For the methyl halides considered here, there must be added to the rotational energy E_r the energy of the nuclear interactions of the halogen, which is given to the first order of approximation by the formula:

$$E_Q=eQ\frac{\partial^2 V}{\partial z^2}\left(\frac{3K^2}{J(J+1)}-1\right)$$
$$\times\left(\frac{3/4C(C+1)-I(I+1)J(J+1)}{2(2J+3)(2J-1)I(2I-1)}\right), \quad (2)$$

where $C=F(F+1)-I(I+1)-J(J+1)$

$$F=J+I,\ J+I-1,\ \cdots |J-I|,$$

and where the selection rules require that $\Delta F=0, \pm 1$. The quadrupole coupling $eQ(\partial^2 V/\partial z^2)$ is constant for a given molecule. Q is the quadrupole moment of the halogen nucleus, and $\partial^2 V/\partial z^2$ is the measure of the rate of variation of the electrical field at the halogen nucleus in the direction of the molecular axis. A summary of the development of this formula is given elsewhere.[7]

TABLE III. Hyperfine structure of the $J=1$ to $J=2$ rotational transition for CH_3I in the ground vibrational state.

	Frequency		Relative intensity	
F transition	Observed	Calculated*	Observed	Theoretical**
	$C^{12}H_3I^{127}$ (98.9% C^{12})			
	For $K=0\rightarrow K=0$			
3/2→1/2	30121.32 mc/sec.	30021.31 mc/sec.	26	20.0
3/2→3/2	29872.52	29872.56	36	28.0
3/2→5/2	29598.95	29598.83	17	18.7
5/2→3/2	30453.46	30453.53	7	12.0
5/2→5/2	30179.71	30179.79	39	36.6
5/2→7/2	30079.72	30079.75	66	51.4
7/2→5/2	29773.95	29774.05	4	4.7
7/2→7/2	29673.95	29674.00	25	28.6
7/2→9/2	30046.99	30046.99	100	100.0
	For $K=1\rightarrow K=1$			
3/2→1/2		30331.48	7	15.0
3/2→3/2	30215.95	30216.01	28	21.0
3/2→5/2	30075.08	30075.04	12	14.0
5/2→3/2	29923.50	29923.63	5	9.0
5/2→5/2	29782.71	29782.66	20	27.4
5/2→7/2	29735.71	29735.61	29	38.5
7/2→5/2	29986.84	29986.98	4	3.5
7/2→7/2	29939.87	29939.93	20	21.4
7/2→9/2	30123.64	30123.55	80	75.0
	$C^{13}H_3I^{127}$ (49% C^{13})			
	For $K=0\rightarrow K=0$			
3/2→3/2	28343.64	28343.71	17	13.9
3/2→5/2	28069.99	28069.98	9	9.3
5/2→5/2	28650.91	28650.94	17	18.1
5/2→7/2	28550.86	28550.90	29	25.5
7/2→7/2	28145.01	28145.15	17	14.2
7/2→9/2	28518.14	28518.14	48	49.6
	For $K=1\rightarrow K=1$			
3/2→3/2	28687.21	28687.16	9	10.4
5/2→5/2	28253.84	28253.81	11	13.6
5/2→7/2	28206.90	28206.76	17	19.1
7/2→7/2	28411.19	28411.08	11	10.6
7/2→9/2	28594.74	28594.70	40	37.2
	Probable error ±0.08 mc/sec.			

* This calculation includes both first- and second-order nuclear effects and a centrifugal stretching term $-D_{J,K}J(J+1)K^2$. The value -1934 mc/sec. was used for $eQ(\partial^2 V/\partial z^2)$ and 95 kc/sec. for $D_{J,K}$.
** The factor $\nu e^{-(E_r/kT)}$ is neglected in the calculations.

The second order theory of the interactions between levels of different J but of the same F and M_F has been derived for linear and symmetric top molecules by Bardeen and Townes.[8] The displacement of the levels caused by this type of interaction is of the form

$$E_Q=\sum_{J'}\frac{(IJFM_F|H_Q|IJ'FM_F)^2}{E_r-E_r'} \quad (3)$$

where J' can differ from J by 1 or 2. These authors have advised us of some typographical errors in their formulae for evaluating the

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[5] G. Herzberg, *Infrared and Raman Spectra of Polyatomic Molecules* (D. Van Nostrand Company, Inc., New York, 1945), p. 26.

[6] Z. I. Slawsky and D. M. Dennison, J. Chem. Phys. **7**, 509 (1939).

[7] J. Bardeen and C. H. Townes, Phys. Rev. **73**, 97 (1948).

[8] J. Bardeen and C. H. Townes, Phys. Rev. **73**, 627 (1948).

squared matrix element in the numerator. The corrected forms are:

$$(IJFM_F|H_Q|IJ+1FM_F)^2$$

$$=\left[\frac{(3eqQK)}{(8I(2I-1)J(J+2)}\right]^2\left[1-\frac{K^2}{(J+1)^2}\right]$$

$$\times\frac{[F(F+1)-I(I+1)-J(J+2)]^2}{(2J+1)(2J+3)}$$

$$\times(I+J+F+2)(J+F-I+1)$$

$$\times(I+F-J)(J+I-F+1), \quad (4)$$

$$(IJFM_F|H_Q|IJ+2FM_F)^2$$

$$=\left[\frac{3eqQ}{16I(2I-1)(2J+3)}\right]^2\left[1-\frac{K^2}{(J+1)^2}\right]$$

$$\times\left[1-\frac{K^2}{(J+2)^2}\right]\frac{1}{(2J+1)(2J+5)}$$

$$\times(F+I+J+3)(F+I+J+2)$$

$$\times(J+I-F+2)(J+I-F+1)$$

$$\times(J+F-I+2)(J+F-I+1)$$

$$\times(I+F-J)(I+F-J-1). \quad (5)$$

Here q is used to represent the form $\partial^2V/\partial z^2$.

Intensities

The intensities of the lines exclusive of nuclear effects are given by the expression:[9]

$$Int(J,K)=C\nu\frac{(J+1)^2-K^2}{(J+1)(2J+1)}g_{JK}$$

$$\times\exp\left[\frac{-E(J,K)}{kT}\right], \quad (6)$$

where $g_{JK}=2(2J+1)$ for $K\neq0$ and

$$2J+1 \text{ for } K=0.$$

TABLE IV. Second-order effects in the hyperfine structure of the $J=1$ to $J=2$ line of $C^{12}H_3I$ in the ground vibrational state. Frequencies are given in mc/sec. relative to the strongest line, $F=7/2$ to $F=9/2$, $K=0\rightarrow0$. eQ $(\partial^2V/\partial z^2)$ $=-1934$ mc/sec.

F transition	Experimental $\Delta\nu$	First-order theory $\Delta\nu$	Experiment minus first-order theory	Second-order theory
	For $K=0\rightarrow K=0$			
3/2→1/2	+74.33	+74.59	−0.26	−0.27
3/2→3/2	−174.47	−174.06	−0.41	−0.37
3/2→5/2	−448.04	−450.35	+2.31	+2.19
5/2→3/2	+406.47	+406.14	+0.33	+0.40
5/2→5/2	+132.72	+129.85	+2.87	+2.95
5/2→7/2	+32.73	+33.15	−0.42	−0.39
7/2→5/2	−273.04	−276.29	+3.25	+3.35
7/2→7/2	−373.04	−372.99	−0.05	0
7/2→9/2	0	—	—	—
	For $K=1\rightarrow K=1$*			
3/2→1/2	—	+281.73	—	+2.76
3/2→3/2	+168.96	+163.02	+5.94	+6.00
3/2→5/2	+28.09	+24.85	+3.24	+3.20
5/2→3/2	−123.49	−127.08	+3.59	+3.72
5/2→5/2	−264.28	−265.25	+0.97	+0.92
5/2→7/2	−311.28	−313.60	+2.32	+2.22
7/2→5/2	−60.15	−62.18	+2.03	+2.17
7/2→7/2	−107.12	−110.53	+3.41	+3.47
7/2→9/2	+76.65	+75.99	+0.66	+0.57

* Because the reference line is a $K=0$ line the second-order corrections for $K=1$ lines include, in addition to the second-order energy predicted by Eq. (3), a constant −0.38 mc/sec. to correct for term $-D_{J,K}J(J+1)K^2$ in the rotational energy, Eq. (1).

Here J and K are for the lower state. In addition, nuclear effects must be taken into account. In general, for molecules having the symmetry of the methyl halides the weight factors caused by the nuclear spin I of the three identical corner atoms are:[10]

$$1/3(2I+1)(4I^2+4I+3) \text{ for } K=0,3,6\cdots$$

and (7)

$$1/3(2I+1)(4I^2+4I) \text{ for } K \text{ not divisible by 3.}$$

For the particular cases here the spin of the hydrogen $I=1/2$, and the ratio of these two factors becomes 2:1. After the over-all intensities (neglecting the halogen nuclear quadrupole splitting of the lines) are calculated as indicated above, the relative intensities of the different hyperfine components of a given rotational transition are determined by the weights $(2F+1)$ of both the upper and lower hyperfine levels with the methods used in atomic spectra to determine the relative intensities of the fine structure or the hyperfine structure. For the transitions studied here, indeed for most cases needed in microwave investigations, the numerical values are already

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[9] See reference 5, p. 32.

[10] D. M. Dennison, Rev. Mod. Phys. 3, 280 (1931).

compiled in tables which may be found in standard texts on atomic spectra.[11]

IV. RESULTS

Nuclear Effects

Because of the interaction of the nuclear quadrupole moment of the halogen, the pure rotational lines of the molecules considered here are split into a number of components. Table I gives the observed and calculated hyperfine structure of the $J=0\rightarrow 1$ transition of CH_3Cl^{35} and CH_3Cl^{37}. The relative intensities and separations of the components were calculated by the methods described above. Equation (2) is in substantial agreement with observation for methyl chloride: that is, in this molecule the second-order effects are negligible, as is predicted by Eq. (3).

In Table II are given the calculated and observed hyperfine structures of the $J=1\rightarrow 2$ transition of CH_3Br^{79} and CH_3Br^{81}. For these cases the second-order effects are outside the range of experimental error. The theory of Bardeen and Townes is found to account for the deviations from the first-order theory.

In methyl iodide, where the nuclear quadrupole coupling is large, the deviations from first-order theory are considerable, in some cases as great as 5 mc/sec. Table III gives the observed and calculated spectrum. From examination of Table IV it may be seen that Eq. (3) accounts well for the deviations from first-order theory.

Table V. The nuclear quadrupole coupling coefficients in mc/sec. for Cl, Br, and I in methyl chloride, bromide, and iodide compared with values found in other compounds.

		Molecule						
Atom	Spin	CH_3Cl	ClCN	ICl	CH_3Br	BrCN	CH_3I	ICN
Cl^{35}	3/2	−75.13	−84[a] −83.5[c]	−82.5[b]				
Cl^{37}	3/2	−59.03	−64[a] −65.0[c]					
Br^{79}	3/2				577.0	686[c]		
Br^{81}	3/2				482.0	573[c]		
I^{127}	5/2			−2930[b]			−1934	−2420[d] −2420[c]

[a] C. H. Townes, A. N. Holden, J. Bardeen, and F. R. Merritt, Phys. Rev. **71**, 644 (1947).
[b] C. H. Townes, F. R. Merritt, and B. D. Wright, privately communicated.
[c] A. G. Smith, H. Ring, W. V. Smith, and W. Gordy, Phys. Rev. (to be published).
[d] See reference 8.

Table VI. Frequencies of hypothetical unsplit rotational lines, ν_0, and resulting moments of inertia for methyl chloride, bromide, and iodide.

Molecule	J transition	ν_0 (mc/sec.)	I_B (10^{-40} g-cm^2)	I_A (10^{-40} g-cm^2)
$C^{12}H_3Cl^{35}$	0→1	26585.77	63.11_{38}	5.52
$C^{12}H_3Cl^{37}$	0→1	26176.37	64.10_{09}	5.52
$C^{12}H_3Br^{79}$	1→2	38272.40	87.68_{85}	5.50
$C^{12}H_3Br^{81}$	1→2	38126:97	88.01_{80}	5.50
$C^{12}H_3I^{127}$	1→2	30005.00	111.8_{43}	5.50
$C^{13}H_3I^{127}$	1→2	28476.16	117.8_{48}	5.50

Table V lists the quadrupole coupling $eQ(\partial^2 V/\partial z^2)$ obtained for the different halide nuclei. In this table are given for comparison the coupling factors of these nuclei in certain other molecules. Since the nuclear quadrupole moment Q does not change, it is apparent that the factor $\partial^2 V/\partial z^2$, which measures the rate of change of the electric field of the molecule at the position of the halogen nucleus, varies appreciably from molecule to molecule. This factor must be evaluated from other sources before microwave data can be used to calculate Q. No method has been evolved for determining the absolute value of $\partial^2 V/\partial z^2$ in molecules of this type, though Townes[12] has suggested a method by which its order of magnitude may be obtained. With the atomic beam method, Davis, Feld, Zabel, and Zacharias[13] have recently measured the hyperfine splitting of $^2P_{3/2}$ ground states for Cl^{35} and Cl^{37}. From this experiment they evaluated the nuclear quadrupole moment of Cl^{35} as $-(7.921\pm 0.05)\times 10^{-26}$ cm^2 and that of Cl^{37} as $-(6.189\pm 0.05)\times 10^{-26}$ cm^2. Using their value of Q with the value of $eQ(\partial^2 V/\partial z^2)$ listed in Table V, the $\partial^2 V/\partial z^2$ at the chlorine nucleus in methyl chloride is found to be 13×10^{15} e.s.u. Our measurements give the ratio of Q for Cl^{35} to that for Cl^{37} as 1.273, in satisfactory agreement with the ratio 1.280 determined by the atomic beam method. Our measurements yield a ratio of 1.197 for the nuclear quadrupole moment of Br^{79} to that of Br^{81}.

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[11] For example: H. E. White, *Introduction to Atomic Spectra* (McGraw-Hill Book Company, Inc., New York, 1934), p. 439; E. U. Condon and G. H. Shortley, *The Theory of Atomic Spectra* (The Cambridge University Press, New York, 1935).

[12] C. H. Townes, Phys. Rev. **71**, 909 (1947).

[13] L. Davis, B. T. Feld, C. W. Zabel, and J. R. Zacharias, Phys. Rev. **73**, 525 (1948); also, L. Davis and C. W. Zabel, private communication.

TABLE VII. Molecular dimensions of the methyl halides.

Molecule	C–X distance (10^{-8} cm)	C–H distance (10^{-8} cm)	∠HCH	Ref.
CH_3F	1.38_4	1.11_2	110° 0′ (assumed)	a, e, 21 e
CH_3Cl	1.779	1.109	110° 0′	b, e
CH_3Br	1.936	1.104	110° 15′	c, e
CH_3I	2.139	1.100	110° 58′	d, e

[a] Using M_X for $F^{19}=19.00452$ a.m.u. as given by M. S. Livingston and H. A. Bethe, Rev. Mod. Phys. **9**, 373 (1937).

[b] Using M_X for $Cl^{35}=34.98107$ a.m.u. and M_X for $Cl^{37}=36.97829$ a.m.u. as given by E. Pollard, Phys. Rev. **57**, 1186 (1940).

[c] Using M_X for $Br^{79}=78.9417$ a.m.u. and M_X for $Br^{81}=80.9400$ a.m.u. as given by F. W. Aston, Nature, **141**, 1096 (1938).

[d] Using M_X for $I^{127}=126.932$ a.m.u. as given by F. W. Aston, Proc. Roy. Soc. **A115**, 487 (1927), and M_C for $C^{13}=13.00761$ a.m.u. as given by M. S. Livingston and H. A. Bethe, Rev. Mod. Phys. **9**, 370 (1937).

[e] Other constants used: $h=6.624_2\times 10^{-27}$ erg-sec., M_H for $H^1=1.00813$ a.m.u., M_C for $C^{12}=12.00386$ a.m.u. and mass of atom of unit atomic mass $=1.6599_0\times 10^{-24}$ g, all as given by R. T. Birge, Rev. Mod. Phys. **13**, 233 (1941).

Molecular Structures

By combining the microwave results obtained here with existing infra-red data it is possible for the first time to determine unambiguously the structure of these molecules. Though the carbon-halogen distances have been determined by electron diffraction[14] to an accuracy of about 3 percent, because of the low electron scattering power of the hydrogens it is not possible to determine either the bond angles or the CH bond lengths by this method.

From the analysis of the microwave hyperfine spectra above, the ν_0, or the frequency of the rotational line which would be observed if no nuclear quadrupole interaction existed, has been determined for each of the J transitions studied. These frequencies, with the I_B values determined from them by Eq. (1), are listed in Table VI. Though the frequency measurements here are accurate to better than four parts in a million, the moments of inertia depend upon Planck's constant, which has not been determined to the same accuracy. Hence, the last two figures in the I_B values have only relative significance.

From infra-red rotation-vibration spectra alone it is not possible to obtain very accurate values for either I_A, the moment of inertia about the symmetry axis, or I_B, that about an axis perpendicular to the symmetry axis. Now that I_B is known, however, it is possible to obtain fairly accurate values of I_A from previously measured separations of certain lines in the fundamental rotation-vibration spectra, which depend on I_A and I_B together. Johnston and Dennison[15] have shown that

$$\sum \Delta\nu_i=\left(\frac{6}{I_A}-\frac{7}{I_B}\right)\frac{h}{8\pi^2 c} \tag{8}$$

where the summation refers to the sums of the average line separations of zero branch lines in the three fundamental perpendicular type vibration bands. The summed values are: for methyl chloride[16] 27.31; for methyl bromide[16] 28.32; and for methyl iodide[16,17] 28.78 cm^{-1}. These, together with the I_B values determined in this work, were used to compute the I_A values listed in Table VI. As pointed out by Herzberg,[18] the accuracy of I_A determined by this equation is limited, because the dependence of I_A and I_B on the vibrational frequency has been neglected and because the sum rule holds exactly for strictly harmonic vibrations only. It is also limited by the accuracy of measurement of the separations of the lines in the vibrational bands. Fortunately, the bond distances can be determined somewhat more accurately since they depend upon the square root of the moment of inertia. Furthermore, the carbon-halogen distance depends primarily upon the I_B value, which is accurately known.

In Table VII are given the molecular dimensions evaluated from the moments of inertia with the following equations, which are readily obtained from the geometry of the molecules:

$$\begin{aligned} d_{CX}^2\left[M_X-\frac{M_X^2}{3M_H+M_C+M_X}\right] &+d_{CX}a\left[2M_X-\frac{2M_X(M_C+M_X)}{3M_H+M_C+M_X}\right]\\ &+a^2\left[(M_C+M_X)-\frac{(M_C+M_X)^2}{3M_H+M_C+M_X}\right]\\ &=I_B-I_A/2, \end{aligned} \tag{9}$$

where

$$a\equiv\left(d_{CH}^2-\frac{I_A}{3M_H}\right)^{\frac{1}{2}}=d_{CH}\cos\beta, \tag{10}$$

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[14] L. R. Maxwell, J. Opt. Soc. Am. **30**, 388 (1940).

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

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

[17] R. T. Lagemann and H. H. Nielsen, J. Chem. Phys. **10**, 668 (1942).

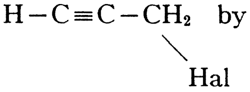
[18] See reference 5, p. 436.

and where X designates halogen and β, the angle of CH with the symmetry axis, is related to $\angle$HCH by

$$\sin\beta = \frac{2}{\sqrt{3}} \sin(1/2 < \mathrm{HCH}). \qquad (11)$$

With regard to the microwave data, the accuracy of the molecular structure determinations depends upon the accuracy of the measurement of the separations of the corresponding lines for the different isotopes. For methyl chloride this difference has been measured to an accuracy of about 0.04 percent, for methyl bromide to an accuracy of about 0.12 percent, and for methyl iodide about 0.01 percent. The structure determinations are also rather sensitive to the ratios of the atomic weights of the isotopes. The atomic weights used are listed in the table. In these calculations it is assumed that the carbon-halogen distances of the ground vibrational state are the same for the two isotopes. Though this is not exactly true, the error introduced by this assumption is probably not as great as that caused by the I_A values. Though the probable limits of error in the values given are not definitely known, in each case the last figure is uncertain.

The *C*-halogen bonds of methyl chloride, bromide, and iodide are somewhat longer than had been anticipated. They are significantly longer than the sum of the covalent radii (1.76, 1.91, and 2.10A) if the value[19] 0.77A is used as the single bond covalent radius of carbon, but they agree fairly well with the sum of the radii if the revised value[20] 0.79A is used for the carbon radius. Resonance with ionic structures of the type $H_3{\equiv}C^+X^-$ would be expected to shorten rather than lengthen the $C-X$ bonds and so would contributions of double bonded structures of the type $H_3^-{=}C{=}X^+$. Small contributions of hyperconjugated structures of the type $H_3^+{=}C\,X^-$ would lengthen both the CH and CX bonds, but significant contributions from such unstable structures does not seem probable. In contrast, the C-halogen interatomic distance in methyl fluoride is appreciably shorter than the sum of the single bond covalent radii (either 1.49A or 1.51A). Microwave measurement in this laboratory[3a] yields a value for the $C-F$ distance (see Table VII) which is in good agreement with the latest electron diffraction value[21] 1.39A.

Though bond lengths shorter than the sum of the single bond covalent radii are of wide occurrence, there are only a few instances known of bonds which are significantly longer than this sum. Carbon to halogen bonds of abnormal length (1.83A, 1.95A, and 2.13A for CCl, CBr, and CI, respectively) have, however, been found in  $H-C{\equiv}C-CH_2-\mathrm{Hal}$ by electron diffraction measurements.[22]

The CH bond-stretching force constants calculated by Linnett[23] for CH_3I, CH_3Br, CH_3Cl and CH_3F are 5.00, 4.95, 4.90, and 4.71×10^{-5} dyne/cm, respectively. The bond lengths, 1.100A, 1.104A, 1.109A, and 1.112A are in accord with this sequence, since the longer bond would have the weaker force constant.

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

[20] W. Gordy, J. Chem. Phys. **15**, 81 (1947).

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

[22] L. Pauling, W. Gordy, and J. H. Saylor, J. Am. Chem. Soc. **64**, 1753 (1942).

[23] J. W. Linnett, J. Chem. Phys. **8**, 91 (1940).