CARBON HALOGEN DISTANCES IN METHYL CHLORIDE AND METHYL BROMIDE

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ABSTRACT

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A brief history of the methyl halides is presented, followed by an introduction to isotope effects and the concept of non-bonded interactions. The theory of rotational spectra is discussed including an explanation of centrifugal distortion and quadrupole coupling. The Kraitchman equations as applied to symmetric top molecules and their application in determining molecular parameters is discussed. A description of the microwave spectrometer used in this investigation is included.

The method of preparation of CD_3Cl and CD_3Br is described. The ground state rotational constants of $^{13}CD_3{}^{35}Cl$, $^{13}CD_3{}^{37}Cl$, $^{13}CD_3{}^{79}Br$ and $^{13}CD_3{}^{81}Br$ have been determined. The transition frequencies of $^{12}CD_3{}^{35}Cl$, $^{12}CD_3{}^{37}Cl$, $^{12}CD_3{}^{79}Br$, $^{12}CD_3{}^{81}Br$ have been remeasured and the rotational constants redetermined. From the rotational constants of the deuterated methyl halides, the C-Cl distance in CD_3Cl and the C-Br distance in CD_3Br were determined to be 1.7804 Å and 1.9377 Å respectively. A literature search was made to determine the best rotational constants of $^{12}CH_3{}^{35}Cl$, $^{12}CH_3{}^{37}Cl$, $^{13}CH_3{}^{35}Cl$, $^{13}CH_3{}^{37}Cl$, and $^{12}CH_3{}^{79}Br$, $^{12}CH_3{}^{81}Br$, $^{13}CH_3{}^{79}Br$, $^{13}CH_3{}^{81}Br$ measured by previous researchers. Appreciable discrepencies in the rotational constant of $^{13}CH_3{}^{37}Cl$ in two different papers required remeasurement of the transition frequencies to determine the best value. Calculations of the carbon halogen internuclear distance allowed a comparison with the deuterated species. It was determined that deuterium substitution reduces the carbon halogen bond length by 11×10^{-4} Å in methyl bromide and 8×10^{-4} Å in methyl chloride.

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To my wife Beverly

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I. HISTORICAL BACKGROUND

Immediately following World War II vast amounts of 1.25 cm, radar equipment were made available to research laboratories in educational institutions. The availability of this equipment at low cost made it possible for many research workers to investigate microwave absorption in gases. It had been realized since the work of Cleeton and Williams(1) in 1933 that ammonia absorbs radiation in the microwave region. This absorption was attributed to transitions between energy levels split by the 6 kilocalories potential barrier hindering the inversion of ammonia.

One of the early investigators, W. D. Hershberger(2), selected a number of gases which he believed to be most likely to absorb microwaves. The requirements he believed to be necessary for absorption were that the molecule have a dipole moment, and that there exist the possibility for hindered rotation of a methyl group with respect to some other group about a single carbon-carbon bond. It was suspected that in the ethyl halides, transitions between energy levels split by hindered rotation should also lie in the microwave region. This hypothesis involving hindered motion was found to be inadequate when it was learned that the methyl halides absorbed microwave radiation. Absorption in this region was then attributed to the rotational motion of the molecule in the lowest vibrational states.

Previously, structural parameters of the methyl halides had been determined by infrared and electron diffraction experiments and discrepancies existed between the two methods(3). The greater precision of microwave spectroscopy combined with existing infrared data reduced the discrepancies considerably.

The first frequency measurements of the rotational spectra of the methyl halides were made by Gordy, Simmons and Smith in 1947(4). Their work indicated the existence of hyperfine structure due to the interaction of the spinning nucleus with the surrounding charge distribution of the molecule. This interaction, known as quadrupole coupling, had been predicted by Kellogg, Rabi, Ramsey and Zacharias in 1940(5). The values of the moments of inertia I_b and the quadrupole coupling constants eQq found by Gordy, et. al. are listed in Table I. The internuclear distances were determined using moments of inertia I_a evaluated from infrared data.

Table I. Methyl chloride and methyl bromide parameters.[a]

Compound	I_b(amu Å^2)	eQq(Mc)	C-X (Å)	Q(cm)
$^{12}CH_3{}^{35}Cl$	38.016	-69	1.79	$.055 \times 10^{-24}$
$^{12}CH_3{}^{37}Cl$	38.558	-56		$.045 \times 10^{-24}$
$^{12}CH_3{}^{79}Br$	52.716	573	1.94	$.17 \times 10^{-24}$
$^{12}CH_3{}^{81}Br$	52.957	485		$.14 \times 10^{-24}$

[a] Reference 4.

In 1947 Gordy, Simmons and Smith (6,7) developed an instrument for multiplying stable 10 mc/sec frequencies. The 10 mc/sec signal was monitored by radio station WWV maintained by the National Bureau of Standards. This new measuring device enabled them to measure frequencies to seven significant figures compared to a maximum of four obtained previously with the cavity wave meter. In addition to more precise measurements using the frequency multiplier, it was determined from discrepancies between measured and theoretical frequencies that second order quadrupole effects were significant in methyl bromide and methyl iodide. When, as in methyl iodide, the effect of quadrupole coupling was large compared to the pure rotational frequency, it was observed that second-order effects were of the magnitude of several megacycles/sec. Improved measuring techniques plus consideration of first and second-order quadrupole effects gave the results listed in Table II(6,7).

The work of Gordy, Simmons and Smith initiated an intense study of the methyl halides by microwave spectroscopy. Much of the work was published in the form of "Letters to the Editor" and provided only a minimum of information. Tables I, and II are a summary of all the available data on methyl bromide and methyl chloride reported since 1947.

Table II. Summary of methyl chloride and methyl bromide data

Compound	Reference	$_0$(Mc/sec)[a]	B(Mc/sec)	eQq	I_b(amu A^2)[b]
$^{12}CH_3{}^{35}Cl$	6	26585.77		-75.13	38.022
	7				38.026
	8			-75.5	
	10		13292.95		
	11			-74.77	
	12			-74.40	
	13	26585.68		-74.77	
	14		13292.86	-74.9	
$^{12}CH_3{}^{37}Cl$	6	26176.37		-59.03	38.618
	7				38.619
	8			-58.03	
	10		13088.24		38.612
	13	26176.26		-58.93	
$^{13}CH_3{}^{35}Cl$	9	25592.43			39.499
	16		12796.2		
$^{13}CH_3{}^{37}Cl$	9	25179.54			40.149
	16		12590.0		
$^{12}CH_3{}^{79}Br$	6	38272.40		577.0	52.824
	7				52.827
	10		9568.188		52.819
	13		9568.20	577.15	
	14		9568.20	577.3	
	15		9568.37	577.3	
$^{12}CH_3{}^{81}Br$	6	38126.97		482.0	53.024
	7				53.028
	10		9531.845		53.023
	13		9531.84	482.16	
	14		9531.82	482.4	
	15		9532.20	482.4	
$^{13}CH_3{}^{79}Br$	17		9119.507	577.3	
$^{13}CH_3{}^{81}Br$	17		9082.86	482.4	

[a] J = 0 ⟶ 1 transition for CH_3Cl and J = 1⟶ 2 for CH_3Br.

[b] I_b has been converted from the original unit of gm cm^2 to amu A^2 for comparison with values given below.

II. INTRODUCTION

Isotope Effects and Non-bonded Interactions

It has been established from theoretical considerations and experimental examples that a reaction which involves the removal of a hydrogen atom in its rate determining step will show a marked difference between the rate of removal of hydrogen and deuterium. The difference in rates, referred to as a primary isotope effect, is not necessarily restricted to hydrogen but is most prominent when hydrogen and its isotopes are involved. A proposed explanation of primary isotope effects is that they are due to the difference in zero point energies of the isotopic species. The lower zero point energy of deuterium requires that a greater energy be expended to dissociate the atom than is required for hydrogen. Therefore the rate of the reaction involving the isotopically substituted species is less.

Kinetic studies(18) have indicated that the effect of substitution on reaction rates is not limited to an isotope directly involved in the reaction but may be extended to other sites. This has been attributed to the effect of the change in the zero point energy on the amplitude of vibration. The unusually large change in the amplitude of vibration upon substitution of deuterium for hydrogen makes hydrogen atoms the most important source of such secondary isotope effects.

Bartell(19) has proposed that deuterium substitution in ethane would lower the non-bonded repulsions thereby decreasing the carbon-carbon bond length. From calculations and electron diffraction experiments, he predicts and finds a decrease in the carbon-carbon bond length of .004 Å with an estimated accuracy of approximately .001 Å.

The precise frequency measurements obtainable with microwave spectroscopy make it the ideal method for determining small variations in the internuclear distances. From the frequency measurements the geometry of the molecule and subsequently the internuclear distances can be determined. The restriction that a molecule have a dipole moment prohibits the measurement of absorption frequencies of ethane by microwave radiation but the same principles should also apply to molecules with a dipole such as the methyl halides. Replacement of the hydrogen atoms by deuterium should reduce the non-bonded repulsions and decrease the carbon-halogen bond distance. The decrease in the carbon-halogen bond distance with substitution is expected to be less than the decrease in the carbon-carbon distance in ethane due to the number of replaceable hydrogen atoms involved, but it is believed that the effect would still be measureable.

III. THEORY OF ROTATIONAL SPECTRA

3.1 Energy of Rotation

For a discussion of their rotational energy molecules may be classified according to the moments of inertia about their principal axes. The moment of inertia about an axis is defined as $I = \sum m_i r_i^2$ where r_i is the perpendicular distance of mass m_i from the axis. The principal axis system (a, b, c system) is located so that its origin is at the center of mass of the molecule and so that $\sum_i m_i a_i b_i = \sum_i m_i a_i c_i = \sum_i m_i b_i c_i = 0$. The three principal moments are called I_a, I_b and I_c and defined so that $I_a \leq I_b \leq I_c$. With this convention all molecules may be grouped as follows:

$I_b = I_c,\ I_a = 0$	Linear molecules
$I_c = I_b + I_a$	Planar molecules
$I_a \neq I_b = I_c$	Prolate symmetric top molecules
$I_a = I_b \neq I_c$	Oblate symmetric top molecules
$I_a \neq I_b \neq I_c$	Asymmetric top molecules
$I_a = I_b = I_c$	Spherical top molecules.

The restrictions for each type of molecule lead to different solutions for the rotational energy. The assumption that a molecule acts as a rigid rotor with no vibration-rotation interaction simplifies the energy expressions and yields a reasonably accurate solution. The potential energy of the molecule due to interactions with other molecules is considered negligible because of the low pressures (10^{-4} atm.) used in microwave spectroscopy. The classical expression for the energy of a rigid rotating body is $W = (1/2)mr^2\omega^2 = I^2\omega^2/2I = P^2/2I$, where I is the moment of inertia about the axis of rotation, P is the angular momentum, and ω is the angular velocity. The quantization of angular momentum requires that $P^2 = (h/2\pi)^2 J(J+1)$; therefore

$$W = \frac{h^2}{8\pi^2 I} J(J+1) = hBJ(J + 1)$$

where J can be zero or a positive integer and B is called a rotational constant. For diatomic molecules the axis of rotation is perpendicular to the axis of the molecule and

$$B = \frac{h}{8\pi^2 I} = \frac{h}{8\pi^2 \mu} \left(\frac{1}{r_0^{\,2}}\right)$$

where μ, the reduced mass, is $\frac{m_1 m_2}{m_1+m_2}$ and r_0 is the internuclear distance.

Molecules classified as symmetric tops include all structures having two equal moments of inertia. Methyl chloride is an example of a prolate top, whereas chloroform is an oblate-top molecule.

The more complex structure of the symmetric top requires the introduction of another quantum number K where $(\frac{h}{2\pi})K$ is the projection of the angular momentum on the unique axis of the molecule, and $K = 0, \pm 1, \pm 2, \ldots \pm J$. The energy level expressions are as follows:

$$W_p = hBJ(J + 1) + h(A - B)K^2 \text{ for a prolate top molecule,}$$

$$W_0 = hBJ(J + 1) + h(C - B)K^2 \text{ for an oblate top molecule.}$$

The selection rules for allowed transitions for a symmetric top are $\Delta J = 1$, $\Delta K = 0$. Application of these selection rules gives for the observed transition frequencies $\nu = 2B(J + 1)$, where J is the quantum number of the lower energy state involved in the transition.

3.2 Centrifugal Distortion

Centrifugal distortion is distortion of the molecule due to the centrifugal force of rotation. If the effects of centrifugal distortion are included the expression for the energy levels of a prolate top molecule becomes

$$W_p = hBJ(J+1) + h(A-B)K^2 - hD_J J^2(J+1)^2 - hD_{JK} J(J+1)K^2 - hD_K K^4$$

where D_J, D_{JK}, and D_K are centrifugal distortion constants related in a complicated way to the geometry and electronic structure of the molecule. Energy level differences previously considered to be simple multiples of J+1 for the rigid rotor, tend to decrease slightly with an increasing value of J. The frequency of a transition for a symmetric top with centrifugal distortion is

$$\nu_{J \longrightarrow J+1} = 2(J+1)(B - K^2 D_{JK}) - 4D_J(J+1)^3$$

The D_J term results from the stretching which arises from the rotation about the B axis, the D_K term compensates for stretching due to rotation about the molecular axis, and D_{JK} is the result of interaction of the two rotations. Numerical values of the stretching constants determined for the methyl halides are given in Table III.

Table III. Centrifugal distortion constants of the methyl halides[a]

Compound	B_0(Mc/sec)	D_J(Kc/sec)	D_{JK}(Kc/sec)
${}^{12}CH_3{}^{3}Cl$	13292.86	18.1	198
${}^{12}CH_3{}^{79}Br$	9568.20	9.9	128.3
${}^{12}CH_3{}^{81}Br$	9531.82	9.7	127.4

[a] Reference 21.

3.3 Nuclear Quadrupole Hyperfine Structure--First Order.

In addition to the angular momentum due to rotation, some molecules have angular momentum resulting from the spin of one or more nuclei. The spinning nucleus being a charge distribution in motion produces a varying magnetic field which may interact with the rotation. As for any spinning system, the square of the angular momentum must be $I(I+1)h^2$ where I, the spin quantum number, is integral or half integral. A spin of 1/2 leads to no interaction between the spin of the nucleus and the rotation of the molecule. For atoms with I greater than 1/2, the interaction of the nuclear quadrupole moment with the surrounding charge distribution causes splitting of the rotational lines. The states are labeled by the total angular momentum quantum number F which has the values F = J+I, J+I-1.... J-I. The splitting of the rotational lines in symmetric top molecules with one quadrupole nucleus is proportional to eQq where Q is the quadrupole moment of the nucleus and $q = \left\langle \frac{\partial^2 V}{\partial Z^2} \right\rangle_{av}$ is the curvature of the electrostatic potential energy in the direction of the unique axis measured at the quadrupole nucleus.

It has been shown by Townes and Dailey (21) that the field gradient along the unique axis is determined most strongly by the valence electrons of the atom in question. The electrons in closed shells have no effect due to spherical symmetry, assuming the distortion due to polarization is negligible. The spherical symmetry of the s orbitals eliminates any effect whereas the low penetrating power of d orbitals would appear to minimize any effect they might have in contributing to a field at the nucleus. As indicated by Townes and Dailey, the only alternative is that the field gradient is produced by the p orbitals in the valence shell. Therefore an evaluation of the field gradient would be a measure of the p character of the bond.

The first order energy expression for the levels split by quadrupole interactions of a symmetric top is

$$W = W_R + W_Q^{(1)} \qquad \text{where } W_R \text{ is the rotational energy}$$

$$W_Q^{(1)} = eQq\left[\frac{3K^2}{J(J+1)} - 1\right] f(IJF)$$

$$f(IJF) = \left(\frac{\frac{3}{4}C(C+1) - J(I+1)J(J+1)}{2(2J+3)(2J-1)I(2I-1)}\right)$$

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

The above equations developed by Bardeen and Townes(22) also apply to linear molecules which are a special case of symmetric tops with $K = 0$.

The frequency of a rotational transition is thus proportional to $\Delta W_R + \Delta W_Q^{(1)}$. The change in rotational energy, ΔW_R, is commonly referred to as the "hypothetical unsplit frequency". Since $\Delta W_Q^{(1)}$ is often much smaller than ΔW_R the transition occurs as a multiplet of lines approximately centered about the hypothetical unsplit frequency.

The quadrupole energy expression for the asymmetric top is more complex, involving three field gradients instead of only one. A complete treatment for all types of molecules may be found in Townes and Schalow(23).

3.4 Nuclear Quadrupole Hyperfine Structure--Second Order.

When the hyperfine splitting becomes large relative to the hypothetical unsplit frequency, calculated first order quadrupole effects do not agree with experimentally determined values. This difference which may be as large as several megacycles per second may be evaluated by second order pertubation theory.

For a symmetric top the energy resulting from second order perturbation is of the form

$$W_Q^{(2)} = \sum_{J'K'} \frac{|(IJFM_F|H_Q|IJ'FM_F)|^2}{W_{JK} - W_{J'K'}}$$

where M_F is the orientation quantum number, H_Q is the part of the Hamiltonian which represents the quadrupole energy and $J' = J+1$ or $J+2$. The equations derived by evaluating the squared matrix elements are of the form(23)

$$|(I, J, F, M_F|H_Q| I, J+1, F, M_F)|^2 =$$

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

$$\times (I+J+F+2)(J+F-I+1), \text{ and}$$

$$|(I, J, F, M_F| H_Q| I, J+2, F, M_F)|^2 =$$

$$\left[\frac{3eQq}{16I(2I-1)(2J+3)}\right]^2 \frac{(F+I+J+3)(F+I+J+2)}{(2J+1)(2J+5)}$$

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

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

Tables enabling easy calculation of $W_Q^{(2)}$ have been prepared(23).

3.5 Stark Effect

In the absence of an external electric or magnetic field, the rotational energy levels are (2J+1) fold degenerate. The introduction of an electric field removes the degeneracy and allows 2J+1 orientations of the total rotational angular momentum with respect to the direction of the applied field. The component of the total rotational angular momentum in the direction of the field is designated by $M_J(\frac{h}{2\pi})$ where the quantum number $M_J = 0, \pm 1, \pm 2, \ldots \pm J$.

The selection rules for allowed transitions are determined by the geometry of the sample cell. If the applied electric field is parallel to the electric field of the microwave radiation, the selection rule is $\Delta M_J = 0$, but if the static electric field is perpendicular to the electric field of the microwave radiation the selection rule is $\Delta M_J = \pm 1$.

The instrument at M.S.U. is constructed such that $\Delta M_J = 0$. For $J = 0$ to $J = 1$ transitions only one stark lobe, $M_J = 0$ to $M_J = 0$, was observed, as would be expected.

3.6 Determination of Atomic Coordinates.

For prolate symmetric top molecules such as the methyl halides, the A rotational constant is $\frac{h}{8\pi^2 I_a}$ where I_a is the moment of inertia of the molecule about the symmetry axis. The B and C rotational constants are both equal to $\frac{h}{8\pi^2 I_b}$ where I_b is the moment of inertia about an axis perpendicular to the symmetry axis passing through the center of mass of the molecule. By definition, the moment of inertia about the b axis is

$$I_b = \sum_i m_i (a_i^2 + c_i^2)$$

where for a prolate top the a axis is the molecular axis. For an atom located on the symmetry axis, the b and c coordinates are zero.

The presently accepted method of determining bond distances from rotational constants is the substitution method(24,31) in which atomic coordinates are determined from differences in moments of inertia of different isotopically substituted molecules.

The equations for the coordinates of a substituted atom which is on the symmetry axis of a symmetric top molecule are particularly simple. Isotopic substitution of the sth atom on the symmetry axis of a symmetric top molecule shifts the center of mass along the a axis by Δa and changes the mass of the molecule by Δm_s. The moment of inertia I_b', of the isotopically substituted molecule is

$$I_b' = \sum_I m_i' \, (a_i'^2 + c_i^2)$$

where $\sum_i m_i' = {}_i \, m_i + \Delta m_s$

$$a_i' = a_i + \Delta a$$

and c_i, a_i and m_i are the parameters of the original molecule. Substituting into the expansion for

$$I_b' = \sum_i m_i \, [(a_i + \Delta a)^2 + c_i^2] + \Delta m_s[(a_s + \Delta a)^2 + c_s^2]$$

Since the sth atom is on the symmetry axis $c_s = 0$. The a_i' are measured from the center of mass of the substituted species. Therefore

$$\sum_i m_i'a_i' = 0 = \sum_i m_i(a_i + \Delta a) + \Delta m_s(a_s + \Delta a)$$

Since ${}_i \, m_i a_i = 0$ is the center of mass condition for the parent species and since $\sum_i m_i = M$, the mass of the parent,

$$(M + \Delta m_s) \, \Delta a + \Delta m_s a_s = 0$$

or

$$\Delta a = - \frac{\Delta m_s a_s}{M + \Delta m_s}$$

where M' = mass of the substituted species.

Substituting the expression for Δa into the expression for I_b' and simplifying finally leads to

$$I_b' = I_b \mu^{-1} a_s^2$$

where $\mu = \frac{M(M' - M)}{M'}$.

It should be emphasized that a_s is the coordinate of the substituted atom in the axis system of the unsubstituted or parent species. Therefore isotopic substitution at different sites gives the coordinates of the substituted atoms all in the same coordinate system. Thus the carbon halogen distance, for example, is simply $a_x - a_c$.

In the methyl halides and deuterated methyl halides using the present experimental data and that previously given, there are a sufficient number of isotopic species to allow four different choices for the parent or unsubstituted species for each carbon-halogen distance to be determined.

IV. DESCRIPTION OF THE MICROWAVE SPECTROMETER

4.1 Introduction

Instrumentation for work in the microwave region is rather different from that used in all other regions. Microwave frequencies (10^{11} cycles/sec) which lie between radio frequencies (10^6 cycles/sec) and visible radiation (10^{15} cycles/sec) require techniques similar to those used in generating radio waves rather than optical methods.

The basic microwave spectrometer consists of a klystron power supply and a klystron to produce monochromatic radiation, a wave guide which acts as a sample holder and a silicon crystal to detect the signal. The signal is amplified and displayed on a recorder or oscilloscope. A block diagram of the components is shown in Figure 1.

4.2 Reflex Klystron

The reflex klystron is an electron tube capable of modulating electron velocities. An electron beam emitted from the cathode is accelerated to pass through a resonant cavity. Further acceleration in the cavity depends on the phase of the oscillation of the fields in the cavity itself. The electrons emerge from the cavity into a drift region where bunching occurs as faster electrons tend to overtake slower ones.

The reflector which is from -150 to -400 volts negative with respect to the cathode, returns the electrons to the cavity. If the returning electrons are properly bunched and in phase with the cavity oscillations which originally accelerated the electrons, the oscillations are enhanced. Microwave radiation is conducted from the cavity

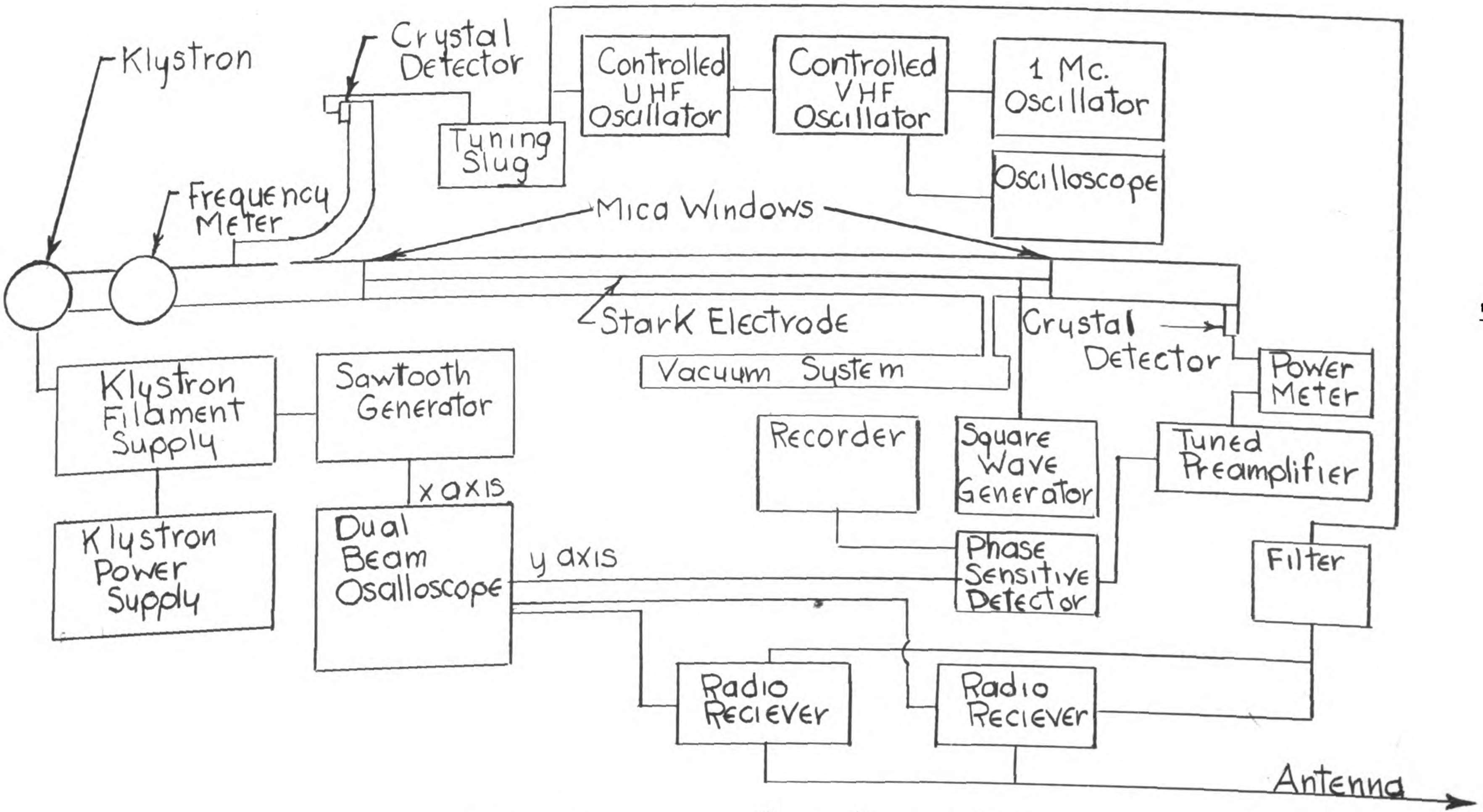

Fig. 1.Microwave Spectrometer

by means of a waveguide outlet. The oscillations tend to be highly monochromatic, and the klystron is tunable over a frequency range of approximately 20% of the center frequency.

4.3 Wavemeter

The wavemeter is a cylindrical cavity of which the dimensions can be varied by a micrometer screw. The cavity is coupled to the wave guide by a thin iris. The geometry of the wave meter is such that the fields in the desired cavity mode and in the wave guide are parallel. As the klystron sweeps through the frequency to which the wavemeter is tuned a fraction of the energy is absorbed which is indicated on the oscilloscope as a decrease in the microwave power.

4.4 Sample Cell

The sample cell consists of a silver lined rectangular pipe (waveguide) capable of transmitting microwave power. The cross sectional dimensions are 0.40 in. x 0.90 in. Along each of the narrow sides of the sample cell is a Teflon tape which holds a silver septum insulated from and parallel to the wider side. Mica windows at each end, of the cell and a sample inlet system permit the waveguide to be used as the sample holder.

4.5 Square Wave Generator

The square wave generator is an electronic device capable of charging and discharging the septum in the waveguide to voltages up to 1200 volts in less than one microsecond at 5 microsecond intervals. The output of the generator is applied to the stark electrode in the waveguide.

The generator serves two purposes. The electric field modifies the absorption frequencies in a way which depends on the dipole moment of the sample, and second, the application of the square wave to the Stark electrode is a means of modulation of the absorption of the sample. The sample is alternately exposed to and isolated from the field at 5 microsecond intervals so that when the klystron frequency is identical to the sample absorption frequency, a small part of the microwave frequency will be modulated due to switching on and off the absorption of the sample by the changes in Stark field.

4.6 Crystal

The crystal rectifier consists of a small silicon wafer with a fine pointed, tungsten wire contact. Contact resistance of the crystal is greater in one direction than the other. The current voltage characteristic is non linear near the origin so that any applied alternating current is rectified. Typical of this type of crystal is the IN26 used with K band wave guide. This type of non-linear device can be used for detection, for mixing two signals, and for frequency modulation.

4.7 Sampling Technique

The sampling technique is determined by the availability and the reactivity of the sample. For samples which do not react with glass, metal, or stopcock grease a vacuum system attached to the waveguide sample cell is satisfactory for introducing the sample to the system. The system is evacuated, then flooded with sample and partially re-evacuated to optimum pressure, generally about 10^{-4} atmospheres. If only a small amount of sample is available, it may be recovered from the cell. A reactive sample is allowed to diffuse into one end of the wave guide while evacuating the waveguide from the other end. This allows for a continual sweeping out of any decomposed or reacted sample.

4.8 Frequency Measurements

Approximate frequency measurements, within 10-20 megacycles, are obtained using the cavity wavemeter (section 4.2) which is attached to the waveguide. When the klystron frequency is identical to the cavity resonance frequency, a small amount of energy is absorbed causing a dip on the Y axis of the oscilloscope.

Exact frequency measurements are referred to a Manson RD 140 high stability one-megacycle/second, crystal-controlled oscillator with a frequency stability of one part in 10^8 per day. The crystal-controlled oscillator is standardized by beating its tenth harmonic against the 10 Mc/sec carrier of radio station WWV from the National Bureau of Standards. The output of the one-megacycle oscillator is connected to the input of a Gertsch AM-1A VHF interpolator where the signal is amplified and multiplied. The output of the multiplier is mixed with the output of a 1-2 megacycle oscillator (LFO). The frequency of the LFO is determined by using only those frequencies which give a stable Lissajous figure when referenced to one megacycle per second. These frequencies may be set to better than one cycle per second. The sum of the multiple of one megacycle and the LFO frequency controls the output of the AM-1A interpolator. This output frequency which is between 20 and 40 Mc/sec is then multiplied and mixed with a ten Mc/sec signal in a second instrument, the Gertsch FM-4A UHF oscillator. The output of the Gertsch FM-4A is controlled by this multiplied and mixed signal. Finally the output of the FM-4A (500-1000 Mc/sec) is multiplied and mixed with the microwave signal on a silcon crystal in the waveguide. The frequency of an absorption line is measured by the difference between the unknown absorption frequency and a multiple of the known frequency of the Gertsch UHF oscillator. The frequency difference is measured by either a Hallicrafters SX-62-A or Collins 51J-4 receiver. The Collins is generally used for fine measurements because of the ease of reading the dial calibrated to .001 megacycle. The Hallicrafters is tuned much more rapidly and is used for determining initial locations.

The exact frequency of an absorption line is determined by moving the frequency difference marker until it is centered on the absorption line. Actually two frequency markers are generated corresponding to positive or negative frequency differences. The positive or high frequency marker is being observed if moving the receiver dial to a higher frequency causes the marker to shift to higher frequencies. With the high frequency marker centered on the absorption line the receiver reading is added to the standard frequency. When the low frequency marker is used the receiver reading is subtracted from the standard frequency. A time delay between the 100 kc signal and the beat marker reaching the oscilloscope requires that measurements be made while sweeping the field in both directions to average out the frequency discrepancies. This method is capable of giving frequency measurements with an absolute precision of 0.01 Mc/sec at 30,000 Mc/sec.

V. DETERMINATION OF STRUCTURE OF METHYL CHLORIDE AND METHYL BROMIDE

5.1 Introduction

In undertaking the study of the structural parameters of the methyl halides the following steps were taken:

1. Preparation of the deuterated carbon-13 methyl halides.
2. Calculation of the rotational spectra using an approximate structure.
3. Assignment of absorption lines.
4. Determination of quadrupole coupling effects, rotational constants and moments of inertia.
5. Calculation of internuclear distances from moments of inertia.
6. Determination of error.

The purpose of the research was to determine the effect of deuteration on the carbon halogen bond distance. Consequently a comparison was made of the results of the present experimental work with those of previous research on the methyl halides.

5.2 Sample Preparation

The preparation of $^{13}CD_3X$ was accomplished in the following steps:

1. Conversion of $Ba^{13}CO_3$ to $^{13}CO_2$
2. Reduction of $^{13}CO_2$ to $^{13}CD_3OH$
3. Halogenation of $^{13}CD_3OH$.

The procedure used in the preparation of $^{13}CO_2$ was that of Nystrom and Yanko.(26) The apparatus consisted of a 100 ml round bottom flask attached to a vacuum manifold through a pressure compensating funnel and a plug of glass wool. Attached to the manifold was a gas collection flask in a liquid nitrogen trap.

A mixture of 3.0 gms of 60% $Ba^{13}CO_3$, 3.5 gms $Ba^{12}CO_3$ and 12 ml of water was frozen out in the 100 ml round bottom flask. The system was evacuated and 25 ml of 70% $HClO_4$ was added to the $BaCO_3$ **mixture** through the pressure compensating funnel. The freezing bath was removed and the system was allowed to reach room temperature slowly. The generator was then closed off to prevent the transfer of the remaining water. The CO_2 was collected in the gas bulb at -196°C.

Reduction of $^{13}CO_2$ to $^{13}CD_3OH$

A modification of the procedure by Nystrom and Yanko(26) was used in the reduction of $^{13}CO_2$ with $LiAlD_4$.

A solution of 2.4 gms of 99.8% $LiAlD_4$ and 250 cc of diethyl carbitol was stirred in a 500 ml, 3 necked round bottom flask for 6 hours. A stoppered dropping funnel containing 60 gms of n-butyl carbitol and a thermometer were inserted in the three necked flask. The system was attached to the vacuum manifold and evacuated to 10 mm Hg. The previously prepared $^{13}CO_2$ was admitted to the system and allowed to react by surface adsorption. After 12 hours the n-butyl carbitol was added through the dropping funnel. Six hours later the system was heated to 60°C and occasionally partially evacuated through two traps cooled by liquid nitrogen. The CD_3OH was collected in the traps and transferred to a gas collection bulb.

Conversion of $^{13}CD_3OH$ to CD_3X

The same general procedure was followed in the preparation of both $^{13}CD_3Cl$ and $^{13}CD_3Br$.

A 50 ml flask was attached to the vacuum manifold thru a cold finger attached to a liquid nitrogen trap. The 50 ml bulb contained three grams of PCl_5 (PBr_3) which was frozen out. The system was evacuated and 0.3 ml of previously prepared $^{13}CD_3OH$ was distilled onto the PCl_5 (PBr_3). A dry ice acetone solution was prepared in the cold finger. All other traps were removed to maintain a continual refluxing of the $^{13}CD_3OH$. After 6 hours of refluxing, one liquid nitrogen bath was placed on the cold trap and one on a U tube in the vacuum manifold. The cold finger was allowed to warm to room temperature and the system was again evacuated through the two cold traps. The samples were immediately transferred to a gas collection bulb. All the bands in the infrared spectra belonged to the methyl deuterides.

5.3 Experimental Procedure

The molecular dimensions used to determine the approximate rotational constants were taken from Townes and Schawlow(23). The values used were compensated for the change in the H-C-H bond angles and C-H bond distances due to the substitution of deuterium for hydrogen. The shortening of the bond was assumed to be 0.009 Å and the bond angle was assumed to increase by 12'. The parameters used were as follows:

	C-D (Å)	D-C-D angle	C-X (Å)
CD_3Cl	1.104	110°31'	1.781
CD_3Br	1.104	111°26'	1.939

The Cartesian coordinates of each atom were calculated using the carbon atom as the arbitrary origin. The translation of the coordinate system to the center of mass and the subsequent determination of the rotational constants were performed on the MISTIC digital computer at Michigan State University.

The completed transformation resulted in the values of B for the deuterated methyl halides given in Table IV.

Table IV. Rotational constants of deuterated methyl chloride and methyl bromide from known parameters[a]

Compound	B(Mc)	Compound	B(Mc)
$^{12}CD_3{}^{79}Br$	7716.77	$^{12}CD_3{}^{35}Cl$	10843.48
$^{12}CD_3{}^{81}Br$	7683.36	$^{12}CD_3{}^{37}Cl$	10660.08
$^{13}CD_3{}^{79}Br$	7442.96	$^{13}CD_3{}^{35}Cl$	10555.89
$^{13}CD_3{}^{81}Br$	7409.22	$^{13}CD_3{}^{37}Cl$	10370.56

[a] Reference 23.

Using the B values from Table IV the following relation was used to minimize the error in approximating the hypothetical unsplit frequencies:

$$B_{^{13}CD_3X}(\text{spec}) = B_{^{13}CD_3X}(\text{calc}) - B_{^{12}CD_3X}(\text{calc}) + B_{^{12}CD_3X}(\text{obs})$$

where the $B_{^{12}CD_3X}(\text{obs})$ were the rotational constants for the deuterated, C-12 methyl halides as determined by Simmons and Goldstein(27).

	B(Mc)
$^{12}CD_3{}^{35}Cl$	10841.88
$^{12}CD_3{}^{37}Cl$	10658.43
$^{12}CD_3{}^{79}Br$	7714.57
$^{12}CD_3{}^{81}Br$	7681.23

The hypothetical unsplit frequencies ($J = 0 \longrightarrow 1$) were calculated as shown in Table V. The halogens in each case have a spin of 3/2 requiring a further calculation of the quadrupole coupling constant due to the interaction of the spin of the halogen nuclei with the field gradient. From the equation developed by Bardeen and Townes(22), and the nuclear quadrupole coupling coefficient determined by Gordy, Simmons and Smith(6) the calculated spectroscopic frequencies are shown in Table VI.

Table V. Approximation of hypothetical unsplit frequencies

Compound	ν_0 (Mc/sec)
$^{13}CD_3{}^{35}CL$	21108.58
$^{13}CD_3{}^{37}Cl$	20739.80
$^{13}CD_3{}^{79}Br$	14881.52
$^{13}CD_3{}^{81}Br$	14814.18

Table VI. Calculated vs. experimental frequencies of deuterated methyl chloride and methyl bromide.

Compound	F -> F'	ν_0 (unsplit)	$\Delta W_Q^{(1)}$	ν calc.[a]	νexp.
$^{13}CD_3{}^{35}Cl$	3/2 - 1/2	21108.58	+ 18.60	21127.18	21128.24
	3/2 - 3/2		- 14.88	21093.70	21094.67
	3/2 - 5/2		+ 3.72	21112.30	21113.33
$^{13}CD_3{}^{37}Cl$	3/2 - 1/2	20737.80	14.64	20752.45	20753.46
	3/2 - 3/2		- 11.72	20726.09	20727.06
	3/2 - 5/2		2.93	20740.73	20741.68
$^{13}CD_3{}^{79}Br$	3/2 - 1/2	14881.52	-143.65	14737.87	14739.37
	3/2 - 3/2		114.92	14996.44	14998.29
	3/2 - 5/2		- 28.73	14852.79	14854.30
$^{13}CD_3{}^{81}Br$	3/2 - 1/2	14814.18	-119.95	14694.23	14695.54
	3/2 - 3/2		95.96	14910.14	14911.77
	3/2 - 5/2		- 23.99	14790.19	14791.46

[a] Based on structure of CH_3X with appropriate changes for CH to CD and HCH to DCD.

5.4 Examination of the Spectra

A survey of the predetermined regions of absorption indicated all lines to be within 1.5 Mc of the calculated values. Each J = 0 -> 1 transition occurred as a set of three lines due to quadrupole splitting. Once the preliminary survey was completed each line was measured at optimum pressure and Stark voltage. A minimum of two measurements was made on each line, in each case reversing the sweep of the oscilloscope and averaging the measurements. The measured frequencies are also shown in Table VI.

5.5 Determination of Molecular Parameters

Using the quadrupole coupling constants determined by Gordy, Simmons and Smith, it was possible to calculate approximately the effects of second order quadrupole coupling for the carbon-13 deuterated methyl halides. From these values and the measured frequencies it was possible to calculate improved values of the quadrupole coupling constants using the relation

$$\Delta W_Q^{(1)} = \nu - \nu_0 - \Delta W_Q^{(2)}$$

where ν is the measured frequency, and ν_0 is the hypothetical unsplit frequency.

Having obtained the average $\Delta W_Q^{(1)}$ for the three lines it was possible to recalculate $\Delta W_Q^{(2)}$ and subsequently the hypothetical unsplit frequency which is equal to 2B for the J = 0 to J = 1 rotational transition. I_B was determined from B in Mc/sec with the equation:

$$I_B = \frac{505531}{B} \text{ amu } \text{Å}^2$$

The calculated constants are included in Tables VII and VIII.

Table VII. Experimentally determined constants of deuterated methyl chloride

Compound	Transition	Frequency in Mc	eQ_q	ν_0	B_0	I_B in Mc	Ref.
$C^{12}D_3Cl^{35}$	3/2 → 1/2	21702.49	-74.62	21683.82	10841.91	46.627485	a
	3/2 → 3/2	21668.93					
	3/2 → 5/2	21687.52					
$C^{12}D_3Cl^{37}$	3/2 → 1/2	21331.60	-58.7	21316.92	10658.46	47.430022	a
	3/2 → 3/2	21305.17					
	3/2 → 5/2	21319.84					
$C^{13}D_3Cl^{35}$	3/2 → 1/2	21128.24	-74.60	21109.59	10554.80	47.895839	a
	3/2 → 3/2	21094.67					
	3/2 → 5/2	21113.33					
$C^{13}D_3Cl^{37}$	3/2 → 1/2	20753.46	-58.7	20738.77	10369.39	48.752241	a
	3/2 → 3/2	20727.06					
	3/2 → 5/2	20741.68					
$C^{12}D_3Cl^{35}$	3/2 → 1/2	21702.36	-74.41	21683.75	10841.88	46.6170631	b
	3/2 → 3/2	21668.88					
	3/2 → 5/2	21687.46					
$C^{12}D_3Cl^{37}$	3/2 → 1/2	21331.51	-58.58	21316.86	10658.43	47.419374	b
	3/2 → 3/2	21305.15					
	3/2 → 5/2	21319.79					

[a] This work. [b] Reference 27.

Table VIII. Experimentally determined constants of deuterated methyl bromide

Compound	Transtion	Frequency in Mc	eQ_q	ν_0	B_0	I_B in Mc	Ref.
$C^{12}D_3Br^{79}$	3/2 → 1/2	15285.77	575.61	15429.25	7714.62	65.528956	a
	3/2 → 3/2	15544.73					
	3/2 → 5/2	15400.69					
$C^{12}D_3Br^{81}$	3/2 → 1/2	15242.50	480.94	15362.43	7681.22	65.813894	a
	3/2 → 3/2	15458.87					
	3/2 → 5/2	15338.55					
$C^{13}D_3Br^{79}$	3/2 → 1/2	14739.37	575.64	14882.85	7441.42	67.934749	a
	3/2 → 3/2	14998.29					
	3/2 →5/2	14854.30					
$C^{13}D_3Br^{81}$	3/2 → 1/2	14695.54	480.60	14815.38	74.07.69	68.244081	a
	3/2 → 3/2	14911.77					
	3/2 → 5/2	14791.46					
$C^{12}D_3Br^{79}$	1/2 → 1/2	30858.29	574.6	30858.29	7714.57	65.514540	b
J=1 → 2	1/2 → 3/2	31002.39					
	3/2 → 3/2	30743.91					
	3/2 → 5/2	30845.98					
	5/2 → 7/2	30846.06					
$C^{12}D_3Br^{81}$	1/2 → 1/2	30724.93	479.8	30724.93	7681.23	65.798907	b
J = 1 → 2	3/2 → 3/2	30629.35					
	3/2 → 5/2	30714.71					
	5/2 → 7/2	30714.65					

[a] This work. [b] Reference 27.

From the equation $a = [\mu^{-1}(\Delta I_b)]^{1/2}$ derived in Section 3.6, the coordinates of the carbon atom and the halogen were determined. The use of four isotopic species permit each one in turn to be used as the parent compound with its appropriate isotopes. The ΔI_b is the difference in the moment of inertia of the substituted species and the chosen parent molecule. The sum of the coordinates of the carbon atom, which lies below the center of mass and the chlorine atom above the center of mass is the internuclear distance. Only absolute values of the coordinates are obtained from this calculation. The sign of the coordinate must be determined from other available information. The calculated bond distances from the experimentally determined moments of inertia for methyl chloride and methyl bromide are given in Table IX.

Identical calculations were performed to determine the carbon halogen distances in the ordinary methyl chloride and bromide. The rotational constants used in the calculations were determined from a literature search of all original experimental work since 1945. The following criteria were used in the order listed to determine the best B value:

1. For any compound in which three measurements agreed within 0.03 Mc, the average of the three values was used.

2. The value of B used was the average determined for any one compound.

The B values of $^{13}CH_3{}^{79}Br$ and $^{13}CH_3{}^{81}Cl$ determined by Matlock, Glockner and Bianco(9) were substantially different from the values determined by Dailey, May and Townes(16). The latter B value was reported in two separate papers by Townes and Kisliuk(28,29) with reference to the

Table IX. Carbon-halogen bond distances of deuterated methyl bromide and methyl chloride

Compound[a]		Coordinate	C-X (Å)
$\underline{^{12}\mathrm{CD}_3{}^{35}\mathrm{Cl}}$	$^{13}\mathrm{CD}_3{}^{35}\mathrm{Cl}$	1.134739	1.780404
$\underline{^{12}\mathrm{CD}_3{}^{35}\mathrm{Cl}}$	$^{12}\mathrm{CD}_3{}^{37}\mathrm{Cl}$	.645665	
$\underline{^{12}\mathrm{CD}_3{}^{37}\mathrm{Cl}}$	$^{13}\mathrm{CD}_3{}^{37}\mathrm{Cl}$	.666756	1.780417
$\underline{^{12}\mathrm{CD}_3{}^{37}\mathrm{Cl}}$	$^{12}\mathrm{CD}_3{}^{35}\mathrm{Cl}$	1.113661	
$\underline{^{13}\mathrm{CD}_3{}^{35}\mathrm{Cl}}$	$^{13}\mathrm{CD}_3{}^{37}\mathrm{Cl}$	1.158197	1.780380
$\underline{^{13}\mathrm{CD}_3{}^{35}\mathrm{Cl}}$	$^{12}\mathrm{CD}_3{}^{35}\mathrm{Cl}$	.622192	
$\underline{^{13}\mathrm{CD}_3{}^{37}\mathrm{Cl}}$	$^{13}\mathrm{CD}_3{}^{35}\mathrm{Cl}$	.642983	1.780431
$\underline{^{13}\mathrm{CD}_3{}^{37}\mathrm{Cl}}$	$^{12}\mathrm{CD}_3{}^{37}\mathrm{Cl}$	1.137448	
$\underline{^{12}\mathrm{CD}_3{}^{79}\mathrm{Br}}$	$^{13}\mathrm{CD}_3{}^{79}\mathrm{Br}$	1.556215	1.937662
$\underline{^{12}\mathrm{CD}_3{}^{79}\mathrm{Br}}$	$^{13}\mathrm{CD}_3{}^{81}\mathrm{Br}$	.381447	
$\underline{^{12}\mathrm{CD}_3{}^{81}\mathrm{Br}}$	$^{12}\mathrm{CD}_3{}^{79}\mathrm{Br}$	.373744	1.937666
$\underline{^{12}\mathrm{CD}_3{}^{81}\mathrm{Br}}$	$^{13}\mathrm{CD}_3{}^{81}\mathrm{Br}$	1.563922	
$\underline{^{13}\mathrm{CD}_3{}^{79}\mathrm{Br}}$	$^{12}\mathrm{CD}_3{}^{79}\mathrm{Br}$	1.540276	1.937664
$\underline{^{13}\mathrm{CD}_3{}^{79}\mathrm{Br}}$	$^{13}\mathrm{CD}_3{}^{81}\mathrm{Br}$	.397378	
$\underline{^{13}\mathrm{CD}_3{}^{81}\mathrm{Br}}$	$^{13}\mathrm{CD}_3{}^{79}\mathrm{Br}$	.389455	1.937680
$\underline{^{13}\mathrm{CD}_3{}^{81}\mathrm{Br}}$	$^{13}\mathrm{CD}_3{}^{81}\mathrm{Br}$	1.548225	

[a] The parent compound is underlined.

original work. Frequency measurements listed in the two papers differed considerably, although the rotational constants were in perfect agreement. The three lines were remeasured in this laboratory and the rotational constant was calculated. The measured quadrupole splittings and the rotational constants were found to compare favorably with the values of Matlock, Glockner and Bianco. Consequently these values were used.

Table X lists the values used in the calculation of the carbon halogen internuclear distances. The calculated values for the carbon halogen bond length in methyl chloride and methyl bromide are shown in Table XI.

Table X. Best Values of methyl chloride and methyl bromide from references

Compound	ν_0	B(Mc/sec)	I_B(amuÅ)	References Used
$^{12}CH_3{}^{35}Cl$	26585.78	13292.89	38.030180	6, 10, 13, 14
$^{12}CH_3{}^{37}Cl$	26176.37	13088.19	38.624974	6, 10, 13
$^{13}CH_3{}^{35}Cl$	25592.42	12796.21	39.506276	9, 16
$^{13}CH_3{}^{37}Cl$	25197.54	12589.77	40.154109	9, 16
$^{12}CH_3{}^{79}Br$		9568.20	52.834493	10, 13, 14
$^{12}CH_3{}^{81}Br$		9531.84	53.036035	10, 13, 14
$^{13}CH_3{}^{79}Br$		9119.51	55.434009	17
$^{13}CH_3{}^{81}Br$		9082.86	55.657689	17

Table XI. Carbon-halogen bond distances of methyl chloride and methyl bromide

Compound[a]		Coordinate	C - X (Å)
$^{12}CH_3{}^{79}Br$	$^{13}CH_3{}^{79}Br$	1.617923	1.938832
$^{12}CH_3{}^{79}Br$	$^{12}CH_3{}^{81}Br$	.320909	
$^{13}CH_3{}^{81}Br$	$^{12}CH_3{}^{81}Br$	1.607804	1.938875
$^{13}CH_3{}^{81}Br$	$^{13}CH_3{}^{79}Br$	.331071	
$^{13}CH_3{}^{79}Br$	$^{13}CH_3{}^{81}Br$	.338038	1.938863
$^{13}CH_3{}^{79}Br$	$^{12}CH_3{}^{79}Br$	1.600825	
$^{12}CH_3{}^{81}Br$	$^{12}CH_3{}^{79}Br$	.314226	1.938845
$^{12}CH_3{}^{81}Br$	$^{13}CH_3{}^{81}Br$	1.624619	
$^{12}CH_3{}^{35}Cl$	$^{13}CH_3{}^{35}Cl$	1.224833	1.781291
$^{12}CH_3{}^{35}Cl$	$^{12}CH_3{}^{37}Cl$	.556485	
$^{12}CH_3{}^{37}Cl$	$^{13}CH_3{}^{37}Cl$	1.246188	1.781273
$^{12}CH_3{}^{37}Cl$	$^{12}CH_3{}^{35}Cl$	.535085	
$^{13}CH_3{}^{35}Cl$	$^{13}CH_3{}^{37}Cl$	.580521	1.781255
$^{13}CH_3{}^{35}Cl$	$^{12}CH_3{}^{35}Cl$	1.200734	
$^{13}CH_3{}^{37}Cl$	$^{13}CH_3{}^{35}Cl$	.558644	1.781233
$^{13}CH_3{}^{37}Cl$	$^{12}CH_3{}^{37}Cl$	1.222579	

[a] Parent compound is underlined.

5.6 Error Analysis

To determine the experimental uncertainty in the internuclear distance an equation relating the distance to the necessary hypothetical unsplit frequencies was derived and differentiated. An experimental uncertainty of ± 0.03 Mc/sec in the frequency measurements was assumed for the calculations.

If a_1 is the a coordinate of a substituted atom on the symmetry axis and I and I_1 are the moments of inertia of the parent and substituted species, respectively, it was shown above that

$$a_1 = [\mu_2^{-1} (I_2 - I)]^{1/2}$$

If the two atoms are on opposite sides of the center of mass

$$r_{12} = r = a_1 + a_2 = [\mu_1^{-1} (I_1 - I)]^{1/2} + [\mu_2^{-1} (I_2 - I)]^{1/2}.$$

Then

$$r = [\mu_1^{-1} K(\frac{1}{B_1} - \frac{1}{B})]^{1/2} + [\mu_2^{-1} K(\frac{1}{B_2} - \frac{1}{B}]^{1/2}$$

$$= [2\mu_1^{-1} K(\frac{1}{\nu_1} - \frac{1}{\nu})]^{1/2} + [2\mu_2^{-1} K(\frac{1}{\nu_2} - \frac{1}{\nu})]^{1/2}$$

$$= [\frac{2K(\nu - \nu_1)}{\mu_1 \nu \nu_1}]^{1/2} + [\frac{2K(\nu - \nu_2)}{\mu_2 \nu \nu_2}]^{1/2}$$

Here $K = 505531$ a.m.u.-Å²-Mc/sec. Since ν, ν_1, and ν_2 are approximately equal

$$r = [\frac{2K\Delta_1}{\mu_1 \nu^2}]^{1/2} + [\frac{2K\Delta_2}{\mu_2 \nu^2}]^{1/2}$$

where $\Delta_1 = \nu - \nu_1$ and $\Delta_2 = \nu - \nu_2$.

Differentiation of the above equation for r then gives

$$r = (R_1 + R_2)\delta\nu - R_1 \delta\nu_1 - R_2 \delta\nu_2,$$

where $R_1 = \left(\frac{K}{2\mu_1\Delta_1\nu^2}\right)^{1/2}$ and $R_2 = \left(\frac{K}{2\mu_2\Delta_2\nu^2}\right)^{1/2}$.

The propagated uncertainty is then

$$\delta r = [(R_1 + R_2)^2 \delta\nu^2 + R_1^2 \delta\nu_1^2 + R_2^2 \delta\nu_2^2]^{1/2}.$$

The values of R_1 and R_2 calculated from the hypothetical unsplit frequencies of the methyl chlorides are shown in Table XII. The propagated experimental uncertainty in the internuclear distances assuming 0.03 Mc/sec uncertainty in the frequency measurements is 4.7×10^{-5} Å.

Table XII. Constants in the error analysis

	$^{12}CH_3{}^{35}Cl$	$^{13}CH_3{}^{35}Cl$	$^{12}CH_3{}^{37}Cl$
$\mu^{-1/2}$		1.0008137	.721523
$K^{1/2}$	711.01		
$_i$	26585.78	25592.42	26176.38
$_i^{1/2}$	163.05	159.98	161.79
Δ_i		993.36	409.40
$\Delta_i^{1/2}$		31.52	20.23
R_i		6.12×10^{-4}	6.80×10^{-4}
R_i^2		36.31×10^{-8}	45.6×10^{-8}
$R_1 + R_2$	12.92×10^{-4}		
$(R_1 + R_2)^2$	16.69×10^{-7}		

VI. DISCUSSION AND CONCLUSIONS

In the previous section it was shown that the carbon-chlorine distance decreases 0.0008 Å and the carbon-bromine distance decreases 0.0011 Å upon deuteration of the appropriate methyl halide. The question then, is what is the origin of the decrease in bond distance.

First to be examined are possible experimental uncertainties. It was also shown in the previous section that the strictly experimental uncertainty in the carbon-halogen distances was approximately 6.6 x 10^{-5} Å, a small fraction of the observed decrease. No account has been taken of the possible effects of centrifugal distortion. However, an estimation of the effect shows it to be completely negligible.

The second and most likely source of the shorter distances is a vibration-rotation interaction. The distances determined are substitution parameters, and though they are often believed to be close to equilibrium values, some differences always remain. Thus if the average C-Cl distance in the deuterated methyl chlorides is less than in the corresponding hydrogen compounds, one would expect the decrease to appear in the substitution parameters.

The changes of 0.0008 Å in the C-Cl distance and 0.0011 Å in the C-Br appear to be consistent with the changes in average bond length suggested by Bartell (19). Bartell predicted a decrease of 0.003 Å in the average C-C bond length upon complete deuteration of ethane. His prediction was based on a consideration of the relaxation of non-bonded repulsions which would occur upon deuteration owing to the smaller amplitude of vibration of deuterium atoms relative to hydrogen. In the methyl halides only three hydrogen atoms are involved, and one would expect the effect to be smaller.

The lower force constant of the carbon-bromine stretch in CH_3Br (2.3×10^5 dyne/cm vs. 3.8×10^5 dyne/cm for C-Cl in CH_3Cl (30)) and the larger size of the bromine atom are consistent with the greater shortening found for C-Br than for C-Cl.

Another important vibration-rotation effect can be ruled out. Laurie (32) has shown that average interatomic distances between non-hydrogenic atoms decrease upon substitution of a heavier isotopic species for one or both of the atoms. This decrease is very small, approximately 0.00005 Å, but is important because it is greatly magnified by the substitution method.

To determine the effect of this decrease a series of calculations were made on $^{12}CH_3{}^{35}Cl$, $^{12}CH_3{}^{37}Cl$, $^{13}CH_3{}^{35}Cl$, $^{13}CH_3{}^{37}Cl$, and the corresponding deuterated methyl chlorides. The moments of inertia of all the species were computed using an assumed structure which was (a) the same for all species, and (b) which was the same for all species except that the $^{12}C^{37}Cl$ and $^{13}C^{35}Cl$ bond lengths were 0.00005 Å shorter, and the $^{13}C^{37}Cl$ bond was 0.0001 Å shorter than the $^{12}C^{35}Cl$ bond length.

The moments of inertia from these calculations were then used to compute the C-Cl bond distances by the substitution method. The results of these calculations and similar ones for CH_3Br are shown in Table XIII. If Laurie's suggestion is correct, and if 0.00005 Å is a reasonable value to use, the C-Cl distance in CH_3Cl is apparently 0.0018 Å longer than the value shown in Table XI and the C-Cl distance is 0.0020 Å longer than the value shown for CD_3Cl in Table IX. Thus we have recovered 0.0002 Å of the apparent shortening but no reasonable parameters would enable recovery of much more. A similar conclusion is reached for CH_3Br.

Table XIII. Carbon-halogen bond distances in methyl chloride and methyl bromide computed assuming 0.00005 Å decrease in the C-X bond distance upon substitution of heavier isotopic species.

Parent Species	C-X (Assumed)	C-X (Calculated)
$^{12}CH_3{}^{35}Cl$	1.78100	1.77923
$^{12}CD_3{}^{35}Cl$	1.78100	1.77903
$^{12}CH_3{}^{79}Br$	1.93900	1.93614
$^{12}CD_3{}^{79}Br$	1.93900	1.93595

A final possibility for the apparent decrease in bond length upon deuteration is a failure of the Born-Oppenheimer approximation. The only way to determine the cause of the decrease would be a completely accurate calculation of vibration-rotation effects, or by a determination of the equilibrium moments of inertia for all of the species. Of these two possibilities the latter seems much more likely, but still represents an extremely difficult experimental problem.

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