

Microwave Spectrum of Chloroform

Peter N. Wolfe

Citation: *The Journal of Chemical Physics* **25**, 976 (1956); doi: 10.1063/1.1743153

View online: <http://dx.doi.org/10.1063/1.1743153>

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Microwave Spectrum of Chloroform*

PETER N. WOLFE†

Department of Physics and Astronomy, The Ohio State University, Columbus, Ohio

(Received November 15, 1955)

A theoretical and experimental examination of the $J=2 \rightarrow 3$ transition in CHCl_3^{35} permits the evaluation of the quadrupole coupling constant of the molecule as $eQV_{zz} = 28.70 \pm 0.08$ Mc, and provides an improved value of the rotational constant, $B = 3302.41 \pm 0.03$ Mc. Two centrifugal distortion coefficients are also obtained: $D_J = 4.12 \pm 0.43$ kc and $D_{JK} = 55 \pm 7$ kc. The $J=2 \rightarrow 3$ transitions in $\text{CHCl}_2^{35}\text{Cl}^{37}$ yield the following, revised structural parameters for chloroform: $\text{C}-\text{H} = 1.073$ Å, $\text{C}-\text{Cl} = 1.762$ Å, and $\text{Cl}-\text{C}-\text{Cl} = 110^\circ 55'$. With the assumption of axial charge symmetry about the $\text{C}-\text{Cl}$ bond direction, a , the revised bond angle gives $eQV_{aa} = -80.39 \pm 0.22$ Mc for the quadrupole coupling constant in CHCl_3^{35} .

INTRODUCTION

PREVIOUS microwave absorption studies of the chloroform molecule¹⁻⁴ have been primarily concerned with structural determinations from the spectra of the symmetric rotor species. In the analysis of the data, the molecule has been treated as a rigid rotor, free from nuclear quadrupole perturbation energies.

The present investigation treats the two abundant species of chloroform, CHCl_3^{35} and $\text{CHCl}_2^{35}\text{Cl}^{37}$, in somewhat greater detail, taking into account the nuclear quadrupole interaction and the effects of centrifugal distortion. The symmetric species is treated conventionally in the evaluation of these effects, and the asymmetric species is considered to be very nearly a symmetric rotor with respect to centrifugal distortion and nuclear effects. The rotational constants for this species then yield a revised set of structural parameters for the molecule.

EXPERIMENTAL

Commercial, chemically pure chloroform was employed as a sample in this investigation. Its relatively high vapor pressure at room temperature facilitates its introduction into the vacuum system. In order to increase the population of the ground vibrational state, the absorption cell was cooled by the application of dry ice. An operating pressure of about 5 microns of mercury, as indicated by a thermocouple vacuum gauge, was found to be a satisfactory compromise between considerations of absorption intensities and pressure broadening of the nuclear quadrupole hyperfine structure components. Since hyperfine detail was of less interest in the case of the asymmetric species, these

spectra were obtained at pressures of about 30 microns, in order to augment the intensities of this less abundant species.

The spectrometer employed in this work is a conventional 6 kilocycle Stark-modulation type of instrument, employing a square-wave modulation system. Radio-frequency power is supplied by a 2K33-type reflex klystron, which is swept mechanically through the frequency region of interest by a 1 rpm synchronous motor, coupled to the klystron's tuning mechanism by a heavy-duty 48:1 speed reducer. A wave-guide tee divides the power into two parts: One portion is supplied to a 1N26 crystal diode associated with the frequency measuring system, where its frequency is determined either approximately by a wave meter preceding that crystal, or more precisely by comparison with standard markers originating in a secondary frequency standard. The remainder of the power passes through the absorption cell to a second 1N26 diode, which serves as a detector.

The absorption cell is a ten-foot length of K -band wave guide, sealed at each end by a mica window and a rubber O-ring, which are compressed between the flush flanges which connect the cell to the remainder of the wave-guide system. A single hole, 0.0635 in. in diameter, in the broad face of the cell serves as a gas port for passing the sample to and from the gas handling system. The cell is fitted with a Stark electrode of 26 gauge (0.0188 in. thick) copper sheet, parallel to the broad face, running the full length of the cell, and supported at either edge by grooved Teflon tape.

Signal voltages from the detector crystal are applied to a narrow-band preamplifier chain, whose output is applied to a square-wave-referenced phase detector,⁵ actuating an Esterline-Angus chart recorder. This recorder is provided with a pair of auxiliary side pens, which are controlled by the frequency measuring system to provide frequency calibration points on the recordings.

The frequency measuring system contains three main components: (i) A crystal controlled secondary frequency standard compared with WWV provides markers at 5 Mc intervals throughout the microwave region, at the terminals of the 1N26 diode. This diode generates

* H. L. Cox, *Rev. Sci. Instr.* **24**, 307 (1953).

* This work was supported in part by a contract between the Office of Scientific Research of the Air Research and Development Command, Baltimore, Maryland, and The Ohio State University Research Foundation.

† National Science Foundation Fellow. Present address: Westinghouse Research Center, Pittsburgh 35, Pennsylvania.

¹ W. V. Smith and R. R. Unterberger, *J. Chem. Phys.* **17**, 1348 (1949).

² Unterberger, Trambarulo, and Smith, *J. Chem. Phys.* **18**, 565 (1950).

³ T. L. Weatherly, Ph.D. Dissertation, The Ohio State University (1951).

⁴ Ghosh, Trambarulo, and Gordy, *J. Chem. Phys.* **20**, 605 (1952).

beat frequencies which are the differences between the standard markers and the unknown klystron frequency. These are detected by (ii) two National HRO-50 communications receivers. One of these is tuned to 5.625 Mc and the other to 6.875 Mc, so that the first receiver gives an indication each time the klystron frequency reaches plus-or-minus 0.625 Mc from a standard marker, while the second receiver performs similarly at plus-or-minus 1.875 Mc. Indications from these receivers pass to (iii) a pen control unit, where they trigger thyratrons which actuate the side pens of the chart recorder, providing marks in the margin of the chart at 1.25 Mc intervals, as the klystron is tuned.

Stark-modulation voltage is supplied by a square-wave generator, whose output is biased to zero on alternate half-cycles. Relatively low Stark fields (about 600 volts/cm) are employed throughout the investigation in order to prevent second order Stark components from being sufficiently displaced to interfere with nuclear quadrupole hyperfine structure components. As a consequence, $K=0$ components are not observed, since these possess no first-order Stark effect. In order to make the $J=2 \rightarrow 3$, $K=0$ transition observable in the light asymmetric species of chloroform, an exception is made and a Stark field of about 1800 volts/cm is employed.

NUCLEAR QUADRUPOLE INTERACTION THEORY

The light, abundant, symmetric species of chloroform, CHCl_3^{35} , contains three identical chlorine nuclei of spin $3/2$, which possess nuclear electric quadrupole moments. By means of these moments, the nuclear spin angular momenta, \mathbf{I}_i , $i=1, 2, 3$, are coupled with the rotational angular momentum, \mathbf{J} , of the molecule to produce a resultant total angular momentum, $\mathbf{F} = \mathbf{J} + \mathbf{I}_1 + \mathbf{I}_2 + \mathbf{I}_3$. As a consequence, the unperturbed rotational energy levels for a rigid symmetric rotor,

$$E = E^0 = BJ(J+1) - (B-C)K^2, \quad (1)$$

are perturbed by the addition of a term, E^1 , the perturbation energy due to the nuclear quadrupole interaction.

In order to follow the method of Bersohn,^{6,7} which makes use of Racah algebra⁸ in determining E^1 , the following, arbitrary, unsymmetrical-appearing coupling scheme is employed in writing the nuclear-rotational wave functions for the F representation:

$$\begin{aligned} \mathbf{I}_1 + \mathbf{I}_2 = \mathbf{L}, \quad L = I_1 + I_2, \quad I_1 + I_2 - 1, \quad \dots, \quad |I_1 - I_2| \\ \mathbf{L} + \mathbf{I}_3 = \mathbf{I}, \quad I = L + I_3, \quad L + I_3 - 1, \quad \dots, \quad |L - I_3| \\ \mathbf{I} + \mathbf{J} = \mathbf{F}, \quad F = I + J, \quad I + J - 1, \quad \dots, \quad |I - J| \end{aligned}$$

The required wave functions are then $\langle I_1 I_2 I_3 L I J K F M |$.

Perturbation theory specifies the E^1 as roots of the secular determinant

$$|H_{rr'} - E^1 \delta(rr')| = 0,$$

where H^1 is the nuclear quadrupole interaction Hamiltonian, r specifies the state $\langle I_1 I_2 I_3 L I J K F M |$, and r' the state $\langle I_1 I_2 I_3 L' I' J K F' M' |$.

A classical consideration of the electrostatic interaction between the nuclear quadrupoles and the electric field of the remainder of the molecule⁶ shows that H^1 may be written as the scalar product of two irreducible tensor operators of order two:

$$H^1 = Q \cdot \nabla E.$$

One of these (Q) operates only on \mathbf{I} , and the other (∇E) operates only on \mathbf{J} , so that the Racah theory⁸ for such operators is applicable.

Rather than write the matrix elements $H_{rr'}$ at this point, it is convenient to take account of the identity of the three quadrupolar nuclei in order to first effect a partial diagonalization of the perturbation energy matrix.

The group of permutations on three identical things has three irreducible representations, A_1 , A_2 , and E . A_1 is the one-by-one identity representation, A_2 is the one-by-one alternating representation, and E is two-by-two. Since three identical nuclei are involved in this problem, the nuclear states, $\langle LI |$, must belong to one or more of these representations. The possible states for nuclei of spin $3/2$ are

$L:$	3	2	1	0
$I:$	9/2			
	7/2	7/2		
	5/2	5/2	5/2	
	3/2	3/2	3/2	3/2
	1/2	1/2		

The representations to which these states belong are:

for L odd—

$I=9/2$	A_1
7/2	E
5/2	A_1 and E
3/2	A_1 and E
1/2	E

for L even—

$I=7/2$	E
5/2	E
3/2	A_2 and E
1/2	E

Because of the identity of the three nuclei, the quadrupole Hamiltonian is invariant under their exchange, and therefore commutes with the operators of the group. Hence it is possible to perform a transformation from the $\langle LI |$ nuclear representation to a representation $\langle SI |$, $S=A_1, A_2, E$, in which the energy matrix elements are diagonal in S . This follows because

⁶ R. Bersohn, Ph.D. Thesis, Harvard University (1949).

⁷ R. Bersohn, J. Chem. Phys. 18, 1124 (1950).

⁸ G. Racah, Phys. Rev. 62, 438 (1942).

TABLE I. The coefficients $\lambda(SII')$.

S	$2I$	$2I'$	λ
A_1	9	9	-2.87228
	5	5	-0.45826
	3	3	0.60000
	9	5	-1.50000
	9	3	0.00000
	5	3	-1.95959
A_2	3	3	-1.00000
E	7	7	0.92582
	5	5	0.13094
	3	3	1.40000
	1	1	0.00000
	7	5	-0.90712
	7	3	1.38564
	7	1	0.00000
	5	3	1.20000
	5	1	-0.64808
	3	1	0.69282

the three S states are mutually orthogonal. When these transformations are employed, the non-vanishing matrix elements of H^1 diagonal in J become:

$$(SIJKF|H^1|SI'JKF) = (-1)^{F-J+\frac{1}{2}}\lambda(SII')G(JK)W(IJI'J;F2). \quad (2)$$

The coefficients $\lambda(SII')$ are given in Table I.⁹ W is the Racah coefficient,⁸ tables of which have been published.¹⁰ The coefficient,

$$G(JK) = \left(\frac{3}{2}\|Q\|\frac{3}{2}\right)(JK\|\nabla E\|JK),$$

where the matrices are the reduced matrices of the

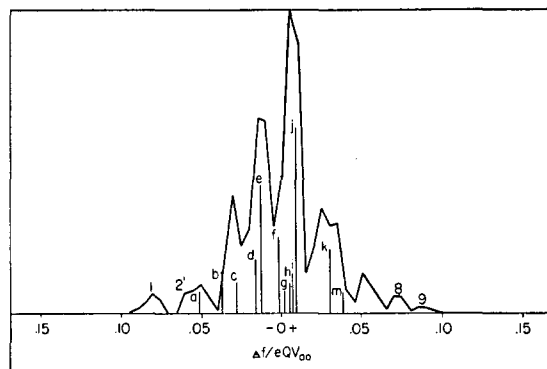


FIG. 1. Predicted hyperfine pattern for $J=2\rightarrow 3$, $K=1$. Shown are the sums of intensities at intervals of $.005eQV_{ao}$, each sum containing all components which lie within $\pm .005eQV_{ao}$ of its center. Also indicated are the most intense hyperfine components, designated as a, b, c , etc. Close multiplets are considered as a single component whose intensity is the sum of the component intensities, and whose frequency is the intensity-weighted mean of the component frequencies.

⁹ The $\langle LI|\rightarrow\langle SI|$ transformations given by Bersohn⁶ contain several errors of sign, which have been corrected here. Consequently, his table of matrix elements (which is essentially equivalent to Table I) contains numerical errors, as well as errors in some of the algebraic signs, due to the factor $(-1)^{F-J+\frac{1}{2}}$.

¹⁰ Simon, Vander Sluis, and Biedenharn, *Tables of the Racah Coefficients* (Oak Ridge National Laboratory publication No. ORNL 1679, 1954).

Racah theory,⁸ can be reduced to common parameters^{6,11}:

$$G(JK) = -g(JK)eQV_{zz}, \quad (3)$$

where

$$g(JK) = \frac{3K^2 - J(J+1)}{2(J+1)} \left[\frac{5(2J+2)(2J+1)}{(2J+3)(2J)(2J-1)} \right]^{\frac{1}{2}}, \quad (4)$$

eQ is the electric quadrupole moment of the chlorine nucleus, and V_{zz} is the second partial derivative of the electric potential at the chlorine nucleus (due to extranuclear charges), with respect to z , the symmetry axis of the molecule.

In order to compare the quadrupole coupling constant for chloroform with that of other methyl chlorides, it is convenient to express V_{zz} in terms of V_{aa} , where a is the C-Cl bond direction. If one assumes axial charge symmetry about the C-Cl bond, which makes an angle β with the molecular symmetry axis, z (the C-H bond direction), one obtains¹¹

$$V_{zz} = -\frac{1}{2}(1 - 3\cos^2\beta)V_{aa}, \quad (5)$$

or

$$G(JK) = \frac{1}{2}(1 - 3\cos^2\beta)g(JK)eQV_{aa}. \quad (6)$$

The perturbation energy matrix elements are now computed from Eq. (2), Table I, and Eq. (6), with

$$\frac{1}{2}(1 - 3\cos^2\beta) = -\cos 2\alpha, \quad (7)$$

where 2α is the angle Cl-C-Cl, here taken to be $110^\circ 24'$.⁴ Diagonalization of this matrix yields the perturbation energies $E^1/g(JK)$, for each value of J of interest, and evaluation of $g(JK)$ for the required values of K completes the energy computation.

The particular transitions of interest in the present investigation involve $J=2\rightarrow 3$, with $K=1, 2$. A consideration of the symmetry properties of the vibrational and rotational states,¹² together with the assumption of a totally symmetric ground electronic state, shows that the nuclear levels associated with these rotational states are those having E character, for the molecule in the ground vibrational state.

Relative intensities of the various hyperfine components of a given transition, $J\rightarrow J+1$, are computed as the square of the matrix elements of the Z -component of the permanent electric dipole moment of the molecule, between the initial and final nuclear-rotational states involved in the transition. This computation yields the following selection rules for the transitions $J\rightarrow J+1$:

$$\begin{aligned} \Delta K &= 0, \\ S &\rightarrow S, \\ \Delta F &= 0, \pm 1, \\ \Delta M &= 0. \end{aligned}$$

Since the hyperfine splitting is independent of M , the intensities are summed over this quantum number.

¹¹ M. Mizushima and T. Ito, *J. Chem. Phys.* **19**, 739 (1951).

¹² D. M. Dennison, *Revs. Modern Phys.* **3**, 280 (1931).

The appearance of the factor, $3K^2 - J(J+1)$, in the expression for $g(JK)$ (Eq. (4)) causes the $J=3$, $K=2$ hyperfine levels to degenerate into a single, unsplit level. For this case, it can be shown that the relative intensities of the hyperfine components belonging to $J=2 \rightarrow 3$, $K=2$ are simply proportional to $2F+1$, where F specifies the initial state.

Predicted nuclear quadrupole hyperfine structure patterns for $J=2 \rightarrow 3$ in chloroform are shown in Fig. 1, for $K=1$, and in Fig. 2, for $K=2$.

For reanalysis of the results of others, for transitions other than $J=2 \rightarrow 3$, it is convenient to have an expression for the frequency shift of the most intense hyperfine component for $J \rightarrow J+1$. An examination of the relative-intensity theory shows that this component belongs to the set $K=1$, and is specified by $F=J+7/2 \rightarrow J+9/2$. The frequency shift associated with this component is then

$$\Delta f = \alpha(J)eQV_{aa}, \quad (8)$$

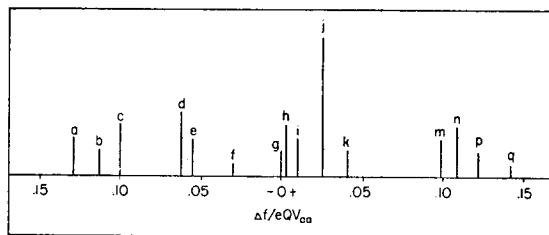


FIG. 2. Predicted hyperfine components for $J=2 \rightarrow 3$, $K=2$.

where

$$\alpha(J) = \frac{(3/8)(1 - 3 \cos^2 \beta)}{(J+1)(J+2) + (4J+7)} \times \frac{(J+1)(J+2) + (4J+7)}{(2J+5)(2J+3)(J+2)(J+1)}. \quad (9)$$

Since the $J=0 \rightarrow 1$ transition does not have a $K=1$ set of components, the expression does not apply to this case.

OBSERVATIONS AND ANALYSIS

Figure 3 shows the $J=2 \rightarrow 3$ transition in CHCl_3^{35} , as observed in the present experiments. Comparison of this tracing with Figs. 1 and 2 indicates qualitative agreement between experiment and theory. However, in order to effect a satisfactory fit, it is necessary to include the effects of centrifugal distortion in the unperturbed rotational frequency expression:

$$f = 2B(J+1) - 4D_J(J+1)^3 - 2D_{JK}(J+1)K^2.$$

The term involving D_{JK} allows different pattern "centers" for the $K=1$ and the $K=2$ components.

The components a , b , c , m , n , p , and q of $K=2$ (Fig. 2) appear to fall in such a position that there is no interference from the $K=1$ pattern. An examination of Fig. 3 suggests that these seven predicted components be taken as the A , B , C , N , P , Q , and R prominences of

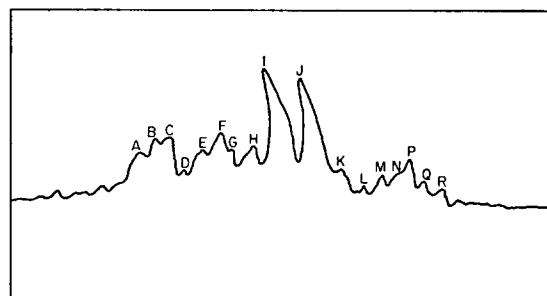


FIG. 3. The observed $J=2 \rightarrow 3$ pattern in CHCl_3^{35} .

the experimental spectrum shown there. With this assignment, a least squares fit is made of the seven theoretical $K=2$ frequencies to the 48 raw data which comprise the averages given in Table II for the foregoing seven prominences. The results of this determination are:

$$eQV_{aa} = -82.35 \pm .22 \text{ Mc}$$

$$6B - 108D_J - 24D_{JK} = 19812.70 \pm .03 \text{ Mc.}$$

This fit predicts $19810.65 \pm .04 \text{ Mc}$ as the frequency of the most intense, j component of the $K=2$ pattern, which must therefore correspond to the observed feature, J , at $19810.57 \pm .05 \text{ Mc}$. The remaining important prominence, K , of the observed pattern can then be attributed only to the most intense $K=1$ component, j . From this assignment,

$$6B - 108D_J - 6D_{JK} = 19813.69 \pm .10 \text{ Mc,}$$

which, combined with the preceding expression, gives

$$D_{JK} = 55 \pm 7 \text{ kc}$$

$$6B - 108D_J = 19814.02 \pm .14 \text{ Mc.}$$

The above parameters yield the predicted hyperfine-component frequencies listed in Table II, which also gives the experimental values for comparison. Theory and experiment are also compared in Fig. 4. The

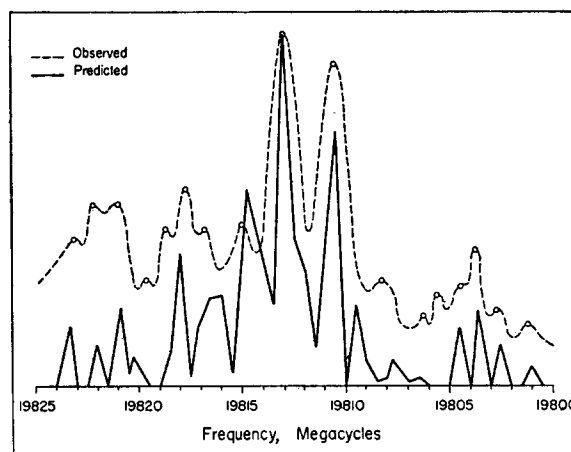


FIG. 4. Comparison of the calculated and observed $J=2 \rightarrow 3$ patterns in CHCl_3^{35} .

TABLE II. Comparison of observed and calculated hyperfine structure features.*

Observation			Calculation			
designation	frequency	intensity	<i>K</i>	designation	frequency	intensity
<i>A</i>	19823.08±.17	M	2	<i>a</i>	19823.30±.05	58
<i>B</i>	19822.19±.12	M	2	<i>b</i>	19822.04±.05	39
<i>C</i>	19821.00±.10	M	2	<i>c</i>	19820.91±.05	78
<i>D</i>	19819.65±.17	W	1	1	19820.29	29
<i>E</i>	19818.73±.17	W	1	2'	19818.35	31
<i>F</i>	19817.66±.13	M	{1	<i>a</i>	19817.91	34
			2	<i>d</i>	19817.83	97
			2	<i>e</i>	19817.21	58
<i>G</i>	19816.76±.14	W	{1	<i>b</i>	19816.74	65
			1	<i>c</i>	19816.03	46
<i>H</i>	19814.95±.10	M	{2	<i>f</i>	19815.21	19
			1	<i>d</i>	19814.97	83
			1	<i>e</i>	19814.72	200
<i>I</i>	19812.92±.10	S	{1	<i>f</i>	19813.81	118
			1	<i>g</i>	19813.52	35
			1	<i>h</i>	19813.26	46
			1	<i>i</i>	19813.07	59
			1	<i>j</i>	19812.92	288
			2	<i>g</i>	19812.70	39
			2	<i>h</i>	19812.47	78
			2	<i>i</i>	19811.91	58
<i>J</i>	19810.57±.05	S	{1	<i>k</i>	19811.17	99
			2	<i>j</i>	19810.65±.04	214
			1	<i>m</i>	19810.45	33
<i>K</i>	19808.28±.12	W	{2	<i>k</i>	19809.33	39
			1	8	19807.70	26
<i>L</i>	19806.21	W	1	9	19806.43	9
<i>M</i>	19805.57±.14	W				
<i>N</i>	19804.43±.16	W	2	<i>m</i>	19804.55±.05	58
<i>P</i>	19803.70±.16	M	2	<i>n</i>	19803.71±.05	78
<i>Q</i>	19802.67±.14	W	2	<i>p</i>	19802.64±.06	39
<i>R</i>	19801.23	W	2	<i>q</i>	19800.97±.06	19

* All frequencies are in megacycles. Intensities are S, strong; M, medium; W, weak. The observed prominences, F, G, H, I, J, and K, are attributed to the unresolved components bracketed on their right.

theoretical pattern of the latter consists of sums of all components at intervals of 0.5 Mc, each sum containing all components which lie within ± 0.25 Mc of the central point. Exceptions to this are cases in which an intense component falls between multiples of 0.5 Mc and would protrude through the line connecting consecutive points. Then the pattern is modified to contain the intense component.

The rotational constant, B , and the centrifugal distortion coefficient, D_J , are evaluated by applying the above results, with Eqs. (8) and (9) for the hyperfine shift of the most intense component, to the experimental determination of the frequency of the $J=6 \rightarrow 7$ transition ($46227.20 \pm .15$ Mc) of Unterberger, Trambarulo, and Smith²:

$$B = 3302.41 \pm .03 \text{ Mc},$$

$$D_J = 4.12 \pm .43 \text{ kc}.$$

THE ASYMMETRIC SPECIES

Three transitions in $\text{CHCl}_2^{35}\text{Cl}^{37}$ were observed in these experiments. The data were analyzed by assuming the molecule to be a rigid asymmetric rotor, modified by

centrifugal distortion effects given by the symmetric rotor expressions, and by nuclear quadrupole effects given by Eqs. (8) and (9). For the latter effect, an effective quadrupole coupling constant was employed,

$$(eQV_{aa})_{\text{effective}} = [N_{35} + N_{37}(Q^{37}/Q^{35})]eQV_{aa}/3.$$

Here N_{35} is the number of Cl^{35} nuclei in the molecule, N_{37} is the number of Cl^{37} nuclei, $Q^{37}/Q^{35} = .79$,¹³ and $eQV_{aa} = -82.4$ Mc as above. Hence,

$$(eQV_{aa})_{\text{effective}} = -77 \text{ Mc}.$$

The observed and calculated frequencies are listed in Table III. The rotational constants for this species which are employed in these calculations are

$$A = 3302.20 \text{ Mc},$$

$$B = 3187.19 \text{ Mc},$$

$$C = 1682.67 \text{ Mc}.$$

By assuming the C—H bond distance to be that given by Ghosh, Trambarulo, and Gordy,⁴ one can obtain the

¹³ R. Livingston, Phys. Rev. **82**, 289 (1951).

following revised set of structural parameters for the chloroform molecule:

C—H	1.073 Å (assumed),
C—Cl	1.762 Å,
Cl—C—Cl	110°55'.

DISCUSSION

In order to take account of the revised value for the bond angle Cl—C—Cl, the value of eQV_{aa} obtained for

TABLE III. Observed and calculated transitions in $\text{CHCl}_2^{35}\text{Cl}^{37}$.

Transition	f_{obs}	f_{calc}
$2_{11} \rightarrow 3_{21}$	$19298.31 \pm .21$	19298.30 Mc
$2_{20} \rightarrow 3_{10}$	$19492.81 \pm .17$	19492.98^a
$2_{21} \rightarrow 3_{11}$	$19643.13 \pm .01$	19643.11

* No correction for nuclear quadrupole effect has been made for this transition.

the symmetric species of chloroform must be modified (Eq. (6)). One obtains from this modification

$$eQV_{aa} = -80.39 \pm .22 \text{ Mc.}$$

Another coupling constant, independent of β , is

$$eQV_{zz} = 28.70 \pm .08 \text{ Mc.}$$

As shown in the theory, all hyperfine component displacements are proportional to this quantity.

Table IV lists the quadrupole coupling constants obtained from both microwave spectra and pure quadrupole resonance studies for the various methyl chlorides. Where necessary for the derivation of eQV_{aa} , the assumption of axial symmetry of charge about the C—Cl bond has been made. The coupling constant for chloroform obtained in the present investigation seems to fit the empirical sequences apparent in the table.

In Fig. 4, although there is general agreement between experiment and theory for the overall pattern, several

TABLE IV. The quadrupole coupling constant of Cl^{35} in the methyl chlorides.

Molecule	Gas		Solid	
	eQV_{aa}	reference	$ eQV_{aa} $	reference
CH_3Cl	-75.50 Mc	a	68.40 Mc	d
CH_2Cl_2	-78.4 ± 2	b	72.47	d
CHCl_3	$-80.39 \pm .22$	c	76.98	d
CCl_4			81.85	d

a R. Karplus and A. H. Sharbaugh, Phys. Rev. **75**, 889 (1949).

b R. J. Myers and W. D. Gwinn, J. Chem. Phys. **20**, 1420 (1952).

c Present investigation.

d R. Livingston, J. Chem. Phys. **19**, 1434 (1951).

discrepancies leave much to be desired. These discrepancies can be attributed to several effects:

(1) Because there are 105 components of non-zero intensity in the $K=1$ pattern alone, it is extremely difficult to find the result of superimposing the components on the basis of a reasonable physical assumption of line shape. Accordingly, with the assumption of rectangular line shapes, the positions of prominent features can be shifted somewhat from their true values, except in cases in which one component is considerably more intense than its neighbors, as in the cases of the $K=1$ and $K=2$, j components.

(2) The omission of all of the $K=0$ components and the neglect of interfering second order Stark components may be fortuitous in some instances.

(3) A lack of knowledge of the rotational constants for the excited vibrational states makes it difficult to quantitatively take into account the possible effects of interference from this source.

It is noteworthy, however, that none of these, except possibly the last, affect the determinations of eQV_{aa} and the stretching constant D_{JK} . The former is determined from transitions well separated from the pattern center and is therefore not susceptible to overlap from strong $K=0$ and $K=1$ components or their second order Stark components. The latter is based on the extremely intense j component for $K=1$, which would not be expected to be significantly displaced by interfering components of weaker intensities.