A PRELIMINARY STUDY OF THE MICROWAVE SPECTRUM OF METHYLCYCLOPROPANE AND THE DETERMINATION OF THE DIPOLE MOMENT OF CYCLOPROPYL CYANIDE

Thesis for the Degree of M. S.
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Lois Cederberg Leffler
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By

Lois Cederberg Leffler

A THESIS

Submitted to the College of Science and Arts
of Michigan State University in partial fulfillment
of the requirements for the degree of

MASTER OF SCIENCE

Department of Chemistry

1959

To "Little Bear"

ACKNOWLEDGMENT

The author wishes to express gratitude to Dr. Richard H. Schwendeman for his willingness to spend long hours answering questions, tracking down the causes of difficulties with the instrument, and for his patience in the many explanations required during the period of time this work was done. Also appreciated were Dr. Harold Hart's suggestions and literature references for the preparation of methylcyclopropane and the financial aid contributed by the Department of Chemistry in the form of a graduate teaching assistantship.

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Approved ________________________________

ABSTRACT

Methylcyclopropane was prepared using zinc and 1, 3-dibromobutane;and preliminary calculations were made which indicated that the $1_{10}-2_{11}$, $1_{01}-2_{02}$, and $1_{11}-2_{12}$ transitions should be visible in the range of the 2K33 klystron then available. A sweep of the entire frequency range (22, 000-25, 000 mc/second) was made and four weak lines were found at 25056.1, 23870.1, 24139.3, and 24532.2 mc/second. No consistent assignment could be obtained using any 3 of these lines.

The Stark effect of certain transitions in the microwave spectrum of cyclopropyl cyanide was studied and the dipole moments about the a and c axes were determined to be $\mu_A = 3.88$ D and $\mu_C = 0.86$ D making the total dipole moment $\mu_{total} = 3.97$ D debye. In addition the frequencies of several previously unreported transitions were measured in an unsuccessful attempt to obtain an accurate value of the smallest principal moment of inertia.

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CHAPTER I

HISTORICAL BACKGROUND AND THEORY

World War II made it possible for research using high resolution microwave spectroscopy to make giant strides. The military had arbitrarily chosen and developed 1.25 cm. radar in an effort to replace 10 cm. equipment, as the latter could not be focussed into a narrow beam because of its long wavelength. The 1.25 cm. microwaves could be sharply focussed but had an extremely short range due to absorption by water vapor in the range of 1.0 to 1.6 cm., with maximum absorption very close to 1.25 cm. Since the equipment was needed principally in the South Pacific area, and since this area abounds in water vapor, the 1.25 cm. equipment had to be discarded in favor of 3 cm. equipment which had been found to be satisfactory. This military defeat proved to be a boon for subsequent research, as it made much 1.25 cm. equipment available to scientists (1).

The first experiments with microwaves were reported in 1933 by Cleeton and Williams (2) who determined the absorption of centimeter radiation by ammonia gas. The first demonstrations of the high resolution available making use of radar electronics were reported in 1946 by Bleaney and Penrose (3, 4) and by Coles and Good (5), also studies of absorption of ammonia. Since 1946 microwave spectroscopy of gases has yielded useful information in a variety of fields. Its high resolution, novel frequency range, and greater accuracy make possible the study of a variety of different phenomena. In addition to pure rotational spectra these include nuclear quadrupole effects, pressure broadening, and Stark and Zeeman effects (6)

General Theory[1]

Absorption of microwave radiation by simple gas molecules is largely the result of transitions between the discrete rotational energy states of the molecule in its ground vibrational and ground electronic energy state. The frequencies at which the absorption of microwaves takes place depends upon the structure of the molecule as may be seen from the expression for the absorption frequencies of a diatomic molecule

$$\nu_{J \rightarrow J+1} = 2B(J+1)$$

where J is zero or a positive integer which measures the total angular momentum of the molecule, and B is a constant called the "rotational constant and is related to the average internuclear distance r_0 of the molecule by

$$B = \frac{h(m_1 + m_2)}{8\pi^2 m_1 m_2 r_0^2}$$

where h is Planck's constant and m_1 and m_2 are the masses of the two atoms in the molecule.

Whereas the diatomic molecule can undergo only end-over-end rotation, non-linear polyatomic molecules can rotate about any of three axes, the principal axes of inertia. Thus the rotational energy levels of polyatomic molecules are much more complicated expressions of the internuclear distances of the molecule; in fact being related through the three principal moments of inertia of the molecule.

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[1] A more comprehensive treatment of the general theory of microwave spectroscopy may be found in References 7, 8 and 9.

The rotational energy levels of non-linear polyatomic molecules may be expressed as follows:

$$W_{J,\tau} = \frac{B+C}{Z} J(J+1) + (\mathbf{A} - \frac{B+C}{Z}) \quad w_{J,\tau}(bp)$$

Here $W_{J,\tau}$ is the rotational energy of a molecule in the τ^{th} of the 2J+1 energy states with total angular momentum $\sqrt{J(J+1)}\ h/2\pi$. The quantum number τ ranges from -J to +J in integral steps. The rotational constants **A**, B and C are related to the principal moments of inertia I_A, I_B, and I_C (conventionally $I_A \leq I_B \leq I_C$) by three expressions of the form

$$\mathbf{A} = \frac{h^2}{8\pi^2 I_A} \ .$$

The quantities $w_{J,\tau}$ are a function of the asymmetry parameter b_p given by

$$b_p = \frac{C-B}{2A-B-C}$$

and are obtained as the eigenvalues of a non-diagonal matrix. However in the case of a near prolate symmetric top (a molecule would be a prolate symmetric top if $\mathbf{A} > B = C$) b_p is very small and the quantity $w_{J,\tau}$ may be obtained by systematic application of perturbation theory as a power series in b_p,

$$w_{J,\tau} = K^2 + C_1 b_p + C_2 b_p^2 + C_3 b_p^3 + C_4 b_p^4 + C_5 b_p^5$$

The values of K^2 and C_1 through C_5 have been tabulated for all energy levels with $J \leq 40$ (10, 11).

The rotational absorption frequencies are given by the Bohr frequency condition

$$h\nu_{J,\tau\,;\,J',\tau'} = W_{J',\tau'} - W_{J,\tau}$$

Not all transitions occur with equal probability however and some are forbidden. Tables giving values of the relative probability of transitions between energy levels with $J \leq 12$ have been prepared for molecules containing components of the dipole moment along any or all of the three principal axes (12). The theory shows that the intensity of a transition is proportional to the square of the component of the dipole moment along a given axis. Those transitions requiring a dipole moment along the A-axis (the axis from which I_A is measured) are called A-type transitions, etc.

It is often useful to replace the index τ with the bipartile index K_{-1}, K_{+1} where $K_{-1}\, h/2\pi$ would be the angular momentum of the molecule about the A axis in the case of a limiting prolate symmetric top ($I_A < I_B = I_C$), and $K_{+1}\, h/2\pi$ would be the angular momentum of the molecule about the C-axis in the case of a limiting oblate symmetric top ($I_A = I_B < I_C$). The quantities K_{-1} and K_{+1} must be zero or positive integers less than or equal to J, whereas τ ranges from -J to +J in integral steps. The relation between the two is

$$\tau = K_{-1} - K_{+1}$$

All the transitions below will be listed as occurring between energy levels $J_{K_{-1}K_{+1}}$ and $J'_{K'_{-1}K'_{+1}}$

The moments of inertia of the molecule are related to the coordinates of the various nuclei in an arbitrary cartesian coordinate system as follows.

$$I_{xx} = \sum_i m_i\,(y_i^2 + z_i^2) - M(y_m^2 + z_m^2)$$

$$I_{yy} = \sum_i m_i\,(x_i^2 + z_i^2) - M(x_m^2 + z_m^2)$$

$$I_{zz} = \sum_i m_i\,(x_i^2 + y_i^2) - M(x_m^2 + y_m^2)$$

where x_i, y_i, and z_i are the coordinates of the i^{th} atom of mass m_i and the summations extend over all the atoms in the molecule. The values x_m, y_m and z_m are the coordinates of the center of mass of the molecule and M is its total mass. The products of inertia are given by

$$I_{xy} = -\sum_i m_i x_i y_i - M x_m y_m$$

$$I_{xz} = -\sum_i m_i x_i z_i - M x_m z_m$$

$$I_{yz} = -\sum_i m_i y_i z_i - M y_m z_m$$

The three principal moments of inertia I_A, I_B, and I_C are the eigenvalues of the moment of inertia tensor

$$I = \begin{pmatrix} I_{xx} & I_{xy} & I_{xz} \\ I_{xy} & I_{yy} & I_{yz} \\ I_{xz} & I_{yz} & I_{zz} \end{pmatrix}$$

The procedure in analyzing the microwave spectrum of a new compound is then as follows:

a) Computation of the principal moments of inertia of the molecule based upon an assumed structure. The rotational energy levels and transition frequencies may then be computed taking into account the region of the spectrum which is available to the spectrometer.

b) Search of the microwave spectrum of the compound for the predicted absorption lines and careful measurement of the frequencies of absorption lines in the regions of those predicted.

c) **A**ssignment of absorption lines to the energy levels involved and recalculation of the principal moments of inertia based upon the experimentally determined frequencies. An assignment is usually assumed confirmed when six or more absorption lines are consistent with the same three rotational constants to within 0.1 mc/sec (about 5 parts in 10^6).

d) **A**nalysis of the structure of the molecule based upon the measured rotational constants. Ordinarily the moments of inertia of one or more isotopic species will be required before very much may be said about the structure of the molecule.

The Stark Effect

The variation of the energy levels of a molecule in a varying electric field is known as the Stark effect. The rotational energy levels are ordinarily at least (2J+1)-fold degenerate corresponding to the 2J+1 orientations of the total angular momentum with respect to an axis fixed in space. Upon the application of an electric field the field direction becomes the space-fixed axis and because of an interaction between the applied field and the dipole moment of the molecule the 2J+1 different orientations of the molecule have slightly different energy levels.

The theory of the Stark effect of asymmetric-rotator molecules has been examined (13). It predicts a shift in energy levels which is proportional to the square of the component of the dipole moment along a given axis and to the square of the field strength. In particular for molecules with $M = 0$ (total angular momentum oriented perpendicular to the field) the shift in energy ($\Delta W_{J,\tau}$) for a molecule with components of the dipole moment along the A and C axes will be

$$\Delta W_{J,\tau} = F^{A}_{J,\tau}\,\mu_{A}^{2}\,E^{2} \quad + \quad F^{C}_{J,\tau}\,\mu_{C}^{2}\,E^{2}$$

where μ_A and μ_C are the components of the dipole moment and **E** is the field strength. The quantity $F^{A}_{J,\tau}$ is given by

$$F^{A}_{J,\tau} = \left[\frac{J}{(4J^{2}-1)} \sum_{\tau'} \frac{\lambda^{(A)}_{J,\tau;J-1,\tau'}}{\nu_{J,\tau\,;\,J-1,\tau'}} + \frac{J+1}{(2J+1)(2J+3)} \sum_{\tau'} \frac{\lambda^{(A)}_{J,\tau\,;J-1,\tau'}}{J,\tau;J-1,\tau'} \right]$$

The quantity $\lambda^{(A)}_{J,\tau\,;\,J-1,\tau'}$ is the transition probability mentioned above for the **A**-type transition of frequency $\nu_{J,\tau\,;J-1,\tau'}$. The summation extends over all the transitions with non-zero λ.

The absorption frequencies in the presence of an electric field will be the result of a transition between two shifted energy levels and consequently the shift in frequency, $\Delta\nu_{J,\tau\,;J'\tau'}$, will be the difference between the energy level shifts, or

$$h\,\Delta\nu_{J,\tau\,;J'\tau'} = (F^{A}_{J'\tau'} - F^{A}_{J\tau})\,\mu_{A}^{2}\,E^{2} + (F^{C}_{J'\tau'} - F^{C}_{J\tau})\,\mu_{C}^{2}E^{2}.$$

Therefore the slope, $d(h\Delta\nu)/d(E^{2})$, will be

$$\frac{d(h\Delta\nu)}{d(E^{2})} = \Delta F^{A}\,\mu_{A}^{2} + \Delta F^{C}\,\mu_{C}^{2}\,.$$

Consequently determination of the slope of the frequency vs. square-of-the-field line for the M = O Stark component of two or more different transitions may be used to determine μ_A^{2} and μ_C^{2} and the total dipole moment may be obtained from

$$\mu^{2} = \mu_{A}^{2} + \mu_{C}^{2}.$$

In the conventional Stark-modulated microwave spectrometer the sample gas is subjected to alternate periods of electric field and zero field. Since the frequency of alternation is usually very large (100,000 c.p.s.) the normal spectrum and the Stark spectrum appear superimposed. The phase-sensitive detector being sensitive to the phase as well as to the frequency of the incoming signal is capable of distinguishing Stark components from the normal spectrum by virtue of the fact that their signals arrive at the detector 180° out of phase. Consequently the output of the phase-sensitive detector is of one polarity for absorption lines in the normal spectrum, zero for no absorption, and of opposite polarity for Stark components. Since the modulating field may be varied at will between 0 and about 1250 volts, determination of the required slope is accomplished by determining the frequency of the M = O Stark component at various settings of the modulation voltage.

CHAPTER II

DESCRIPTION OF THE MICROWAVE SPECTROMETER

Figure I shows a block diagram of the instrument in use at Michigan State University in the Department of Chemistry.

The klystron power supply is a FXR, Type Z815B manufactured by the Electronics and X-Ray Division, FR Machine Works, Inc., Woodside 77, New Jersey. It must supply -500 to-2500 volts to the cathode, depending on the particular klystron being used, -50 to -1000 volts (measured from the cathode) to the reflector of the klystron, 0 to -300 volts to the grid, again measured from the cathode, and 6.3 volts AC or DC for the heater.

The klystron used for most of this work was a Raytheon[*] QK306 requiring 1800 volts at the cathode at 9 ma, and 6.3 volts at .58 amperes for the heater. Its frequency range was approximately 18,000 to 22,000 megacycles/second. However, some work was done with the Raytheon 2K33 klystron whose range was 22,000 to 25,000 megacycles/second.

The frequency meter used for approximate frequency measurements was of the absorption type, causing a dip in the transmitted power when the size of the cavity was of the proper dimensions for the radiation. The frequency meter used here was a De Mornay Bonardi, Serial No. 715-2 720. The calibration chart sent with the meter appeared to be in error so a recalibration was made. The results appear in Chapter III.

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[*] Raytheon Manufacturing Co., Tube Power Division, Waltham, Mass.

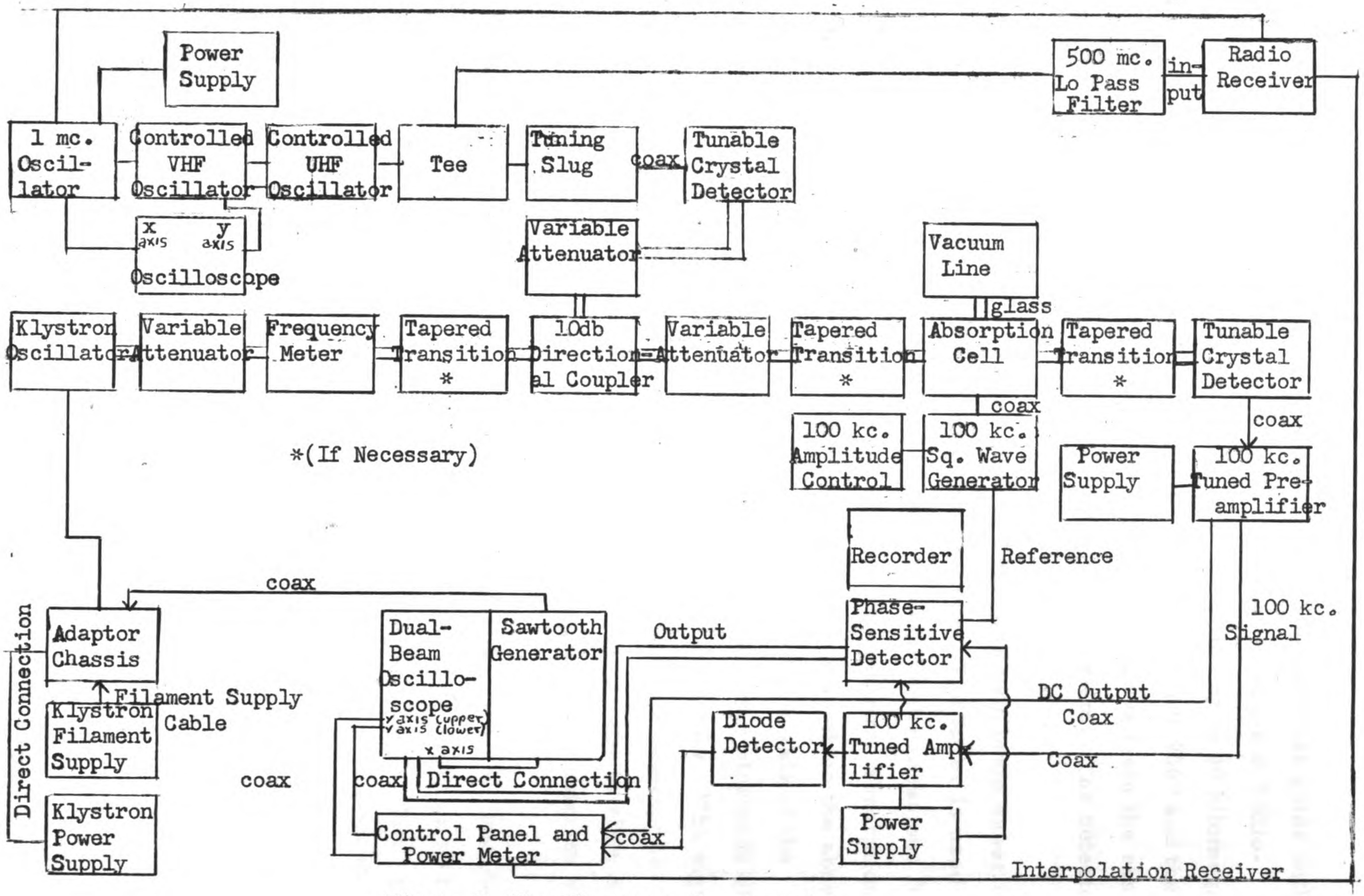

Figure I The Microwave Spectrometer

The waveguide is a ten foot length of X-band brass guide with a silvered inside surface which conducts radiation above 8.2 kilomegacycles/second and can be used for radiation up to 40 kilomegacycles/second. Its inside dimensions are 0.400" x 0.900" and the walls are 0.050". It is sealed off with mica windows from the rest of the instrument and is filled via the vacuum system. The detector is a silicon rectifier.

Two oscilloscopes are in use; a Tektronix twin beam experimental model and a Dumont single beam oscilloscope. The latter is used in connection with the frequency standard to observe the Lissajous figures while the Tektronix oscilloscope is used to monitor the absorptions of the molecule and also to determine the frequency at which the absorption occurs. The sawtooth voltage sweeping across the x-axis of the oscilloscope is simultaneously applied to the reflector electrode of the klystron varying the microwave frequency uniformly. The signal from either the phase-sensitive detector or the diode detector is applied to the y axis causing the face of the oscilloscope to show a plot of the amplitude of the amplified A.C. signal at the detector vs. microwave frequency.

The square wave generator was designed by L. C. Hedrick and patterned after a model described by him (14). It provides up to 1250 volts of zero based square wave output at 100 KC/second. The square wave voltage is applied to a coin silver septum (0.032" x 0.796") which is mounted between Teflon tapes (0.062" x 0.400" with a 0.032" groove 0.010" deep). The Stark field applied to the sample produces changes in frequency or splitting of absorption lines by exerting a torque on the rotating molecules upon interaction with their dipole moments. This "Stark effect", which can be used for the determination of dipole moments as described in the previous chapter, is also extremely useful in the differentiation of noise from the absorption line. The generator exposes the sample to electric fields during alternate 5 μ-second periods, thus alternating zero-field absorption and Stark absorption. Only signals modulated in this manner appear on the face of the oscilloscope. From the crystal detector the signal goes through a preamplifier-amplifier system which blocks all frequencies but the ones near 100 kc. The 100 kc amplifier used was adapted from one designed by C. C. Costain of the National Research Council at Ottawa, Canada, while the preamp was designed by J. C. Williams of Harvard University. The amplifier output then may go either to a crystal diode or to a phase-splitter and phase-shifter. If the output is sent to the diode the 100 kilocycle signal is rectified, averaged, and applied to the input of the oscilloscope. If sent to the phase-splitter-phase-shifter combination the phase splitter splits the signal into 2 signals which are equal but 180° out of phase, while the phase shifter makes it possible to make the phase of the incoming signal identical to that of a reference produced by the square-wave modulator. The net result is that the Stark absorption signal being 180° out of phase to the normal spectrum is of opposite polarity causing Stark lobes to be in the opposite direction to the normal absorption at the oscilloscope or recorder. The great advantage of this latter system is the rejection of 100 kc noise components having the wrong phase, as well as noise having a frequency different from 100 kc.

If use of the recorder is desired the signal from the phase-sensitive detector is sent directly to the recorder and the klystron is driven mechanically over the frequency range.

The frequency standard consists of a Hallicrafters SX-62-A receiver, a Manson Laboratories RD-140 high-stability 1 mc oscillator, a Gertsch products AM-1A VHF interpolator, and a Gertsch FM-4A microwave frequency multiplier (see Figure II). It is possible to measure frequencies to 0.02 mc at 20,000 mc but with compounds containing broad absorption lines considerably less precision is possible, 0.1 mc at 20,000 mc seemingly the limit.

The 1 mc oscillator is calibrated by comparison of its 10th harmonic with the 10 mc carrier of WWV, of the National Bureau of Standards. It is adjusted so that the background noise of a receiver tuned to WWV pulsates less than once every 2 seconds indicating an error in the 1 mc oscillator of less than 0.1 c.p.s. The 1 mc output of the RD-140 is then fed to the input of the AM-1A VHF interpolator where it is amplified and selectively multiplied 19-38 times. The output of the multiplier is mixed with the output of a 1-2 mc. oscillator and the sum frequency used to control the frequency of a 20-40 mc oscillator. The frequency of the 1-2 mc oscillator (LFO) is determined by the appearance of a stable Lissajous figure on the face of the oscilloscope, whose frequency of rotation is kept less than one c.p.s. in order to keep the error in the LFO frequency below 1 c.p.s. The output of the AM-1A is then a single signal of some frequency between 20 and 40 mc plus a 1 mc reference signal which are input to the FM-4A. This latter instrument is locked on a harmonic of the AM1A ± 10 mc. This signal (between 500 and 1000 mc) is then sent, by means of a coaxial cable, to the mixer-multiplier crystal where its harmonics are generated and mixed with the microwave signal. The difference frequencies (between the harmonics of the 500-1000 mc signal and the microwave frequency) are then sent back along the same cable through a filter which blocks all frequencies above 500 mc.

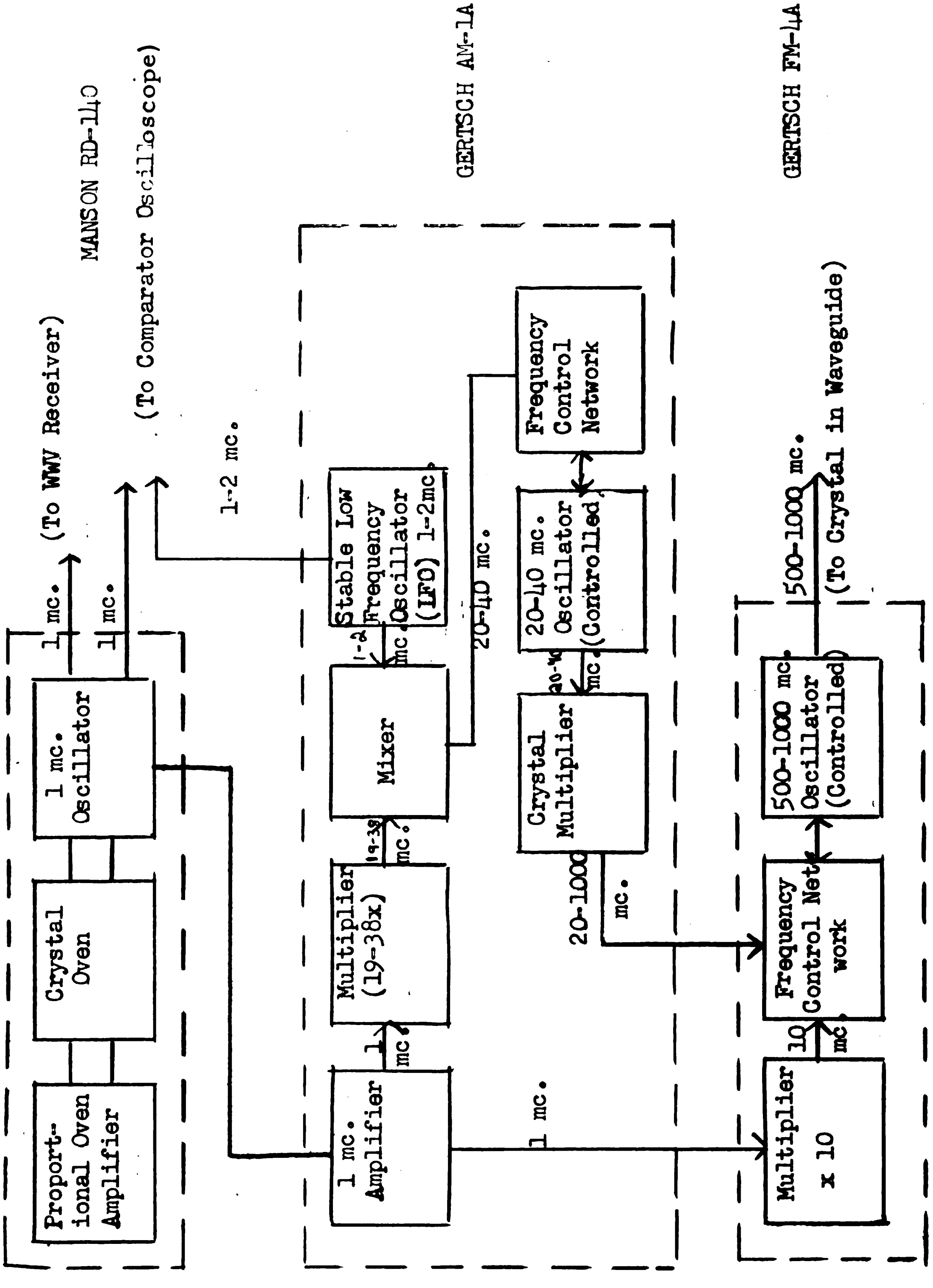

Figure II Reference Frequency Generator

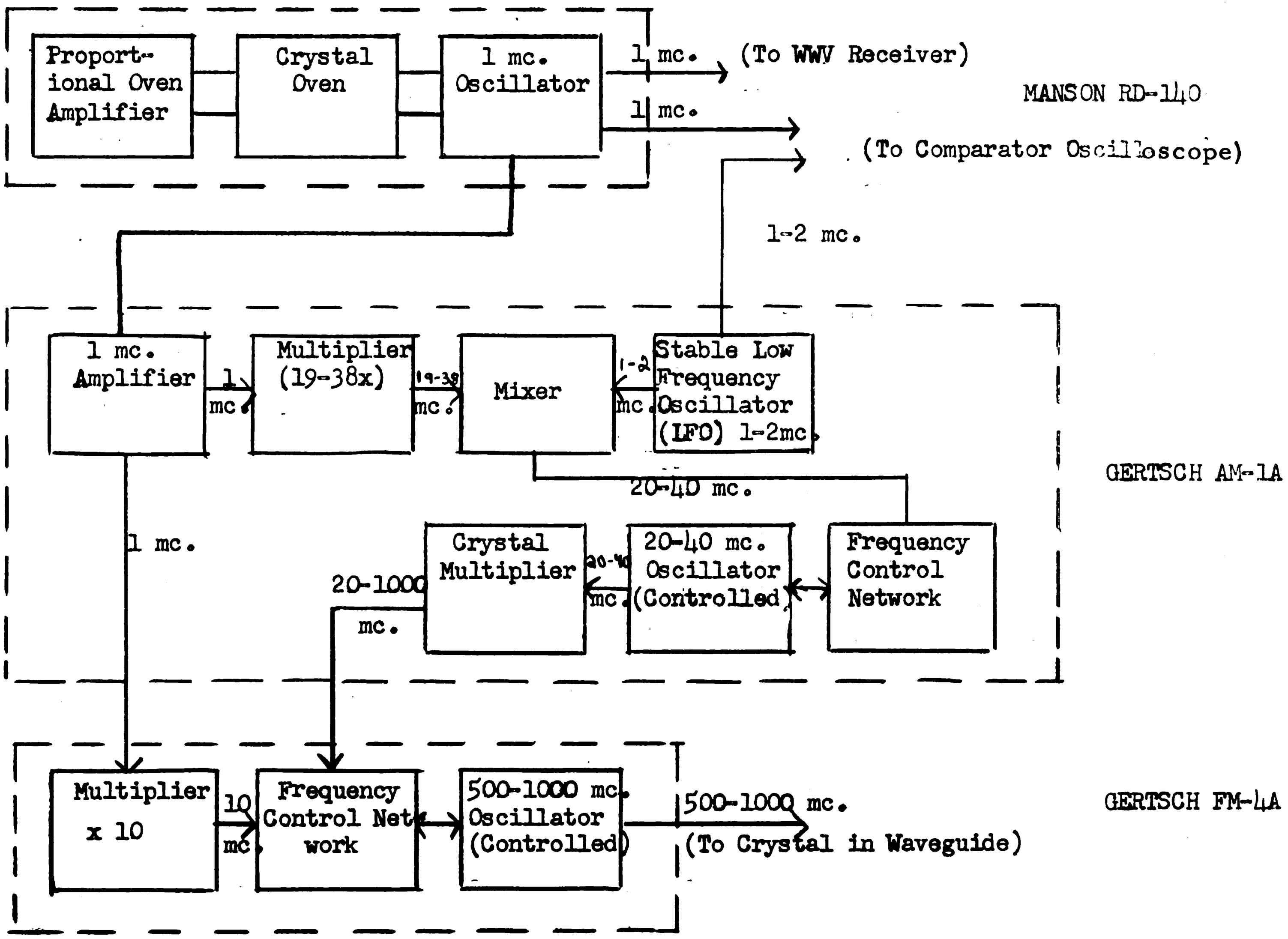

Figure II Reference Frequency Generator
)

This difference frequency then may be measured on the interpolation receiver. Each time the klystron sweeps over the frequency measured by the system there will be "pip" on the oscilloscope and a sound will be heard in the speaker of the interpolation receiver.

The dual beam oscilloscope makes it possible to place an absorption line on one trace and measure it with the frequency standard marker placed on the second trace. If desired the recorder may be used in connection with the frequency measuring device. The output of the phase sensative detector is fed to the recorder. As the klystron sweeps over the frequency which has been set up a sound is heard. At this instant a telegraph key may be closed causing a momentary change in the voltage which the recorder sees that is duly registered on the recorder paper.

CHAPTER III

CALIBRATION OF THE FREQUENCY METER

The De Mornay Bonardi Frequency meter was calibrated by putting a known frequency marker generated by the frequency standard on the oscilloscope and then adjusting the frequency meter until the power dip in the klystron output caused by the absorption by the meter and the frequency marker were superimposed. The correction term was obtained by noting the actual reading of the scale and the chart reading corresponding to the frequency at which the standard was set. The correction term must be added algebraically to the actual frequency meter reading to give the chart value corresponding to the true frequency, or subtracted algebraically from the chart value to obtain the actual reading.

CALIBRATION OF THE De MORNAY BONARDI WAVEMETER, No. 715-2 720

KLYSTRON QK306

Actual Wavemeter Reading	Frequency Standard Base (mc)	Interpolation Receiver	True Frequency	Wavemeter Reading Should Be (From Chart)	Correction Term
234.8	18050	-40	18010	234.6	-0.2
230.45		+40	18090	230.2	-0.25
226.7	18200	-40	18160	226.5	-0.2
222.5		+40	18240	221.25	-0.25
216.4	18400	-40	18360	216.25	-0.15
212.4		+40	18440	212.3	-0.1
206.6	18600	-40	18560	206.5	-0.1
202.8		+40	18640	202.75	-0.05
197.3	18800	-40	18760	197.2	-0.1
193.8		+40	18840	193.6	-0.2
188.6	19000	-40	18960	188.4	-0.2
185.2		+40	19040	185.1	-0.1
182.2	19150	-40	19110	182.4	+0.2
179.0		+40	19190	179.4	+0.4
172.3	19400	-40	19360	172.7	+0.4
169.2		+40	19440	169.4	+0.2
164.7	19600	-40	19560	164.6	-0.1
161.7		+40	19640	161.6	-0.1
157.4	19800	-40	19760	157.3	-0.1
154.5		+40	19840	154.5	0.0
150.4	20000	-40	19960	150.4	0.0
147.7		+40	20040	147.7	0.0
143.7	20200	-40	20160	143.7	0.0
141.2		+40	20240	141.1	-0.1
137.3	20400	-40	20360	137.2	-0.1
134.8		+40	20440	134.7	-0.1
131.1	20600	-40	20560	131.0	-0.0
128.7		+40	20640	128.75	+0.05
125.2	20800	-40	20760	125.3	+0.1
122.9		+40	20840	123.1	+0.2
119.6	21000	-40	20960	119.65	+0.05
117.3		+40	21040	117.4	+0.1

Continued

Klystron QK306 - Continued

Actual Wavemeter Reading	Frequency Standard Base (mc)	Interpolation Receiver	True Frequency	Wavemeter Reading Should Be (From Chart)	Correction Term
114.0	21200	-40	21160	114.1	+0.1
111.9		+40	21240	112.0	+0.1
108.7	21400	-40	21360	108.9	+0.2
106.7		+40	21440	106.8	+0.1
103.7	21600	-40	21560	103.8	+0.1
101.7		+40	21640	101.8	+0.1
98.7	21800	-40	21760	98.85	+0.15
96.7		+40	21840	97.0	+0.3
94.0	22000	-40	21960	94.3	+0.3
92.1		+40	22040	92.4	+0.3

KLYSTRON 2K33

Actual Wavemeter Reading	Frequency Standard Base (mc)	Interpolation Receiver	True Frequency	Chart Wavemeter Reading	Correction Term
92.8	22050	-40	22010	93.1	+0.3
91.0		+40	22090	91.3	+0.3
88.2	22250	-40	22210	88.5	+0.3
86.4		+40	22290	86.7	+0.3
79.8	22550	+40	22590	80.2	+0.4
77.4	22750	-40	22710	77.7	+0.3
75.7		+40	22790	76.1	+0.4
73.3	22950	-40	22910	73.6	+0.3
71.7		+40	22990	72.0	+0.3
69.3	23150	-40	23110	69.6	+0.3
67.7		+40	23190	68.1	+0.3
65.5	23350	-40	23310	65.8	+0.3
63.9		+40	23390	64.3	+0.4
61.7	23550	-40	23510	62.1	+0.4
60.2		+40	23590	60.6	+0.4
58.0	23750	-40	23710	58.5	+0.5
56.5		+40	23790	57.0	+0.5
54.5	23950	-40	23910	54.9	+0.4
53.1		+40	23990	53.6	+0.5
51.0	24150	-40	24110	51.5	+0.5
49.6		+40	24190	50.2	+0.6
47.7	24350	-40	24310	48.2	+0.5
46.4		+40	24390	46.9	+0.5
44.5	24550	-40	24510	44.9	+0.4
43.2		+40	24590	43.7	+0.5
41.3	24750	-40	24710	41.8	+0.5
40.0		+40	24790	40.6	+0.6
37.9	24960	-40	24920	38.6	+0.7
36.7		+40	25000	37.4	+0.7

CHAPTER IV

METHYLCYCLOPROPANE

Introduction

It is known that the chemical properties of cyclopropyl compounds are similar in some respects to the chemical properties of vinyl compounds. The barrier to internal rotation of the methyl group in ethyl derivatives is of the order of 3 kcal/mole, whereas the barrier to rotation of the methyl group in vinyl derivatives is approximately 2 kcal/mole (15). It was thought that a study of the potential barrier in methylcyclopropane would give further insight into the nature of bonding in the cyclopropyl ring, and specifically the degree of resemblance to the vinyl system. It was also hoped that a dipole moment could be obtained for the compound.

Preparation

Methylcyclopropane was prepared using the method of Shortridge <u>et al.</u> (16). This method was first applied to the preparation of methylcyclopropane by J. D. Roberts and R. H. Mazur (17). However some important unreported differences in the preparation of the two compounds came to light during the actual operation. 1, 3-Dibromo butane (purchased from Matheson, Coleman, and Bell, highest possible purity) was added to a gently refluxing mixture of 95% ethanol, distilled H_2O and an excess of zinc dust while vigorous stirring was maintained. Whereas they had added 1, 3-dibromo-2, 2-dimethyl propane to the mixture and then continued heating and stirring for a period of 24 hours to prepare the dimethyl compound, it was found that the preparation of methylcyclopropane went much faster. The 1, 3-dibromobutane was added over a period of approximately 1 hour. The methyl cyclopropane came over during the addition of the 1, 3-dibromobutane and was captured in a trap immersed in a dry-ice acetone bath. It was distilled into a sample bulb and an infrared spectrum taken. This spectrum checked very well with the spectrum obtained and reported by F. E. Condon, and D. E. Smith (18).

From literature vapor pressure data (18) a graph of log p vs 1/T was made and the vapor pressure at -22.8°C of methyl cyclopropane (the freezing point of CCl_4) was found to be approximately 269.2 mm. A rough determination of the vapor pressure at this temperature was made on the methyl cyclopropane prepared by the above method and was found to be 288 mm.

Later an attempt was made to remove possible alkenes and water from the methyl cyclopropane by running it through $KMnO_4$, activated charcoal, and $CaCl_2$, but no changes were observed in the infrared spectrum. A literature check was made in an effort to find methods of purification but the only method given was that of passing the sample through activated charcoal (19).

Calculations

The moments of inertia and rotational constants, for cyclopropyl cyanide were calculated using the following structural parameters (20).

d_{C-C}	1.53 Å
d_{C-H}	1.08 Å
$\measuredangle$ C-C-H	116°24'
$\measuredangle$ H-C-$H_{(ring)}$	118°12'
$\measuredangle$ H-C-$H_{(methyl\ group)}$	109°30'

The results were as follows:

I_A = 33.347

I_B = 79.214

I_C = 89.598

A = 15154.627

B = 6381.84

C = 5642.12

On the basis of the above calculation methyl cyclopropane was expected to show a-type selection rules and the transitions $1_{10}-2_{11}$, $1_{01}-2_{02}$, and $1_{11}-2_{12}$ were predicted to lie at 24787.75, 24003.32, and 23308.53 mc/second respectively.

Experimental

A sweep of the entire range covered by the 2K33 klystron (22,000-25,000 mc/sec) was made in a search for absorption lines. Only four weak lines were found. The measured frequencies were:

25056.1 mc/second
23870.1 mc/second
24139.3 mc/second
24532.2 mc/second

with the frequencies considered accurate to ± .1 mc/sec. No combination of any three of these lines are compatible with the expected assignment for any values of the three rotational constants.

Discussion

When the predicted pattern of lines did not appear it became apparent that the wiser course to follow would be to defer further study of the compound until the capability of the instrument could be increased in two ways:

1. since 2→3 transitions would be predicted in the 35-37,000 mc/sec. frequency range it would be desirable to obtain a klystron for use in this region, and
2. the general sensitivity of the instrument should be increased in order to bring out any weaker lines.

CHAPTER V

CYCLOPROPYL CYANIDE

Preliminary Considerations

In the September, 1958 issue of The Journal of Chemical Physics an article was published by Friend and Dailey entitled "Microwave Studies of the Structure of Cyclopropyl Derivatives" (21). In this paper data were presented to lend support to the theory of Coulson and Moffitt (22), which states essentially that the C-C internuclear distance in the cyclopropyl system is shorter than a normal C-C bond, the H-C-H angle is equal to $116^{\circ} \pm 2^{\circ}$, and the ring has a greater ability to conjugate with halogens and multiple bonds than the corresponding unstrained hydrocarbons (21).

Friend and Dailey assigned transitions involving the component of the dipole moment along the a-axis, and due to the insensitivity of the frequencies of these transitions to the value of the moment of inertia along the a-axis, the uncertainty in the a-moment is stated to be 0.4% (compared to 0.001% in the other two moments). Furthermore, the reported structure based upon the spectra of the parent compound and cis and trans C_3H_4DCN predicts a-moments of inertia which differ by 3.7%, 3.1%, and 5.1% respectively from the measured values. Such large deviations certainly detract from the validity of their reported structure.

Calculations based upon the structure given by Friend and Dailey, assuming the dipole moment to lie entirely along the CN bond, suggested that transitions involving a component of the dipole moment along the c-axis should be visible. These calculations were later verified by a measurement of the dipole moment along the c-axis as described below.

Materials

The cyclopropylcyanide used for this work was obtained from the Columbia Organic Chemical Company, Inc., and was of "the highest possible" purity. It was placed in a suitable sample bulb for use on the vacuum line and was used without further purification.

TABLE I

ROTATIONAL CONSTANTS AND STRUCTURAL PARAMETERS OF CYCLOPROPYL CYANIDE (21)

d $C\text{-}C_{(ring)}$	1.5131 ± 0.001 Å	d $C \equiv N$	1.1574 ± 0.0005 Å
d $C\text{-}C_{(CN)}$	1.4720 ± 0.001 Å	∡ H-C-H	114°36' ± 1°
d C-H	1.107 ± 0.002 Å	∡ $C_{(CN)}\text{-}C\text{-}H$	119°34' ± 30'

	Calculated (mc)	Observed (mc)
A	15339.4	15917 ± 58
B	3461.4	3465.06 ± 0.02
C	3289.7	3286.22 ± 0.02
b_p	-0.00718	-0.00713 ± 0.00003

TABLE II

OBSERVED FREQUENCIES FOR CYCLOPROPYL CYANIDE (21)

Transition	Frequency (mc)
$2_{11} \longrightarrow 3_{12}$	20,521.10
$2_{20} \longrightarrow 3_{21}$	20,261.17
$2_{21} \longrightarrow 3_{22}$	20,253.82
$2_{02} \longrightarrow 3_{03}$	20,246.27
$2_{12} \longrightarrow 3_{13}$	19,984.59
$3_{12} \longrightarrow 4_{13}$	27,358.91
$3_{21} \longrightarrow 4_{22}$	27,022.79
$3_{30} \longrightarrow 4_{31}$	27,008.78
$3_{31} \longrightarrow 4_{32}$	
$3_{22} \longrightarrow 4_{23}$	27,003.61
$3_{03} \longrightarrow 4_{04}$	26,985.78
$3_{13} \longrightarrow 4_{14}$	26,643.54

Attempted Assignment of C-Type Transitions

The 2-3 transitions observed by Dailey were remeasured and found to be good to ± .1 mc. Using Dailey's values of B and C and assuming first his variation in A (± 58 mc/second)and then ± 100 mc/second the following C-type transitions were predicted to lie in the regions of the QK306 klystron indicated:

TABLE III

PREDICTED LINES AND FREQUENCIES FOR C-TYPE TRANSITIONS

Line	Relative Intensity	Frequency Range in mc/second Assuming A to Change by ± 58 mc/sec.	Frequency Range in mc/second Assuming A to Change by Approximately ± 100 mc/sec.
$10_{37}-9_{45}$	1.05	19750-20600	19475-20875
$14_{4,10}-13_{5,8}$	1.5	17,900-18,750	17,500-19100
$7_{25}-8_{17}$	1.31	19125-19490	19000-19600
$8_{27}-9_{19}$	1.56	18850-19210	18725-19325
$4_{13}-5_{05}$	2.0	20200-20300	20160-20360

These ranges were scanned, many rough frequencies and some exact frequencies were obtained, and an attempt made to fit lines observed to a reasonable value of $A - \frac{B+C}{2}$. Also various lines were used to calculate the rotational constants. These constants were then used to predict other lines. No consistent assignment was found although many lines were found that could be C-type transitions.

Lines Measured

The following unreported lines were measured during the course of the work:

17984.0 mc/second
18100.6
18937.6
19185.0
19349.4
19411.8
19808.5
20341.7 mc/second
20547.2
20555.2
20587.2
20830.6
21449.5
21709.3
21737.1 mc/second
21742.1
21832.5
21907.3
22309.5
22338.5

All these frequencies are considered accurate to ± .1 mc/second.

Determination of Dipole Moment

From the study of the M = O Stark component of the 2_{11}-3_{12} (20,521.10 mc/second), 2_{02}-3_{03} (20246.27 mc/second) and 2_{12}-3_{13} (19984.59 mc/second) lines a plot of the square of the voltage vs. frequency (see Tables IV, V, and VI, and Figures III, IV, and V) gives experimental slopes of $-.1746 \times 10^{-4}$, $-.1905 \times 10^{-4}$, and -1.234×10^{-4} mc/volts^2 respectively. Using calculations based on the theory of Chapter I

$$\mu_A = 3.88 \text{ D}$$

$$\mu_C = 0.86 \text{ D}$$

$$\mu_{total} = 3.97 \text{ D}$$

TABLE IV

(See Figure III)

TRANSITION 2_{11}-3_{12} (20521.1 mc)

Voltage	(Voltage)^{2}x10^{-4}	Frequency
300	9.00	20519.70
400	16.00	20518.12
500	25.00	20516.56
600	36.00	20514.46
696	48.44	20512.36
706	49.84	20512.46
800	64.00	20509.70
900	81.00	20507.18

TABLE V

(See Figure IV)

TRANSITION 2_{12}-3_{13} (19984.6 mc)

Voltage	$(\text{Voltage})^2 \text{x} 10^{-4}$	Frequency
406	16.48	19981.08
508	25.81	19979.00
602	36.24	19977.50
706	49.84	19974.77
800	64.00	19972.00
898	80.64	19969.69
904	81.72	19970.00
994	98.80	19966.75

TABLE VI

(See Figure V)

TRANSITION 2_{02}-3_{03} (20246.27 mc)

Voltage	$(\text{Voltage})^2 \text{x} 10^{-4}$	Frequency
150	2.25	20243.71
200	$4.0^0 \times 10^4$	20241.43
250	6.25	20238.625
300	$9.0^0 \times 10^4$	20235.20
400	$16.0^0 \times 10^4$	20227.00

See Table VII for a comparison of dipole moment values for ethyl cyanide, cyclopropyl cyanide, and acrylonitrile in solution (benzene at 25°C) and as obtained in the vapor phase using microwave techniques.

TABLE VII

DIPOLE MOMENTS OF ETHYL CYANIDE, CYCLOPROPYL CYANIDE AND ACRYLONITRILE IN SOLUTION AND USING MICROWAVE TECHNIQUES

	Solution	Microwave
Ethyl Cyanide	3.56 D (23)	4.02 D (25) *
Cyclopropyl Cyanide	3.75 D (24)	3.97 D
Acrylonitrile	Not available	3.89 D (26) *

If the structure of Friend and Dailey is used the -C-C≡N configuration (21) is calculated to make an angle of 18° with the a-axis. Since the sign of the dipole moment is undetermined from the Stark effect measurements, there are two possible orientations of the dipole moment. One forms an angle of ~ 31° with the CN bond while the other forms an angle of ~ 5°. Because of the polar nature of the CN bond, the smaller is the most probable.

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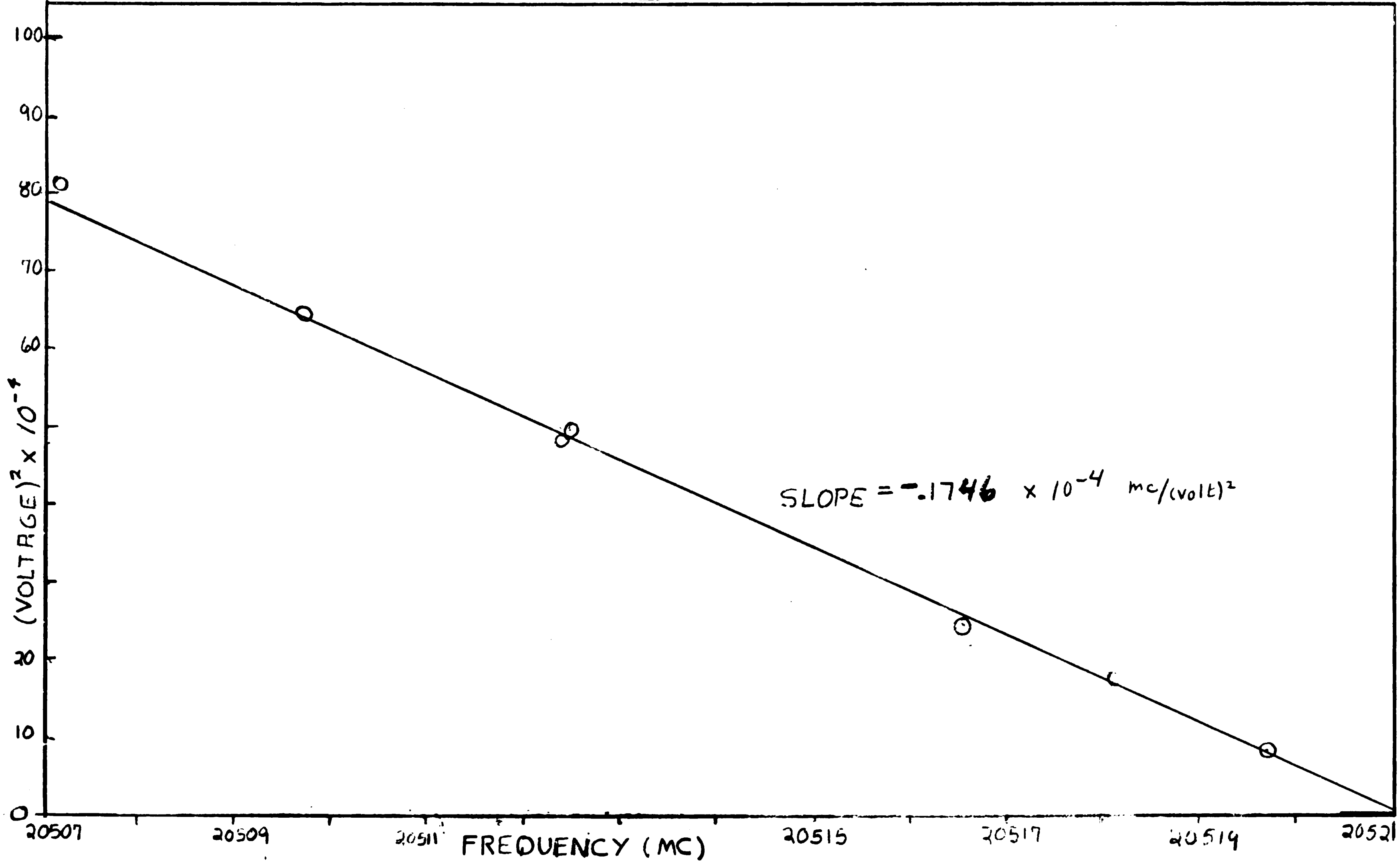
* The dipole moments of these compounds using microwave techniques are in excellent agreement with those determined using dielectric measurements (27, 28).

The uncertainty in the slope of the lines is estimated to be 2%, compared with 1% uncertainty in the very sharp OCS lines, leading to 1% uncertainty in the total dipole moment. The 2% uncertainty in the slope may be attributed to a) broadness of the line; b) the fact that frequency standard markers are not sharply detectable, c) the variation in line voltage which causes a variation in the Stark field seen by the molecule, and d) meter inaccuracy.

FIGURE III



TRANSITION $2_{11} - 3_{12}$ (20521.10 MC)

FIGURE IV

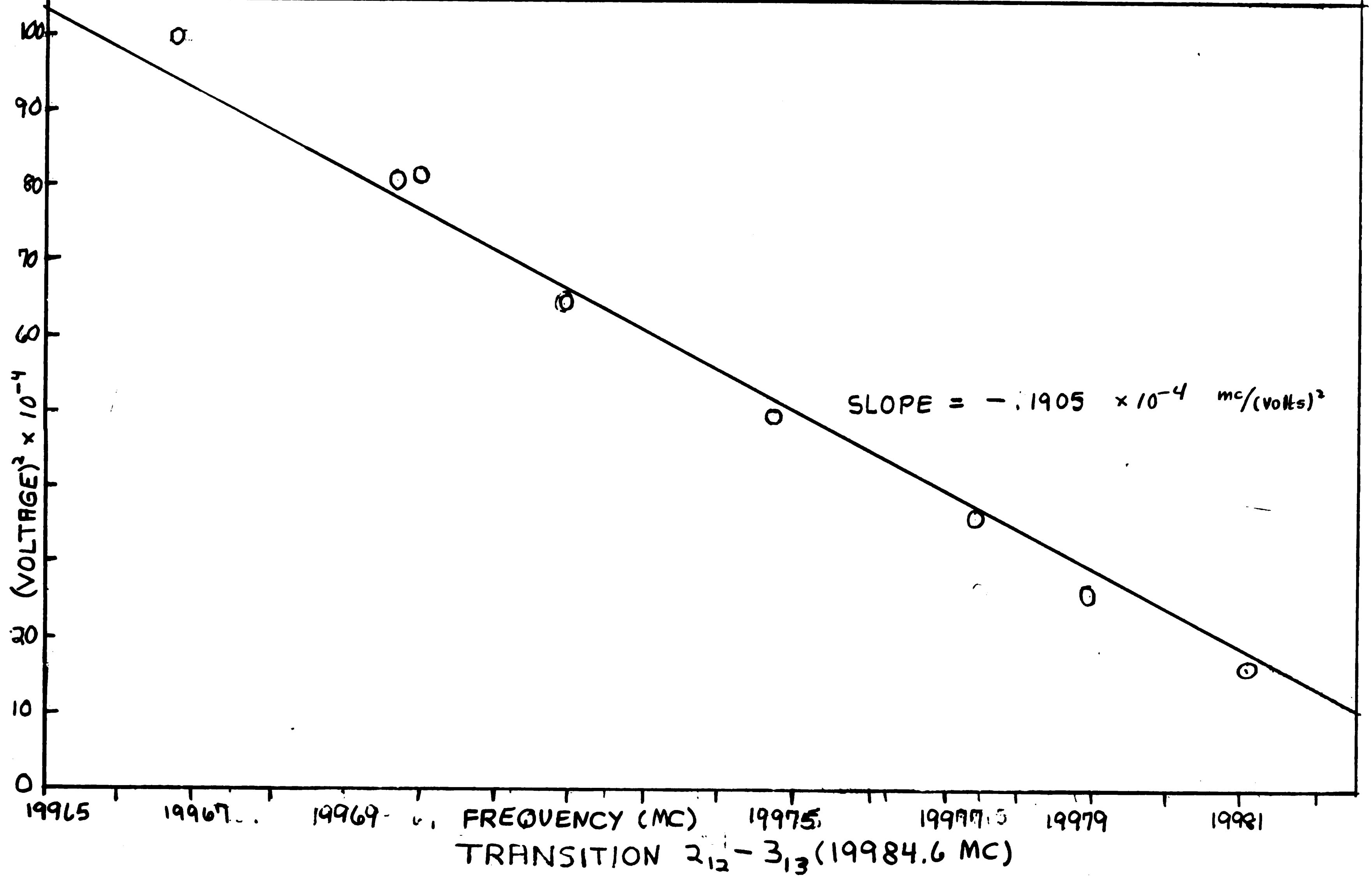
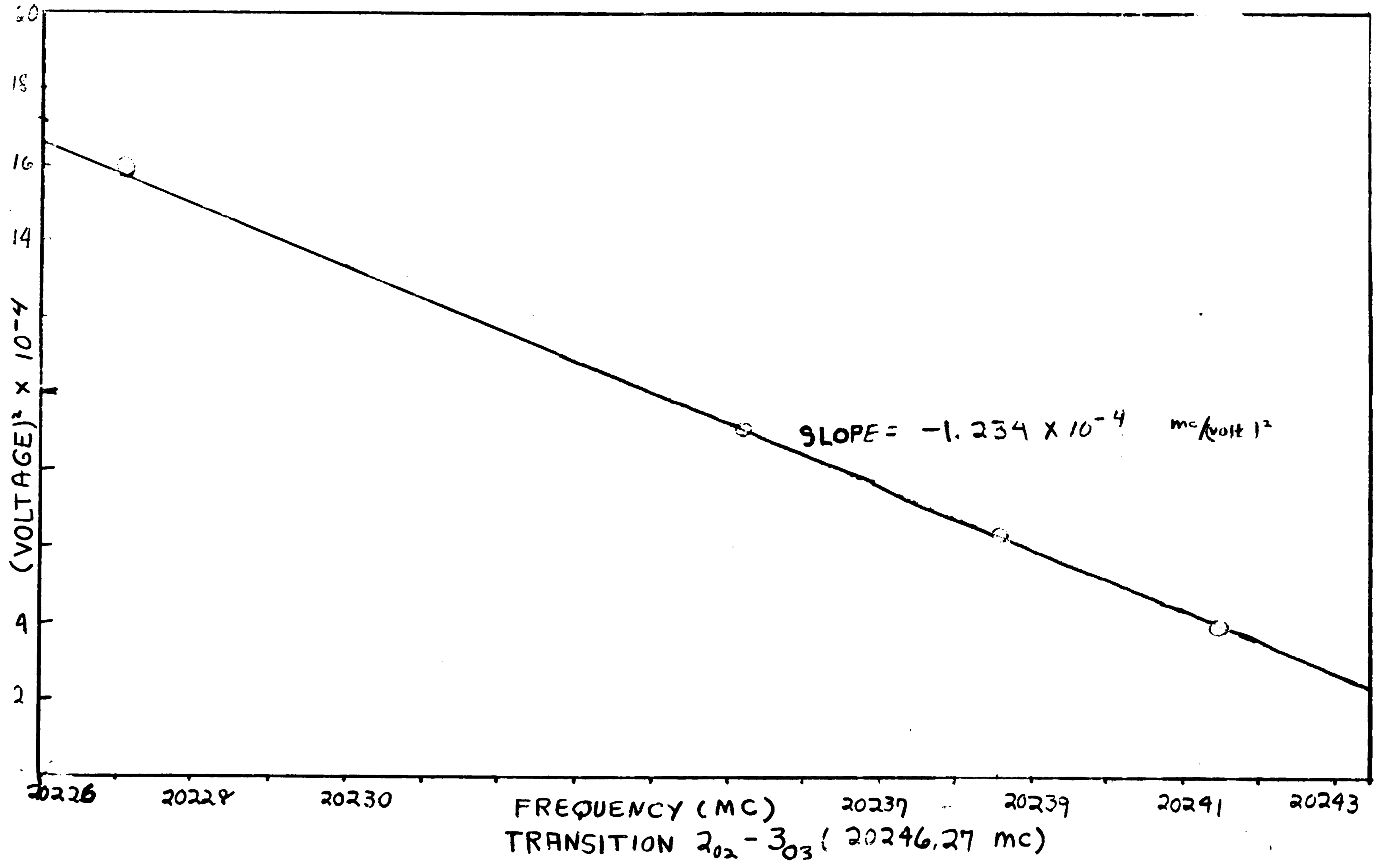

100
90
80
70
60
10
0
$(\text{VOLTAGE})^2 \times 10^{-4}$
SLOPE = −.1905 × 10^{-4} mc/(volts)^2
19965
19967
19969
19975
19977.5
19979
19981
FREQUENCY (MC)
TRANSITION $2_{12} - 3_{13}$ (19984.6 MC)

FIGURE V


20
18
16
14
(VOLTAGE)^2 x 10^{-4}
4
2
SLOPE = -1.234×10^{-4} mc/(volt)^2
20226
20228
20230
20237
20239
20241
20243
FREQUENCY (MC)
TRANSITION $2_{02} - 3_{03}$ (20246.27 mc)

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