MICROWAVE SPECTRUM OF METHYL AMINE

Part I. Experimental Details and Spectrum of CD_3NH_2

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ABSTRACT

The microwave spectrum of CD_3NH_2 has been studied in the region 24·9–38 KMc. The general experimental arrangements for observing the lines and measuring their frequencies using known spectral lines as frequency standards are described. About fifty lines are recorded and the lower J and ΔJ values for some of these lines have been assigned. The transition $J = 0_{00} - 1_{01}$ has been identified and found to be a doublet with the components at 36,436·8 Mc./sec. and 36,436·2 Mc./sec.

INTRODUCTION

THE microwave spectrum of CH_3NH_2 has been studied earlier by Hershberger and Turkevitch,[1] Shimoda and Nishikawa[2] in the region 15 to 27 KMc./sec. Later, Shimoda *et al.*[3] obtained the spectrum in the region 7 to 30 KMc./sec. Independently Lide[4] also studied the spectrum of CH_3NH_2 in the region 11 to 38 KMc./sec. Since then the spectrum was extended up to 50 KMc./sec. by Venkateswarlu[5] and Nishikawa.[6] The spectrum of CD_3ND_2 has been obtained recently by Lide[7] in the region 22 to 32 KMc./sec. The microwave spectrum of CH_3ND_2 and CD_3NH_2 are not reported in the literature. It is expected that a study of the microwave spectra of the above two isotopic species along with the known spectral data on CD_3ND_2 and CH_3NH_2 will throw more light on the structure of the molecule and the involved internal motions. A systematic study of these isotopic species CD_3NH_2 and CH_3ND_2 has been undertaken in this laboratory along with a reinvestigation of the spectra of CD_3ND_2 and CH_3NH_2. The present paper deals with the general experimental details and the spectrum of CD_3NH_2. The spectra of the other isotopic species and the discussion on molecular structure will be taken up in later papers.

EXPERIMENTAL DETAILS

A 100 Kc. Stark modulation spectrograph[8] has been set up for this purpose. The spectrograph consists of a 10½ ft. X-band copper absorption cell. The frequency region 22 to 39 KMc./sec. has been covered by Raytheon klystrons, QK–292, QK–291, QK–290, QK–289, QK–288 and QK–463. A 100 Kc. square-wave modulation of variable voltage 0–1,200 V. is applied to the central electrode. The square-wave generator suitable for this modulation was originally designed by L. C. Hedrik.[9] The one that was used is a modification of the original instrument purchased commercially. This instrument was designed to yield a maximum voltage of 1,200 V. across a cell having a capacity not greater than 1,000 mmfd. and the square-wave is automatically zero based at all voltages. After transmission through the cell the microwave power is rectified by a crystal detector. Sylvania IN 26 crystals were used for the region 22–26 KMc./sec. and IN 53 crystals for the region 26–39 KMc./sec. The crystal output was fed to a low frequency receiver (National HRO-60) tuned to 100 Kc. The output of the receiver was displayed on an oscilloscope (Dumont-304 A or 322). In order to resolve the precise structure of Stark patterns an automatic recording spectrograph[8] was used. In this set-up the klystron was tuned mechanically by motor assembly. The crystal output was fed to a Lock-in-amplifier tuned to 100 Kc. which is coupled to a phase shifter. The output of the Lock-in-amplifier was recorded on an Esterline Angus D.C. milliammeter recorder.

Measurement of frequencies.—Frequencies of the lines were first measured roughly by using different suitable cavity wavemeters for different regions. A PRD type 568B was used for the region 18–22 KMc./sec. Sperry types 349 A and 350 A were used for the regions 19–26 KMc./sec. and 26-39 KMc./sec. respectively. Precise frequency measurements were made by using frequencies of known spectral lines or their harmonics as secondary standards. The experimental arrangement for measurement of frequencies in the region 36–44 KMc./sec., where the first harmonic frequencies of appropriate spectral lines in the region 18–22 KMc./sec. were used as secondary standards, is shown in Fig. 1. Here a K-I band multiplier using a slotted IN26 crystal or a K-J band multiplier using a PRD modified IN26 crystal has been used for harmonic production. In this arrangement two spectrographs are used together simultaneously. Spectrograph A consists of a 3 ft. coin silver K-band Stark cell and is used for observing the known standard lines and may be called a secondary standard spectrograph. After setting the klystron of the secondary standard spectrograph for the frequency of the proper standard line the sawtooth sweep of the klystron is removed. Spectrograph B which may be called the search spectrograph is used for observing new lines and its description has been given earlier. A small amount of power from klystron 1 is taken through a Tee and its frequency is doubled by a crystal multiplier. The harmonic frequency is then mixed with a small

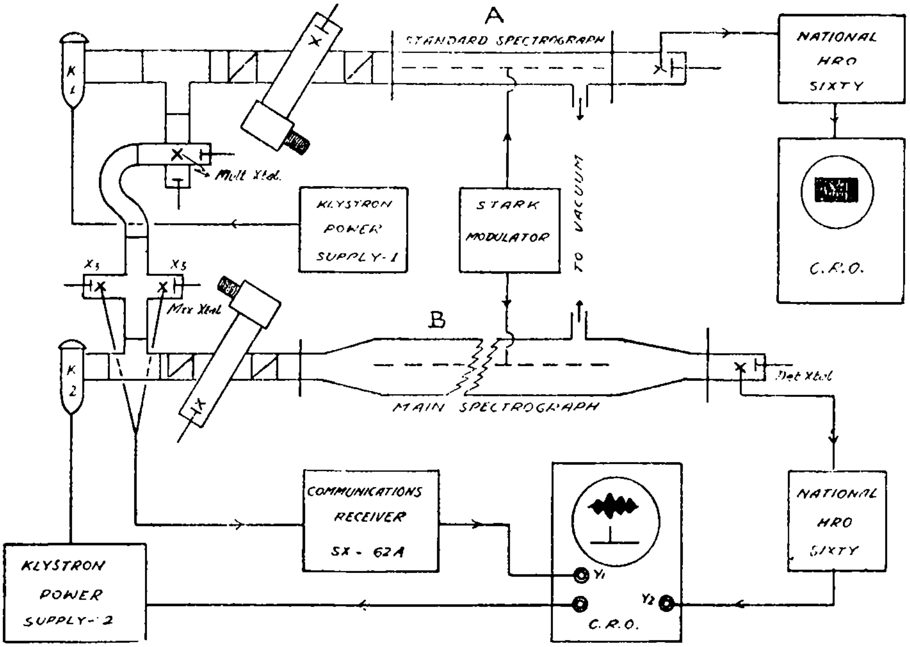


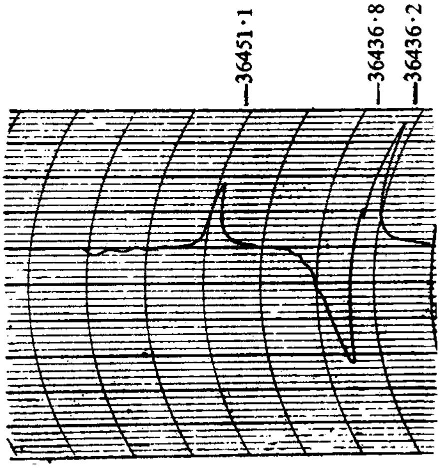
FIG. 1. **Block diagram of the experimental arrangement for measurement of the microwave spectral lines in the region 36–40 KMc./sec.**

amount of power from 2 through a magic tee. Crystal mixers X_3 are connected to the opposite arms 2 and 3 of the magic tee. The use of the magic tee helps to have a balanced mixer as well as to isolate the klystrons. For measurement of frequencies in the region 18–36 KMc./sec., where frequencies of appropriate spectral lines in this region are taken as secondary standards, a small amount of power from klystron 1 is directly mixed without multiplication, with small amount of power from klystron 2 through a magic tee and necessary directional couplers. The resulting beat frequencies from the crystal mixers X_3 are fed into a communications receiver (Hallicrafters type SX-62 *a*). The output of the receiver is displayed on a double beam oscilloscope (Dumont 322) along with the line to be measured. The receiver output appears as a marker whenever one of the beat frequencies from the mixers X_3 corresponds to the frequency to which the communications receiver is tuned. The receiver setting is adjusted so that the marker coincides with the centre of the search line. In this way the beat frequencies between the two oscillators, one of which is stabilised at the frequency of the known line (within the range of about 110 Mc. from the search line) while the other at the line to be measured, are measured. Whenever it was necessary to extend the frequency range of the measurements with respect to the frequency of a standard absorption line an output of a r.f. signal generator (GR 1,001 A) was mixed with the beat frequencies from mixers X_3. In this way known lines lying within ± 215 Mc. from the search line could be used as secondary standards. The receiver and the signal generator were calibrated with a GR-620 A heterodyne frequency meter. The accuracy of the lines measured is expected to be better than ± 0·5 Mc./sec.

SPECTRUM OF CD_3NH_2 IN THE REGION 24·9-38 KMC./SEC.

The spectrum of CD_3NH_2 has been studied in the region 24·9-38 KMc./sec. and fifty lines have been recorded and measured. The sample has been kindly provided by Dr. A. P. Gray and Prof. R. C. Lord who have published[10] earlier the details of the chemical preparation. The observed lines can be classified into three kinds: (1) those that show first order Stark pattern, (2) those that show second order Stark pattern and (3) those that show a Stark pattern which is a mixture of first and second orders. All the lines are listed in Table I. Some of the lines are having well resolved Stark patterns and their lower J and △J values could be well ascertained from the relative intensities of the Stark components and their relative mutual separations.[11, 12, 13] For those lines, that have partially resolved Stark patterns, only the limit of the J value could be set. Finally there are a number of lines with unresolved Stark patterns.

The lines at 36436·2 Mc. and 36436·8 Mc./sec., shown in Fig. 2, are identified as belonging to the transition $J = 0_{00} \rightarrow 1_{01}$. The observed splitting



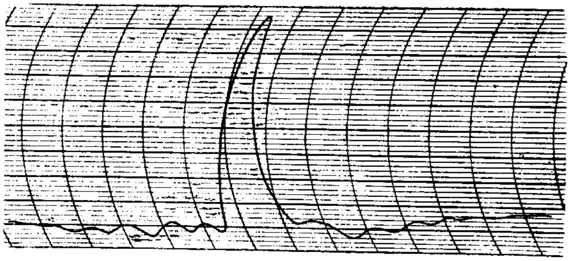


FIG. 2 FIG. 3

FIG. 2. $J = 0_{00} — 1_{01}$ line and 36451·1 line showing 4 first order Stark components.

FIG. 3. The line at 34670 Mc. showing 6 first-order Stark components.

TABLE I

Frequency Mc./Sec.	Intensity	Order of Stark effect	Number of Stark components	Lower J	± ΔJ
38023·7	M	2	..	..	..
37951·4	S	1	3	3	0
37840·5	W	1	..	..	..
37812·2[a]	M	2	..	..	..
37807·9[a]	M	1	..	..	..
37427·1[b]	M	2	6	6	0
37386·3[c]	M	1	4	4	0
37320·9[d]	S	2	..	..	..
37230±10	W	2	..	..	..
37148±10	W	2	..	..	..
37015·4[e]	M	2	3	3	0
36856·9[f]	M	1 & 2	..	..	..
36816·6	W	1 & 2	..	..	..
36753·7	W	1	..	..	..
36451·1	M	1	4	4	0
36436·8 36436·2	S	2	1	($J = 0_{00} \rightarrow 1_{01}$)	
35590·6 35588·1	S	2	5	5	0
35324·7	M	1 & 2	..	..	..
35202·1	W	1	..	..	..
35171·4[g]	S	1 2	6	6	0
35135·7[h]	S	2	..	..	..
35100*	M	2	..	..	..
34995·0	W	2	..	..	..
34962·4[i]	S	1 & 2	..	..	..
34670*	W	1	6	6	1

TABLE I (*Contd.*)

Frequency Mc./ Sec.	Intensity	Order of Stark effect	Number of Stark components	Lower J	±ΔJ
34625*	W	1	..	..	..
33900*[j]	W	1	..	..	..
33860*	W	1	..	..	..
33692·1	S	2	..	..	..
33664·2	S	1 & 2	..	..	..
33160·4	M	2	..	..	..
32968·3	W	2	..	..	..
32298·0	W	1	..	..	..
32267·4	S	2	..	..	..
32178·0[k]	W	1 & 2	..	..	..
31933·7[l]	M	1 & 2	..	..	..
31656·2[m]	S	2	3	3	1
31422·9[n]	S	2	..	..	..
30057·2	M	2	..	..	..
30010·5[o]	W	1 & 2	..	..	..
29913·2[p]	S	2	..	..	..
29507·2	M	2	..	..	..
28601·6[q]	S	2	2	2	0
27815·0[r]	S	2	2	2	1
27472·5[s]	S	2	..	..	..
25834·5[t]	W	1 & 2	..	..	..
25570·4[u]	W	2	2	2	1
24913·1[v]	W	2	3	3	1

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* Frequencies of these lines are measured with wavemeter only.

(*a*) These lines lie close together. A first-order line and a second-order neighbouring one has been observed in many cases.

(*b*) Very likely there are six Stark components. Five components are well seen.

(*c*) There is a weak line on the low frequency side of this line which shows second-order Stark effect.

(*d*) Shows three components the farthest being well separated. The nearest one shows up some unresolved structure at high voltages and probably is a mixture of some components. It appears that the total number of components is probably more than five or six and $\Delta J = 0$, but this conclusion is not definite.

(*e*) Has a neighbouring line on the low frequency side showing first-order Stark effect, the Stark pattern for which is not resolved.

(*f*) Shows three first-order Stark components on each side and one more Stark component on high frequency side which is more intense. The strong component at high voltages shows three broad envelopes.

(*g*) The Stark component on the high frequency side resolves into six while the one on the low frequency side stays as one.

(*h*) Three components are seen. Probably there are more. But these are mixed up with a weak second-order line that lies between 35171·4 Mc. and 35135·7 Mc. lines.

(*i*) There are two or three broad envelopes for the Stark pattern on the high frequency side while only one on the low frequency side.

(*j*) Two Stark components on high frequency side seen clearly and only one Stark component is seen on the low frequency side which is mixed up with the Stark component of the 33860 Mc. line. It is not clear whether this line is showing a first-order or a mixture of first and second-order Stark effect.

(*k*) There are two Stark components on each side. But at high voltages the one on the low frequency side goes down gradually and disappears.

(*l*) There is one Stark component on each side at low voltage. At high voltages the one on the high frequency side splits into two while the one on the low frequency side moves towards the main line and slowly disappears.

(*m*) The Stark component nearest to the main line is strongest and probably corresponds to M = 0,1. The mutual separation increases for the component away from the main line.

(*n*) Shows three Stark components at 300 V. the nearest one to the main line being the most intense. At 900 volts the intense component begins to show up more components.

(*o*) At low voltages this line shows one Stark component on each side. At high voltages the one on the high frequency side broadens into two envelopes while the one on the low frequency side slowly disappears (probably moves towards the main line).

(*p*) Appears to show four or probably more Stark components, the one away from the zero-field line being more intense. The farthest ones have smaller mutual separations.

(*q*) At low pressures there appears to be a weak main component on the high frequency side. There are two Stark components, the farthest one being more intense. The mutual separation for the two Stark components is more than the separation between the main line and the nearest Stark component.

(*r*) Similar to the line marked *m*.

(*s*) Shows irregularly spaced Stark components. This may be due to superposition of a weak line.

(*t*) There is one Stark component on each side at low voltages. At high voltages the one on the high frequency side appears to split into more than one component and the one on the low frequency side, slowly goes down in intensity like that for the line marked *l*.

(*u*) Similar to the line marked *r*.

(*v*) At 250 volts this line appears to show four Stark components. The farthest one probably corresponds to M = 0. At 225 volts this shows three Stark components of which the farthest one being more intense, probably corresponds to M = 0, 1. It looks like $\Delta J = \pm 1$ the lower J being 3, but this cannot be said definitely as there is a weak line superposed on the Stark components.

is probably due to the involved hindered rotations. The line at 36451·1 Mc. in Fig. 2 has four first-order Stark components and the outer components are most intense. The lower J for this transition has been assigned as 4 and ΔJ as 0.

Figure 3 shows a line at 34,670 Mc. with six first-order Stark components. Since the inner components are most intense, the ΔJ for this transition is assigned as ± 1 and the lower J as 6. Figure 4 shows a line at 37,951·4 Mc. with 3 first-order Stark components with lower J = 3 and $\Delta J = 0$.

Figure 5 shows the line at 37015·4 with three second-order Stark components. The intensity and the mutual separation for the Stark components of this line increases as one goes off from the zero-field line. This suggests that $\Delta J = 0$ for the transition and the lower J as 3.

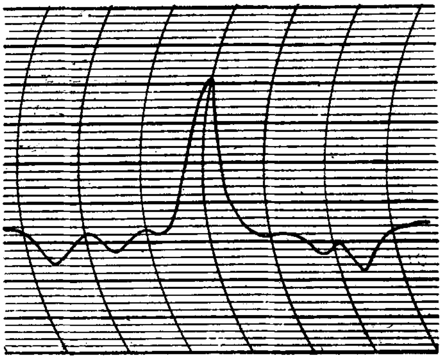

FIG. 4

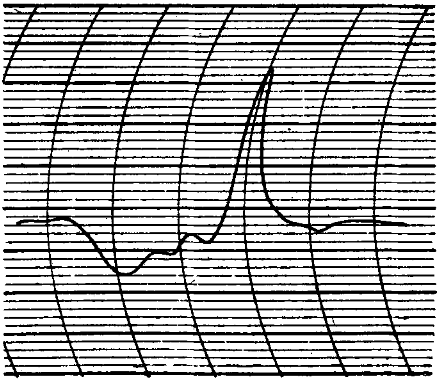

FIG. 5

FIG. 4. The line at 37951·4 showing 3 first-order Stark components.

FIG. 5. The line at 37015·4Mc. showing 3 second-order Stark components.

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