The Rotation Spectrum of Methyl Alcohol from 20 cm^{-1} to 80 cm^{-1}

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The rotational spectrum of methanol vapor has been measured from 20 cm^{-1} to 80 cm^{-1}. The observations have been compared with the predictions of Burkhard and Dennison and for the most part good agreement is found. Some differences are found and since the new observations offer more reliable data with which to determine the energy levels a re-examination of the problem has been made.

I. INTRODUCTION

In a recent account of the rotation spectrum of methyl alcohol Burkhard and Dennison (1) using existing microwave and infrared data, have presented tables of the frequencies and intensities of the strongest spectral features to be expected in the far infrared region.

As they have pointed out, observations in the region below about 70 cm^{-1} are of particular interest for two main reasons. One is that the end-over-end rotational transitions occurring with no change in the internal rotor energy have their greatest intensity in this region. The second concerns the energy levels of the hindered rotor in the torsional ground state $n = 0$. In the Burkhard and Dennison work these levels were obtained by calculation and since they were involved in the deduction of levels for higher n values an important check would be allowed by the direct observation of transitions between them. These transitions again occur mainly in the region below 70 cm^{-1}.

The experimental situation is that only one set of results of rather low resolution exists for the range 50–70 cm^{-1}, and none below 50 cm^{-1} has been published. It is the purpose of this paper to present new experimental observations for the region 20 to 80 cm^{-1}, which have been made by a Michelson interferometer and Fourier transformation and using these new data, to re-examine the determination of energy levels made by Burkhard and Dennison.

II. EXPERIMENTAL METHODS

These have been briefly described in Reference *2* and will be treated fully in forthcoming publications. Specific points which should be recorded here are as follows.

Analar grade MeOH was vacuum distilled into the cell without further purification.

The whole optical path outside the cell was evacuated to a pressure of about 10^{-3} mm mercury and a liquid nitrogen trap further reduced the amount of water vapor present. The sample cell was 30 cm long and a pressure of 13 mm of methyl alcohol was used for all observations. The cell could also be evacuated and the spectra in Fig. 1 are the ratios of the spectral intensity with gas in the cell to intensity with the cell empty. Those in Fig. 2 are not ratioed.

To compare the results with theoretical predictions we have calculated spectral profiles from these data. The theory gave lines of delta function form with frequencies, $\nu(r)$, and intensities, $I(r)$. The computed profile here is given by

$$I_\tau(k) = \sum_r \frac{I(r)}{[k - \nu(r)]^2 + \tau^2}. \tag{1}$$

Thus the delta functions are replaced by Lorentzian's with a width at half height of 2τ cm^{-1}. In computing $I_\tau(k)$ for a particular frequency k cm^{-1} the
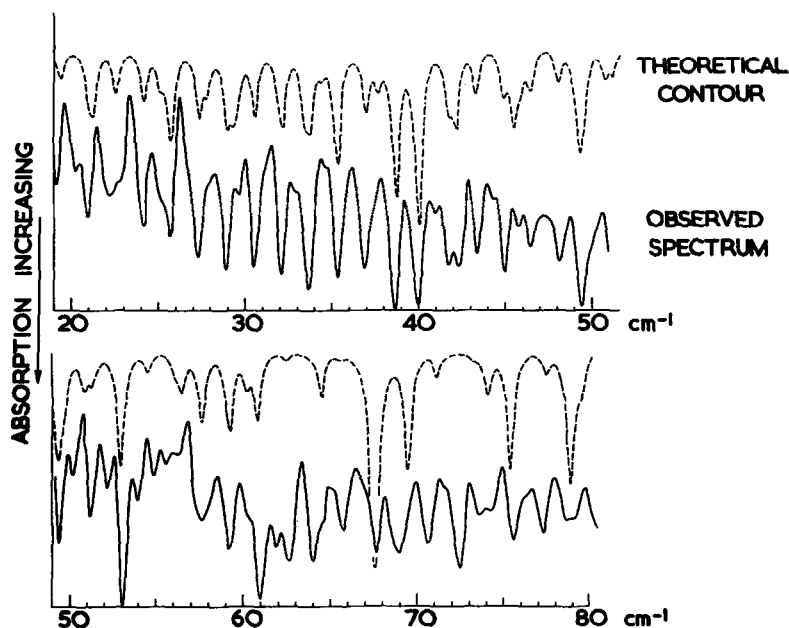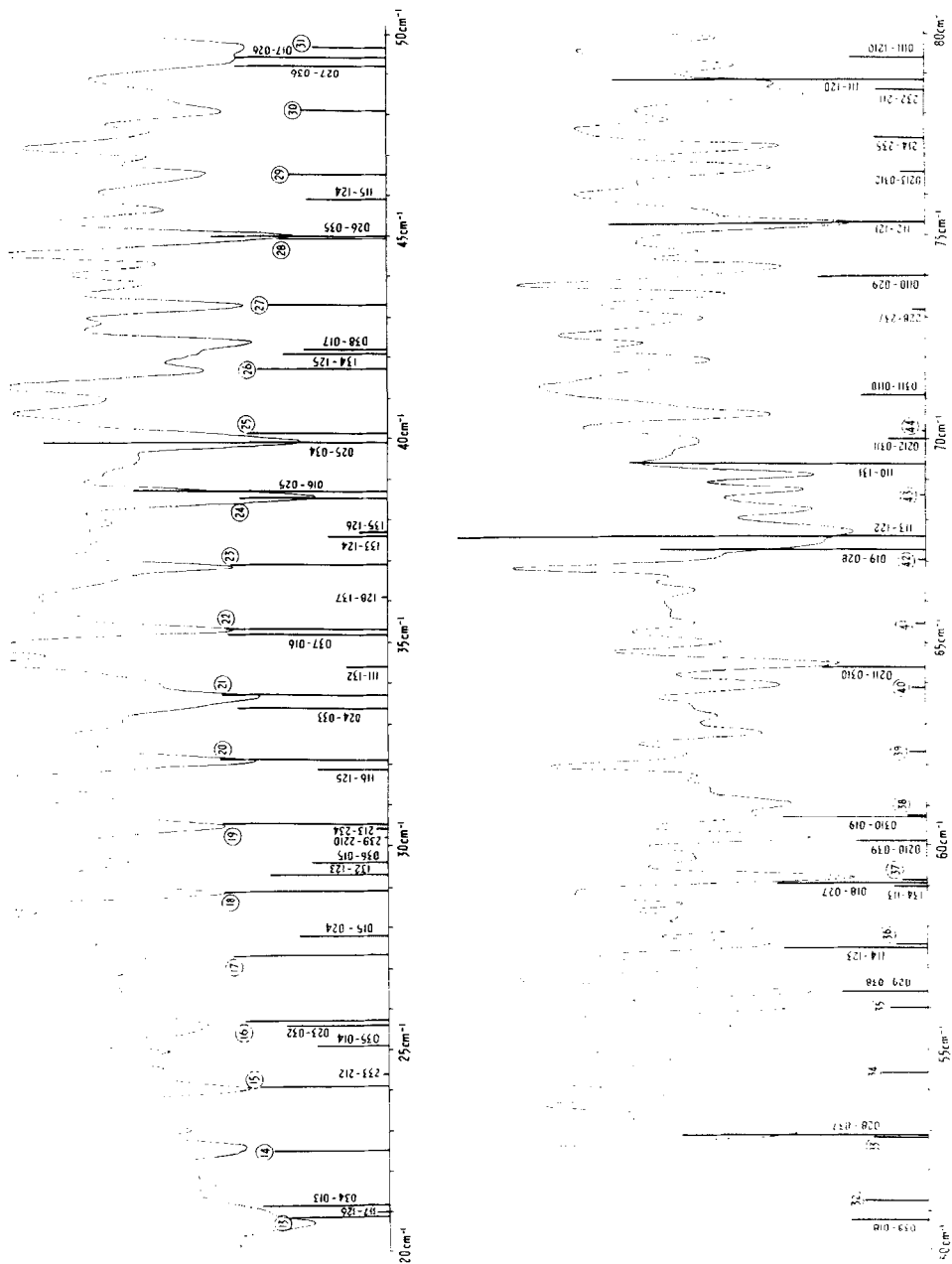

Fig. 1. Observed spectrum of methyl alcohol vapor in the range 20 cm^{-1} to 80 cm^{-1} with a theoretical profile at the same resolution of 0.5 cm^{-1}.

FIG. 2. Observed spectrum of methanol at 0.25-cm⁻¹ resolution with line assignments marked below.

contribution of every line in Tables I and III which lies between 20 and 80 cm^{-1} has been included.

The resolution in this spectroscopic technique is determined by the maximum path difference introduced by the interferometer and may conveniently be defined as the reciprocal of this difference. Thus, in the spectrum of Fig. 1 the resolution is given as 0.5 cm^{-1} corresponding to a 2-cm maximum path difference. The shape of the spectral window, which is the function corresponding to the "slit function" of a grating or prism spectrometer can be varied in this type of spectroscopy by applying different weighting functions to the ordinates of the interferogram before transformation. Its form in these experiments has been chosen to have a width at half height approximately equal to the resolution as defined above. To make the spectral profiles correspond as closely as possible to the observed spectra, the whole width of the Lorentzian at half intensity was made equal to the resolution.

One further remark should be made about the experimental technique. In the interferometer an unfiltered quartz mercury lamp is used as source and thus ultraviolet light may pass through the sample cell. Though it is felt unlikely that this causes observable changes in the spectrum no control experiments were made to check this assumption.

III. RESULTS

Two series of spectra were taken with the same observation time of about 2 hours for each. The first series had a resolution of 0.5 cm^{-1} and a better signal to noise ratio than the second which had a resolution of 0.25 cm^{-1}. Each series consists of four independent runs whose results were averaged. Figure 1 shows the spectrum between 20 and 80 cm^{-1} at 0.5 cm^{-1} resolution together with the theoretical profile computed from Eq. (1). Figure 2 shows the 0.25-cm^{-1} resolution spectrum, without background ratioing and with line assignments marked.

IV. DISCUSSION

The agreement between observed and simulated spectra is for the most part very satisfactory although a number of differences are to be noted.

In the first place, more lines are observed than are predicted. This feature is a result of the fact that the computed spectrum ignores the existence of the very numerous, but individually weak lines resulting from the $\Delta J = \pm 1$, $\Delta K = \pm 1$ transitions. These may be expected to form a relatively strong background which, for the most part, will be unresolved by the present observations. At certain points, however, coincidences between the lines will no doubt occur and these will be recorded as single lines although in this particular sense they are spurious.

The second type of difference between the two spectra concerns the failure of the predicted lines to coincide with the observed lines by amounts ranging up to several tenths of a wave per centimeter. In some cases it is probable that these

discrepancies are due either to experimental errors or to displacements covered by the unresolved background lines mentioned above. In many other cases, however, the new measurements offer a more reliable source of data with which to determine the energy levels than that available to Burkhard and Dennison. It is from this viewpoint that the present re-examination is being undertaken. An attempt will be made to identify as many lines as possible in the observed spectrum. The measured positions of these lines will then be used for re-evaluations of the energy levels and comparisons will be made with the theoretical treatment. In the following discussion the notation used will be that employed by Burkhard and Dennison.

The allowed rotational transitions for methyl alcohol may be divided into two classes characterized by the change in the quantum number K. In the first of these ΔK, as well as the changes in the internal rotation numbers $\Delta\tau$ and Δn are all zero while the total angular momentum number J changes by one. The methyl alcohol molecule possesses only a relatively slight asymmetry and, aside from the internal rotation terms, its rotational energy is well represented by that of a symmetrical top. Thus the principal J dependence of the energy has the form $Be(J^2 + J)$ where Be was determined by Ivash and Dennison (3) to be 0.8066 hc. It is to be expected that centrifugal stretching will introduce the small terms $-D_{JK}(J^2 + J)K^2 - D_{JJ}(J^2 + J)^2$ where the coefficients D_{JK} and D_{JJ}, as will be seen later, may be estimated from the force constants of the molecule. That part of the rotational energy which is of importance for the class of lines under consideration is therefore $B_{\text{eff}}(J^2 + J) - D_{JJ}(J^2 + J)^2$ and the resulting frequencies are given by the formula

$$h\nu_{J-1,J} = 2B_{\text{eff}}J - 4D_{JJ}J^3. \tag{2}$$

The intensities of these absorption lines can be readily calculated and it will be shown that their strength increases with increasing J, reaches a broad maximum, and then decreases rather rapidly. For methyl alcohol the maximum is found to occur near $J = 20$, that is, in the region of 32 cm^{-1}.

An inspection of the experimental curves shows that the most prominent feature of the spectrum from 20 cm^{-1} to 50 cm^{-1} is a set of nearly equi-spaced lines with a spacing of around 1.6 cm^{-1}. Clearly these lines may be identified with the predicted lines just discussed. In most cases the observed lines follow a concordant intensity pattern but in others the lines are either too intense when compared with their neighbors or are abnormally broad. The obvious inference is that these lines coincide or nearly coincide with lines belonging to the other class of transition and hence may be designated as multiple. The process of analysis which was followed consisted in selecting the single lines of this series as measured in the high resolution (0.25 cm^{-1}) plot and fitting them to a formula containing a linear and a cubic term in J. The result of this fitting was

$$\nu/c = 1.610J - 0.79 \times 10^{-5}J^3. \tag{3}$$

TABLE I

J	I	(ν)calc.	(ν)obs.	$\Delta\nu$	J	I	(ν)calc.	(ν)obs.	$\Delta\nu$
12	2.0	19.31	19.25	-0.06	29	2.4	46.50	46.6	+0.10
13	2.4	20.91	20.75M	-0.16	30	2.1	48.09	48.1	+0.01
14	2.5	22.52	22.75M	+0.23	31	1.8	49.67	49.7M	+0.03
15	3.2	24.12	24.1	-0.02	32	1.6	51.26	51.1M	-0.16
16	3.5	25.73	25.7M	-0.03	33	1.3	52.85	53.0M	+0.15
17	3.8	27.33	27.3	-0.03	34	1.1	54.43	54.4	-0.03
18	4.0	28.93	28.9M	-0.03	35	0.9	56.01	56.0	-0.01
19	4.0	30.54	30.5	-0.04	36	0.7	57.59	57.7M	+0.11
20	4.1	32.14	32.1	-0.04	37	0.6	59.17	59.2M	+0.03
21	4.0	33.74	33.7M	-0.04	38	0.46	60.75	60.8	+0.05
22	4.0	35.34	35.35M	+0.01	39	0.37	62.32	62.25	-0.07
23	3.8	36.93	36.9	-0.03	40	0.29	63.90	64.0M	+0.10
24	3.6	38.53	38.6M	+0.07	41	0.22	65.47	65.5	+0.03
25	3.4	40.13	39.9M	-0.23	42	0.16	67.04	67.2M	+0.16
26	3.2	41.72	41.75	+0.03	43	0.12	68.60	–	–
27	2.9	43.31	43.3	-0.01	44	0.09	70.17	–	–
28	2.7	44.91	45.0M	+0.09	45	0.07	71.73	–	–

The accuracy with which the coefficient of J^3 could be determined was unfortunately low and of the order of $\pm 10\%$.

Table I summarizes the results. The first column gives the value of J assuming that the line in question corresponds to the transition $J - 1 \rightarrow J$. The second column lists the computed intensities (see later) while the third column gives the frequency as calculated from the above formula. This is followed by the observed frequency. The letter M means that the line appears to be multiple. The last column lists the differences between the observed and calculated frequencies. It will be noted that these latter are satisfactorily small for all except certain of the clearly multiple lines. Since most of the observed frequencies are only given to three significant figures while the computed ones are given to four, deviations of less than 0.05 cm^{-1} may be properly considered to be zero.

In the paper by Burkhard and Dennison (1) a formula was given for calculating the intensities of the second class of transitions, namely, those for which $\Delta K = \pm 1$. A similar formula may be obtained for the lines corresponding to $\Delta K = 0$. The following modifications must be introduced:

1. The constant A is to be replaced by $(\mu_\parallel/\mu_\perp)^2 A = 0.378A$ where $\mu_\parallel$ and $\mu_\perp$ are, respectively, the components of the permanent dipole moment parallel to

and perpendicular to the methyl axis of the molecule. The numerical values of these components are listed by Ivash and Dennison (3).

2. Since the lines of the $\Delta K = 0$ class are in reality very close multiplets, a sum must be made over the internal rotation number τ. τ may assume the values 1, 2, and 3 and the weight of two of these is unity while that of the third is 2. Thus the factor $f_{\tau' k'}$ has the value 4.

3. A further sum must be made over the internal rotation number n. This results in replacing $e^{-E'_{n\tau k}/kT}$ by $\sum_{n=0}^{\infty} e^{(-E_{n\tau})_{\text{av}}/kT}$. Here $\langle E_{n\tau} \rangle_{\text{av}}$ is the average of the internal rotational energy. It does not include the rotational term proportional to K^2. In accordance with the convention used by Burkhard and Dennison, this energy will be calculated relative to the ground-state energy. Thus, estimating from their Fig. 1, $\langle E_{n\tau} \rangle_{\text{av}}$ has the values 0, 230, 465, and 845 hc for $n = 0$, 1, 2, 3, respectively. The sum in question becomes 1.46.

4. Since these transitions are between the same internal rotation states, the matrix elements of M are all equal to unity.

5. The sum over the external rotation amplitudes and weights will be accomplished by the formula given by Gerhard and Dennison (4). Taking account of the pertinent numerical factors, one finds that $F_{K'K''}$ is to be replaced by

$$F_{J,J-1} = (2/\beta) \left[(2x - 1/x) \int_0^x e^{-u^2} \, du + e^{-x^2} \right] e^{-x^2/\beta} \qquad (4)$$

where $x^2 = \sigma\beta J^2 = 0.0169 J^2$ and $\beta = C/A - 1 = 4.37$. The complete formula for the intensity of the Jth line is therefore

$$I_J = (1.006) A\nu (1 - e^{-h\nu/kT})(\tfrac{1}{2}\beta) F_{J,J-1} . \qquad (5)$$

In deriving this formula it is clear that many approximations have been made in that integrals have replaced sums and averages for the internal rotation energy levels employed. However, the final results should be correct to the two significant figures listed.

As is well known, the centrifugal distortion constant D_{JJ} may be calculated very simply from the condition of minimizing the rotational energy. Following the notation of Hecht and Dennison (5) one finds from their Eq. (6)

$$D_{JJ} = \left(\frac{h^4}{32} \right) \sum_i \left[\frac{A_i^{(1)}}{A_0^2} + \frac{B_i^{(1)}}{B_0^2} \right]^2 \frac{1}{k_i} . \qquad (6)$$

Here A_0 and B_0 are the equilibrium values of the large moments of inertia. For methyl alcohol $A_0 \cong B_0$ since the asymmetry is small. $A_i^{(1)}$ and $B_i^{(1)}$ are first derivatives of the moments of inertia with respect to the normal coordinate q_i and k_i is the coefficient of $(\delta q_i)^2$ in the potential energy expression $\tfrac{1}{2} \sum_i k_i (\delta q_i)^2$. Let q_i equal the H—O distance, q_2 the C—O distance and q_3 the C—H distance. Since the D_{JJ} measures the centrifugal distortion for an end-over-end rotation in which K may, for convenience, be set equal to zero, all

<div align="center">TABLE II</div>

Mode	γ/c	$k_i \times 10^{-5}$	$D_{JJ}/hc \times 10^{+6}$
O - H stretch	3682	7.58	0.004
C - O stretch	1033	5.04	1.763
C - H stretch	2911	4.8	0.027
H - O - C bend	1346	1.08	0.035
H - C - O bend	1453	1.25	0.108

C—H distances may be taken equal. Further let $q_4 = (q_1)_0 \alpha$ where α is the HOC angle and $q_5 = (q_3)_0 \beta$ where β is the HCO angle. Again β will be the same for all three of the methyl hydrogens.

The q's which have been introduced are not, strictly speaking, normal coordinates. However, as is well known, the stretching of the valence bonds and of the valence angles, are good approximations for the normal coordinates in the case of the simpler hydrocarbons.

Knowing the equilibrium dimensions of the molecule it is now easy to write the moments of inertia as functions of the q's and thus obtain the requisite first derivations.

To obtain estimates of the potential constants, use was made of the analysis of the vibration bands of methyl alcohol given by Ivash, Li, and Pitzer (6). These are shown in Table II, together with the contribution which each normal coordinate makes to D_{JJ} .

The sum of the centrifugal distortion contributions is therefore $D_{JJ}/hc = 0.194 \times 10^{-5}$. The coefficient of J^3 is four times this figure or 0.776×10^{-5} in nearly perfect agreement with the value obtained from the observed lines. It should be remembered that the above calculation involves the approximation of identifying the normal coordinates with the valence coordinates. In addition the k_i were found by using reasonable values for the reduced masses rather than through a complete normal vibration analysis. In spite of these shortcomings, it is believed that the final figure for D_{JJ} is quite reliable, particularly since the largest contribution comes from the C—O stretching for which the approximations employed should be most valid.

As a final remark concerning the lines belonging to this first class of transition for which $\Delta K = 0$, it will be noted that the observed coefficient of J, namely, 1.610 cm^{-1} differs slightly from the value 1.6132 deduced by Ivash and Dennison

from an analysis of the very accurate microwave spectrum. A rough estimate shows that a difference of this magnitude results from the average value of the centrifugal stretching term $-D_{JK}(J^2 + J)K^2$. An accurate calculation of D_{JK} would be difficult but from the experience with other symmetrical top molecules one concludes that $D_{JK} \cong D_{JJ}(A/C)^2$ where C and A are, respectively, the moments of inertia along axes parallel and perpendicular to the symmetry axis. Substituting the numbers for methyl alcohol one estimates $D_{JK}/hc \cong 5.6 \times 10^{-5}$. The centrifugal stretching term in question will result in splitting apart the multiple lines of the transition so that their positions, relative to the original line are given by $-2D_{JK}JK^2$ where $K = 0, 1, \cdots, J - 1$. The intensities of the individual lines are approximately proportional to $(J^2 - K^2)e^{-\sigma\beta K^2}$. The spacing of the lines is much too small to be observed with the present experimental arrangement and consequently one should calculate their center of gravity. For the large values of J here encountered (in distinction to the small J values for the microwave lines considered by Ivash and Dennison) it may be shown that the center of gravity will lie close to $-D_{JK}J/\sigma\beta$. Substituting the numbers, it is found that the centrifugal stretching will decrease the coefficient of J by approximately 0.0033 cm^{-1}. The agreement with what may be called the observed difference of 0.0032 cm^{-1} is certainly fortuitously good since the above calculations are little better than order of magnitude estimates.

The second class of dipole transitions which will be considered are those for which $\Delta J = 0$ and $\Delta K = \pm 1$. These involve changes in the internal rotation. The possible changes in the quantum numbers τ and n are given in the paper by Burkhard and Dennison. These lines are also multiple since J may assume all values from the higher of the two values of K to ∞. In the absence of higher order perturbations, the components of these multiple lines exactly coincide but it is to be expected that effects such as that of centrifugal stretching may cause displacements of the order of one or more tenths of a wave number.

The Burkhard–Dennison paper lists the energy levels [designated by the symbols $(n\tau K)$] as obtained from an analysis of the spectrum observed in the region from 50 cm^{-1} to 625 cm^{-1}. The expected positions of the lines together with their calculated intensities are also given. Those lines which fall in the range of the present experiment were plotted and compared with the observed spectrum. The attempt was then made to identify each line. The high resolution $(0.25$ cm$^{-1})$ plot was used in listing observed frequencies although frequent use was made of the 0.5-cm^{-1} plot.

The results of this procedure are shown in Table III. The first column gives the transition $(n''\tau''K'') \to (n'\tau'K')$ where, for the sake of uniformity with earlier papers, the first state is the one of higher energy and thus the line is given in emission rather than absorption. The second column lists the calculated intensity and the third the calculated frequency. The fourth column represents the observed frequency. The letter M indicates that the observed line is probably

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TABLE III

Transition	I	(ν)calc.	(ν)obs.	Transition	I	(ν)calc.	(ν)obs.
229 - 238	0.01	20.2	-	027 - 036	3.7	49.2	49.3M
117 - 126	0.2	21.0	-	017 - 026	3.7	49.4	49.3M
034 - 013	3.1	21.2	(20.75)M	039 - 018	1.9	50.8	51.1M
233 - 212	0.1	24.4	-	028 - 037	6.1	52.9	53.0M
035 - 014	1.7	25.1	25.0	029 - 038	2.2	56.4	56.4
023 - 032	2.5	25.6	25.7M	114 - 123	3.6	57.5	57.7M
015 - 024	2.1	27.8	27.7	134 - 113	0.8	59.0	(59.2)M
132 - 123	2.9	29.3	28.9M	018 - 027	3.7	59.1	59.2M
036 - 015	1.8	29.6	29.65	0210 - 039	1.7	60.1	60.2
239 - 2210	0.03	30.2	-	0310 - 019	3.6	60.7	61.0
213 - 234	0.2	30.4	-	0211 - 0310	2.5	64.4	64.5
116 - 125	1.7	31.9	(32.1)M	019 - 028	6.5	67.3	67.5
024 - 033	3.6	33.4	(33.7)M	113 - 122	11.6	67.6	67.75
111 - 132	1.0	34.4	(34.7)	110 - 131	7.3	69.4	69.1
037 - 016	3.9	35.2	35.35M	0311 - 0110	1.5	71.1	(70.9)M
128 - 137	0.1	36.1	36.0	228 - 237	0.4	73.2	(73.0)M
133 - 124	1.4	37.6	(37.6)M	0110 - 029	2.6	74.0	74.3
135 - 126	0.6	37.7	(37.6)M	112 - 121	7.8	75.3	75.3
016 - 025	6.3	38.7	38.6M	214 - 235	1.2	77.4	(77.25)M
025 - 034	8.6	39.9	39.9M	232 - 211	1.2	78.6	(78.75)M
134 - 125	2.5	42.1	42.4M	111 - 120	7.8	78.8	78.75M
038 - 017	2.0	42.2	42.4M	0111 - 0210	1.9	79.4	79.2
026 - 035	4.3	45.5	45.5M				
115 - 124	2.0	45.9	45.7				

multiple. In some cases the other coinciding, or nearly coinciding lines are identifiable while in others the multiplicity is inferred from the fact that the observed intensity is much greater than that calculated. The treatment of the data presented by the multiple lines requires an element of judgment. In those instances where the observed lines appear to be narrow and sharp and where the predicted intensity is high, it will be assumed that the observed frequency can be properly identified with the transition. In other cases, however, where there is doubt as to the validity of this assumption the frequency will be bracketed.

For the most part the identifications shown in Table III are very satisfactory.

In particular it is gratifying to note that almost every line of the series where $n = 0 \to 0$ is observed and that there is good agreement between the calculated and measured frequencies. The levels obtained by Burkhard and Dennison for the higher n values were obtained from differences which ultimately involved the $n = 0$ levels. These levels, however, could not be obtained directly from the measured spectrum then available but were obtained from calculation. The present observations therefore serve to validate the higher n levels.

A number of transitions associated with $n = 1 \to 1$ are also identified. In many cases such as the lines 112–121 and 113–122 among others, the frequency agreement is good while in other cases divergences of the order of 0.3 or 0.4 cm^{-1} occur. These probably indicate the necessity for small revisions in the values of the levels as given previously.

An examination was made of the observed and predicted spectra over the whole range from 20 cm^{-1} to 80 cm^{-1}. The following points were noted:

1. There are no strong predicted lines for which there does not exist a strong observed line. In all such cases the identification both in frequency and in intensity is satisfactory.

2. From 20 cm^{-1} to 50 cm^{-1} there are no strong lines in the experimental spectrum which are not accounted for. Over much of this region indeed there are few lines of even low intensity (excluding the very weak lines) which cannot be identified.

3. From 50 cm^{-1} to 80 cm^{-1}, however, a good many lines are observed which have no counterpart in the predicted spectrum. These are probably due to the fortuitous coincidence or near coincidence of what may be termed the third class of lines, namely, those for which $\Delta J = \pm 1$ and $\Delta K = \pm 1$. These, in distinction to the lines of the first two classes already considered, are indeed single lines whose individual intensities are relatively low. In the aggregate, however, they are more intense than the sum of the intensities of the second class lines by a factor of approximately two. In an attempt to explore this explanation further all the lines of the third class falling within the arbitrarily chosen region from 60 to 65 cm^{-1} were listed. It was found that these were some 300 entries, and that the individual intensities varied over a considerable range. Many close coincidences occurred and there appeared to be concentrations of intensity near 62.4 and 62.8 cm^{-1}. Moreover these concentrations tended to repeat with a spacing of 1.6 cm^{-1}. An examination of the experimental spectrum shows features of this type although the systematic repetition was not pronounced. It is to be expected however that higher order terms such as those from centrifugal stretching will alter the pattern to some extent. The only conclusion which appears warranted is that the combined effect of this third class of lines can indeed give rise to the extra lines which are observed but that a precise identification of these intensity maxima cannot be made without further detailed studies.

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