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# The Structure of the Ultraviolet Absorption Spectrum of Formaldehyde. I

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The ultraviolet absorption spectrum of formaldehyde was photographed under high dispersion so that the rotational structure could be analyzed. The present paper gives details of six bands at 3530, 3430, 3390, 3370, 3295 and 3260A. The bands are due to transitions in which the electric moment is in the plane of the molecule and perpendicular to the CO-axis. As the asymmetry of the molecule is very slight, the structure of the bands is very nearly the structure of vertical bands due to a symmetrical top. The position and intensity of the lines is in very good agreement with this except if the component $K$ of the angular momentum along the CO-axis is smaller than four. In this case, the effect of the asymmetry makes itself felt in a shift and doubling of the lines in agreement with the theoretical expectations. A rigorous check of all the regularities is furnished by combination relations. The distortion of the molecule by the rotation can be studied in the deviations of the observed energy values from those of a rigid top. A value for the force between the two C—H bonds results from this. In the bands 3430 and 3295 there are strong perturbations which affect the dependence of the rotational energy on the quantum number $K$ only, not that on the total angular momentum $J$. The molecular constants for the normal state of the molecule and six vibrational states of the excited electronic level can be obtained with good accuracy (see Table V and §10).

SOME time ago we reported on the analysis of the rotational structure of some ultraviolet absorption bands of formaldehyde.[3] Since then we photographed a number of additional bands under high dispersion and analyzed their structure. In the present paper the detailed results for six bands are given. Three of these, the bands at 3530, 3430 and 3390A were already described in the preliminary report, but the data on which the results were based were withheld then. They are given in full now, besides three more bands of the same structure at 3370, 3295 and 3260A. We hope to report on some more bands, some of them of different structure, in a subsequent paper and shall reserve also the discussion of the vibrational structure until then, as those bands are essential for its understanding.

## §1. EXPERIMENTAL

All the bands discussed in this paper were photographed in the third order of the 40 ft. Tuxedo spectrograph[4] with a six-inch plane grating with 15,000 lines per inch. The Steinheil Uviol glass lens allowed one to photograph down to about 3200A. The light source for the continuous spectrum was a water-cooled quartz hydrogen tube described by one of us previously.[5] It took a current of about 1.5 amperes which was supplied by a 6500 volt transformer. The exposure times varied between two and ten hours. At the shorter wave-lengths the absorption of the uviol lens required a prolonged exposure. The whole spectrograph was thermostated, and the temperature fluctuations were of the order of 0.01°C.

In the earlier work a 30-cm long quartz absorption tube was used. At the high pressures which were necessary to obtain the fainter bands the formaldehyde polymerized rapidly, and it was difficult to keep the windows clean. Also, at the high pressures, the lines tend to broaden which has a detrimental influence on the resolution of the crowded parts of the bands. For that reason a two-meter long absorption tube was substituted. This tube was all quartz with two flat windows fused to the ends and could be heated electrically in order to study the absorption at higher temperatures. In order to avoid a deposit on the windows it was necessary in all

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[1] The Johns Hopkins University.

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[3] G. H. Dieke and G. B. Kistiakowsky, Proc. Nat. Acad. **18**, 367 (1932).

[4] A. L. Loomis and G. B. Kistiakowsky, J. Sci. Inst. **4**, 201 (1932).

[5] G. B. Kistiakowsky, Rev. Sci. Inst. **2**, 549 (1931).

cases to heat the windows separately to a slightly higher temperature than the rest of the tube.

Formaldehyde was obtained by heating commercial C.P.-grade paraformaldehyde. Early in the course of the work it was found that to obtain satisfactory photographs it was necessary to keep the formaldehyde pressure in the absorption tube very constant. This was accomplished by means of an automatic pressure regulating device. The solid paraformaldehyde was kept in a small glass vessel connected to the absorption tube and to a differential mercury manometer provided with electric contacts. On the other side of the differential manometer was a ballast flask and a closed-end manometer. The vessel with the paraformaldehyde was wound with Nicrome wire in series with a resistance and a relay operated through the contacts on the differential manometer. This latter had to be heated slightly (to 40–50°C) to prevent fouling of the contacts by the condensing paraformaldehyde. Air was admitted on one side of it to the desired pressure whereupon the formaldehyde pressure built up in the course of some 10–20 minutes and then stayed constant for prolonged time intervals, seldom varying by more than ±1 mm.

At pressures above some 100 mm the condensation of paraformaldehyde was so rapid that the connecting tubes were rapidly clogged.

Here the regulation was accomplished by electric contacts on an open-end manometer and all the connecting lines as well as the manometer were electrically heated. We used pressures from a few mm to about 600 mm. Pressures above about 100 mm were, however, not of very much use, as the lines became too diffuse, and the resolution of the bands insufficient.

## §2. MEASUREMENTS

The plates which were obtained in this way have a dispersion of about 0.4A per mm. The absorption lines were measured under the comparator in the usual way against iron standards. As the number of lines was very large, in most cases the wave numbers of the lines were evaluated directly without the wave-lengths. Two plates, often more than two, were measured for every band. That was necessary, because on the low pressure plates the strong lines showed with very good definition and resolution, whereas on the high pressure plates, on which many fainter lines came out, the stronger lines, especially in the center of the bends, flowed together and could not be measured with any accuracy.[6] The centers of the bands are only partly resolved on all plates and the measurements there are at best very difficult. The agreement between the measurements of good lines on different plates was as a rule within a few hundreds of a wave number; for the congested regions the agreement was naturally less. Lines which are separated by less than 0.2 $\mathrm{cm}^{-1}$ could not be resolved. We believe that this is due to the character of the formaldehyde lines rather than to limitations of the spectrograph, as the full theoretical resolving power was obtained with other spectra.

## §3. THE THEORETICAL STRUCTURE OF THE ROTATIONAL LEVELS

The formaldehyde molecule must have a Y-shaped form (Fig. 1) and has therefore three different moments of inertia, i.e., it can be regarded in first approximation as an asymmetric top. The quantum-mechanical theory of the asymmetrical top has been given by Kramers

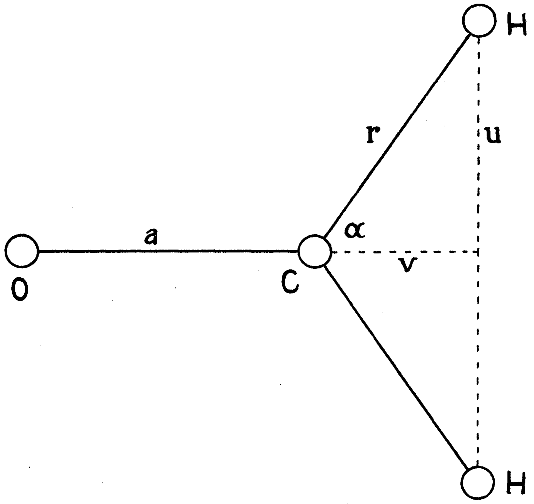

FIG. 1.

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[6] In order to obtain the best results for a given region of a band it was essential that the pressure had a value deviating by not more than 50 percent from its optimum value. This means that a much larger number of plates had to be taken than were afterwards measured.

and Ittmann[7] and Wang.[8] All the rotational energy levels can be found from the general formulae given by these authors, but the process is somewhat laborious. Fortunately the asymmetry of the formaldehyde molecule is only very slight, and therefore most of the peculiarities of the absorption spectrum of formaldehyde can be understood from a consideration of the properties of the *symmetrical* top.

We shall therefore use the symmetrical top as starting point and investigate further on what changes are introduced when we take the asymmetry of the formaldehyde molecule into consideration. We call $A$, $B$, $C$ the three principal moments of inertia of the molecule in the order of their size. $A$ is then the moment about the axis perpendicular to the plane of the molecule, $B$ about the axis in the plane perpendicular to the CO-axis, and $C$ the moment of inertia about the CO-axis. We have

$$A=B+C \tag{1}$$

and, as $C$ is very small on account of the small mass of the hydrogen atoms, $A$ is very nearly equal to $B$. We consider now a symmetrical top with the moment of inertia $C$ about the symmetry axis and the moment of inertia $D$ about any axis perpendicular to it. $D$ is connected with the moments of inertia $A$ and $B$ of our molecule by

$$1/D=\tfrac{1}{2}(1/A+1/B). \tag{2}$$

The rotational energy of this symmetrical top is[9]

$$W_0=\frac{h^2}{8\pi^2 D}J(J+1)+\frac{h^2}{8\pi^2}\left(\frac{1}{C}-\frac{1}{D}\right)K^2. \tag{3}$$

$J$ is the total angular momentum, $K$ its component along the axis of symmetry, both expressed in units $h/2\pi$.

If the deviations from the symmetrical top are small, this expression can be regarded as a good approximation, and the deviations from it can be calculated by the method of perturbations. This is what Wang did. The corrections can be expressed with the help of a parameter $b$ which gives the degree of asymmetry.

$$b=[1/B-1/A]/[2(1/C-1/D)], \tag{4}$$

$b=0$ for the symmetrical top. If $W$ is the energy of the asymmetrical top we can write

$$W=W_0+(h^2/8\pi^2)(1/C-1/D)x \tag{5}$$

and if $y=K^2+x$, $y$ can be found immediately as the solution of the secular determinant characteristic of the perturbation problem. For every value of $J$ there results an algebraic equation of degree $2J+1$ which splits up into four equations, three of degree $J/2$ and one of degree $J/2+1$ if $J$ is even and three equations of degree $J/2+1$ and one of degree $J/2-1$, if $J$ is odd. The coefficients of these equations contain the parameter $b$. The equations are given explicitly for $J\leq 8$ by Dennison[9] and for $J\leq 10$ by Nielsen.[10]

They are still rather inconvenient for numerical calculations and therefore we used the corresponding equations in $x$ which have small quantities as solutions. They can be found for $J\leq 10$ from Nielsen's equations or directly from the secular determinants given by Wang. We found the latter course safer, as there are a few misprints in Nielsen's numbers. We used this method up to $J=15$ although for such high values of $J$ the resulting equations became rather involved and an approximation method is better used.

There seems to be no need to reproduce here all the results of these calculations[11] especially in view of the fact that our hope to be able to use them to find an unambiguous assignment of quantum numbers also for the centers of the bands was not fulfilled.

A few general characteristics of the energy levels which can be obtained directly from the papers of Wang or Kramers and Ittmann are, however, useful for a discussion of the structure of the bands. For $b=0$, i.e., for the symmetrical

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[7] H. A. Kramers and G. P. Ittmann, Zeits. f. Physik **53**, 553 (1929); **58**, 217 (1929); **60**, 663 (1930).

[8] S. C. Wang, Phys. Rev. **34**, 243 (1929).

[9] See D. M. Dennison, Rev. Mod. Phys. **3**, 280 (1931), where the literature is also given.

[10] H. Nielsen, Phys. Rev. **38**, 1432 (1931).

[11] In some of these calculations we were aided by Dr. J. W. Mauchly with the help of a special grant from The Johns Hopkins University for which we wish to express our appreciation.

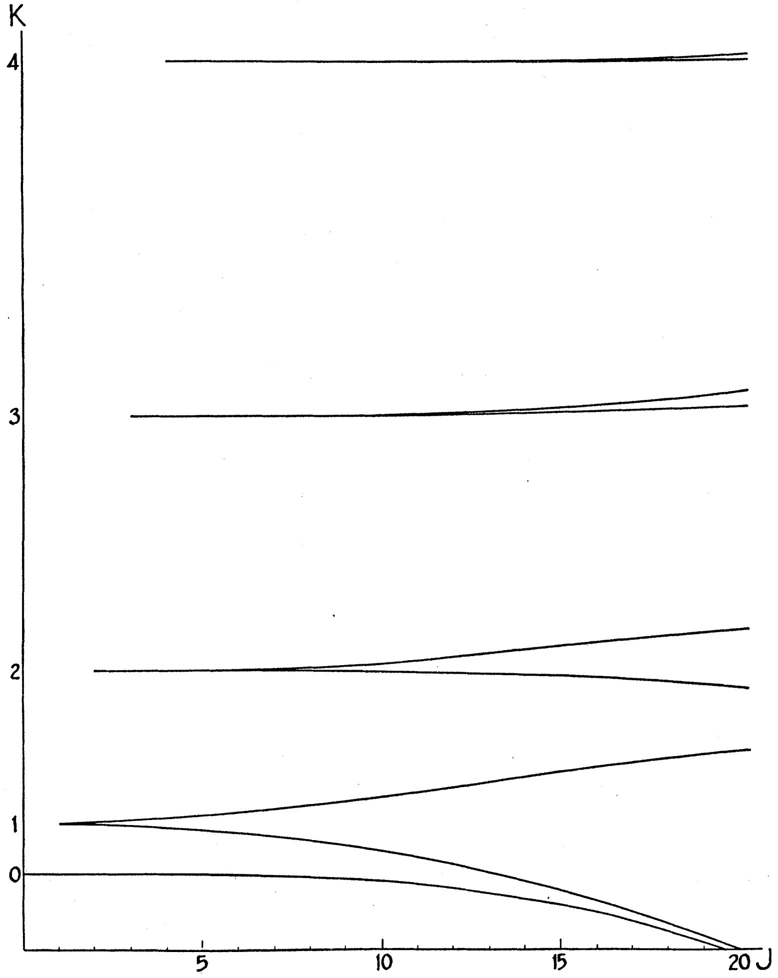

FIG. 2. The rotational energy of a slightly asymmetric top. ($b$ about 0.01.) The term $h^2J(J+1)/8\pi^2D$ is subtracted. The deviations from the horizontal lines represent the deviations from the symmetrical top.

top there are $J+1$ different energy levels for each value of $J$, which are distinguished by different values of $K$, $(0 \leq K \leq J)$. As $b$ gradually increases, all these energy levels split up into doublets except the ones with $K=0$. This splitting up is closely analogous to the $\Lambda$-doubling in the rotational energy levels of diatomic molecules. The doublet separation is negligible for large values of $K$ and moderate values of $J$. Energy levels of this type are not appreciably affected by the small asymmetry of the molecule. That this must be the case can be seen easily from a classical model. If the rotation about the CO-axis is much faster than the precession about the invariable axis, only an average of the two large principal moments of inertia is of importance for the motion of the top. Therefore if

$$J/D \ll (1/C-1/D)K$$

the asymmetrical top has acquired the properties of a symmetrical one.

For small values of $K$ (for $K \leq 3$ for the degree of asymmetry found in the formaldehyde molecule) the deviations from the values for the symmetric top become appreciable. There is not only the doubling, but also the center of gravity of the doublet is shifted. The behavior of these levels is illustrated for $K \leq 4$ in Fig. 2.

## §4. Selection Rules and Intensities

In order to find the appearance of a band it is not only necessary to know the rotational energy levels of the upper and lower electronic states, but we need also the selection rules and the expressions for the intensities of the lines. For our purpose it is first entirely sufficient to make use of the selection and intensity rules of the symmetrical top, as the deviations which are treated in §6 are only small for a very small degree of asymmetry.

There are two different cases to be considered for which the selection rules are different.

(A) The electric moment is perpendicular to the axis of symmetry. In this case we can have $pP$-, $pQ$-, $pR$-, $rP$-, $rQ$-, and $rR$-branches.[12]

(B) If the electric moment is parallel to the axis of symmetry $qP$-, $qQ$-, and $qR$-branches occur.

There are bands of both types in the ultraviolet absorption spectrum of formaldehyde, but as the bands given in this paper are all of type A, we need only consider this case here.

As the moment of inertia about the CO-axis is so much smaller than the other two principal moments of inertia, the factor of $K^2$ in (3) is much larger than the factor of $J(J+1)$, and a consequence of this is that a change of $K$ by one results in a much larger energy change than a corresponding change in $J$. This means that all the lines belonging to a given $K' \rightarrow K''$ transition but different values of $J$ lie much closer together than lines which have different values of $K$. Therefore the whole band can be divided up into a number of sub-bands each of which corresponds to a fixed $K$-transition and has a $P$-, $Q$- and $R$-branch. Each of these sub-bands is therefore closely analogous to a band of a diatomic molecule. The $K=1 \rightarrow K=0$ sub-band, e.g., is in every respect analogous to a $^1\Pi \rightarrow {}^1\Sigma$ band of a diatomic molecule. The number of missing lines near the origin of each sub-band is determined by the condition $K \leq J$. For example, the $K=1 \rightarrow K=0$ sub-band has one missing line in the $P$-branch and one in the $Q$-branch, the band $2 \rightarrow 1$ two in the $P$-branch, two in the $Q$-branch and one in the $R$-branch, etc. If, therefore, the $K$-values are increased by one, that means that there is one more missing line in every branch for the corresponding sub-band.

The relative intensities of the individual lines in an absorption band are given by

$$J = P^{K',\,J'}_{K'',\,J''}\, e^{-W''/kT}, \tag{6}$$

in which $W''$ is the energy in the lower electronic states, and $P^{K',\,J'}_{K'',\,J''}$ factors in which the transition probabilities and weights *a priori* are contained. These intensity factors are for the different branches occurring in a vertical band.

$$\begin{array}{ll} \left.\begin{array}{l} rR(K-1,\,J-1) \\ pP(K,\,J) \end{array}\right\} & \dfrac{A(J+K-1)(J+K)}{8J}, \\[2ex] \left.\begin{array}{l} pQ(K,\,J) \\ rQ(K-1,\,J) \end{array}\right\} & \dfrac{A(2J+1)(J-K+1)(J+K)}{8J(J+1)}, \\[2ex] \left.\begin{array}{l} pR(K,\,J-1) \\ rP(K-1,\,J) \end{array}\right\} & \dfrac{A(J-K+1)(J-K)}{(J+K)(J+K-1)}, \end{array} \tag{7}$$

If the constants of the molecule are known, so that the energy levels can be calculated, these expressions allow one to find the relative intensities of all lines in a given band. The formulae for the intensity factors show that the different branches have very unequal strengths. For not too small values of $K$ only those branches are strong for which $K$ and $J$ change in the same direction, i.e., the $pP$- and $rR$-branches. The $Q$-branches though very strong for small values of $K$ are much weaker for higher $K$'s and the $pR$- and $rP$-branches are so weak that they are

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[12] For the designation of the branches the following nomenclature which is an extension of that for the diatomic molecules is simple and useful. The change in $J$ is designated, as for diatomic molecules, so that if $\Delta J = -1$, 0, or $+1$ we have $P$-, $Q$-, and $R$-branches. The corresponding $K$-transitions are given by the equivalent small letters. A $pQ$-branch, e.g., is a branch for which $\Delta K = -1$ and $\Delta J = 0$. If it is desired to label a definite line, the quantum numbers of the lower state are given between brackets. $pQ(K, J)$ means a line for which $K-1 \rightarrow K$ and $J \rightarrow J$. In this paper all the transitions are written as if they occurred in *emission.* This nomenclature is very convenient for symmetrical or slightly asymmetrical molecules. In the latter case the two doublet components can be distinguished by subscripts. If the asymmetry is considerable, this nomenclature is still possible, and may in certain cases be preferable, as $K$ always can be used to label the levels, even if it has lost its significance as component of the angular momentum along the symmetry axis.

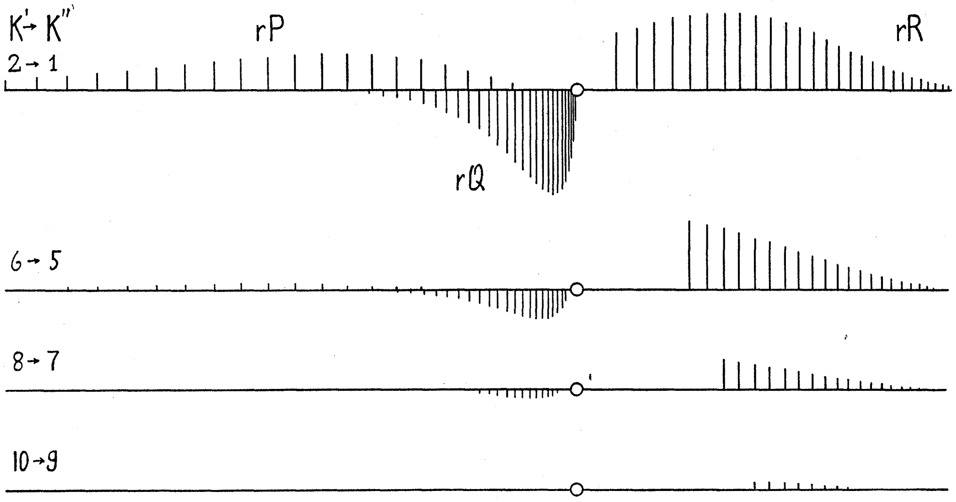

FIG. 3. The intensity distribution in a few typical sub-bands at room temperature. The spacing and convergence of the lines is chosen arbitrarily.

completely absent except for the lowest $K$-values. Fig. 3 gives an idea of the expected intensities for some characteristic values of $K$.

## §5. ALTERNATING INTENSITIES

The formaldehyde molecule is symmetric with respect to a rotation of 180° about the CO-axis. It behaves in this respect exactly as an $H_2$-molecule. On account of the nuclear spin 1/2 in the hydrogen molecule successive rotational levels have alternately weights one and three, which results in the well-known alternating intensities in the molecular spectrum of hydrogen. In the formaldehyde molecule the same state of affairs must exist with respect to rotations about the CO-axis. As these rotations are characterized by the quantum number $K$, successive $K$-transitions will be alternately strong and weak and the intensities must correspond to a ratio three to one in the weights of the respective energy levels. Further on it will be shown that this is exactly what is observed in the absorption bands.

## §6. DEVIATIONS FROM THE SYMMETRIC TOP

The statements of the preceding paragraphs are strictly true only if the molecule is symmetric. There will be only slight changes in this picture if the asymmetry is only small. In the first place there will be a doubling of the lines. We have seen in §3 that a slight asymmetry results in a doubling of the energy levels and that this doubling is analogous to the Λ-doubling of diatomic molecules. The same kind of selection rules must hold here (see below) which means that only two of the possible four combinations are allowed, i.e., that all the lines (except those which involve levels with $K=0$) must be double. This doubling decreases rapidly with increasing $K$ but increases roughly with the $2K$th power of $J$. For small values of $K$ we have to expect besides a shift of the whole doublet from its position for the symmetric top.

The selection rules for the asymmetrical top can be derived from the symmetry properties of the rotational wave functions. The results can be expressed in a very simple way with the help of the quantum numbers $K$ and $J$.

We have to consider two transformations. The first is an inversion at the $C$-axis, the axis of the smallest moment of inertia, the second a reflection at a plane perpendicular to this axis. The rotational wave functions can be either symmetric or antisymmetric to these transformations. If, as is customary, we designate by a $+$ that the wave function is symmetric and by a $-$ that it is antisymmetric, the symmetry properties of every state can be described by a pair of

TABLE I. *The bands at 3530, 3390, 3260, 3370, 3430 and 3295A.*

An * with a wave number means that the line has been used more than once. It is liable to be less accurate for this reason. The absence of an * does not mean that the line is necessarily single, as it may be confused with an unclassified line.

A wave number between [ ] means that a weak line should fall very close to a strong line of different origin, so that it cannot be separated from it. In this case the wave-length is entirely unreliable.

The intensities (numbers between ( )) are rough estimates only. Their values for different bands cannot be compared. The meaning of the letters attached to the intensity figures is

| | | | |
|---|---|---|---|
| b | line broad. | h | only found on the high temperature plates. |
| c | line very close to another line and not completely resolved from it. | r | degraded toward longer wave-lengths. |
| d | line diffuse. | v | degraded toward shorter wave-lengths. |

*Band at 3530A.*

| $J''$ | $K''=3$ | | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | *pP-Branches* | | | | | | |
| 3 | 282 61.44*(3) | | | | | | | | | | | |
| 4 | 58.12 (1) | | 28200+<br>39.24 (1b) | | | | | | | | | |
| 5 | 54.54 (2) | | 35.73 (1) | 28200+<br>15.90 (3) | | | | | | | | |
| 6 | 50.70 (3) | | 31.87 (1) | 12.03 (2) | 28100+<br>91.33 (1) | | | | | | | |
| 7 | 46.43 (2d) | | 27.57 (1) | 07.87 (2) | 87.15 (2c) | 28100+<br>65.59 (3d) | | | | | | |
| 8 | 41.93 (2d) | | 23.16 (2) | 03.35 (2) | [82.52] (2b) | 61.07 (2) | | | | | | |
| 9 | 37.32 (0) | 37.07 (0d) | 18.33 (0) | 28100+<br>98.60 (2) | — | 56.35 (2c) | | 28100+<br>10.61 (0) | | | | |
| 10 | 32.35 (1) | 31.87 (1) | 13.29 (0) | 93.53 (2d) | — | 51.24 (1) | | 05.52 (0) | | | | |
| 11 | 27.08 (0) | 26.51 (2b) | [07.87] (2) | 88.16 (2) | 67.46 (0) | 45.88 (2) | | 00.13*(1) | | 28000+<br>51.35*(0bh) | | |
| 12 | 21.62 (2) | 20.65 (1) | 02.26 (0d) | 82.55*(2b) | — | 40.25 (1) | | 28000+<br>94.44 (0) | | 45.54 (0h) | | |
| 13 | 15.90*(3) | 14.45 (1) | | 76.56 (2) | 55.85 (0) | 34.30 (1) | | 88.57 (0) | | 39.64 (0ch) | | |
| 14 | 09.87 (1) | 07.87*(2c) | | 70.32 (2) | [49.72] (2) | 28.03 (1) | | 82.31 (0) | | 33.42 (0h) | | |
| 15 | 03.63 (1) | 01.20 (0) | | 63.74 (2) | — | 21.56 (0) | | 75.80 (0ch) | | 26.81 (0h) | | |
| 16 | 28100+<br>97.16 (1d) | 93.99 (1d) | | 56.90 (2) | 36.32 (0) | 14.63 (0) | | 68.94 (1h) | | 19.94 (0bh) | | |
| 17 | 90.38 (0) | 86.33 (1c) | | 49.72 (2) | | 07.54*(0c) | 28000+<br>85.00 (0h) | 61.75*(2h) | | | | |
| 18 | | | | 42.31 (1) | | 00.13*(1) | 77.63 (0h) | 54.34 (0bh) | | | | |
| 19 | | | | 34.58 (1) | | 28000+<br>92.27 (0h) | 69.84 (0bh) | 46.59 (0h) | | | | |
| 20 | | | | 26.51 (1) | | 84.29 (0h) | 61.75*(2h) | 38.61 (0h) | | | | |
| 21 | | | | 18.20 (0) | | 75.98 (0ch) | | 30.21 (0h) | | | | |
| 22 | | | | 09.52 (0) | | 67.35 (0ch) | | 21.56 (0ch) | | | | |
| 23 | | | | 00.57 (0) | | 58.41 (1h) | | | | | | |
| 24 | | | | 28000+<br>91.31 (0) | | 49.18 (0h) | | | | | | |
| 25 | | | | 81.78 (0h) | | 39.64 (1ch) | | | | | | |
| 26 | | | | 72.06 (0hc) | | 29.79 (0h) | | | | | | |
| 27 | | | | 61.75*(2h) | | 19.52 (0h) | | | | | | |
| 28 | | | | 51.35 (0bh) | | | | | | | | |

+ and − signs, the first referring to the first and the second to the second of the transformations mentioned above. For a given $K$ and $J$ we have two levels, and if we designate the upper one by $D_1$ and the lower one by $D_2$ the following scheme gives all the necessary information

| | | | | |
|---|---|---|---|---|
| $K+J$ | even | even | odd | odd |
| $K$ | even | odd | even | odd |
| $D_1$ | ++ | +− | −+ | −− |
| $D_2$ | −+ | −− | ++ | +− |

For $K=0$ there is only $D_1$.

The selection rules are different according to whether the matrix component of the electric moment belonging to the transition in question has a component along the $A$-, $B$-, or $C$-axis. The selection rules are

| *Electric moment along* | *first sign* | *second sign* |
|---|---|---|
| $A$ | unchanged | changes |
| $B$ | changes | changes |
| $C$ | unchanged | unchanged |

The connection between the possible branches and the values of $K$ and $J+K$ is

| Branch | $\Delta(K+J)$ | $\Delta K$ |
|---|---|---|
| $pP$, $rR$ | $\pm 2$ | $\pm 1$ |
| $pR$, $rP$ | 0 | $\pm 1$ |
| $pQ$, $rQ$ | $\pm 1$ | $\pm 1$ |
| $qP$, $qR$ | $\pm 1$ | 0 |
| $qQ$ | 0 | 0 |

The combination of the last three schemes gives

Table I. (*Continued.*) *Band at 3530A.*

| J'' | K''=3 | | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | *pQ-Branches* | | | | | | |
| 3 | 282 67.80 (1d) | | | | | | | | | | | |
| 4 | 66.64 (3c) | | 28200+<br>47.84 (0d) | | | | | | | | | |
| 5 | 65.23 (2) | | [46.43] (3) | 28200+<br>26.83 (0) | | | | | | | | |
| 6 | 63.48 (2) | | — | 24.85 (1) | | | | | | | | |
| 7 | 61.44*(3) | | 42.56 (0) | 22.79 (1) | | | | | | | | |
| 8 | 59.21 (0) | 58.95 (0) | 40.04 (2c) | 20.45 (1) | | | | | | | | |
| 9 | 56.73 (3) | 56.27 (2) | 37.59 (0) | 17.82 (1) | | 28100+<br>75.45 (0c) | | | | | | |
| 10 | 53.81 (1) | 53.28 (1) | 34.64 (0) | 14.87 (1) | | — | | | | | | |
| 11 | 50.70*(3) | 49.97 (1) | 31.39 (2) | 11.69 (2) | | 69.21*(1d) | | | | | | |
| 12 | 47.38 (1) | 46.43*(3) | | 08.07 (2c) | | — | | | | | | |
| 13 | 43.73 (2) | 42.35 (1) | | 04.27 (2c) | | — | | | | | | |
| 14 | 39.91 (2c) | 38.07 (0) | | 00.22 (1) | | 57.91 (1) | | | | | | |
| 15 | 35.73 (1) | 33.43 (1r) | | 28100+<br>95.75 (1) | | 53.39 (0) | | 28100+<br>07.54*(0c) | | | | |
| 16 | 31.39*(2) | 28.47 (1) | | 91.03 (1d) | | 48.83 (1b) | | 02.95 (0) | | | | |
| 17 | | | | 86.06 (1c) | | 43.73 (0) | | | | | | |
| 18 | | | | 80.72 (1) | | — | | 28100+<br>92.76 (0h) | | | | |
| 19 | | | | 75.12 (1c) | | 32.76 (0) | | | | | | |
| 20 | | | | 69.21 (1d) | | 26.87 (0) | | | | | | |
| 21 | | | | 63.01 (0) | | | | | | | | |
| | | | | | | *rQ-Branches* | | | | | | |
| 4 | 283 58.73 (2) | | | | | | | | | | | |
| 5 | 57.22*(3b) | | 28300+<br>[68.88] (3) | | | | | | | | | |
| 6 | 55.48*(2d) | | 67.19 (0) | 28300+<br>78.01*(2) | | | | | | | | |
| 7 | 53.40 (1) | | 65.17 (0) | 75.82*(2d) | — | | | | | | | |
| 8 | 51.07*(3d) | | 62.84 (0) | 73.49 (1) | — | — | | | | | | |
| 9 | 48.42*(2) | | 60.16*(2) | 70.84 (0) | | | | | | | | |
| 10 | 45.39 (2c) | | [57.22] (3b) | [67.77] (4) | 28300+<br>77.46 (0h) | 28300+<br>86.10 (0) | | | | | | |
| 11 | 42.13 (3) | | 53.83 (1d) | 64.61*(2c) | 74.22*(1) | 82.79 (0c) | | 28300+<br>96.85 (0h) | | | | |
| 12 | 38.51* (4) | | 50.28 (0) | 61.02 (2) | | 79.20 (1c) | | 93.34 (0h) | | | | |
| 13 | 34.57 (2b) | | [46.49] (2c) | 57.22*(3b) | | 75.32 (1) | | — | | | | |
| 14 | 30.56 (2b) | 30.22 (1) | | 52.98*(1) | | 71.20 (0) | | 85.27 (0h) | | | | |
| 15 | 26.00 (1) | 25.64 (1) | | 48.42*(2) | | 66.70 (0h) | | [80.63] (1b) | | | | |
| 16 | 21.24 (2) | 20.67 (0) | | 43.68 (2) | | 61.92 (0) | | [75.82] (2d) | | | | |
| 17 | 16.10 (1) | 15.34 (3c) | | 38.51*(4) | | | | | | | | |
| 18 | 10.71 (2c) | 09.69 (0c) | | | | | | | | | | |
| | | | | | | *rR-Branches* | | | | | | |
| 3 | 283 68.46 (3) | | | | | | | | | | | |
| 4 | 69.40 (3) | | 28300+<br>81.15 (1) | | | | | | | | | |
| 5 | 70.09*(3c) | | 81.88*(2) | 28300+<br>92.54*(3) | | | | | | | | |
| 6 | 70.49*(3c) | | 82.20*(2) | 92.87*(3) | 28400+<br>02.51*(2) | | | | | | | |
| 7 | 70.49*(3c) | | 82.20*(2) | 92.87*(3) | 02.51*(2) | 28400+<br>11.14 (2) | | | | | | |
| 8 | 70.25 (3c) | | 81.88*(2) | 92.54*(3) | 02.31 (1) | 10.93 (2) | 28400+<br>18.41 (0) | | | | | |
| 9 | 69.72 (3) | | 81.49 (1) | 92.13*(3) | 01.75 (1) | 10.35 (2) | 17.89 (0) | 28400+<br>24.43 (1) | | | | |
| 10 | 68.88 (3) | | 80.63 (1b) | 91.31 (3) | 00.92 (1c) | 09.49 (2) | 17.04*(1) | 23.56 (1) | 28400+<br>29.02*(1h) | | | |
| 11 | 67.77 (4) | | 79.49 (1) | 90.16 (3) | 28300+<br>99.74 (1) | 08.35 (2) | 15.90 (0) | 22.37 (1) | 27.90 (0h) | 28400+<br>32.37 (0h) | | |
| 12 | 66.24*(3) | | 78.01*(2) | 88.71 (3) | 98.33 (1) | 06.88 (2) | 14.38 (0) | 20.88 (1) | 26.36 (0bh) | 30.80 (0h) | 28400+<br>34.40 (0h) | |
| 13 | 64.61*(2c) | 64.39 (2c) | 76.30 (1) | 86.99 (2) | 96.62 (0) | 05.12 (1) | 12.68 (0) | 19.11 (0) | [24.43] (1) | 29.02*(1h) | | 28400+<br>34.98 (0h) |
| 14 | 62.54 (1) | 62.24 (1) | 74.22 (1) | 84.94 (2) | 94.52 (0) | 03.07 (1) | 10.57 (0h) | 17.04*(1) | [22.37] (1) | 26.92 (0h) | | 32.84 (0h) |
| 15 | 60.16 (1) | 59.73 (1) | 71.88 (1) | 82.57 (1) | 92.13*(3) | 00.72 (1c) | 08.35*(2) | 14.71 (0) | | [24.43] (1) | | 30.42 (0h) |
| 16 | 57.54 (2) | 56.89 (0) | | 79.94 (1) | 89.50 (0) | 28300+<br>98.09 (1) | 05.65*(0h) | 11.98 (0d) | | 21.80 (0h) | | 27.64 (0h) |
| 17 | 54.46*(1d) | 53.83 (1d) | | 76.96 (2) | — | 95.09 (0) | | 09.05 (0h) | | 18.77 (0h) | | |
| 18 | | | | 73.68 (1) | 83.21 (0) | 91.77 (0) | | 05.65 (1bh) | | 15.44 (0h) | | |
| 19 | | | | 70.09*(3) | | 88.23 (0) | | 02.13 (0h) | | | | |
| 20 | | | | 66.24*(3) | | 84.36 (0) | | | | | | |
| 21 | | | | 61.90 (10) | | 80.12 (0h) | | | | | | |
| 22 | | | | 57.54*(2c) | | 75.82*(2d) | | | | | | |
| 23 | | | | | | 70.84*(0) | | | | | | |

TABLE I. (*Continued.*) *Band at 3390A.*

| $J''$ | $K''=3$ | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 |
|---|---|---|---|---|---|---|---|---|---|
| | | | | *pP-Branches* | | | | | |
| 3 | 294 43.82 (2c) | | | | | | | | |
| 4 | 40.45 (2) | 29400+<br>21.36 (0) | | | | | | | |
| 5 | 36.74 (2) | 17.67 (1) | 29300+<br>97.57 (2) | | | | | | |
| 6 | 32.71 (2) | 13.66*(3) | 93.58 (2) | 29300+<br>72.48 (0) | | | | | |
| 7 | 28.37 (2) | — | 89.24 (2) | 68.18 (0) | 29300+<br>46.19*(2) | | | | |
| 8 | 23.79 (1c)  23.64 (1c) | 04.66 (0) | 84.62 (2) | 63.58 (0) | 41.53 (1) | 29300+<br>18.59 (0) | | | |
| 9 | 18.92 (1c)  18.71*(1c) | 29300+<br>99.84*(3r) | 79.71*(2c) | 58.68*(1c) | 36.57*(2) | 13.60*(2) | 29200+<br>89.89 (1) | | |
| 10 | 13.66*(3)  13.19 (0) | 94.46 (0) | 74.34 (2c) | 53.28 (0) | 31.29 (1) | 08.37 (1) | 84.66 (1) | 29200+<br>59.97 (0) | |
| 11 | 08.25*(2)  [a] | — | 68.77 (1) | 47.70 (1) | 25.74 (1) | 02.77 (0d) | 79.04 (1) | 54.54*(0d) | 29200+<br>29.14 (0d) |
| 12 | 02.46*(1c)  01.53 (0c) | 82.99 (1) | 62.88 (1) | 41.84 (0) | 19.80 (1) | 29200+<br>96.91 (0d) | 73.12 (2d) | 48.58 (0) | 23.21 (0c) |
| 13 | 96.45 (1)  95.11 (0) | 76.72 (0) | 56.64 (1) | 35.54 (1) | 13.60*(2) | 90.60 (0d) | 66.91*(1) | 42.32 (0) | 16.99 (0c) |
| 14 | 90.10 (0)  88.27*(1d) | 70.15 (0) | 50.11 (1) | 29.05 (0) | 07.05 (1) | 84.08 (0) | 60.41 (1) | 35.70 (0) | 10.48*(0c) |
| 15 | 83.56 (0)  81.17 (0) | 63.33 (1c)  63.13*(1c) | 43.27 (1) | 22.13 (2) | 00.17 (1) | 77.23 (0) | 53.56 (0) | | 03.57 (0) |
| 16 | 76.72*(1)  73.66 (0) | 57.06 (0d)  55.57*(1) | 36.06 (1) | — | 29200+<br>93.02 (1) | 70.00 (0) | 46.38*(1) | | |
| 17 | 69.81*(1r)  65.64 (1) | 48.42 (1)  47.70 (0) | 28.52 (1) | 07.48 (0) | 85.48 (2c) | 62.50 (0) | 38.87 (0) | | |
| 18 | 62.83 (0)  57.27 (0) | | 20.69 (1) | — | 77.69 (1) | 54.54 (0) | 31.08 (0) | | |
| 19 | | | 12.54 (1) | 29200+<br>91.50 (0d) | 69.52 (1) | 46.38*(1) | 22.85*(1) | | |
| 20 | | | 03.99 (1c) | 83.08 (0) | 61.09 (1) | 38.15 (0d) | 14.48 (0) | | |
| 21 | [a] Emission line superimposed | | 29200+<br>95.26 (1) | 74.23 (0c) | 52.30 (1) | | 05.73 (0c) | | |
| 22 | | | 86.13 (1) | 65.14 (0) | 43.14 (0c) | | | | |
| 23 | | | 76.66 (1) | | 33.70 (0) | | | | |
| 24 | | | 66.91*(1) | | 24.07 (1c) | | | | |
| 25 | | | 56.70 (0) | | 13.91 (0) | | | | |
| | | | | *pQ-Branches* | | | | | |
| 3 | 29400+<br>50.13 (2c) | | | | | | | | |
| 4 | 48.84 (2) | — | | | | | | | |
| 5 | 37.34 (4v) | — | 29400+<br>08.25*(2) | | | | | | |
| 6 | 45.41 (1) | 29400+<br>26.14 (2) | 06.24 (0) | 29300+<br>85.03 (0) | | | | | |
| 7 | 43.25 (1d)  43.10 (0) | 24.04 (1) | 04.09*(1d) | 82.99*(1) | — | | | | |
| 8 | 40.80 (1)  40.45*(2) | 21.61 (0) | 01.53 (1) | 80.43 (0) | 29300+<br>58.50 (1c) | — | | | |
| 9 | 38.02 (1)  37.66 (1c) | 18.71*(1c) | 29300+<br>98.68 (1) | — | 55.57 (1) | 29300+<br>32.60 (1) | | | |
| 10 | 34.98 (1)  34.46 (1) | 15.62 (0) | 95.48*(1) | 74.55 (1c) | 52.39 (1) | 29.38 (0) | — | | |
| 11 | 31.61 (1)  30.89 (1) | 12.15 (0) | 92.02 (1) | — | 48.88 (1) | — | 29300+<br>02.17 (0d) | | |
| 12 | 27.96 (1)  26.95 (1) | 08.25*(2) | 88.27*(1d) | 67.13 (1d) | 45.13 (1) | 22.13*(2) | 29200+<br>98.41 (0d) | | |
| 13 | 24.04 (1)  22.71 (0c) | 04.09*(1d) | 84.10 (1) | 63.13 (1c) | 40.97 (1) | — | — | | |
| 14 | 19.81 (1)  18.09 (1) | | 79.71*(2c) | 58.68*(1dc) | 36.57*(2) | 13.60*(2) | 89.89*(1) | | |
| 15 | 15.29 (0)  13.19*(0d)[a] | | 74.79 (1) | 53.82 (0) | 31.78 (1) | | 85.18 (1c) | | |
| 16 | 10.80 (0)  08.25*(0) | | 69.81 (1r) | | 26.75 (1) | | 80.07 (1v) | | |
| 17 | 06.24*(0)  03.22 (0) | | 64.42 (1) | | 21.33 (1) | | 74.60 (1dc) | | |
| 18 | | | 58.68*(1c) | | 15.64 (1d) | | 68.96 (0c) | | |
| 19 | [a] close to Emission line. | | 52.64 (1) | | 09.61 (2) | | 62.95 (0) | | |
| 20 | | | 46.19*(2) | | 03.24 (1) | | 56.70 (1b) | | |
| 21 | | | 39.62*(1) | | 96.50 (0d) | | | | |
| 22 | | | | | 89.53 (0) | | | | |
| 23 | | | | | 82.23 (0) | | | | |
| 24 | | | | | 74.60 (1dc) | | | | |

the following selection rules:

| Electric moment along | *A* | *B* | *C* |
|---|---|---|---|
| *pP, rR, pR, rP* | $D_1\rightarrow D_1$, $D_2\rightarrow D_2$ | $D_1\longleftrightarrow D_2$ | absent |
| *pQ, rQ* | $D_1\longleftrightarrow D_2$ | $D_1\rightarrow D_1$, $D_2\rightarrow D_2$ | absent |
| *qP, qR* | absent | absent | $D_1\longleftrightarrow D_2$ |
| *qQ* | absent | absent | $D_1\rightarrow D_1$, $D_2\rightarrow D_2$ |

The selection rules for the symmetrical top given in §4 are a special case of the rules given here. The two first cases which interest us here differ in that there is crossing over in the *Q*-branches if the electric moment is along the greatest moment of inertia, and in the *P*- and *R*-branches if it is along the middle moment of inertia. (Figs. 4 and 5.)

TABLE I. (*Continued.*) *Band at 3390A.*

| $J''$ | $K''=0$ | | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | *rQ-Branches* | | | | | |
| 3 | | | | | | | | | | |
| 4 | 29500+<br>40.36 (2) | | | | | | | | | |
| 5 | 38.94*(3d) | | 29500+<br>50.13 (2c) | | | | | | | |
| 6 | 36.89 (1) | | 48.25 (0) | 29500+<br>58.52 (2) | | | | | | |
| 7 | 34.68 (2) | | 46.06*(0) | 56.32 (1d) | 29500+<br>65.47 (1c) | | | | | |
| 8 | 32.10 (2) | | — | 53.78 (0) | 62.86*(2) | 29500+<br>[70.90] (3) | | | | |
| 9 | 29.22 (2) | | 40.63 (0) | 50.99*(3c) | 60.00 (1) | 68.19 (1) | — | | | |
| 10 | 26.00*(2) | | 37.45 (1c) | 47.77*(4) | 56.85 (0) | 64.97 (2) | — | — | | |
| 11 | 22.47 (2c) | | 33.87 (0) | 44.13 (3c) | | 61.46 (2c) | 29500+<br>68.56 (0) | — | | |
| 12 | 18.30 (3) | | 30.04 (0) | 40.36*(2) | | 57.54*(2) | 64.64 (0) | 29500+<br>70.69 (c) | | |
| 13 | 14.40 (2) | | 26.00*(2) | — | | | [60.50] (2c) | 66.41 (0) | | |
| 14 | 10.02 (1) | 09.67 (1) | 21.37 (2) | 31.70 (1) | | | | [61.71] (2c) | | |
| 15 | 05.13 (1) | 04.73*(2) | | 26.75 (2) | | | | 57.20 (0) | | |
| 16 | 00.01 (2c) | 99.45*(1d) | | 21.77 (0) | | | | — | | |
| 17 | 94.51 (0) | 93.76 (2) | | 16.26 (1c) | | | | 46.46 (0) | | |
| 18 | 88.73 (0) | 87.65 (0) | | 10.49 (0) | | | | 40.63 (0) | | |
| 19 | | | | 04.32 (1) | | | | | | |
| 20 | | | | 29400+<br>97.82 (0) | | | | | | |
| 21 | | | | 90.96 (1) | | | | | | |
| 22 | | | | 83.95 (0) | | | | | | |
| | | | | | *rR-Branches* | | | | | |
| 3 | 29500+<br>50.13 (2c) | | | | | | | | | |
| 4 | 50.99*(3c) | | 29500+<br>62.29 (2c) | | | | | | | |
| 5 | 51.57*(4) | | 62.86 (2) | 29500+<br>73.19 (3c) | | | | | | |
| 6 | 51.57*(4) | | 63.06*(2) | 73.33*(4c) | 29500+<br>82.40*(2) | | | | | |
| 7 | 51.57*(4) | | 63.06*(2) | 73.33*(4c) | 82.40*(2) | 29500+<br>90.46 (2) | | | | |
| 8 | 51.11 (3c) | | 62.48 (2c) | 72.73 (3c) | 81.84 (2) | 90.00*(2) | 29500+<br>97.06 (1) | | | |
| 9 | 50.35 (3c) | | 61.71 (2c) | 71.98 (2b) | 81.10 (2) | 89.24 (3) | 96.30 (1) | 29600+<br>02.33 (2v) | | |
| 10 | 49.26 (2) | | 60.68 (2c) | 70.90 (3c) | 80.01 (2) | 88.16 (3) | 95.16 (1) | 01.22 (2) | 29600+<br>06.22 (0c) | |
| 11 | 47.77*(4) | | 59.29 (2c) | 69.52 (3b) | 78.54 (2) | 86.77 (3) | 93.75 (1c) | 29500+<br>99.78 (2) | 04.78*(1c) | 29600+<br>08.78 (0) |
| 12 | 46.06 (2) | | 57.54*(2) | 67.74 (3) | 76.85 (2c) | 85.00 (3r) | 92.06 (1r) | 98.01 (2) | 02.96 (1) | 07.02 (0c) |
| 13 | 44.13*(3) | 43.91 (1) | 55.39 (2c) | 65.68 (3c) | 74.82*(3) | 82.95 (2) | 90.00*(2) | 95.90 (2r) | — | 04.78*(1c) |
| 14 | — | 41.37 (1) | 52.96 (0) | 63.30 (2) | 72.38 (1) | 80.60 (2) | 87.49 (0c) | 93.56 (1c) | 98.45 (0) | [02.33] (2v) |
| 15 | 38.94*(3d) | 38.49 (1d) | | 60.50 (2c) | 69.52*(3b) | 77.89 (2) | [85.00] (3r) | 90.80 (1) | [95.90] (2r) | [99.78] (2) |
| 16 | — | — | | 57.54*(2) | 66.60 (2) | 74.82*(3) | | 87.71 (0c) | | |
| 17 | 32.62 (0) | 31.70 (0) | | 54.19 (0d) | | 71.47 (1) | | 84.39 (0) | | |
| 18 | | | | — | | 67.74*(3) | | [80.60] (2) | | |
| 19 | | | | 46.46 (0) | | 63.80 (2c) | | 76.59 (2c) | | |
| 20 | | | | — | | 59.51 (2c) | | [72.38] (1) | | |
| 21 | | | | 37.29 (1c) | | | | | | |

These selection rules are, of course, the same as those given by Kramers and Ittmann or Dennison. They are, however, in a form much more convenient for our purpose. Even if the asymmetry is larger so that the symmetrical top is no more a good approximation, the quantum number $K$ can be used for the classification of the levels, and this may often be found convenient. In that case it cannot be interpreted, however, as the angular momentum about the symmetry axis.

It needs hardly mentioning that all these considerations, even if the deviations due to the asymmetry are strictly taken into account, lead only to approximative results for an actual molecule. The results are true only to such an extent as the molecule can be regarded as a rigid top. Especially for higher values of the rotational quantum numbers deformations will take place, which are of an analogous though more complicated nature, as those observed for diatomic molecules. The effect of such deformations can be detected in the formaldehyde bands, but it is in general very small compared with the total rotational energy.

TABLE I. (*Continued.*) *Band at 3260A.*

| $J''$ | $K''=3$ | 4 | 5 | 6 | 7 | $K''=3$ | 4 | 5 | 6 | 7 |
|---|---|---|---|---|---|---|---|---|---|---|
| | *pP-Branches* | | | | | *rQ-Branches* | | | | |
| 3 | 306 07.07 (1c) | | | | | | | | | |
| 4 | 03.64 (2) | 30500+<br>84.40 (0) | | | | 307 03.10 (0) | | | | |
| 5 | 305 99.79 (2c) | 80.57 (0) | 30500+<br>60.21 (1) | | | 01.28 (0) | | | | |
| 6 | 95.75 (2) | 76.53 (1) | 56.13 (1) | 30500+<br>34.67 (0) | | 306 99.32 (1) | | 30700+<br>20.15*(0) | | |
| 7 | 91.27 (2) | 72.01 (0) | 51.62 (2) | [30.46] (1b) | 30500+<br>07.86 (1) | 96.91 (1) | | 17.79 (0) | | |
| 8 | 86.53 (2b) | 67.25 (1) | 46.85 (2c) | — | 03.04 (1) | 94.16 (1c) | | 15.22 (0c) | | 30700+<br>31.52 (0c) |
| 9 | 81.52 (0c) 81.21 (0c) | 62.17 (1) | 41.77 (2) | 20.31 (0r) | 30400+<br>97.94 (1) | 91.12 (1c) | | 12.01*(2) | | 28.52 (0) |
| 10 | 76.01 (1) 75.63 (1c) | 56.60*(1) | 36.30 (1) | 14.94 (0d) | 92.49 (1) | 87.66 (1) | | 08.56 (0) | | 24.94*(1) |
| 11 | 70.38 (1) 69.79 (1) | 50.82 (1) | 30.46 (1b) | — | 86.69 (1) | 83.92 (1) | | 04.96 (0c) | | 21.13*(0) |
| 12 | 64.39 (0) 63.55*(1) | 44.63*(1c) | 24.35 (2b) | 03.04*(1) | 80.58 (0) | 79.74 (1c) | | 00.82 (0) | | |
| 13 | 57.98 (0) 56.60*(1) | 38.12 (1) | 17.87 (1) | 30400+<br>96.44*(1c) | 74.02 (1) | 75.43 (1c) 75.13 (1c) | | | | |
| 14 | 51.37 (0) 43.49 (0) | | 10.97 (1) | | — | 70.58 (0b) 70.25 (0) | | | | |
| 15 | 44.63 (1) 42.23 (1) | | 03.77 (0b) | | 60.07 (0) | 65.44 (1) 64.98 (1) | | | | |
| 16 | 37.40 (1) 34.67 (0) | | 30400+<br>96.23 (1c) | | | 59.81 (2c) 59.26 (1c) | | | | |
| 17 | | | 88.45 (1d) | | | | | | | |
| | *pQ-Branches* | | | | | *rR-Branches* | | | | |
| 3 | 306 13.35 (0) | | | | | 307 12.98*(2) | | | | |
| 4 | 12.03 (1) | 30500+<br>92.80*(1) | | | | 13.52*(3c) | 30700+<br>24.62*(1d) | | | |
| 5 | 10.36 (2c) | 91.27*(2) | 30500+<br>70.77 (1) | | | 13.90*(3c) | 24.94*(1r) | 30700+<br>34.81*(2c) | | |
| 6 | 08.29 (0) | 89.01 (1) | 68.65 (1) | | | 13.90*(3c) | 24.94*(1r) | 34.81*(2c) | | |
| 7 | 06.07 (1c) 05.92 (1c) | [86.53] (2b) | 66.31 (1) | 30500+<br>44.99*(2) | | 13.52*(3c) | 24.62*(1d) | 34.50 (1c) | | 30700+<br>50.94 (0) |
| 8 | 03.40 (0c) 03.16 (1c) | 84.00*(1d) | 63.55 (2) | 42.23*(1) | 30500+<br>19.75 (0) | 12.98*(2) | 24.10 (0) | 33.90 (1) | | 50.27 (0) |
| 9 | 00.46 (1c) 00.07 (1c) | 80.81*(1b) | 60.59 (1) | 39.19 (0) | 16.73 (0) | 12.01 (2) | 23.06 (1c) | 32.96 (1) | | 49.18 (0) |
| 10 | 97.03 (1) 96.60 (1) | 77.61 (2) | 57.17 (1) | 35.93 (0) | 13.32 (0) | 10.69 (1) | 21.77 (0) | 31.63 (1c) | | 47.80 (0) |
| 11 | 93.41 (2) 92.80 (1) | | 53.53 (0) | | 09.68 (0) | 09.00 (1) | 20.15*(0) | 29.95 (1) | | 46.15 (0) |
| 12 | 89.49 (1) 88.65 (0) | | 49.49 (0) | | 05.58 (0) | 06.95 (1) | 18.13 (0) | 27.90 (1) | | 44.06 (0) |
| 13 | 85.29 (2) 84.00*(1d) | | 44.99*(2) | | 01.19 (0) | 01.80 (1d) 01.54 (1) | | 25.62 (1) | | 41.60 (0) |
| 14 | 80.81 (1b) 79.16 (0) | | 40.28 (1) | | 30400+<br>96.44 (1c) | 30600+<br>98.83 (1b) 98.36 (0) | | 22.83 (1c) | | 38.72 (0) |
| 15 | 76.01*(1) 74.29 (1) | | 35.11 (1) | | 91.40 (0) | 95.67 (0) 94.90 (0) | | 19.75*(0c) | | |
| 16 | | | 29.71 (1) | | | | | 16.37 (0) | | |
| 17 | | | | | | | | [12.72] (2c) | | |

## §7. OBSERVED STRUCTURE

All the absorption bands under consideration have the following features in common. In the center of the bands the absorption is strongest, but the lines are so close together that this region is only partly resolved and there are no obvious regularities. On the violet end there is a number of regular progressions of lines (called further on the violet branches) each of which comes to a head toward the shorter wave-length side. The heads themselves form also a regular sequence. It can be observed that in this sequence of violet branches subsequent members are alternately strong and weak. The intensity of the branches diminishes gradually toward the outside of the band. Furthermore it is at once apparent that the outermost branches have fewer lines than those nearer to the center, and a closer inspection reveals that as one goes from the center of the band toward its violet side every subsequent progression has one line less near its head than the preceding one.

On the red side of the bands some regular progressions are also apparent (called in this paper the red branches). The spacing of the lines in these red branches is much wider than in the violet branches and they do not form heads. Also there is no such *apparent* connection between the different red branches as was found between the violet ones.

These are the empirical facts which can be deduced from the plates even without a measurement of the lines. An inspection of the frequencies of the lines shows that the lines in the branches satisfy Deslandres' law very closely and that in most bands also the corresponding lines of the violet branches satisfy a quadratic

TABLE I. (*Continued.*) *Band at 3370A.*[a]

| $J''$ | $K''=3$ | 4 | 5 | 6 | 7 | 8 | 9 | 11 |
|---|---|---|---|---|---|---|---|---|
| | | | | *rQ-Branches* | | | | |
| 4 | 296 82.88 (0) | | | | | | | |
| 5 | 81.43 (2) | | | | | | | |
| 6 | 79.60 (2) | | 29700+<br>[04.92] (2) | | | | | |
| 7 | 77.56 (2) | 29600+<br>90.59 (0) | 02.92 (1) | | | | | |
| 8 | 75.17 (2c) | 88.21 (1c) | 00.53*(2) | | 29700+<br>22.85 (0) | | | |
| 9 | 72.46 (2b) | — | 29600+<br>97.79*(2b) | | — | | | |
| 10 | 69.46 (2c) | 82.54 (0) | 94.99 (1c) | | 17.15*(3) | | | |
| 11 | 66.16 (2c) | 79.26 (0) | 91.55 (2c) | | 13.88*(3) | | | |
| 12 | 62.57 (3)58 | 75.75 (0) | 88.00 (2c) | | 10.29 (0) | | | |
| 13 | 58.64 (1) | 71.76 (1c) | 84.11*(2) | | 06.44*(1) | | | |
| 14 | 54.50 (1c) 54.30 (2c) | 67.56 (0c) | 79.89 (1) | | 02.21 (1d) | | | |
| 15 | 50.03 (2b) 49.56 (2b) | 63.13 (0) | 75.44 (1c) | | 97.79*(2b) | | | |
| 16 | 45.18 (2) 44.65 (1) | | 70.62 (1) | | 92.59*(2) | | | |
| 17 | 40.12 (1) 39.29 (1) | | 65.48 (1r) | | 87.82 (1) | | | |
| 18 | | | 60.06 (1) | | 82.34 (0) | | | |
| | | | | *rR-Branches* | | | | |
| 3 | 296 92.59 (2) | | | | | | | |
| 4 | 93.50 (2c) | 29700+<br>06.77*(2c) | | | | | | |
| 5 | 94.18 (3c) | 07.29*(2c) | 29700+<br>19.55*(3c) | | | | | |
| 6 | 94.53*(3c) | 07.62*(2c) | 19.91*(3c) | 29700+<br>31.45*(3b) | | | | |
| 7 | 94.53*(3c) | 07.62*(2c) | 19.91*(3c) | 31.45*(3b) | 29700+<br>42.25 (3) | | | |
| 8 | 94.36 (3c) | 07.29*(2c) | 19.55*(3c) | 31.45*(3b) | 41.98 (3) | 29700+<br>52.05 (1) | | |
| 9 | 93.79 (2c) | 06.77 (2c) | 19.11 (3) | 30.66 (1) | 41.43 (2) | 51.43 (1c) | 29700+<br>60.73 (1) | |
| 10 | 92.94 (2) | 05.97 (1b) | 18.26 (3) | 29.79 (2) | 40.56 (2) | 50.62*(1b) | 59.79 (1) | |
| 11 | 91.75 (2c) | 04.92*(2b) | 17.15*(3) | 28.61 (2) | 39.39 (2) | 49.32 (0) | 58.58 (1) | 29700+<br>74.86 (1) |
| 12 | 90.36 (2) | 03.36 (1) | 15.66 (3) | 27.17 (2) | 37.91 (2) | 47.90*(1) | 57.08 (1c) | 73.37 (0) |
| 13 | 88.45 (2c) | 01.62 (1) | 13.88*(3) | 25.40 (1) | 36.15 (2) | 46.02 (0) | 55.25 (1) | 71.31 (0) |
| 14 | 86.52 (1c) 86.27 (1c) | 29600+<br>99.54 (1) | 11.86 (2v) | 23.27 (0) | 34.05 (2) | 43.94 (0) | 53.15 (1) | 69.36 (0) |
| 15 | 84.11*(1) 83.74 (0) | | 09.45 (2) | 20.87 (0) | [31.45] (3b) | | 50.62*(1b) | |
| 16 | 81.43*(2) 80.89 (1c) | | 06.77*(2c) | [18.26] (3) | 29.01 (1) | | 47.90*(1) | |
| 17 | 78.44 (2c) 77.56*(2) | | 03.79 (1) | 15.21 (0) | 26.03 (1) | | 44.96 (0) | |
| 18 | | | 00.53*(2) | | 22.65 (1c) | | | |
| 19 | | | 29600+<br>96.85 (1) | | | | | |
| 20 | | | 92.94*(2) | | | | | |
| 21 | | | 88.64 (2c) | | | | | |
| 22 | | | 84.11*(2) | | | | | |

[a] The *p*-branches of the 3370 band fall in the region where the much stronger 3390 band is well developed. At pressures sufficiently high to bring out the lines of λ3370, the absorption of 3390 is so strong that there is no chance to observe any of the *p*-branches of the 3370 band.

formula. All the violet branches have very nearly the same constants, i.e., they can be shifted in such a way that they all coincide. One can do the same thing with the red branches and in this way identify corresponding lines. It becomes then at once apparent that corresponding lines of the different red branches also follow Deslandres' law and that also in these sequences the branches are alternately strong and weak. The spacing of the red branches is much wider than the spacing of the violet progressions. Also in the red branches, as in the violet ones, there is one more line missing in every branch, as one goes toward the outside of the band.

## §8. INTERPRETATION

These are roughly the observed facts. With the results of §3–§5 in mind, it is not difficult to see how they must be interpreted. Let us consider first the sequence of violet branches. The fact that subsequent branches in this sequence show the intensity alternations indicates that they must be due to subsequent *K*-transitions. The individual lines of each branch are then due to a fixed *K*-transition and different *J*-transitions. The behavior of the missing lines shows clearly that they are *rR*-branches. In the same way it is shown that the red branches must be *pP*-branches. This explains also the fact that their

TABLE I. (*Continued.*) *Band at 3430A.*

| $J''$ | $K''=3$ | 4 | 5 | 6 | 7 | 8 | 9 | $K''=3$ | (4) | 5 |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | *pP-Branches* | | | | | | *rQ-Branches* | |
| 3 | 290 84.03 (3) | | | | | | | 291 79.70 (2r) | | |
| 4 | 80.72 (2) | 29000+<br>61.02 (1) | | | | | | 78.14*(2) | | |
| 5 | 77.15 (3v) | 57.43 (1) | 29000+<br>36.84 (2c) | | | | | 76.36 (3d) | | |
| 6 | 73.19 (3) | 53.58 (1) | 32.94 (2) | 29000+<br>11.72*(2) | | | | 74.31*(3d) | | 29100+<br>98.73 (1d) |
| 7 | 68.97 (3d) | 49.47 (1c) | 28.80*(3v) | 07.59 (0) | 28900+<br>86.27*(3) | | | 71.92*(2) | | 96.58 (2c) |
| 8 | 64.61 (1c) 64.46 (1c) | 44.89 (1) | 24.27 (2c) | 03.05 (0c) | 81.78 (1) | | | 69.27 (3c) | | 94.23 (2d) |
| 9 | 59.87 (1c) 59.59 (1c) | 40.16 (2d) | 19.41 (3) | 98.21 (2) | 76.90 (2) | | 28900+<br>36.57 (0) | 66.24 (2) | | 91.37*(3) |
| 10 | 54.86 (2) 54.49 (1) | 35.00 (1) | 14.41 (3) | 93.14 (1) | 71.87 (2) | | 31.45 (0) | 62.94 (2) | | 88.50*(2) |
| 11 | 49.70 (1c) 49.04 (1) | 29.63 (0) | 08.99 (3) | 87.75 (0) | 66.43 (1) | | 26.01 (0) | 59.38 (2) | | 85.15 (2v) |
| 12 | 44.03 (1) 43.26 (2) | 23.93 (1c) | 03.30 (2c) | 82.08 (0) | 60.69 (1) | | 20.35 (0c) | 55.49 (2) | | 81.48 (1) |
| 13 | 38.18 (1) 37.12 (1c) | 17.94 (0) | 28900+<br>97.34 (2) | 76.06 (0) | 54.64 (1) | | 14.33 (0c) | 50.97 (2db) | | 77.49 (2) |
| 14 | 32.03 (1) 30.59 (0) | 11.72*(2) | 91.05 (2) | 69.84 (1) | 48.38 (1) | | 07.99 (0) | 46.74 (0) 46.17 (0) | | |
| 15 | 25.82 (2) 23.75 (0) | 05.25 (1c) | 84.40 (1) | 63.20 (0) | 41.69 (1) | | 01.40 (0) | 41.97 (2c) 41.34 (2) | | |
| 16 | 19.43*(3) 16.48 (2) | | 77.56 (1) | | 34.85 (1) | | 28800+<br>94.46 (0) | 36.78 (1) 35.87 (1c) | | |
| 17 | | | 70.38 (1) | | 27.58 (0) | | 87.22 (0c) | 31.21 (1c) 30.24 (1) | | |
| 18 | | | 62.86 (1c) | | 20.06 (0c) | | 79.70 (0) | | | |
| 19 | | | 55.13 (1v) | | 12.24 (0r) | | | | | |
| 20 | | | 46.99 (1) | | 04.15 (0) | | | | | |
| 21 | | | 38.57 (0) | | 28800+<br>95.34 (0) | | | | | |
| 22 | | | 29.88 (0) | | 86.78 (0) | | | | | |
| 23 | | | 20.85 (0) | | | | | | | |

| $J''$ | $K''=3$ | 4 | 5 | 6 | 7 | $K''=3$ | 4 | 5 | 6 | 7 |
|---|---|---|---|---|---|---|---|---|---|---|
| | | *pQ-Branches* | | | | | *rR-Branches* | | | |
| 3 | 290 90.49 (1) | | | | | 291 89.40 (3) | | | | |
| 4 | 89.35 (2v) | | | | | 90.35 (3c) | 29200+<br>01.59 (2c) | | | |
| 5 | 87.87 (3d) | 29000+<br>68.14 (1) | 29000+<br>47.54 (0) | | | 91.02 (4d) | 02.27*(3) | 29200+<br>13.24*(4) | | |
| 6 | 96.09 (2) | 66.34 (1) | 45.76 (2) | 29000+<br>24.49 (0c) | | 91.37*(2c) | 02.63*(3) | 13.56*(4) | 29200+<br>25.86*(2d) | |
| 7 | 84.03*(3) | 69.31 (1c) | 43.67 (1) | 22.49 (0) | 29000+<br>01.27*(1) | 91.37*(4c) | 02.63*(3) | 13.56*(4) | 25.86*(2d) | 29200+<br>37.20 (1d) |
| 8 | 81.76 (1c) 81.59 (1c) | 62.00 (2) | 41.33 (2c) | 00.09 (0) | 98.79 (0) | 91.20 (2c) | 02.27*(3) | 13.24*(4) | 25.50 (1) | 36.90 (1d) |
| 9 | 79.15 (2c) 78.83 (2) | 59.33 (1c) | 38.62 (2) | 17.40 (0) | 96.08 (0) | 90.59 (3c) | 01.73 (2c) | 12.69 (3) | 25.00 (2c) | 36.26 (0d) |
| 10 | 76.24 (2) 75.86 (1) | — | 35.70 (1) | 14.41*(3) | 93.14*(1) | 89.71 (3) | 00.88 (1d) | 11.82 (3) | 24.15 (2d) | 35.32 (0d) |
| 11 | 73.19*(3) 72.53 (2) | [53.20] (2d) | 32.45 (1) | 11.17 (0) | 89.70*(1d) | 88.50*(2) | 29100+<br>99.72 (1c) | 10.56 (3) | 22.93 (2) | 34.77 (0) |
| 12 | 69.71 (3d) 68.97*(3d) | 49.47*(1c) | 28.80*(3v) | 07.59 (0) | 86.27*(3) | 86.94 (2c) | 98.20 (1) | 09.11 (2) | 21.53 (0) | 32.60 (0) |
| 13 | 66.02 (1) 64.93 (1) | 45.76*(2) | 25.05 (1) | 03.78 (0c) | 82.34 (0) | 85.15 (2v) | 96.45 (2c) | 07.27 (2) | 19.61 (0) | 30.90 (0) |
| 14 | 62.00*(2) 60.63 (1) | | 20.90 (1) | 99.62 (1d) | 78.15 (0) | 83.19 (1c) 82.96 (1c) | | 05.15 (1d) | 17.52 (0) | |
| 15 | 57.96 (2c) 55.97 (1d) | | 16.47 (2) | | 73.68 (0) | 80.80 (1) 80.42 (1) | | 02.63*(3) | | |
| 16 | | | 11.72*(2) | | 68.84 (0) | 78.14*(1) 77.49 (1) | | 29100+<br>99.96 (1c) | | |
| 17 | | | 06.63 (1) | | 63.71 (0b) | 75.11 (0) 74.31*(2d) | | | | |
| 18 | | | 01.27 (1) | | 58.33 (1) | 71.92*(2) 70.67 (1) | | | | |
| 19 | | | 95.59 (1) | | 52.63 (0) | 68.35 (2d) 66.64 (0) | | | | |
| 20 | | | 89.70*(1d) | | 46.53 (0) | | | | | |
| 21 | | | 83.41 (1c) | | 40.24 (0) | | | | | |

spacing is so much wider than that of the violet branches, for the band is degraded toward the red. We have seen that the *rR*- and the *pP*-branches are for not too small values of *K* the only ones with an appreciable intensity, but that for smaller values of *K* also *rQ*- and *pQ*- branches must exist and, with a smaller intensity, also *rP*- and *pR*-branches. If the *rR*-branches are given, the position of the *rP*-lines can be found by extrapolation, and with a suitable assumption about the numbering of the lines also the *rQ*-branches. (In each sub-band everything is exactly as in a band of a diatomic molecule.) These calculated branches are actually found and are more intensive if we go toward the center of the band where the sub-bands with small values of *K* lie. In this way the numbering of the lines can be fixed, as only with one definite numbering the *Q*-branches are found in their right places.

In Table I the wave numbers and intensities of the classified lines are given. Whereas on both sides of the bands almost all the observed lines are classified, there is a large number of unclassified lines in the center of the bands. These lines

TABLE I. (*Continued.*) *Band at 3925A.*

| $J''$ | $K''=3$ | 4 | 5 | (6) | 7 | $K''=3$ | (4) | 5 | (6) | 7 |
|---|---|---|---|---|---|---|---|---|---|---|
| | | *pP-Branches* | | | | | | *rQ-Branches* | | |
| 3 | 302 86.95 (1) | | | | | | | | | |
| 4 | 83.58 (1c) | 30200+<br>[62.39] (1c) | | | | 303 78.51 (2c) | | | | |
| 5 | 79.89 (1) | 58.56 (0c) | 30200+<br>35.55 (1c) | | | 76.76 (2) | | | | |
| 6 | 75.90 (1) | 54.58 (0d) | 31.50 (1) | | | 74.76 (1) | | 30300+<br>89.34*(2c) | | |
| 7 | 71.73 (2b) | 50.22 (0c) | 27.11 (0) | | 30100+<br>77.00 (0) | 72.54 (1) | | 87.10*(2) | | |
| 8 | 67.00 (2c) | 45.58 (1b) | 22.48 (1) | | 72.36 (1) | 69.94 (1) | | 84.73 (0) | | |
| 9 | [62.39] (1c) 61.94*(1c) | 40.60*(1b) | 17.47*(1b) | | 67.51 (0) | 67.08 (1c) | | 81.81*(1d) | | 30300+<br>93.71 (0) |
| 10 | 56.83 (0c) 56.52*(2c) | 35.35 (1c) | 12.23 (1) | | 62.29 (0) | 63.94 (2d) | | 78.81 (0) | | 90.49 (0) |
| 11 | 51.35 (1) 50.87 (1) | 29.81*(1) | 06.64 (1) | | 56.77 (0) | 60.30 (2) | | 75.35 (1c) | | 87.10*(2) |
| 12 | 45.58*(1b) 44.89*(0b) | 23.79 (0d) | 00.71 (0) | | 50.96 (0) | 56.48 (1c) | | 71.67*(2dc) | | 83.21 (0) |
| 13 | 39.37 (0) 38.51 (0) | 17.65*(0c) | 30100+<br>94.42 (0) | | 44.84 (0) | 52.37 (2c) 52.12 (0c) | | 67.45 (1c) | | 78.81*(1d) |
| 14 | | 11.37 (0) 11.08 (0) | 87.87 (0) | | | | | 63.11*(0c) | | 74.21 (0) |
| 15 | | | 81.00 (0) | | | | | 58.27 (1) | | 69.44*(0) |
| 16 | | | 73.80 (0) | | | | | 53.31 (1) | | |
| 17 | | | 66.27 (0) | | | | | 48.17 (1c) | | |
| 18 | | | 58.44 (0) | | | | | | | |
| | | *pQ-Branches* | | | | | | *rR-Branches* | | |
| 3 | 302 93.30 (1) | | | | | 303 87.92 (2c) | | | | |
| 4 | 92.09 (1) | 30200+<br>[70.99] (1b) | | | | 88.85*(2c) | | | | |
| 5 | 90.48 (1c) | 69.07 (0) | 30200+<br>46.15 (1b) | | | 89.34*(2c) | | 30400+<br>03.84*(1c) | | |
| 6 | 88.29 (0) | 67.35 (0c) | 44.17 (0) | | | 89.52*(2c) | | 04.17*(2c) | | |
| 7 | 86.40 (1) | 64.97 (0) | 41.84 (0) | | 30100+<br>91.90 (0) | 89.52*(2c) | | 04.17*(2c) | | 30400+<br>15.81 (0) |
| 8 | 84.15 (1c) 83.89 (1) | 62.39 (1c) | 39.37 (0) | | 89.37 (0) | 88.85*(2) | | 03.84*(1c) | | 15.32 (0) |
| 9 | 81.21 (1c) 80.91 (1c) | 59.55 (1) | 36.55 (1) | | 86.46 (0) | 88.21 (2c) | | 03.04 (1b) | | 14.63 (0) |
| 10 | 78.11 (0) 77.66 (2) | 56.53 (3c) | 33.35 (1) | | 83.35 (0) | 87.10*(2) | | 02.07 (1) | | 13.62 (0c) |
| 11 | 74.75 (1) 74.19 (1) | 52.91 (1) | 29.81 (1) | | — | 85.33 (2c) | | 00.72 (1) | | 12.18 (0) |
| 12 | 70.99*(1b) 70.29 (1) | 49.06 (0c) | 26.01 (1) | | 76.29 (0d) | 83.84 (1) | | 30300+<br>99.03 (1d) | | 10.53 (0) |
| 13 | 67.00*(2c) 66.09 (1) | 44.94(0) | 21.83 (0) | | — | 81.81*(1d) | | 97.09 (2r) | | |
| 14 | 62.82 (1c) 61.50 (1) | | 17.47*(1v) | | 67.51*(0) | 79.27*(2b) | | 94.73 (1) | | |
| 15 | | | 12.65 (0) | | | 76.76* 76.26 (0) | | 92.48 (0d) | | |
| 16 | | | 07.55 (0) | | | | | 89.52*(2c) | | |
| 17 | | | 02.19 (0) | | | | | | | |
| 18 | | | 96.38 (0) | | | | | | | |
| 19 | | | 90.66 (0) | | | | | | | |
| 20 | | | 84.40 (0) | | | | | | | |

belong to the branches with low values of $K$ which were omitted from the tables for reasons discussed in §11. The *rP*- and *pR*-branches are omitted as their intensity is so low that they can be observed only very incompletely and only in the crowded center portion of the bands where many strong lines interfere with them.

After the bands have been analyzed, the values for the rotational energies of the lower state can be found, and therefore the intensities of all the lines calculated according to (6) and (7). The observed intensities agree very well with the calculated values although a very accurate comparison is not possible, as only intensity estimates are available. However by comparing lines which are just at the limit of visibility it is possible to get nevertheless a fairly good confirmation of the intensity relations. In particular it is found that the intensity ratio between the strong and weak branches conforms with the expected ratio 3 : 1 (§5).

In order to obtain a further check of the classification and the intensity relations the band at 3530A was photographed with the formaldehyde vapor at varying temperatures up to 300°C. The changes which occurred in the bands are exactly those to be expected. Lines belonging to higher rotational quantum numbers come out relatively more strongly. In this way the *rR*-branches up to $K=14 \rightarrow K=13$ could be identified. There is, however, a limit to the usefulness of increased temperatures for the development of higher lines. At room temperature practically all the molecules are in the lowest vibrational state. With rising temperatures an increasing number of molecules is brought into the next higher vibrational states, and there is accordingly the possibility of a great number of new bands arising from the absorption of molecules in these higher vibrational levels. These bands are partly confused with the low temperature bands, and

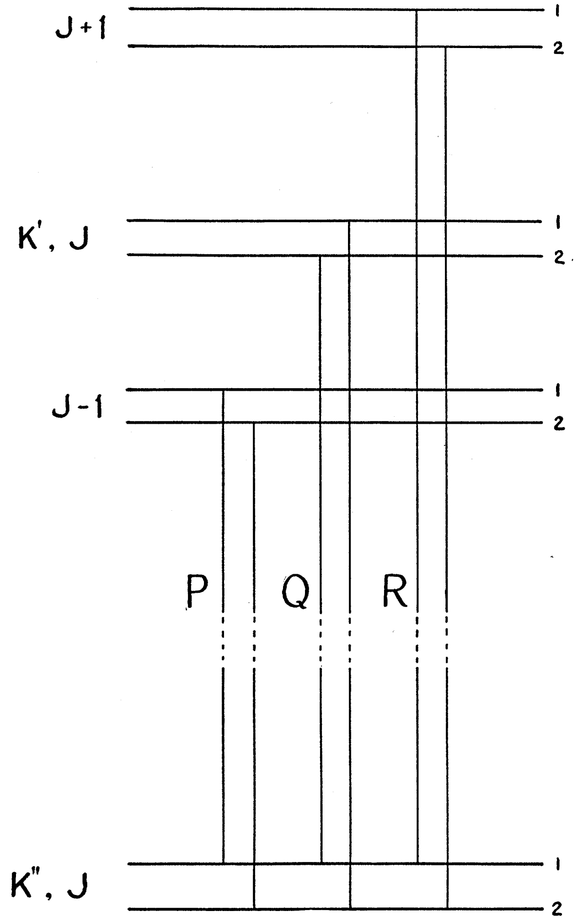

FIG. 4. Allowed transitions, if the electric moment is along the axis of the greatest moment of inertia.

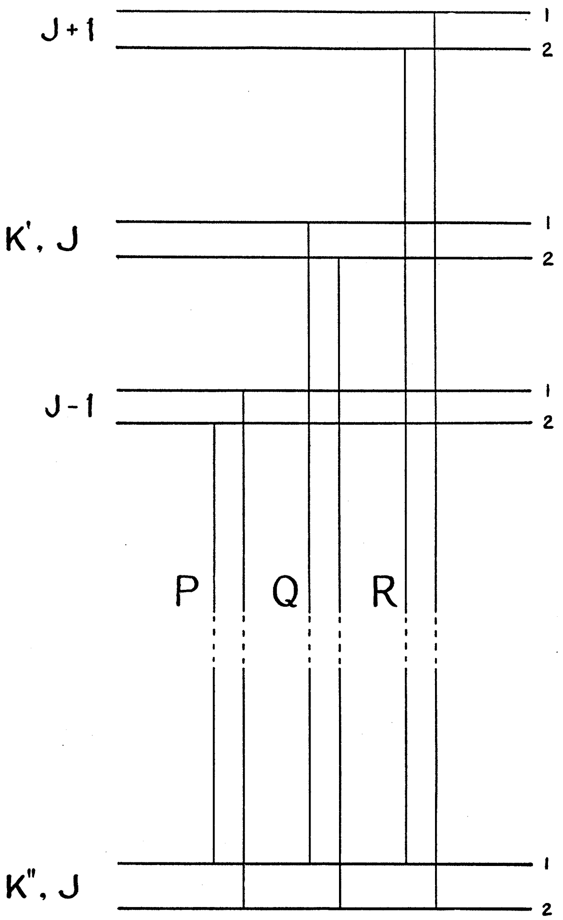

FIG. 5. Allowed transitions, if the electric moment is along the axis of the middle moment of inertia.

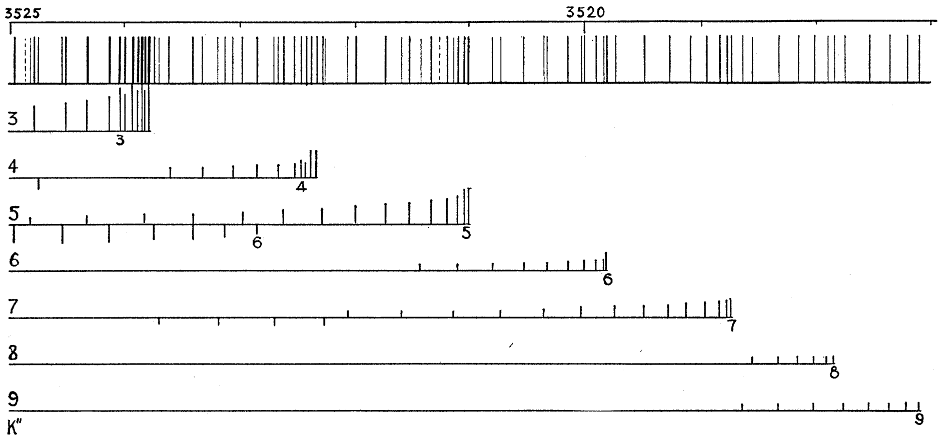

FIG. 6. Short wave-length end of the 3530 band at room temperature, with the classification into the different sub-bands. Lines drawn upward represent *rR*-lines, those drawn downward *rQ*-lines.

form an almost continuous background against which weak lines disappear.

In order to give an idea of the actual appearance of the bands in Fig. 6 the violet side of the 3530 band is drawn. The intensity of the lines is roughly indicated by their thickness. Below, the arrangement of the lines into different branches is shown. Each horizontal line represents one sub-band. Only two weak lines, shown in the figure as dotted lines could not be classified in this region. At higher pressures more lines appear some of which do not fit into the band. This is not surprising, as at high enough pressures new bands appear almost everywhere so that the absorption becomes almost continuous.

## §9. COMBINATION RELATIONS

The correctness of the numbering of the lines can be tested in a much more direct way with the help of combination relations, which also furnish a general proof of the correctness of the interpretation, which is free from any particular assumption about the shape of the molecule or any formula for the rotational energy levels. If $F(K, J)$ is the rotational energy (divided by $h$) of the upper state as function of $J$ and $K$, and $f(K, J)$ that of the lower state we can write the six kinds of branches.

$$\left.\begin{aligned} pP(K, J)&=F(K-1, J-1)-f(K, J),\\ pQ(K, J)&=F(K-1, J)-f(K, J),\\ pR(K, J)&=F(K-1, J+1)-f(K, J),\\ rP(K, J)&=F(K+1, J-1)-f(K, J),\\ rQ(K, J)&=F(K+1, J)-f(K, J),\\ rR(K, J)&=F(K+1, J+1)-f(K, J).\end{aligned}\right\} \quad (8)$$

From this it follows that

$$\left.\begin{aligned} rR(K-1, J-1)-pP(K+1, J+1)&=f(K+1, J+1)-f(K-1, J-1),\\ rR(K, J-1)-rP(K, J+1)&=f(K, J+1)-f(K, J-1),\\ pR(K, J-1)-pP(K, J+1)&=f(K, J+1)-f(K, J-1),\\ rR(K, J)-rQ(K, J+1)&=f(K, J+1)-f(K, J),\\ pQ(K, J)-pP(K, J+1)&=f(K, J+1)-f(K, J).\end{aligned}\right\} \quad (9)$$

The right sides of all these equations contain only term differences of the lower state. If we form these differences for different bands which have all the same lower but different upper states they must be identical for all the bands. All the bands considered here have the normal state of the formaldehyde molecule as lower state. The fact that the differences for the six bands turn out to be identical proves that the interpretation and the numbering of the lines must be correct.

In Tables II and III the combination relations are given, and it is seen that the agreement is very satisfactory. These combination relations were a very great help for the analysis of additional bands when the analysis of one or two were completed, as it was possible then to calculate the position of all other lines, if one set of branches only was known.

## §10. CALCULATION OF THE CONSTANTS

If we restrict ourselves to those lines which follow Deslandres' formula well (those deviating from it will be discussed in the next paragraph), and show no doubling, we can be assured that (3) is a good approximation for the rotational energy levels, and by substituting this expression for $f(K, J)$ in (9) we can calculate the moments of inertia from the values of Tables II and III. If we introduce the abbreviations

$$\alpha=\frac{h}{8\pi^2cA};\ \beta=\frac{h}{8\pi^2cB};\ \gamma=\frac{h}{8\pi^2cC};\ \delta=\frac{h}{8\pi^2cD}, \quad (10)$$

we have

$$f(K, J+1)-f(K, J)=2\delta(J+1), \quad (11)$$

$$f(K+1, J+1)-f(K-1, J-1) =4(\gamma-\delta)K+4\delta(J+\tfrac{1}{2}). \quad (12)$$

TABLE II. $pQ(K, J)-pP(K, J+1)$.

| J | K=3 | | | | | | | | | | K=4 | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 3530 | | 3390 | | 3200 | | 3430 | | 3295 | | 3530 | 3350 | 3260 | 3430 | 3295 |
| 3 | 9.68 | | 9.68 | | 9.71 | | 9.77 | | 9.72 | | | | | | |
| 4 | 12.10 | | 12.10 | | 12.24 | | 12.20 | | 12.25 | | 12.11 | — | 12.23* | — | [12.43] |
| 5 | 14.53 | | 14.63 | | 14.61 | | 14.68 | | 14.58 | | [14.56] | — | 14.74* | 14.56 | 14.49 |
| 6 | 17.05 | | 17.04 | | 17.02 | | 17.12 | | 16.92 | | — | — | 17.00 | 16.87 | 17.15 |
| 7 | 19.51* | | 19.46 | 19.46 | 19.54 | 19.39 | 19.41* | 19.57* | 19.40 | | 19.40 | 19.38 | [19.28] | 19.42 | 19.39 |
| 8 | 21.89 | 21.88 | 21.88 | 21.76* | 21.88 | 21.95 | 21.89 | 22.00 | — | 21.95 | 21.71 | 21.77 | 21.83* | 21.84 | 21.79* |
| 9 | 24.38 | 24.40 | 24.36* | 24.47 | 24.45 | 24.44 | 24.29 | 24.34 | 24.38 | 24.39 | 24.30 | 24.25* | 24.21* | 24.33 | 24.20 |
| 10 | 26.73 | 26.77 | 26.73* | — | 26.65 | 26.81 | 26.54 | 26.82 | 26.76 | 26.79 | [26.77] | — | 26.79 | — | 26.72* |
| 11 | 29.08* | 29.32 | 29.15* | 29.36 | 29.02 | 29.25* | 29.16* | 29.27 | 29.17 | 29.30 | 29.13 | 29.16 | | [29.27] | 29.12 |
| 12 | 31.48* | 31.98* | 31.51 | 31.84 | 31.51 | 32.05* | 31.53 | 31.85* | 31.62 | 31.78 | | 31.53* | | 31.73* | 31.41* |
| 13 | 33.86 | 34.48* | 33.94 | 34.44* | 33.92 | 34.51* | 33.89 | 34.34 | | | | 33.94* | | 34.04 | |
| 14 | 36.28 | 36.87 | 36.25 | 36.92 | 36.18 | 36.93 | 36.18* | 36.88 | | | | 36.51 | | | |
| 15 | 38.57 | 39.44 | 38.57* | 39.53 | 38.61* | 39.62 | 38.53* | 39.49 | | | | | | | |
| 16 | 41.01* | 42.14 | 40.99* | 42.61 | | | | | | | | | | | |
| 17 | | | 43.36* | 45.95 | | | | | | | | | | | |

| J | K=5 | | | | | K=6 | | | K=7 | | | | | K=9 | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 3530 | 3390 | 3260 | 3430 | 3235 | 3390 | 3260 | 3430 | 3530 | 3390 | 3260 | 3430 | 3295 | 3530 | 3390 |
| 3 | | | | | | | | | | | | | | | |
| 4 | | | | | | | | | | | | | | | |
| 5 | 14.80 | 14.67 | 14.64 | 14.58 | 14.65 | | | | | | | | | | |
| 6 | 16.98 | 17.00 | 17.03 | 16.98* | 17.06 | 16.85 | — | 16.90 | | | | | | | |
| 7 | 13.44 | 19.47* | 19.46 | 19.39 | 19.36 | 19.41* | — | 19.44 | — | — | — | [19.48] | 19.54 | | |
| 8 | 21.85 | 21.82* | 21.78 | 21.88 | 21.90* | 21.75* | 21.92 | 21.88 | — | 21.93* | 21.79 | 21.88 | 21.86 | | |
| 9 | 24.29 | 24.34 | 24.29 | 24.20 | 24.32 | — | 24.25 | 24.26 | 24.21 | 24.28 | 24.24 | 24.21 | 24.17 | — | — |
| 10 | 26.70 | 26.71* | 26.71 | 26.69 | 26.69 | 26.85 | | 26.66 | — | 26.65 | 26.63 | 26.73* | 26.58 | — | — |
| 11 | 29.14* | 29.14* | 29.18 | 29.14 | 29.11 | — | | 29.09 | 28.96* | 29.08 | 29.10 | 29.02* | — | — | 29.05 |
| 12 | 31.51 | 31.63* | 31.62 | 31.45* | 31.59 | 31.59 | | 31.53 | — | 31.53 | 31.56 | 31.64* | 31.45* | — | 31.50* |
| 13 | 33.95 | 33.98 | 34.02 | 33.99 | 33.96 | 34.08 | | 33.94 | — | 33.92 | | 33.95 | | — | — |
| 14 | 36.48 | 36.44* | 36.51 | 36.49 | 36.47* | 36.55* | | 36.42 | 36.35 | 36.40* | | 36.46 | | — | 36.63* |
| 15 | 38.85 | 38.91 | 38.88 | 38.92 | 38.85 | | | | 38.76 | 38.76 | | 38.83 | | 38.60* | 38.80* |
| 16 | 41.31 | 41.29 | 41.26 | 41.34* | 41.28 | | | | 41.29 | 41.27 | | 41.26 | | 41.20* | 41.20 |
| 17 | 43.75 | 43.73 | | 43.83 | 43.75 | | | | 43.60* | 43.64 | | 43.65 | | | 43.58 |
| 18 | 46.14 | 46.14* | | 46.15 | | | | | — | 46.12 | | 46.09 | | 46.17 | 46.11* |
| 19 | 48.61 | 48.65 | | 48.63 | | | | | 48.47 | 48.52 | | 48.48 | | | 48.47 |
| 20 | 51.01 | 50.93* | | 51.13* | | | | | 50.89 | 50.94 | | — | | | 50.97 |
| 21 | 53.49 | 53.49* | | 53.53 | | | | | | 53.36 | | 53.48 | | | |
| 22 | | | | | | | | | | 55.83 | | | | | |
| 23 | | | | | | | | | | 58.16 | | | | | |
| 24 | | | | | | | | | | 60.69 | | | | | |

TABLE II. (*Continued.*) $rR(K, J)-rQ(K, J+1)$.

| J | K=3 | | | | | | | | | | | | K=4 | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 3530 | | 3390 | | 3260 | | 3370 | | 3430 | | 3295 | | 3530 | 3350 | 3370 |
| 3 | 9.73 | | 9.77* | | 9.88* | | 9.71* | | 9.70 | | 9.41 | | | | |
| 4 | 12.18* | | 12.05* | | 12.14* | | 12.07 | | 12.21* | | 12.09* | | [12.27] | 12.16 | — |
| 5 | 14.51* | | 14.68* | | 14.58* | | 14.58 | | 14.64 | | 14.58* | | 14.69* | 14.61 | — |
| 6 | 17.09* | | 16.89* | | 16.99* | | 16.97* | | 17.06* | | 16.98* | | 17.03* | 17.00* | 17.03* |
| 7 | 19.42* | | 19.47* | | 19.36* | | 19.36* | | 19.45* | | 19.58* | | 19.36* | — | 19.41* |
| 8 | 21.83* | | 21.89 | | 21.86* | | 21.90 | | 21.93 | | 21.77* | | 21.72* | 21.85 | — |
| 9 | 24.33 | | 24.35* | | 24.35 | | 24.33 | | 24.35 | | 24.27 | | [24.27] | 24.26 | 24.23 |
| 10 | 26.75 | | 26.79 | | 26.77 | | 26.78 | | 26.77 | | 26.80* | | 26.80 | 26.81 | 26.71 |
| 11 | 29.26* | | 29.17 | | 29.26 | | 29.18 | | 29.12* | | 29.15 | | 29.21 | 29.25 | 29.17* |
| 12 | 31.67* | | 31.66 | | 31.52 | 31.82 | 31.62 | | 31.45 | | 31.47 | 31.69 | [31.52] | 31.54* | 31.60 |
| 13 | 33.83 | 34.39* | 33.89 | 34.46 | 33.95 | 34.28 | 33.95 | 34.15 | 34.18 | | 33.91* | | | 34.02 | 34.06 |
| 14 | 36.24 | 36.80 | 36.24 | — | 36.30 | 36.82 | 36.24 | 36.96 | 36.22 | 37.02 | | | | | 36.41 |
| 15 | 38.47 | 39.49 | 38.48 | 39.49* | 38.55 | 39.57 | 38.56 | 39.46* | 38.45 | 39.46 | | | | | |
| 16 | 40.79 | 42.20 | — | — | | | 40.77 | 42.14* | 40.71 | 42.27* | | | | | |
| 17 | 43.12 | 44.77 | 42.97 | 44.97 | | | | | 42.10 | 44.87 | | | | | |

| J | K=5 | | | | | | K=6 | | K=7 | | | | K=8 | K=9 | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 3530 | 3390 | 3260 | 3370 | 3430 | 3295 | 3530 | 3390 | 3530 | 3390 | 3260 | 3370 | 3390 | 3530 | 3390 |
| 3 | | | | | | | | | | | | | | | |
| 4 | | | | | | | | | | | | | | | |
| 5 | 14.53* | 14.67 | 14.66* | [14.63] | 14.51* | 14.50* | | | | | | | | | |
| 6 | 17.05* | 17.01* | 17.02* | 16.98* | 16.98* | 17.07* | — | 16.93 | | | | | | | |
| 7 | 19.38* | 19.55* | 19.28 | 19.38* | 19.33* | 19.44* | — | 19.54* | — | — | 19.42 | 19.40 | | | |
| 8 | 21.70* | 21.74* | 21.89* | 21.76* | 21.87* | 22.03* | — | 21.84 | — | [21.81] | 21.75 | — | — | | |
| 9 | 24.36 | 24.21* | 24.40 | 24.23 | 24.19* | 24.23 | 24.29 | 24.25 | 24.26 | 24.27 | 24.24* | 24.28* | — | — | — |
| 10 | [26.92] | 26.77 | 26.93 | 26.71 | 26.67 | 26.72 | 26.70* | | 26.70 | 26.70 | 26.67* | 26.68* | 26.60 | 26.72 | — |
| 11 | 29.14* | 29.16* | 29.13 | 29.15* | 29.08 | 29.05* | | | 29.17 | 29.23* | | 29.10 | 29.11 | 29.03 | 29.03 |
| 12 | 31.49 | — | | 31.55 | 31.62 | 31.58 | | | 31.55 | | | 31.47* | [31.56] | — | 31.60 |
| 13 | 34.01* | 33.98 | | 33.99* | | 33.98* | | | 33.92 | | | 33.94 | | 33.84 | [34.19] |
| 14 | 36.52* | 36.55 | | 36.42 | | 36.46 | | | 36.38 | | | 36.26* | | [36.41] | 36.36 |
| 15 | 38.89* | 38.73 | | 38.83 | | 39.17 | | | 38.80 | | | [38.86] | | [38.89] | — |
| 16 | 41.43* | 41.28* | | 41.29* | | 41.35* | | | | | | 41.19 | | | 41.25 |
| 17 | | 43.70 | | 43.73 | | | | | | | | 43.69 | | | 43.76 |
| 18 | | — | | | | | | | | | | | | | |
| 19 | | 48.64 | | | | | | | | | | | | | |
| 20 | | — | | | | | | | | | | | | | |
| 21 | | 53.34 | | | | | | | | | | | | | |

TABLE III. $rR(K-1, J-1)-pP(K+1, J+1)$.

| $J$ | $K=4$ | | | | | $K=5$ | | | |
|---|---|---|---|---|---|---|---|---|---|
| | 3530 | 3390 | 3260 | 3430 | 3295 | 3530 | 3390 | 3260 | 3430 |
| 4 | 152.56 | 152.56 | 152.77* | 152.55 | 152.37 | | | | |
| 5 | 157.37 | 157.41* | 157.39* | 157.41 | 157.35* | 189.82 | 189.81 | 189.95* | 189.81* |
| 6 | 162.22* | 162.33* | 162.28* | 162.25* | 162.23* | 194.73 | 194.68 | — | 194.68* |
| 7 | 167.14* | 166.95* | 167.05* | 166.93* | 167.03* | [199.65] | 199.48* | — | 199.58* |
| 8 | 171.89* | 171.86* | 171.75* | 171.94 | 171.87* | — | 204.38* | 204.31* | 204.42* |
| 9 | 176.72 | 176.77 | 176.68* | 176.79 | 176.60* | — | 209.20 | 209.16 | 209.13* |
| 10 | 181.56 | 181.58* | 181.55 | 181.60 | 181.57 | 214.03 | 214.01 | — | 213.98 |
| 11 | 186.33* | 186.38 | 186.34 | 186.41* | 186.40* | — | 218.84 | 218.73* | 218.80 |
| 12 | 191.21 | 191.13* | 191.13 | 191.16 | 191.21 | 223.64 | 223.75 | 223.71* | 223.66 |
| 13 | 195.92* | 195.95 | 195.98 | 195.89 | 195.97 | [228.29] | 228.49* | | 228.36 |
| 14 | 200.87* 200.65 | 200.86* 200.64 | 200.76 | 200.75 | 200.81* | — | 233.26 | | 233.25 |
| 15 | 206.04 205.34 | — 205.31 | 205.57 205.31 | 205.63 205.40 | 205.47* | 237.90 | | | |
| 16 | 210.44 210.01 | 210.42* 209.97 | 210.38 209.91 | 210.42 210.04 | 210.49* 209.99 | | | | |
| 17 | 215.23 214.58 | — — | | 215.26* 214.63 | | | | | |
| 18 | | 220.08 219.16 | | 219.98 219.18* | | | | | |
| 19 | | | | 224.93* 223.68 | | | | | |
| 20 | | | | 229.78 228.07 | | | | | |

| $J$ | $K=6$ | | | | | $K=7$ | | $K=8$ | | | $K=9$ | $K=10$ | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 3530 | 3390 | 3260 | 3430 | 3295 | 3530 | 3390 | 3530 | 3390 | 3430 | 3390 | 3530 | 3390 |
| 4 | | | | | | | | | | | | | |
| 5 | | | | | | | | | | | | | |
| 6 | 226.95* | 227.00* | 226.95* | 226.96* | 226.84* | | | | | | | | |
| 7 | 231.80* | 231.80* | 231.77* | 231.78* | 231.81* | — | 263.81* | | | | | | |
| 8 | 236.52* | 236.76* | 236.56 | 236.66* | 236.66* | — | 268.80* | 300.53 | 300.57 | 300.63 | | | |
| 9 | 241.30* | 241.44 | 241.41 | 241.36* | 241.55* | — | 273.47 | 305.41 | 305.34* | 305.45 | 337.09 | | |
| 10 | 246.25* | 246.24 | 246.27 | 246.28 | 246.27 | — | 278.33 | 310.23* | 310.19 | 310.25 | 341.76* | 373.07 | 373.19 |
| 11 | 251.06 | 251.10 | 251.05 | 251.13 | 251.11 | — | 283.10 | 315.05 | 315.03 | 314.97 | 346.58 | 378.02 | 378.01 |
| 12 | 255.86 | 255.92 | 255.93 | 255.95 | 255.83 | — | 287.94 | 319.80 | 319.85* | 319.84 | 351.43 | 382.71 | 382.79 |
| 13 | 260.68 | 260.69 | — | 260.72 | | — | 292.77 | 324.56 | 324.58 | 324.61 | 356.36 | 387.46 | 387.53 |
| 14 | 265.43 | 265.51 | 265.55 | 265.58 | | — | 297.59* | 329.32 | 329.39 | 329.50 | | 392.30 | |
| 15 | 270.31 | 270.28 | | 270.30 | | — | 302.38 | 334.14 | 334.22* | | | 397.11 | |
| 16 | 275.03* | 275.01 | | 275.05* | | 307.13* | 307.02* | 338.97* | 339.02 | | | 402.47 | |
| 17 | 279.81* | 279.83* | | 279.90 | | 311.87 | 312.06 | 343.75 | 343.74* | | | | |
| 18 | 284.69 | 284.67 | | | | — | | 348.50 | 348.62* | | | | |
| 19 | 289.39 | — | | | | 321.46* | | 353.16 | 353.26* | | | | |
| 20 | 294.11* | 294.16 | | | | | | 358.02 | 358.07 | | | | |
| 21 | 298.89* | — | | | | | | 362.80 | | | | | |
| 22 | 303.49 | 303.59 | | | | | | | | | | | |
| 23 | 308.36* | | | | | | | | | | | | |

Table II gives the observed values of $f(K, J+1)-f(K, J)$. They can be represented within the limits of experimental errors by (11). The values for $K=5$, and $K=7$ may serve here as an example (Table IV).

TABLE IV.

| $J$ | $K=5$ obs. | $K=5$ calc. | $K=7$ obs. | $K=7$ calc. |
|---|---|---|---|---|
| 5 | 14.61 | 14.57 | | |
| 6 | 16.99 | 17.00 | | |
| 7 | 19.44 | 19.43 | 19.41 | 19.40 |
| 8 | 21.83 | 21.86 | 21.83 | 21.83 |
| 9 | 24.28 | 24.29 | 24.24 | 24.25 |
| 10 | 26.71 | 26.72 | 26.67 | 26.68 |
| 11 | 29.15 | 29.15 | 29.08 | 29.10 |
| 12 | 31.57 | 31.58 | 31.55 | 31.53 |
| 13 | 34.00 | 34.01 | 33.93 | 33.95 |
| 14 | 36.49 | 36.44 | 36.39 | 36.38 |
| 15 | 38.89 | 38.87 | 38.79 | 38.80 |
| 16 | 41.31 | 41.29 | 41.25 | 41.23 |
| 17 | 43.74 | 43.72 | 43.65 | 43.65 |
| 18 | 46.14 | 46.15 | 46.10 | 46.08 |
| 19 | 48.63 | 48.58 | 48.49 | 48.50 |
| 20 | | | 50.92 | 50.93 |
| 21 | | | 53.42 | 53.35 |

The second column gives the averages for $K=5$ obtained from Table II and the fourth column those for $K=7$. In forming these averages all values originating from obviously bad lines were excluded. Assuming now the validity of (11) a value for $\delta$ can be calculated by dividing the sum of the values in one column by the sum of the $J+1$ values involved. We obtain thus $2\delta=2.4291$ for $K=5$ and $2\delta=2.4250$ for $K=7$. If we calculate $2\delta(J+1)$ with these values for $\delta$ we get the third and fifth columns. Table IV shows clearly that the agreement between the calculated and observed values is as perfect as the experimental errors permit, and that therefore (11) holds within the limits of experimental errors. The value of $\delta$ for $K=7$ is a little smaller than that for $K=5$, and this difference is real and outside the limits of experimental errors. It shows in the table in that the observed values for $K=7$ are systematically all a little smaller than those for $K=5$. More generally it was found that in all the states investigated the value of $\delta$ depends on $K$ and that it decreases with $K$.[13] It is easy to verify that for the lower electronic state from Table II.

The reason for the variation of $\delta$ with $K$ must be sought in the deformation of the molecule by the rotation. We can disregard it for the purpose of this paper, except that it necessitates small corrections for the calculation of the other constants of the molecule.

With the help of (12) and the values of Table III, it is possible to calculate $\gamma$. As $\delta$ is not a constant, (12) must be modified to

$$f(K+1, J+1)-f(K-1, J-1)=(4\gamma-\delta)K \\ +4\delta_{K+1}(J+\tfrac{1}{2})-(\delta_{K-1}-\delta_{K+1})(J-\tfrac{1}{2})^2. \quad (13)$$

As $\delta_K$ is known this equation can be used to calculate $\gamma$. In order to do so we subtract $4\delta_{K+1}(J+\frac{1}{2})-(\delta_{K-1}-\delta_{K+1})(J-\frac{1}{2})^2$ from the observed average values of Table III. The result should be a constant independent of $J$. It appears that this is in general not the case, but that there is a slight though definite variation. That is due to the fact that the quadratic term is not known with sufficient accuracy. It is easy however to adjust in every case the value of $\delta_{K-1}-\delta_{K+1}$ in such a way that there is no more systematic variation. This is then at the same time a method to obtain more accurate information about the variation of $\delta$ with $K$.

This procedure is carried out in the same way for all the available values of $K$. The result is

| $K$ | 4 | 5 | 6 | 7 | 8 | 9 | 10 |
|---|---|---|---|---|---|---|---|
| obs. | 130.83 | 163.26 | 195.45 | 227.67 | 259.51 | 291.33 | 322.59 |
| calc. | 130.71 | 163.18 | 195.52 | 227.68 | 259.54 | 291.41 | 322.92 |

and the values (obs.) thus found should be proportional to $K$. It is found that this is not the case, but that there are deviations which exceed by far the observational errors. Also here these deviations are due to the deformation of the molecule by the rotation. The main effect here is easily accounted for quantitatively. It is the centrifugal force acting on the hydrogen atoms due to the rapid rotation about the CO-axis. This force is of the same nature as the centrifugal expansion of a diatomic molecule and we expect therefore that it can be represented by a negative term of the form $-\mu K^4$. The value of $\mu$ turns out to be $5.8\times10^{-4}$. If this correction term is taken into account, the above values are fairly well proportional to $K$. The value of $\gamma-\delta$ turns out to be 8.189, the values of $4(\gamma-\delta)K-8\mu(K^3+K)$ calculated with these values for $\gamma$ and $\mu$ are given in the row "calc." of the above table. The agreement between the observed and calculated values is fairly good, although there are still some slight systematic deviations, which, however, are too small to be of any interest to us here.

Combination relations analogous to (9) allow us to obtain the rotational differences of the upper electronic level. They are omitted here in order to save space. From these combination differences we obtain the constants of the six upper levels by the same process which was used for the calculations of the constants of the ground state. All the constants obtained in this way are collected in Table V.

A few comments concerning these constants are necessary. It was already mentioned that the expression (3) for the energy of a symmetrical top, though a very good approximation, does not represent exactly the rotational states of the formaldehyde molecule. The deviations which are due to the fact that the molecule is slightly asymmetric, and which occur for low $K$-values only, will be discussed in §11. Besides, we saw that the rotational distortion of the molecule has the effect that the moments of inertia are not constants but depend on $K$. Due to uncertainty about the exact nature of the deviations an extrapolation to the rotationless state of the molecule cannot be carried out exactly. For this reason the constant $\delta$ is given for $K=5$ for the ground level and for $K=4$ for the upper levels. The possible deviations of this value from that for the rotationless molecule are very small, probably of the same order as the uncertainty

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[13] As the variation of $\delta$ with $K$ is very small the exact law of the variation cannot be established from the present data. The values for $K=3$, 5 and 7 which are the most reliable ones seem to indicate a linear decrease with $K$. It seems highly probable though that this apparent linear decrease results from two terms of higher power with opposite sign. This would also agree better with the theoretical results. Preliminary calculations about the distortion of the formaldehyde molecule by rotation have shown that there is no possibility of a linear term, but that there is a term proportional to $K^2$ and one proportional to $K^3$ with opposite sign.

TABLE V. *Rotational constants of formaldehyde.*

| | $\delta$ | $\gamma-\delta$ | $\gamma$ | $\mu\times10^4$ | $\nu_0$ | $\alpha$ | $\beta$ | $A\times10^{40}$ | $B\times10^{40}$ | $C\times10^{40}$ | $b$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Normal state | 1.215 | 8.189 | 9.404 | 5.8 | | 1.137 | 1.293 | 24.33 | 21.39 | 2.941 | 0.0095 |
| Upper level of | | | | | | | | | | | |
| 3530 | 1.067 | 7.682 | 8.749 | | 28,312.66 | 1.002 | 1.132 | 27.61 | 24.44 | 3.162 | 0.0084 |
| 3390 | 1.056 | 7.645 | 8.701 | 3.8 | 29,495.12 | 0.992 | 1.120 | 27.88 | 24.70 | 3.179 | 0.0084 |
| 3260 | 1.046 | 7.606 | 8.653 | | 30,658.67 | 0.983 | 1.110 | 28.14 | 24.92 | 3.197 | 0.0083 |
| 3370 | 1.066 | 7.827 | 8.893 | | 29,634.45 | 1.002 | 1.130 | 27.61 | 24.48 | 3.110 | 0.0081 |
| 3430 | 1.067 | 7.546 | 8.613 | | 29,136.6 | | | | | | |
| 3295 | 1.055 | 7.19 | 8.24 | | 30,340.1 | | | | | | |

due to experimental errors. Besides, for further information about the nature of the upper electronic state, the absolute values of the constants are not as important as their variation with the vibrational states. If, therefore, the way in which the constants are calculated might introduce a slight systematic error, this will be of no great importance provided it is the same for all the different levels. For this reason the constants of all the bands were as much as possible calculated in exactly the same manner, so that very probably the relative values of the constants are free from any, even slight, systematic errors.[14]

In all cases it was found that the dependence of the rotational energy on $J$ was strictly of the form $\delta_K J(J+1)$. No deviations from this formula could be detected. It was already mentioned that there occur, however, appreciable deviations from the quadratic dependence of the rotational energy on $K$, and that these deviations can be expressed satisfactorily by a term in $K^4$. The same thing is true for the initial levels of the bands 3530, 3390, 3260, and 3370. This is illustrated by Table VI in which the $K$ differences extrapolated to $J=0$ are tabulated for the upper levels of the different bands. They are compared with the values calculated from the formula $4(\gamma-\delta)K-8\mu(K^3+K)$. The value $\mu=3.8\times10^{-4}$ is obtained from the 3390 band for which the most complete and reliable data are available. The same value for $\mu$ was used for the upper levels of the other bands, as it must be expected that it does not depend much on the vibrational state. Table VI shows that the agreement between calculated and observed values is satisfactory for the bands 3530, 3390, and 3260. The same is true for the band 3370 for which, however, as the $p$-branches could not be observed, a slightly different mode of procedure had to be adopted.

If one tries, however, to represent the differences for the upper levels of the 3430 and 3295 bands by a formula of the same type, there is no possible way to get any agreement. Table VI shows that if the calculated values are made to agree for $K=3$ there is a wide discrepancy for the higher values of $K$. This discrepancy does not seem to obey a simple law. This is shown, e.g., by the following figures which are the $K$ differences of Table VI (corrected for the fourth power term) for the 3430 band divided by $K$.

| 3 | 4 | 5 | 6 | 7 | 8 | 9 |
|---|---|---|---|---|---|---|
| 30.19 | 30.41 | 30.67 | 31.23 | 30.72 | —— | 30.71 |

If no anomaly were present, all these values should be identical and equal to $4(\gamma-\delta)$.

In view of the fact that no adequate formula can be found to represent the rotational levels of these two bands, and that certainly the expression (3) cannot be valid even with the corrections for the nonrigidity of the molecule, the question may be raised, in how far we can be sure of the correctness of the analysis of the bands. As far as the four regular bands are concerned, we believe that there is hardly any possibility for doubt. Most of the regularities suggest themselves readily and the fact that they agree in all details with the theoretical expectations is a strong confirmation for their genuineness. In the band 3430 some of the branches are quite as regular and well developed as those of the other bands and the Tables II and III show that the

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[14] To give an example the value for $\delta$ given in Table V, is 1.067 for the 3530 band and 1.066 for the 3370 band. Although there may be an error of a few units of the last decimal in the absolute values of these constants, their difference 0.001 is accurate to a fraction of this value.

TABLE VI.

| | 3530 | | 3390 | | 3260 | | 3430 | | 3295 | |
|---|---|---|---|---|---|---|---|---|---|---|
| $K$ | obs. | calc. | obs. | calc. | obs. | calc. | obs. | calc. | obs.* | calc. |
| 3 | 92.32 | 92.18 | 91.58 | 91.62 | 91.17 | 91.17 | 90.47 | 90.47 | 86.44 | 86.44 |
| 4 | 122.98 | 122.91 | 122.06 | 122.07 | | | 121.39 | 120.53 | | 115.16 |
| 5 | 153.66 | 153.64 | 152.44 | 152.43 | 151.64 | 151.67 | 152.89 | 150.51 | 142.24 | 143.79 |
| 6 | 184.45 | 184.37 | 182.59 | 182.69 | | | 186.62 | 180.38 | | |
| 7 | 215.06 | 215.10 | 212.86 | 212.82 | 211.78 | 211.75 | 213.83 | 210.12 | 208.24 | 200.72 |
| 8 | | | 242.83 | 242.80 | | | | | | |
| 9 | 276.35 | 276.55 | 272.62 | 272.61 | | | 273.75 | 269.14 | | |
| 10 | | | 302.25 | 305.23 | | | | | | |
| 11 | | | 331.61 | 331.63 | | | | | | |

* Obtained from the zero lines of the sub-bands.

combination relations are fulfilled with the same accuracy as for the other bands. It is hard to imagine how all these regularities could be anything but genuine. We must have then here a perturbation of the rotational energy levels, as far as we know the first one of this type observed in a polyatomic molecule. The perturbation affects only the dependence of the energy levels on $K$.

The band at 3295A is a little less well developed than the other bands, and the regularities are less obvious. But also in this case we believe that the analysis presented here is essentially correct and that we have here a similar perturbation.

In order to clear up completely the nature of the perturbations further investigations are necessary which are still under way. The perturbations must originate from the interaction of the level in question with another level which is very close to it. This second level might be another vibrational level of the same electronic state, or might belong to a different electronic state. Because of the predissociation in the higher vibrational states we know that there is a second electronic state close to the upper state of our bands which is at least partly continuous. Whether this level is also responsible for the perturbations observed here is doubtful though not impossible.

The fact that the rotational levels of the upper state of the bands 3430 and 3295 do not follow a quadratic formula makes an accurate calculation of the constant $\gamma$ impossible. As the figures on the preceding page show, the apparent value of $\gamma-\delta$ in 3430 decreases for decreasing values of $K$ and if this decrease continues it seems plausible that the value for 4 $(\gamma-\delta)$ should be smaller than 30.19. For the band 3295 the value for $\gamma-\delta$ is also calculated from the lowest $K$ available, but this is, of course, no guarantee that it is very close to the real value.

## The zero lines

The wave numbers for the lines in the $rR$-branches can be written

$$rR(K_1J)=\nu_0+\gamma''+2K(\gamma''-\delta'')$$
$$-(\gamma''-\gamma'+\delta'-\delta'')(K+1)^2-\mu'(K+1)^4+\mu''K^4$$
$$+(2J+1)\delta_K''-(\delta_K''-\delta_{K+1}')(J+1)^2 \quad (13)$$

and, as all the other constants are known, $\nu_0$ can be calculated with the help of this expression. In doing so it is most convenient to calculate first the zero lines of the individual sub-bands. The difference $(\delta''-\delta')$ is multiplied with much larger numbers than $\delta''$ and should therefore be known with about the 20-fold accuracy. Therefore often a slight adjustment of $\delta''-\delta'$ is necessary in order to assure that the zero line calculated from the different lines of a branch has the same value. With such an adjustment it is not difficult to get a perfect agreement within the limits of experimental errors. Naturally for the bands 3430 and 3295 no accurate value for the zero lines can be obtained and the value given in Table V may be in error by several wave numbers.

The relations (1), (2) and (10) allow us to calculate the three principal moments of inertia, if $\gamma$ and $\delta$ are known. We get, e.g., $\alpha$ as the positive root of the quadratic equation

$$\alpha^2-2(\gamma+\delta)\alpha+2\gamma\delta=0.$$

Finally the asymmetry constant $b$ can be found from (4) which can be written

$$b=(\beta-\alpha)/2(\gamma-\delta)\cong\delta^2/2\gamma.$$

## §11. THE DEVIATIONS FROM THE SYMMETRICAL TOP

The deviations from the symmetrical top must be noticeable for small values of $K$. It is unfortunate that the lines due to the low $K$-transitions fall into the very crowded center region of the bands. Some of the strongest sub-bands are crowded together here. Each of these sub-bands is much richer in lines than those due to higher $K$-values, as fewer lines near the origin are missing. Besides, the $P$-, $Q$- and $R$-branches have much more nearly the same intensity and each line is split into a doublet. All this causes the structure in this part of the band to be extremely complex, many lines fall so close together that they cannot be separated and no obvious structure is apparent. For these reasons it is rather futile to attempt an analysis of this section. It is perfectly possible to find all the lines to be expected, but such an analysis would have very little value, as there would be no way to test its correctness. Because of the incomplete resolution one would have to allow much larger errors in the combination relations and the intensities would have no meaning. Under these conditions almost any expected arrangement of lines could be verified.

Only in the 4→3 and 2→3 sub-bands conditions are more favorable so that an unambiguous identification of the lines seems possible. Both are strong sub-bands, and both have still the symmetric top characteristics for small values of $J$. But if one tries to find the higher lines with the help of the symmetrical top formula, it appears that they show deviations from about $J=13$ in the 4→3 sub-band and from about $J=8$ in the 2→3 sub-band. As must be expected the lines become doublets of increasing width. As all the constants of the molecule are known, the position of the lines can be calculated with the help of the formulae for the asymmetrical top. But in order to obtain entirely unbiased results an empirical analysis was first attempted, and only after this was completed it was compared with the theoretical expectations. The procedure was as follows: The approximate positions for all the lines under the assumption that the molecule is strictly a symmetrical top were calculated. For high enough values of $J$, of course no lines were found in these positions, but there would be several lines near. As for all the bands the asymmetry is about the same, the deviations of the correct lines from their calculated positions should be about the same. Therefore the lines which showed about the same deviation from the calculated positions in all the bands were taken to be the correct ones. This allowed in general an unambiguous identification of the lines except near the end of the branches where the lines became too weak in some bands.

It is now necessary to investigate, how the lines found in this way without any assumption about the theoretical structure of the bands, fit into the theoretical scheme. In the 4→3 sub-band the doublet separation will be due almost entirely to the separation of the lower level (see Fig. 2) whereas in the 2→3 sub-bands the situation will be just the opposite. The Figs. 4 and 5 show, that in order to obtain the differences for the final state it is necessary to subtract the longer wave-length doublet component from the shorter wave-length one and *vice versa*, if the doublet separation of the upper levels is less than that of the lower ones. We have therefore, if the index 1 refers to the upper and the index 2 to the lower component of a given doublet level

$$\left.\begin{aligned} R_s(K,\,J)-Q_l(K,\,J+1)&=f_1(K,\,J+1)-f_2(K,\,J),\\ R_l(K,\,J)-Q_s(K,\,J+1)&=f_2(K,\,J+1)-f_1(K,\,J)\end{aligned}\right\}\tag{14}$$

independent on whether the electric moment is in the plane of the molecule or perpendicular to it. If the doublet separation in the upper level is bigger than in the lower one we have to take the differences

$$\left.\begin{aligned} Q_l(K,\,J)-P_l(K,\,J+1)&=f_1(K,\,J+1)-f_2(K,\,J),\\ Q_s(K,\,J)-P_s(K,\,J+1)&=f_2(K,\,J+1)-f_1(K,\,J).\end{aligned}\right\}\tag{15}$$

The right sides are correct if the electric moment is in the plane of the molecule (Fig. 4). If it is perpendicular to it, (Fig. 5) the indices 1 and 2 must be interchanged. The differences of the two Eqs. (15) give

$$P_s(K,\,J+1)-P_l(K,\,J+1)-[Q_s(K,\,J)-Q_l(K,\,J)]=\Delta P(K,\,J+1)-\Delta Q(K,\,J)$$
$$=f_1(K,\,J+1)-f_2(K,\,J+1)+f_1(K,\,J)-f_2(K,\,J).$$

TABLE VII. $\Delta f(3,\,J)+\Delta f(3,\,J+1)$.

| | 1. From 2→3 sub-band | | | | | 2. From 4→3 sub-band | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| *J* | 3530 | 3390 | 3260 | 3430 | 3295 | 3530 | 3390 | 3260 | 3370 | 3430 | Ave.₁ | Ave.₂ | Calc. |
| 8 | −0.01 | −0.14 | +0.07 | 0.11 | — | | | | | | 0.01 | | 0.02 |
| 9 | + .02 | + .11 | − .01 | .05 | 0.01 | | | | | | .04 | | .05 |
| 10 | .04 | — | + .17 | .28 | .03 | | | | | | .10 | | .10 |
| 11 | .24 | .21 | .23 | .11 | .13 | | | | | | .18 | | .17 |
| 12 | .50 | .33 | .54 | .32 | .16 | | | | | | .37 | | .26 |
| 13 | .62 | .50 | .59 | .35 | | 0.34 | 59 | 0.33 | 0.20 | — | .52 | 0.37 | .41 |
| 14 | .57 | .67 | .75 | .70 | | .66 | — | 72 | .72 | 0.80 | .67 | .72 | .62 |
| 15 | .87 | .96 | 1.01 | .66 | | 1.00 | 1.01 | 1.02 | .90 | 1.01 | .95 | .99 | .91 |
| 16 | 1.13 | 1.62 | | | | 1.41 | — | | 1.37 | 1.56 | | 1.44 | 1.32 |
| 17 | | | | | | 1.65 | 2.00 | | | 1.77 | | 1.81 | 1.88 |
| 18 | | | | | | 2.15 | | | | 2.75 | | | |

TABLE VIII. *Doublet separation in the $K'=2\rightarrow K''=3$ sub-band.*

| | *pP-Branch* | | | | | | *pQ-Branch* | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| *J* | 3530 | 3390 | 3260 | 3430 | 3295 | calc. | 3530 | 3390 | 3260 | 3430 | 3295 | calc. |
| 7 | 0 | 0 | 0 | 0 | 0 | 0.10 | 0 | 0.15 | 0.15 | 0 | 0 | 0.20 |
| 8 | 0 | 0.15 | 0 | 0.15 | 0.17 | .20 | 0.26 | .35 | .24 | 0.17 | 0.26 | .33 |
| 9 | 0.25 | .21 | 0.31 | .28 | .32 | .34 | .46 | .36 | .39 | .32 | .30 | .51 |
| 10 | .48 | .47 | .38 | .37 | .38 | .55 | .53 | .52 | .42 | .38 | .45 | .74 |
| 11 | .57 | — | .59 | .66 | .66 | .84 | .73 | .72 | .61 | .66 | .56 | 1.03 |
| 12 | .97 | .93 | .84 | .77 | .74 | 1.20 | .95 | 1.01 | .84 | .74 | .70 | 1.42 |
| 13 | 1.45 | 1.34 | 1.38 | 1.06 | 1.09 | 1.68 | 1.38 | 1.33 | 1.29 | 1.09 | .91 | 1.88 |
| 14 | 2.00 | 1.83 | 1.88 | 1.44 | 1.37 | 2.29 | 1.84 | 1.72 | 1.65 | 1.37 | 1.32 | 2.40 |
| 15 | 2.43 | 2.39 | 2.40 | 2.07 | 1.99 | 3.04 | 2.30 | 2.10 | 1.72 | 1.99 | | 3.00 |
| 16 | 3.17 | 3.06 | 2.73 | 2.65 | | 3.92 | 2.92 | 2.55 | | | | 3.64 |
| 17 | 4.05 | 4.17 | | | | 4.96 | | | | | | |

The right side, a positive quantity, is the sum of the doublet separations of two successive rotational levels. It would change its sign, if the electric momentum were not in the plane of the molecule, but perpendicular to it.

In the formaldehyde bands the doublet separation of the $pQ(3,\,J)$ lines is consistently smaller than that of the $pP(3,\,J+1)$ lines, which proves that for the electronic transition in question the resultant electric moment is in the plane of the molecule and perpendicular to the CO-axis.

In Table VII the sum of the doublet separations of two successive rotational levels is given for $K=3$ of the lower electronic level. The method of calculation is indicated by the heads of the table. In each of the values so obtained four lines are involved of which one or more, as a rule, are incompletely resolved. In view of this circumstance the rather large differences between the values of the individual bands is not surprising. The averages are compared with the theoretical values calculated with the value $b=0.0095$ given in Table V. The agreement is very satisfactory.

In Table VIII the observed doublet separations in the 2→3 sub-bands are compared with the theoretical ones. We have

$$\Delta pP(K,\,J)=\Delta F(K,\,J-1)+\Delta f(K,\,J),$$
$$\Delta pQ(K,\,J)=\Delta F(K,\,J)-\Delta f(K,\,J).$$

The calculated values are those for the band 3390. The values for the other bands should not be more than about 3 percent different. The observed values are all systematically lower than the calculated ones. One would get agreement within the limits of experimental errors if the asymmetry constant were about $b=0.0073$ instead of 0.0083. We see, therefore, that although the general trend of the doublet separation agrees well within the theoretical one, there is a definite discrepancy in the exact numerical agreement. It is probable that the cause for this discrepancy is the same which produces the perturbations in the 4330 and 3295 bands. In the normal state where there is no such possibility for the interaction of different levels the agreement between the observed and theoretical values is entirely within the limits of experimental errors.

## §12. The Shape of the Formaldehyde Molecule

From the values for the moments of inertia (see Table V) the shape of the formaldehyde molecule can be determined to a certain extent. A complete determination of the shape is not possible, as we have only two independent data, say the moments of inertia $B$ and $C$ (the third moment of inertia is not independent of the two others as it is given by the relation $A=B+C$) for the determination of the three quantities which determine the structure of the molecule. These three quantities are (see Fig. 1) the CO-distance $a$, the CH-distance $r$ and the angle $2\alpha$ between the two CH-bonds. If we call $u=r\sin\alpha$ and $v=r\cos\alpha$, we have

$$C=2m_{\mathrm{H}}u^2.$$

From the observed values of $C$ we obtain for the distance $2u$ between the hydrogen atoms 1.88A for the normal state of the molecule and 1.95A cm for the excited state of 3530. In the normal hydrogen molecule the distance between the two H-atoms is 0.75A.

We have further

$$B=[m_{\mathrm{O}}(m_{\mathrm{C}}+2m_{\mathrm{H}})a^2+4m_{\mathrm{O}}m_{\mathrm{H}}av+2m_{\mathrm{H}}(m_{\mathrm{O}}+m_{\mathrm{C}})v^2]/M, \tag{16}$$

in which $m_{\mathrm{O}}$, $m_{\mathrm{C}}$, and $m_{\mathrm{H}}$ are the masses of the oxygen, carbon and hydrogen atoms and $M=m_{\mathrm{O}}+m_{\mathrm{C}}+2m_{\mathrm{H}}$ the total mass of the molecule. By substituting the values for the masses we obtain

$$B=7.471(a^2+0.2876\,av+0.2516\,v^2)m_1$$

in which $m_1=1.649\times10^{-24}$ g is the mass of an atom with atomic weight one.

It is necessary to know one of the two quantities $a$ or $v$ in order to determine the other one from this relation. If we assume that the angle $2\alpha$ between the two CH-bonds is the tetrahedron angle (110°), $v=u\operatorname{ctg}\alpha=0.659$A. We obtain then for the CO-distance $a=1.185$A, and the CH-distance becomes $r=1.15$A. In the normal state of the CO-molecule the internuclear distance is 1.15A. It is perhaps better to compare the CO-distance in formaldehyde with that in $CO_2$, where it is 1.16A.[16] In almost all compounds the CH-distance is found to be about 1.1A (for the lowest state of the CH-molecule the internuclear distance is 1.13A). We see therefore that the dimensions obtained for the formaldehyde molecule are about what we should expect.

It is rather problematic whether we are justified in assuming that also in the excited state of formaldehyde the angle between the CH-bonds is about 110°. If we make this assumption nevertheless for want of something better, we get for the CO-distance $\alpha=1.27$A and for the CH-distance 1.19A.

In §10 we saw that the centrifugal force due to the rotation about the CO-axis enlarges the distance between the two H-atoms. The amount of this centrifugal expansion depends on the strength of the CH-bond and the force between the two CH-bonds. A quantitative relation between the different constants involved can easily be obtained by the following simple calculation.

If we call $x_1$ a displacement of an H-atom from the equilibrium position in the direction of the CH-bond, and $x_2$ a displacement perpendicular to it, the restoring forces can be written $f_1x_1$ and $2f_2x_2$. (Both hydrogen atoms are affected in the same way.) If $k$ is the angular momentum

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[16] From the value $70.6\cdot10^{-40}$ g cm$^2$ for the moment of inertia given by Barker and Adel, Phys. Rev. **44**, 185 (1933).

about the CO-axis, ($k=Kh/2\pi$) the centrifugal force acting on a hydrogen atom is $k^2/2Cu$ and the equilibrium is determined by

$$\left.\begin{aligned} k^2/2Cu &= f_1x_1 \sin\alpha + 2f_2x_2\cos\alpha, \\ 0 &= f_1x_1\cos\alpha - 2f_2x_2\sin\alpha, \\ x &= x_1\sin\alpha + x_2\cos\alpha, \end{aligned}\right\} \quad (17)$$

in which $x$ is the increase in the distance $u$ from the CO-axis. The potential energy is $f_1x_1{}^2+2f_2x_2{}^2$ and the kinetic energy in first approximation

$$k^2/2C=(k^2/2C_0)(1-2x/u_0);$$

therefore the total change in energy in first approximation

$$E=-\frac{k^2x}{C_0u_0}+f_1x_1{}^2+2f_2x_2{}^2 \\ =-\frac{k^4m_{\rm H}}{2C_0{}^3}\left(\frac{\sin^2\alpha}{f_1}+\frac{\cos^2\alpha}{2f_2}\right). \quad (18)$$

If we call $2\pi\omega_1=(f_1/m_{\rm H})^{\frac{1}{2}}$ and $2\pi\omega_2=(2f_2/m_{\rm H})^{\frac{1}{2}}$ we obtain

$$\Delta E/h=-\mu K^4 \quad (19)$$

with

$$\mu=4\gamma^3[(\sin^2\alpha)/\omega_1{}^2+(\cos^2\alpha)/\omega_2{}^2]. \quad (20)$$

$\omega_1$ is the frequency with a force constant $f_1$ and a reduced mass $m_{\rm H}$, $\omega_2$ the frequency with $f_2$ as force constant and a reduced mass $\frac{1}{2}m_{\rm H}$. For $\alpha=90°$ the expression for $\mu$ becomes the well-known expression for the diatomic molecule.

(20) can be used to obtain a rough value for the frequency $\omega_2$, as the value for $\omega_1$ is well known from Raman and infrared data of other molecules which contain a CH-bond. With the observed value $5.8\times10^{-4}$ for $\mu$ and $\omega_1=3000$ cm$^{-1}$, we obtain $\omega_2=2000$ cm$^{-1}$. The accuracy of this value is not very great, probably not better than about 20 percent, but it seems to be definitely larger than the value generally assumed. With the above value for $\omega_2$ it follows that the CH-force is about four times larger than the apparent force between the two hydrogen atoms.

In conclusion it is a great pleasure to express our sincere thanks to Mr. A. L. Loomis for his continued hospitality and the opportunity to use the facilities of his laboratory. We are also grateful to Mrs. Hildegard Kistiakowsky for her help with the wave-length calculations.