# Stark Effect on the Electronic Bands of a Symmetric-top Molecule

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Calculations have been performed on the energy matrix of a rigid symmetric-top molecule, HCHO, in order to determine the transition energies and intensities of the rotational sub-bands of the electronic spectrum under various magnitudes of external electrostatic fields. Though HCHO is an asymmetric-top molecule, the rotational structure of the 3390 Å band of this molecule is close to that of a perpendicular band of a symmetric-top molecule, at least, for not too small values of $K$. The variation in the band structures with the applied fields can be illustrated by the behavior of several selected bands, $^pP$, $^pQ$, $^rR$, and $^rQ$. Below 100 kV/cm, the overall Stark splittings have been linearly dependent on the field strength, regardless of the branch types. Over 100 kV/cm, however, a deviation from the linear dependence has been found for a certain branch. Changes in the band shape have appeared at such small values of external fields that no deviation from the linear field dependence of the overall Stark splitting has been observed. Such changes are dependent on the branch types, especially in the cases of branches with small $J$ values and with $K<J$. The intensity enhancement of some forbidden bands has also been observed, the magnitude of which is proportional to the square of the field strength below 100 kV/cm. However, the relation between the intensity enhancement and the electric fields has been found to be complicated at fields over 100 kV/cm, the enhanced intensity being proportional to a coupled sum of $E^2$ and higher terms. At a fixed electric field, a linear relation has been found between the overall Stark splitting and the various $\mu$ values assumed for the excited state. The analysis of the data has enabled us to determine the electric dipole moment of the lowest $n\rightarrow\pi^*$ excited state of HCHO as 1.65 D.

Electric dipole moments in excited electronic states of gaseous molecules have been measured by means of electric-field-induced spectra, or the optical Stark effect.[1] When an electric field is applied to a molecule with a fine rotational structure in the electronic spectrum, some rotational lines may split into their Stark components. The splitting will be a function of the magnitude of the applied field and the dipole moments of the molecule in both states related to the transition. Thus, this method affords an important means for us to obtain some exact structural information on the short-lived excited molecules as well as on the ground-state molecules.

The first-order perturbation theory is usually used for the estimation of the dipole moments of electronic excited states from the Stark splittings of a symmetric-top molecule. However, the value of the splitting calculated on the basis of this theory differs greatly from the one observed at high electric fields, and sometimes gives a significant discrepancy even at low electric fields.

Therefore, in order to improve the calculation, we need to include higher-order terms in the perturbation theory. From this point of view, Shirley[2] has given an extensive treatment of the energy levels for all the rotational states through $J=4$, obtained from the direct diagonalization of the energy matrix of a rigid symmetric-top molecule under an electric field. On the other hand, as for an asymmetric-top molecule, West and Mizushima[3] have calculated the Stark effect of the lower rotational levels of $H_2S$ and $SO_2$. However, both these calculations have been carried out only for molecules in one electronic state, *i.e.*, the electronic ground state.

Lombardi[4] was the first to make calculations of the Stark splittings and the band shapes of certain selected rotational sub-branches associated with *an electronic transition* of an asymmetric-top molecule under an electric field. In principle, Lombardi's calculation appears to cover all cases, and so it may seem unnecessary to do a similar calculation on a symmetric-top molecule.

However, for asymmetric-top molecules, the Stark effect is essentially of the second order, while it is of the first order for symmetric-top molecules. Moreover, so far there have been no such calculations made on symmetric-top molecules or on asymmetric-top ones whose behavior may be actually considered to be those of symmetric-top ones. For these molecules, it will be necessary to get detailed information about the Stark effect on their electronic transitions, because so far there has been no discussion on how large magnitudes of electric fields can make invalid the results obtained by the first-order perturbation theory, on how the band shapes in various branches may change with the electric fields, and on how the forbidden bands of a symmetric-top molecule in a zero field can get their intensities with electric fields, *etc.*

Moreover, the recent progress of very high resolution spectroscopy[5] free from Doppler broadening, especially the progress of a tunable cw dye laser technique, has attracted much attention. Then, also in the very-high-resolution spectra of the Stark splitting of electronic bands, it would be necessary to know the detailed $M$ structures rather than the overall doublet splitting usually observed in moderately-high-resolution spectra, even though such very-high-resolution spectroscopy has not yet been well established.

In consideration of these circumstances, our calculation has been performed with special interest taken in the details of the intensity variation of each Stark component in different types of transitions with the field strengths and in the limits of the application of the perturbation theory for a symmetric-top molecule under an external electric fields.

## Theoretical

The main program of the diagonalization of the energy matrix of a symmetric-top molecule under an external electric field closely parallels Shirley's. However, here we need eigenfunctions for the intensity calculation as well as the eigenvalues of the energy matrices for each set of $J$, $K$, and $M$. Therefore, we must directly diagonalize the fixed dimensions of the energy matrices.

The term values of each rotational state are expressed as

$$F(\mathrm{II}) = B(\mathrm{II}) \times E(\mathrm{II}, J, K, M) + \{A(\mathrm{II})-B(\mathrm{II})\}\times K^2, \tag{1}$$

where $A(\mathrm{II})$ and $B(\mathrm{II})$ are the rotational constants of the related states and where $E(\mathrm{II},J,K,M)$ are the eigenvalues of the matrix to be mentioned below. The frequencies of the rotational bands associated with an electronic transition are given by

$$\nu = \nu_0 + F(2) - F(1), \tag{2}$$

where $\nu_0$ is the frequency of vibronic origin.

The energy matrix for the determination of $E(\mathrm{II},J,K,M)$ is

$$\begin{vmatrix} a_1-E & \sqrt{b_2} & 0 & \cdot & \cdot \\ \sqrt{b_2} & a_2-E & \sqrt{b_3} & \cdot & \cdot \\ 0 & \sqrt{b_3} & a_3-E & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot \end{vmatrix} = 0, \tag{3}$$

where

$$a_k = (J_0+k-1)\times(J_0+k) - \frac{R(\mathrm{L,II})\times M\times K}{(J_0+k-1)\times(J_0+k)}, \tag{4}$$

$$b_k = \frac{R(\mathrm{L,II})^2\times\{(J_0+k-1)^2-K^2\}\times\{(J_0+k-1)^2-M^2\}}{(J_0+k-1)^2\times\{4\times(J_0+k-1)^2-1\}}, \tag{5}$$

and

$$R(L,\mathrm{II}) = \mu(\mathrm{II})\times V(L)/B(\mathrm{II}).$$

Throughout these equations, the notation II is used to distinguish the ground state (II=1) or the excited state (II=2). $\mu(\mathrm{II})$ denotes the dipole moment of the ground or excited state, and $V(L)$, various field strengths, with $L=1, 2, 3,\cdots$ $J_0$ is the lowest $J$ value for the special set of the $K$ and $M$ quantum numbers; it is equal to the larger of the two quantities, $|K|$ and $|M|$. For example, $J_0=5$ for each set of $|K|=0$—5 and $|M|=5$.

The energy matrices are diagonal for the $K$ and $M$ quantum numbers, but not for the $J$ quantum number because the nondiagonal element, $b_k$, induces the mixing between the rotational states of $\Delta J=\pm 1$, $\Delta K=\Delta M=0$. Therefore, the exact energy matrices for each set of $K$ and $M$ are infinite in dimensions. For the purpose of computation they must be truncated. The truncated matrices of definite dimensions are then expanded to give two types of continued fractions, both of which are solved by an iteration method improved by the application of the Newton-Raphson procedure discussed by Swalen and Pierce.[6] A program which has been written for this purpose is available from the authors on request.

Table 1. Comparison of the eigenvalues for the energy matrices of $5\times 5$ and $6\times 6$[a)]

| II | $L$ | $J_0$ | $J$ | $K$ | $M$ | $K2$ | $W(k2)$ | $W(k2)$ |
|---|---|---|---|---|---|---|---|---|
| 1 | 9 | 5 | 5 | 5 | 5 | 1 | 29.24844 | 29.24844 |
| 1 | 9 | 5 | 6 | 5 | 5 | 2 | 41.46239 | 41.46239 |
| 1 | 9 | 5 | 7 | 5 | 5 | 3 | 55.59698 | 55.59698 |
| 1 | 9 | 5 | 8 | 5 | 5 | 4 | 71.68682 | 71.68682 |
| 1 | 9 | 5 | 9 | 5 | 5 | 5 | 89.75537 | 89.74968 |
| 1 | 9 | 5 | 10 | 5 | 5 | 6 | | 109.8012 |

a) The first and second columns show those eigenvalues obtained for the ground state (II=1) and under an applied electric field of $V(L=9)=28.1$ kV/cm. The last two columns show the eigenvalues of the energy matrices of $5\times 5$ and $6\times 6$ respectively.

In the present calculation, we truncated all the matrices into $5\times 5$, whose eigenvalues are classified by $J_0$, $J_1$, $J_2$, $J_3$, and $J_4$, $J_0$ being the lowest. However, as is shown in Table 1, the truncation of the matrices into $5\times 5$ will remain a sufficiently good approximation for at least the lower four states from $J_0$ to $J_3$ unless extremely high fields are achieved. Table 1 shows the comparison of each eigenvalue of the $5\times 5$ and $6\times 6$ matrices for the states of $J_0=5$, $K=5$, and $M=5$ at an applied field of $V(9)=28$ kV/cm.

Table 2. Rotational sub-states $J_{KM}$ calculated in the present work[a)]

| $J_0$ | Rotational sub-states |
|---|---|
| 0 | $0_{00}$, $1_{00}$, $2_{00}$, $3_{00}$ ; |
| 1 | $1_{01}$, $2_{01}$, $3_{01}$, $4_{01}$ ; $1_{11}$, $2_{11}$, $3_{11}$, $4_{11}$ ; $1_{1-1}$,$2_{1-1}$,$3_{1-1}$,$4_{1-1}$; |
| 2 | $2_{02}$, $3_{02}$, $4_{02}$, $5_{02}$ ; $2_{12}$, $3_{12}$, $4_{12}$, $5_{12}$ ; $2_{22}$, $3_{22}$, $4_{22}$, $5_{22}$ ;<br>$2_{1-2}$,$3_{1-2}$,$4_{1-2}$,$5_{1-2}$; $2_{2-2}$,$3_{2-2}$,$4_{2-2}$,$5_{2-2}$; |
| 3 | $3_{03}$, $4_{03}$, $5_{03}$, $6_{03}$ ; $3_{13}$, $4_{13}$, $5_{13}$, $6_{13}$ ; $3_{23}$, $4_{23}$, $5_{23}$, $6_{23}$ ;<br>$3_{33}$, $4_{33}$, $5_{33}$, $6_{33}$ ; $3_{1-3}$,$4_{1-3}$,$5_{1-3}$,$6_{1-3}$; $3_{2-3}$,$4_{2-3}$,$5_{2-3}$,$6_{2-3}$;<br>$3_{3-3}$,$4_{3-3}$,$5_{3-3}$,$6_{3-3}$; |

a) The energy matrices are symmetric for $K$ and $M$. Therefore, the eigenvalues for $J_{\pm K\pm M}$ and $J_{\pm M\pm K}$ are the same, but the state energies of Eq. 1 are different for $|K| \doteqdot |M|$. In the table the states of $J_{\pm M\pm K}$ and also of higher $J_0$ values than $J_0=3$ are not written because the space is limited, though we have calculated all the states through $J_0=9$.

In the case of $J_0=5$, the present truncation limits the states of $K=5$ and $M=5$ to the states of $J=5$ to 8. The highest state $9_{55}$, (in the notation of $J_{KM}$), of the $5\times 5$ matrix has been omitted because the approximation obtained is not good enough compared with that for lower states, as is shown in Table 1. Accordingly, if we take the energy matrices to be of definite dimensions, we will inevitably get only limited information for each set of $K$ and $M$, as is shown in Table 2. Table 2 shows the rotational sub-states of $J_{KM}$ calculated by the present method, but the states of $J_{\pm M\pm K}$ and $J_0$ values higher than $J_0=3$ are not shown.

The eigenfunctions corresponding to each eigenvalue have been obtained by solving the simultaneous equations derived from Eq. 3 and by using the normalization conditions. In the present approximation, the general form of the eigenfunctions of a symmetric-top molecule under the Stark effect is written as

$$\Psi(\mathrm{II}, J_0^{KM}) = T(\mathrm{II}, 1, 1)\times\phi(J_0^{KM}) + T(\mathrm{II}, 2, 1)\times\phi(J_1^{KM}) + \cdots + T(\mathrm{II}, 5, 1)\times\phi(J_4^{KM}), \tag{7}$$

where the superscript in $J^{KM}$ denotes a state that has a definite $K$ and $M$, and $T(\mathrm{II}, \xi+1, \eta+1)$, the coefficients of the symmetric-top bases, $\phi(J_\xi^{KM})$, in $\Psi(\mathrm{II}, J_\eta^{KM})$.

The transition moment, $TM$, of a rotational sub-band associated with an electronic transition is, then, given by

$$\begin{aligned} TM &= \int\Psi(1, J_{\eta''}^{K''M''})\times\phi_{Fg}\times\Psi(2, J_{\eta'}^{K'M'})\times \mathrm{d}\tau \\ &= \sum_{\xi'',\xi'} T(1, \xi''+1, \eta''+1)\times T(2, \xi'+1, \eta'+1) \\ &\quad \times\int\underline{\phi(J_{\xi''}^{K''M''})\times\phi_{Fg}\times\phi(J_{\xi'}^{K'M'})\times \mathrm{d}\tau}, \end{aligned} \tag{8}$$

where $\phi_{Fg}$ are the direction cosines between space-fixed $F$ and molecule-fixed $g$ coordinate axes and where $''$ and $'$ refer to the ground and excited states respectively.

The transition intensity, $I$, is written as

$$I = |TM|^2\times\exp\{-E(1, J'', K'', M'')/kT\}. \tag{9}$$

In Figs. 1—4 the transition intensities have been calculated with Eqs. 8 and 9, although the matrix element associated with the direction consine, the integral underlined in Eq. 8, is taken from the table given by Allen and Cross.[7]

## Results and Discussion

To carry out the numerical calculation with the program stated in the previous section, it is necessary to know the rotational constants of the ground and excited states of a symmetric-top molecule.

In the previous experimental work,[8] we studied the Stark effect on the 3390 Å band of formaldehyde. Several reports[1] have also been given on the same problem of this molecule. In this calculation we shall take the rotational constants of formaldehyde given in Table 3. The following discussion will be mainly concerned with the Stark effect on the spectrum of formaldehyde.

TABLE 3. ROTATIONAL CONSTANTS OF $H_2CO$[a]

| States | $a$ | $b$ | $c$ |
|---|---|---|---|
| $^1A''$ | 8.7517 | 1.1245 | 1.0123 |
| $^1A_1$ | 9.4053 | 1.2953 | 1.1342 |

a) Taken from "Molecular Spectra and Molecular Structure," III, ed by G. Herzberg, Van Nostrand Reinhold Company (1966), p. 612.

Strictly, formaldehyde is an asymmetric-top molecule, but it is very close to a symmetric-top one, the two larger moments of inertia being nearly equal and much greater than the moment of inertia around the C=O axis. When the value of $K$ is not too small, the rotational structure of the 3390 Å band is almost the same as that of a perpendicular band of a symmetric-top molecule* whose rotational constants are taken as $A=a$, $B=(b+c)/2$ at both states related to the transition, where $a$, $b$, and $c$ are those of formaldehyde.

For the perpendicular transition of a symmetric-top, the selection rules are $\Delta K=\pm1$ and $\Delta J=0$ and $\pm1$. The transitions are designated as $^r$R, $^r$P, and $^r$Q for $\Delta K=+1$, and $^p$R, $^p$P, and $^p$Q for $\Delta K=-1$. In the series of sub-bands with $\Delta K=+1$, the $^r$R branches are much stronger than the $^r$Q branches, while the $^r$P branches are too weak to be observed. In the series with $\Delta K=-1$, the situation is reversed, the $^p$P and $^p$Q branches being observed, while the $^p$R branches are absent.

In the present work we have calculated the transition energies and intensities for all possible transitions among the Stark components of the rotational sub-branches shown in Table 2. However, it is impossible to show all of them in our limited space. Thus, it will be more instructive to choose the intense branches in a zero field, such as $^r$R, $^r$Q, $^p$P, and $^p$Q, and to show how the band splittings and shapes of these branches vary with the increase in the electric field.

The results of our calculation are shown in Figs. 1—4. Figures 1 and 2 show the field dependence of the Stark splittings of the $^r$R 5(5) and $^p$P 5(5) sub-branches of

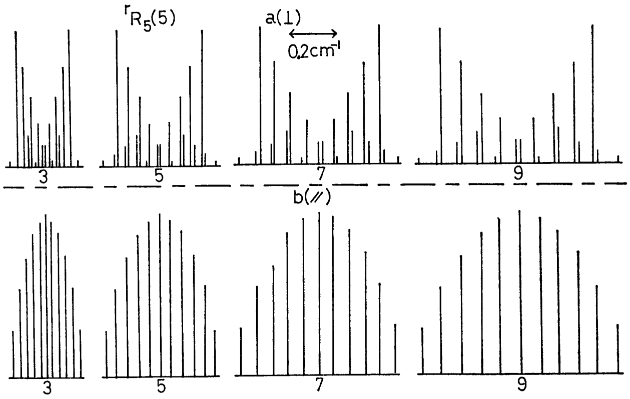

Fig. 1. The Stark splitting of $^r$R 5(5) branch and its change with field strengths. Throughout Figs. 1 to 4 (a) and (b) correspond to the absorption with perpendicular and parallel polarizations to the direction of the applied field, and $\mu(2)=1.44$ D is assumed. The numbers written under each figure mean the values of the field strength $10\times\mu(1)\times V(L)/B(1)$.

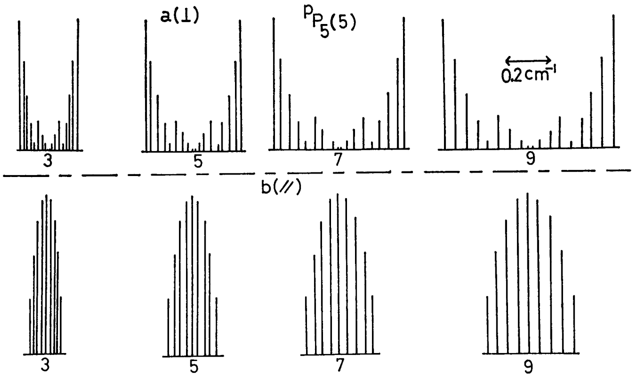

Fig. 2. The Stark splitting of $^p$P 5(5) branch and its change with field strengths.

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* For a slightly asymmetric-top, the asymmetric splitting is, in general, unobservably small for the state with $K>3$.

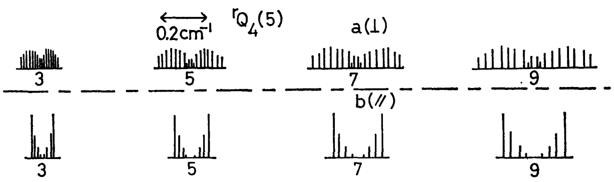

Fig. 3. The Stark splitting of $^{r}$Q 4(5) branch and its change with field strengths.

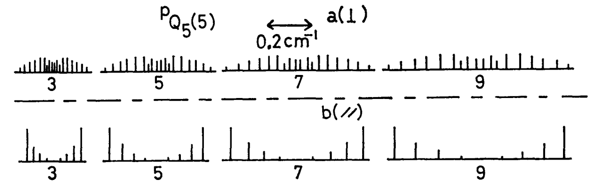

Fig. 4. The Stark splitting of $^{p}$Q 5(5) branch and its change with field strengths.

the 3390 Å absorption band for the light polarized perpendicular and parallel respectively to the field direction. Here, to show explicitly the lower-state quantum numbers of the $^{r}$R and $^{p}$P transitions, the notation $K''(J'')$ has been inserted after the branch notations. Figures 3 and 4 also show the field dependence of the Stark splittings for the $^{r}$Q 4(5) and $^{p}$Q 5 (5) sub-branches under the same conditions as in Figs. 1 and 2.

Table 4. Intensity criteria of the profiles of incompletely resolved Stark patterns

| | $\Delta J=-1$ | $\Delta J=0$ | $\Delta J=+1$ |
|---|---|---|---|
| $\Delta M=0$ (parallel polarization) | broadening | doublet | broadening |
| $\Delta M=\pm 1$ (perpendicular polarization) | doublet | broadening | doublet |

Throughout Figs. 1—4 the general features of each band are in agreement with those suggested by the criteria based on the intensity rule shown in Table 4. Certainly, the envelopes of the $^{r}$R and $^{p}$P absorption lines in the perpendicular spectra seem to show a doublet splitting, while those for the parallel spectra seem to show line-broadenings. However, it must be noted that the detailed features of these spectra are rather different from those obtained by the usual perturbation theory, especially for the $^{r}$Q and $^{p}$Q branches in the perpendicular spectra shown in Figs. 3 and 4.

Figure 5 shows how the overall splittings $\Delta\nu$ of the $^{p}$P 5(5) branch in the perpendicular spectra vary with the increase in the electric field. There, we can see a linear relation between the overall splittings, $\Delta\nu$, and the field strengths. This linear relation indicates the validity of the usual perturbation theory, which we shall consider in our later discussion of the same problem in other branches.

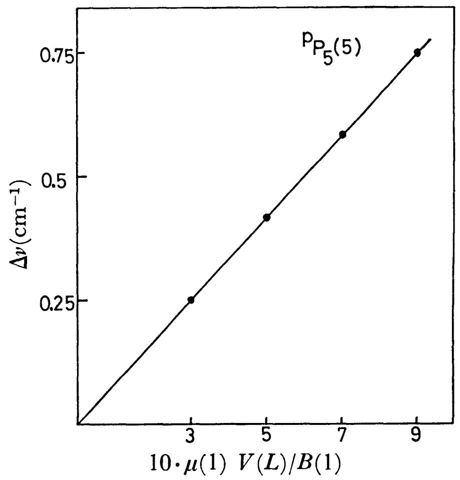

Fig. 5. The linear relation between the overall splittings of $^{p}$P 5(5) and the field strengths. $10\times\mu(1)\times V(9)/B(1)=9$ corresponds to a field strength 28.1 kV/cm, and $\mu(2)=1.44$ D is assumed.

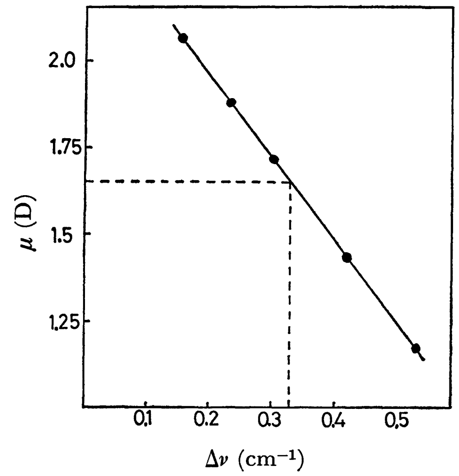

Fig. 6. The change of the overall Stark splitting of $^{p}$P 5(5) branch with various assumed dipole moments of the excited state under a constant electric field 15.6 kV/cm. The dotted line is drawn to determine the dipole moment of the excited state corresponding to the observed doublet splitting of HCHO spectrum under the same field strength.

The calculated spectra shown in Figs. 1—4 are obtained by assuming the dipole moments in the electronic ground and excited states to be 2.34[9] and 1.44 D respectively. Figure 6 shows how the overall splitting, $\Delta\nu$, of $^{p}$P 5(5) varies when only the dipole moment of the molecule in the electronic excited state is changed, while other quantities, such as the dipole moment in the ground state and the applied field strength, keep constant. In this figure we see that, as the value of the dipole moment in the excited state becomes smaller compared with that in the ground state, the overall splitting becomes larger.

The dipole moment of the excited state can be determined from Fig. 6 if the overall splittings $\Delta\nu$ have been established experimentally. However, it must be noted that the available data on the overall splittings have been obtained from moderately-high-resolution spectra, that is, from a blended doublet splitting, but not from well-resolved splittings such as were those in Figs. 1—4.

Before making use of the experimental overall splitting values, it will be useful to know how to get a blended doublet pattern from the resolved splitting, or *vice versa*. For this purpose, we have assumed a Gaussian distribution with a half-band width of 0.1 cm$^{-1}$ for each resolved splitting line.**

Naturally the band shapes obtained through such blending depend not only on the type of branch, but also on the magnitude of the assumed excited state dipole moment and on the applied fields. We have obtained a factor of 1.13 to be multiplied for the transformation from an observed blended doublet to a resolved overall splitting, especially for the case of the $^{p}$P 5(5) branch under the same conditions as those of our experiment.

The value on the abscissa shown by a dotted line in Fig. 6 shows the $\Delta\nu$ recalculated from the observed doublet splitting with the above factor. The intersection of the dotted line with the ordinate gives the value of the dipole moment of the excited state obtained by this calculation.

The value of 1.65 D obtained here for the excited-state dipole moment is comparable with the 1.61 D obtained when the first-order perturbation theory (also *cf.* Ref. 1a) is applied to our experimental results. It should be noted that there is a little discrepancy between the dipole moment obtained by the first-order perturbation theory and that obtained in the present work, because the present calculation includes implicitly higher-order perturbation terms together with the usual first-order perturbation theory.

The calculated $\mu$ value is, of course, obtained from the experimental correspondence, as has been stated above. The experimental value of the Stark splitting has been obtained from the spectra observed by the use of a newly designed Fabry-Perot interferometer spectroscope, whose details have previously been described.8,10) The Stark cell is a parallel-plate condenser, the two brass plates (100 cm long, 5 cm wide, 0.7 cm thick) being separated (0.5 cm) by Teflon spacers. The overall errors of our experimental work are within 5%. The value of 1.65 D obtained here for the $n \to \pi^*$ excited state of formaldehyde is, then, in good agreement with the other data: 1.56±0.1 D,1a) 1.67±0.15 D (Method I), and 1.4±0.1 D (Method II).1b)

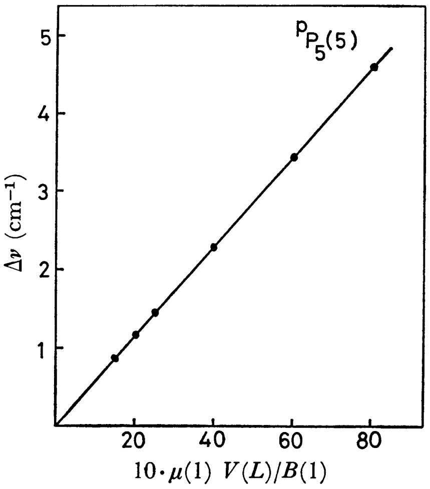

Fig. 7. The linear relation between the overall splittings of $^{p}$P 5(5) and the field strengths over 30 kV/cm. The abscissa shows the field strengths $10\times\mu(1)\times V(L)/B(1)$, and $\mu(2)=1.75$ D is assumed.

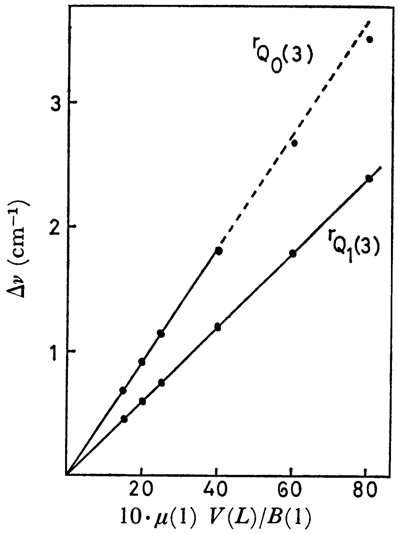

Fig. 8. The change of the overall Stark splittings of $^{r}$Q 0(3) and $^{r}$Q 1(3) branches with field strengths.

Let us return to the problem of the linear relation between the overall splitting of $^{p}$P 5(5) and the applied field strength observed in Fig. 5, where applied fields are varied below 30 kV/cm. In Fig. 7 it should be noted that the linear relation holds up to such a high field strength as 200 kV/cm or more. Certainly this seems to reflect the validity of the usual first-order perturbation theory in such a high field. However, it is certain that the linear relation is also dependent on the type of branch. In Fig. 8 the same relation is shown for $^{r}$Q 0(3) and $^{r}$Q 1(3).*** Especially for the $^{r}$Q 0(3) branch, we can observe a noticeable departure from the linear relation around 100 kV/cm, while the $^{r}$Q 1(3) branch still shows a linear field dependence. However, as for the band shape of the latter branch as well as of the former, the symmetric pattern at low fields changes to an asymmetric one even at rather small field strengths, and presents a quite different appearance around 200 kV/cm, as is shown in Fig. 9.

It may be considered that such characteristic behavior of the $^{r}$Q 0(3) and $^{r}$Q 1(3) branches clearly shows the existence of higher-order interactions, even at rather low field strengths.

At least under field strengths below 100 kV/cm, and so long as the magnitude of the overall splittings is in question, there seems to be no serious disagreement between the first-order perturbation theory and the

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** The value of 0.1 cm$^{-1}$ was taken from the observation for half-band widths in a field-free spectrum.

*** These branches with $K<3$ should show a large asymmetric effect in the spectrum of HCHO, and so here they were only chosen as prototypes of such bands in a symmetric-top molecule.

Table 5. The intensity enhancement of the forbidden band $1''_{01}$ to $1'_{01}$ in a zero-field limit[a)]

| Field strength | 0.1 | 0.3 | 0.5 | 0.7 | 0.9 | 1.5 | 2.0 | 2.5 | 4.0 | 6.0 | 8.0 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Intensity | 0.0001 | 0.0006 | 0.0017 | 0.0035 | 0.0057 | 0.0181 | 0.0310 | 0.0463 | 0.0999 | 0.1735 | 0.2377 |

a) As the field strength we used the value of $\mu(1)V/B(1)$. The intensities at the field strengths from 0.1 to 0.9 are those obtained under the assumption of $\mu(2)=1.44$ D, but the others were obtained under the assumption of $\mu(2)=1.75$ D.

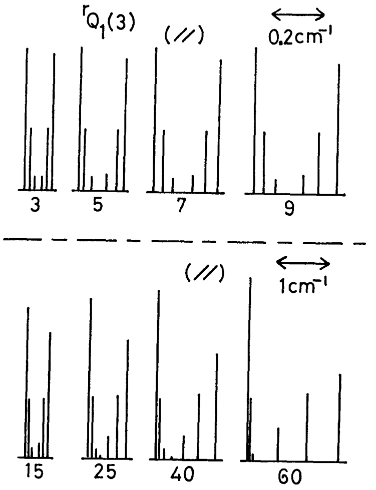

Fig. 9. The Stark splitting of $^rQ$ 1(3) branch and its change with field strengths.

present treatment, regardless of the type of branch. However, as for the band shapes or the band structure, it should be noted that a serious discrepancy may occur depending on types of the branches. This is especially remarkable for the branches with small $J$ values and with $K<J$.

Lastly, we shall discuss the intensity enhancement of the forbidden branches of a symmetric top in a zero field. Table 5 shows the intensities of the transition from the $1''_{01}$ to the $1'_{01}$ rotational sub-branch. This transition is, of course, a forbidden one† due to the selection rule of $\Delta J=\pm 1$ for $K=0$ of a symmetric-top in a zero field. From the table we can see that the intensity of the transition is appreciable at a field strength of 30 kV/cm, and that it increases with a quadratic dependence on the field strengths. With a further increase in the field strengths, the intensity increases more and more, until beyond 100 kV/cm it is no longer distinguishable from that of the allowed transition and also shows an appreciable deviation from the quadratic-field dependence.

## Conclusion

By way of conclusion, we may summarize the present work as follows:

(1) By the direct diagonalization of the energy matrices of a symmetric top under an external electric field, we have calculated the Stark splittings and intensities of the rotational sub-branches associated with the 3390 Å band of HCHO. For some selected branches we have given the detailed band structures, which can, it is hoped, be used as model spectra of the Stark splittings in very-high-resolution spectroscopy.

(2) Below 100 kV/cm, the overall Stark splittings are dependent linearly on the field strength, regardless of the branch type. Over 100 kV/cm the deviation from the linear-field dependence becomes appreciable, depending on the branch type.

(3) The change from a symmetric to an asymmetric appearance of the band shapes of a certain band occurs even below 30 kV/cm, and becomes appreciable with a further increase in the field strength. The effects depending on the branch types stated in (2) and (3) are especially remarkable for the branches with small $J$ values and with $K<J$.

(4) Between the assumed dipole moments of the excited state and the overall splitting of the $^pP$ 5(5) branch, there exists a linear relation at field strengths below 100 kV/cm. From this relation, the value of 1.65 D has been determined for the dipole moment of the first excited $n\rightarrow\pi^*$ state of HCHO.

(5) The intensity enhancement of the forbidden bands of a symmetric-top molecule in a zero field shows a quadratic dependence on the applied field strength below 100 kV/cm, but comes to show an appreciable deviation from the quadratic-field dependence over 100 kV/cm.

The numerical calculations have been carried out with an NEAC 2200-700 electronic computer at Tohoku University.

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† In this work we carried out the calculations for both parallel- and perpendicular-type bands of a symmetric-top. The transition from $1''_{01}$ to $1'_{01}$ is the forbidden branch $^qQ$ 0(1) of a parallel-type band.

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