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Internal Rotation of Propane from the Microwave Spectrum

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The microwave spectrum of propane was observed in the first-excited states of the CH_3 torsion. Each transition was split into a symmetric triplet; the splittings were 14—19% larger for the (−) state than for the (+) state. The top-top interaction and its effect on the rotational spectra were treated by the perturbation theory, and the results were applied to the analysis of the triplet splittings. The two barrier parameters, V_3 and V_3'', were thus determined to be 3325 ± 20 and -170 ± 30 cal/mol respectively.

The internal rotation in propane is an important problem, since propane is one of the simplest hydrocarbon molecules and the barrier height for the internal rotation in this molecule is referred to in the discussion of the structure of high-polymeric systems. Lide has successfully observed the microwave spectra of propane and its isotopic species, and has thus determined the r_s structure and dipole moment.¹⁾ The rotational spectra he observed were, however, in the ground vibrational state and did not show any splitting due to the internal rotation. Thus he placed a lower limit of 2700 cal/mol on the barrier height to the internal rotation; this limit was compatible with the thermodynamic value of 3100—3300 cal/mol obtained by Kistiakowsky and Rice.²⁾ Recently Scharpen and Laurie³⁾ observed the spectra in the excited torsional states and analyzed them using a single-top approximation to get the barrier to internal rotation to be 3.55 kcal/mol. In the present paper the rotational spectra in the excited torsional states were observed as triplets, and the splittings were analyzed by taking into account the top-top interactions.

The theory of the two-top internal rotation has been discussed by many authors,⁴⁻⁶⁾ but such consideration has primarily been devoted to the ground torsional state. Typical of the two-top problem, an additional complication comes in the rotational spectra in the first-excited states, since the latter ($v=1$) are degenerate because of the presence of two equivalent tops. The degeneracy is, however, removed by the coupling terms of the two tops, producing the (+) and (−) states. It may thus be inferred that the effect of the top-top coupling is more conspicuous for the $v=1$ than for the $v=0$ states. In the present paper a perturbation calculation was carried out to the first order in the coupling terms and applied to the analysis of the torsional satellites.

Rotational Spectra

The rotational spectrum was observed with a 100 kc sine-wave Stark modulation spectrometer described elsewhere.⁷⁾ All measurements were made at dry-ice temperature. The signal-to-noise ratio was about 3 for the weakest line observed, that is, the AA or AE and EA (not resolved) lines of the $1_{10}\leftarrow1_{01}$ transition.

The observed frequencies of the spectra in the first-excited states are listed in Table 1. All the transitions are triplets, symmetric both in splitting and in intensity. The assignment of the lines to the (+) and (−) states was made by observing the relative intensities of the triplet components: in the (+) state the intensity ratio, (A_1A_2) : (EE) : (A_1E and EA_2), was expected to be 36 : 64 : 36 for the ee↔oo transitions and 28 : 64 : 28 for the eo↔oe transitions, whereas the (A_2A_1) : (EE) : (A_2E and EA_1) ratio of the (−) state was 28 : 64 : 28 for the former and 36 : 64 : 36 for the latter transitions.⁸⁾ The observed relative intensities are shown in Table 2, where the intensities of the (EE) components are normalized to 64 and the averages of the side components, (AA) and (AE and EA), are compared with the theoretical values, 36 or 28. The spectral lines assigned to the (+) state were found to be stronger than those to the (−) state. This is also consistent with the assignments, as will be shown by an analysis given below.

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TABLE 1. TRANSITION FREQUENCIES AND ROTATIONAL CONSTANTS[a)] OF PROPANE IN THE FIRST EXCITED STATES OF THE TORSION[b)]

Transition	(+) state			(−) state		
	A_1A_2	EE	A_1E+EA_2	A_2A_1	EE	A_2E+EA_1
$1_{11}-0_{00}$	36616.05	36617.73	36619.24	36534.10	36535.95	36537.80
$2_{12}-1_{01}$	51514.95	51516.55	51518.15	51425.55	51427.45	51429.25
$1_{10}-1_{01}$	21717.05	21718.67	21720.33	21642.31	21644.27	21646.21
$2_{11}-2_{02}$	22733.90	22735.68	22737.35	22645.06	22647.00	22648.99
$3_{12}-3_{03}$	24322.78	24324.54	24326.37	24210.73	24212.82	24214.99
$4_{13}-4_{04}$	26556.51	26558.40	26560.30	26411.06	26413.30	26415.55
$5_{14}-5_{05}$	29525.87	29527.91	29529.98	29334.72	29337.18	29339.60
A (α^A)	29166.55 (40.81)			29088.18 (119.18)		
B (α^B)	8432.45 (13.62)			8415.31 (30.76)		
C (α^C)	7449.47 (9.51)			7445.81 (13.17)		

a) For A_1A_2 and A_2A_1 states b) In Mc/sec

TABLE 2. RELATIVE INTENSITIES OF THE TORSIONAL SATELLITES

Transition	(+) state		(−) state	
	Obs.[a)]	Calcd.	Obs.[a)]	Calcd.
$1_{11}-0_{00}$	34±5	36	—	28
$1_{10}-1_{01}$	30±5	28	37±8	36
$2_{11}-2_{02}$	38±4	36	34±3	28
$3_{12}-3_{03}$	30±3	28	39±6	36
$4_{13}-4_{04}$	32±2	36	30±5	28
$5_{14}-5_{05}$	30±4	28	37±4	36

a) Average of the two side components, (AA) and (AE+EA). The intensity of the center line, (EE), is normalized to 64.

TABLE 3. TRIPLET SPLITTING, (AE+EA)−(AA), IN THE TORSIONAL SATELLITES OF PROPANE (Mc/sec)

Transition	Obs.				Calcd.[b)]
	(+)	(−)	Av.	Corrected for linear term[a)]	
$1_{11}-0_{00}$	3.19	3.70	3.44_5	3.51_2	3.54_5
$2_{12}-1_{01}$	3.20	3.70	3.45	3.47_2	3.54_5
$1_{10}-1_{01}$	3.28	3.90	3.59	3.52_3	3.54_5
$2_{11}-2_{02}$	3.45	3.93	3.69	3.66_8	3.67_3
$3_{12}-3_{03}$	3.59	4.26	3.92_5	3.91_4	3.86_9
$4_{13}-4_{04}$	3.79	4.49	4.14	4.13_3	4.14_2
$5_{14}-5_{05}$	4.11	4.88	4.49_5	4.49_1	4.50_0

a) Corrections for the linear term are $\pm 2\times 0.067/J(J+1)$, where + holds for $J_{1,J-1}$ and − for $J_{1,J}$.
b) Calculated by assuming $\Delta A=3.54_5$ and $\Delta B=0.124_4$ Mc/sec.

The spectra of the (AA) level were analyzed using the rigid-rotor model, except for the introduction of a centrifugal term, $k\ J^2(J+1)^2$, for the Q-branches, as Lide has assumed, where the value of k was taken to be the same as that for the ground states. The rotational constants and vibration-rotation interaction constants, α, are given in Table 1.

The internal-rotation splitting is 14—19% larger for the (−) state than for the (+) state, as is shown in Table 3. The difference may be ascribed to the contributions of the top-top coupling terms, as will be shown later. It should also be noted that the splittings in the Q-branch lines are slightly larger than those in the R-branches.

Perturbation Calculation of the Top-Top Interaction

The Hamiltonian for the overall and internal rotations[4−6,8)] is divided into three parts:

$$\mathscr{H}=\mathscr{H}_r'+\mathscr{H}_t+\mathscr{H}_{r,t} \tag{1}$$

where

$$\mathscr{H}_r'=\mathscr{H}_r+F(\mathcal{P}_1^2+\mathcal{P}_2^2)+F'(\mathcal{P}_1\mathcal{P}_2+\mathcal{P}_2\mathcal{P}_1) \tag{1a}$$

$$\mathscr{H}_t=\mathscr{H}_t^{(0)}+\mathscr{H}_t^{(1)} \tag{1b}$$

and

$$\mathscr{H}_{r,t}=-2F(p_1\mathcal{P}_1+p_2\mathcal{P}_2)-2F'(p_1\mathcal{P}_2+p_2\mathcal{P}_1) \tag{1c}$$

represent the overall rotation, the internal rotation (torsion), and the interaction between the two motions respectively. The Hamiltonian for the overall rotation is different from the rigid-rotor formula, $\mathscr{H}_r=AP_a^2+BP_b^2+CP_c^2$, by small contributions from the internal rotation. Of the interaction terms, those dependent on the torsional coordinates are contained in Eq. (1c). Only these terms can combine the overall and internal rotations. The two terms in the torsional Hamiltonian Eq. (1b) are given by:

$$\mathscr{H}_t^{(0)}=F(p_1^2+p_2^2)+\frac{1}{2}V_3(1-\cos 3\alpha_1)+\frac{1}{2}V_3(1-\cos 3\alpha_2) \tag{2a}$$

and

$$\mathscr{H}_t^{(1)} = F'(p_1p_2 + p_2p_1) + V_3'\cos 3\alpha_1 \cos 3\alpha_2 + V_3''\sin 3\alpha_1 \sin 3\alpha_2 \quad \text{(2b)}$$

Here Eq. (2a) denotes the Hamiltonian for the torsional motion of the two independent tops, whereas Eq. (2b) denotes the coupling between them. The notation used in Eqs. (1) and (2) is apparent from the following relations:

$$\begin{aligned} \mathcal{P}_1 &= \rho_a P_a + \rho_b P_b & \rho_a &= \lambda_a I_a / I_a \\ \mathcal{P}_2 &= -\rho_a P_a + \rho_b P_b & \rho_b &= \lambda_b I_a / I_b \end{aligned} \quad (3)$$

It is more convenient to introduce sums and differences in such a way that:

$$p_\pm = (p_1 \pm p_2) \qquad \alpha_\pm = (\alpha_1 \pm \alpha_2)/2 \quad (4)$$

$$\begin{aligned} \mathcal{P}_+ &= \mathcal{P}_1 + \mathcal{P}_2 = 2\rho_b P_b \\ \mathcal{P}_- &= \mathcal{P}_1 - \mathcal{P}_2 = 2\rho_a P_a \end{aligned} \quad (5)$$

Then Eqs. (1a) and (1c) may be rewritten as:

$$\mathscr{H}_r' = \mathscr{H}_r + \frac{1}{2}(F + F')\mathcal{P}_+^2 + \frac{1}{2}(F - F')\mathcal{P}_-^2 \quad \text{(6a)}$$

$$\mathscr{H}_{r,t} = -(F+F')\mathcal{P}_+ p_+ - (F - F')\mathcal{P}_- p_- \quad \text{(6c)}$$

The solutions of Eq. (2a) are well-known, but it should be noted that only some linear combinations of the wave functions belong to an irreducible representation of the $(C_{3v}^- \times C_{3v}^+)$ group.[6,8] With this implication, eigenfunctions and eigenvalues are denoted by $|V_0)$ and $E_V{}^0$ respectively. Then the solutions of the whole torsional equation, Eq. (1b), are given by:

$$|V) = |V_0) + \sum_{\substack{V_0' \\ (V_0' \neq V_0)}} \frac{(V_0'|\mathscr{H}_t^{(1)}|V_0)}{E_V{}^0 - E_{V'}{}^0} |V_0') + \cdots \quad (7)$$

$$E_V = E_V{}^0 + (V_0|\mathscr{H}_t^{(1)}|V_0) + \sum_{\substack{V_0' \\ (V_0' \neq V_0)}} \frac{|(V_0'|\mathscr{H}_t^{(1)}|V_0)|^2}{E_V{}^0 - E_{V'}{}^0} + \cdots \quad (8)$$

where the non-degenerate perturbation theory is used, since the coupling term (2b) is usually smaller than (2a). If this conditions were not satisfied, the secular equation should be solved, as will be discussed below (see Discussion). The degeneracy inherent in the two-top problem can be ignored in Eqs. (7) and (8), because symmetrized wavefunctions, $|V_0)$, are used as the bases for the perturbation calculation. The V_0' states in Eqs. (7) and (8) belong to the same symmetry species as the V_0 state.

By using Eqs. (6)—(8), the effective rotational Hamiltonian is derived for the V state as follows:

$$\begin{aligned} \mathscr{H}_r^{eff}(V) = \mathscr{H}_r &+ \frac{1}{2}(F + F')\mathcal{P}_+^2 + \frac{1}{2}(F - F')\mathcal{P}_-^2 && \text{(9a)} \\ &- (F + F')\mathcal{P}_+(V|p_+|V) - (F - F')\mathcal{P}_-(V|p_-|V) && \text{(9b)} \\ &+ (F + F')^2\mathcal{P}_+^2 \sum_{V'} \frac{|(V'|p_+|V)|^2}{E_V - E_{V'}} \\ &+ (F-F')^2\mathcal{P}_-^2 \sum_{V'} \frac{|(V'|p_-|V)|^2}{E_V - E_{V'}} \\ &+ (F^2 - F'^2)\left[\mathcal{P}_-\mathcal{P}_+ \sum_{V'} \frac{(V|p_-|V')(V'|p_+|V)}{E_V - E_{V'}} + \mathcal{P}_+\mathcal{P}_- \sum_{V'} \frac{(V|p_+|V')(V'|p_-|V)}{E_V - E_{V'}}\right] && \text{(9c)} \\ &+ 0(\mathcal{P}^3) + 0(\mathcal{P}^4) + \cdots \end{aligned}$$

Here (9b) denotes the so-called linear term, while (9c) and the last two terms in Eq. (9a) are the second-order term. Since the AE and EA lines were not split in the spectrum of propane, the following approximation was assumed for the matrix elements of Eq. (9b):

$$(V|p_\pm|V) \cong (V_0|p_\pm|V_0)$$

The third- and fourth-order terms seemed to be unimportant in the low-J transitions observed in the present work. The denominator corrections, which need not be considered either, are neglected in Eq. (9c) by simply inserting the pure torsional energies, E_v, in the denominators. The second-order terms are by far the most important. The coefficients of $\mathcal{P}_\pm^2$ in Eq. (9) are given by:

$$FW_V{}^{(2\pm)} = \frac{1}{2}(F \pm F') + (F \pm F')^2 \sum_{V'} \frac{|(V'|p_\pm|V)|^2}{E_V - E_{V'}} \quad (10)$$

The perturbation sum is expanded in terms of parameters, F', V_3', V_3'', as follows:

$$\begin{aligned} \sum_{V'} \frac{|(V'|p_\pm|V)|^2}{E_V - E_{V'}} &\equiv (4/9F) \textstyle\sum^\pm \\ &= (4/9F)\left(\textstyle\sum_0^\pm + \sum_1^\pm + \sum_2^\pm + \cdots\right) \end{aligned} \quad (11)$$

where $\sum_n^\pm$ contains the nth power of the interaction parameters. By substituting Eq. (11), Eq. (10) becomes:

$$\begin{aligned} FW_V{}^{(2\pm)} &= [(1/2)F + (4/9)F\textstyle\sum_0^\pm] && \text{(12a)} \\ &+ [\pm(1/2)F' \pm (8/9)F'\textstyle\sum_0^\pm + (4/9)F\sum_1^\pm] && \text{(12b)} \\ &+ [(4F'^2/9F)\textstyle\sum_0^\pm \pm (8/9)F'\sum_1^\pm + (4/9)F\sum_2^\pm] && \text{(12c)} \\ &+ \cdots \end{aligned}$$

It is to be noted that Eq. (12a) is independent of, and Eqs. (12b) and (12c) are the first- and second-order terms in, the interaction parameters.

The first and second terms of Eq. (11) were evaluated by using Eqs. (7) and (8):

$$(4/9F)\Sigma_0{}^{\pm} = \sum_{V_0'} \frac{|(V_0'|p_\pm|V_0)|^2}{E_V{}^0 - E_{V'}{}^0} \tag{13}$$

$$\begin{aligned}
(4/9F)\Sigma_1{}^{\pm} = &- \sum_{V_0'} \frac{|(V_0'|p_\pm|V_0)|^2}{(E_V{}^0 - E_{V'}{}^0)^2} \\
&\times [(V_0|\mathscr{H}_t{}^{(1)}|V_0) - (V_0'|\mathscr{H}_t{}^{(1)}|V_0')] \\
&+ \sum_{V_0'} \sum_{\substack{V_0'' \\ (V_0'' \neq V_0)}} \left[\frac{(V_0|\mathscr{H}_t{}^{(1)}|V_0'')}{E_V{}^0 - E_{V''}{}^0} \right. \\
&\quad \times \frac{(V_0''|p_\pm|V_0')(V_0'|p_\pm|V_0)}{E_V{}^0 - E_{V'}{}^0} \\
&\quad + \frac{(V_0|p_\pm|V_0')(V_0'|p_\pm|V_0'')}{E_V{}^0 - E_{V'}{}^0} \\
&\quad \left. \times \frac{(V_0''|\mathscr{H}_t{}^{(1)}|V_0)}{E_V{}^0 - E_{V''}{}^0} \right] \\
&+ \sum_{V_0'} \sum_{\substack{V_0''' \\ (V_0' \neq V_0''')}} \left[\frac{(V_0'''|\mathscr{H}_t{}^{(1)}|V_0')}{E_{V'}{}^0 - E_{V'''}{}^0} \right. \\
&\quad \times \frac{(V_0|p_\pm|V_0''')(V_0'|p_\pm|V_0)}{E_V{}^0 - E_{V'}{}^0} \\
&\quad + \frac{(V_0|p_\pm|V_0')(V_0'''|p_\pm|V_0)}{E_V{}^0 - E_{V'}{}^0} \\
&\quad \left. \times \frac{(V_0'|\mathscr{H}_t{}^{(1)}|V_0''')}{E_{V'}{}^0 - E_{V'''}{}^0} \right]
\end{aligned} \tag{14}$$

For the first-excited torsional states, Eq.(13) can be expressed, in a simple form, in terms of a single-top perturbation sum[9] as follows:

$$(4/9F)\Sigma_0{}^{\pm} = (4/9F)\left[\left(\frac{pp}{\Delta}\right)_{v=1}^{(A)} + \left(\frac{pp}{\Delta}\right)_{v=0}^{(A)}\right]$$

for A_1A_2 and A_2A_1 (15a)

$$= (4/9F)\left[\left(\frac{pp}{\Delta}\right)_{v=1}^{(E)} + \left(\frac{pp}{\Delta}\right)_{v=0}^{(E)}\right]$$

for A_1E, A_2E, EA_1 and EA_2 (15b)

$$= (2/9F)\left[\left(\frac{pp}{\Delta}\right)_{v=1}^{(A)} + \left(\frac{pp}{\Delta}\right)_{v=0}^{(A)} + \left(\frac{pp}{\Delta}\right)_{v=1}^{(E)} + \left(\frac{pp}{\Delta}\right)_{v=0}^{(E)}\right]$$

for EE states. (15c)

Small correction terms have been neglected in deriving Eqs. (15b) and (15c). By introducing the perturbation coefficients in the single-top problem given by:

$$W_{10}{}^{(2)} = 1 + (16/9)\left(\frac{pp}{\Delta}\right)_{v=1}^{(A)}$$

$$W_{11}{}^{(2)} = 1 + (16/9)\left(\frac{pp}{\Delta}\right)_{v=1}^{(E)}$$

$$W_{00}{}^{(2)} = 1 + (16/9)\left(\frac{pp}{\Delta}\right)_{v=0}^{(A)}$$

$$W_{01}{}^{(2)} = 1 + (16/9)\left(\frac{pp}{\Delta}\right)_{v=0}^{(E)}$$

Eq. (12a) becomes:

$$FW_{(AA)}{}^{(2\pm)} = (1/4)F(W_{10}{}^{(2)} + W_{00}{}^{(2)}) \tag{16a}$$

$$FW_{(AE,EA)}{}^{(2\pm)} = (1/4)F(W_{11}{}^{(2)} + W_{01}{}^{(2)}) \tag{16b}$$

$$FW_{(EE)}{}^{(2\pm)} = (1/8)F(W_{10}{}^{(2)} + W_{00}{}^{(2)} + W_{11}{}^{(2)} + W_{01}{}^{(2)}) \tag{16c}$$

This is in accordance with the result expected for the case where there are two independent tops, one in the $v=1$ state and the other in the $v=0$ state.

TABLE 4. FIRST-ORDER CORRECTIONS, EQ. (14)

State	Correction
A_1A_2	$+I_A+II_A$
A_2A_1	$-I_A+II_A+III_A$
A_1E	$+I_E+II_E \qquad +IV_E+V_E$
A_2E	$-I_E+II_E+III_E-IV_E$
EA_2	$+I_E+II_E \qquad -IV_E$
EA_1	$-I_E+II_E+III_E+IV_E+V_E$
A_1E'[a]	$+I_E+II_E$
A_2E'[b]	$-I_E+II_E+III_E$

a) Average of A_1E and EA_2, when V_E is neglected.
b) Average of A_2E and EA_1, when V_E is neglected.

The first-order corrections, Eq. (14), consist of several terms, I—V, as is shown in Table 4. These terms are all expressed by the matrix elements and eigenvalues of the single-top problem; the subscripts A and E indicate that the eigenfunctions and eigenvalues involved are appropriate for the A and E sublevels. The corrections for the EE state are not given in Table 4 because they are immaterial in analyzing the symmetric triplets. It is convenient to take the average of A_1E and EA_2 and that of A_2E and EA_1; these averages are denoted by A_1E' and A_2E' respectively. When AE and EA lines are not resolved, as in the present case, a weighted average should be taken rather than a simple average, because AE and EA lines have different spin weights.[8] However, when the splitting is much smaller than the line width, a simple average is a good approximation. It may also be noted that IV_E contributes to the splitting of AE and EA lines as the linear term, but these two lines were not resolved in the present case. The corrections for A_1E' and A_2E' are shown in Table 4. Since the V_E term was found to be negligible, it was omitted from the corrections for A_1E' and A_2E'.

It is worth considering further the expressions for AA, the average of A_1A_2 and A_2A_1, and for AE′, the average of A_1E' and A_2E', which are given by $II_A+(1/2)III_A$ and $II_E+(1/2)III_E$ respectively.

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[9] Notations are due to Herschbach; D. R. Herschbach, Tables for the Internal Rotation Problem, Harvard University, 1957.

It can be shown that $II+(1/2)III$ does not involve V_3''. Furthermore, the term linear in F' reduces, for an A level, for example, to:

$$\begin{aligned} & II_{\mathrm{A}} + (1/2)III_{\mathrm{A}} \\ & = \cdots \pm 8F'(4/9F)^2\left(\frac{pp}{\Delta}\right)^{(\mathrm{A})}_{v=0}\left(\frac{pp}{\Delta}\right)^{(\mathrm{A})}_{v=1} \\ & = \cdots \pm (F'/2F^2)(1 - W_{10}{}^{(2)} - W_{00}{}^{(2)}) \qquad (17) \end{aligned}$$

It may thus be shown, by substituting Eq. (17) into Eq. (12b), that $FW_V{}^{(2\pm)}$ is independent of F'.

The contribution of the first-order correction to the splitting of the triplets is given by:

$$(I_{\mathrm{A}} - I_{\mathrm{E}}) + (II_{\mathrm{A}} - II_{\mathrm{E}})$$

for the (+) state, which is the difference in the corrections for $\mathrm{A_1A_2}$ and $\mathrm{A_1E'}$, while it is given by:

$$-(I_{\mathrm{A}} - I_{\mathrm{E}}) + (II_{\mathrm{A}} - II_{\mathrm{E}}) + (III_{\mathrm{A}} - III_{\mathrm{E}})$$

for the (−) state, where it is equal to the difference in the corrections for $\mathrm{A_2A_1}$ and $\mathrm{A_2E'}$. Thus the difference between the splitting in the (+) state and that in the (−) state is proportional to:

$$2(I_{\mathrm{A}} - I_{\mathrm{E}}) - (III_{\mathrm{A}} - III_{\mathrm{E}}) \qquad (18)$$

The expressions of I_{A}, I_{E}, III_{A}, and III_{E} are given in Appendix I, where the V_3'-dependent parts are not listed, since they do not contriubute to (18).

Application to the Analysis of the C_3H_8 Spectra

The linear term (9b) is not large enough to split the AE and EA lines, but its effect appears in the difference in the splittings in the Q-branch and R-branch lines. Since ρ_{a} is much larger than ρ_{b}, Eq. (9b) is simplified to $-2(F-F')\rho_{\mathrm{a}}P_{\mathrm{a}}(V_0|p_-|V_0)$, which is zero for $\mathrm{A_1A_2}$, $\mathrm{A_2A_1}$, $\mathrm{A_1E}$, and $\mathrm{A_2E}$, but is equal to $-2(F-F')\rho_{\mathrm{a}}P_{\mathrm{a}}[(1|p|1)+(0|p|0)]$ for $\mathrm{EA_1}$ and $\mathrm{EA_2}$ and equal to $-(F-F')\rho_{\mathrm{a}}P_{\mathrm{a}}[(1|p|1)+(0|p|0)]$ for EE. Here $(v|p|v)$ is the matrix element appearing in the one-top problem. These small terms have a sizable effect only on the K-type doublets, $J_{1,J-1}$ and $J_{1,J}$. After being treated by second order perturbation, they become:

$$\pm\frac{8(F-F')^2\rho_{\mathrm{a}}{}^2P_{\mathrm{a}}{}^2}{(B-C)J(J+1)}[(1|p|1)+(0|p|0)]^2 \qquad \text{for } \mathrm{EA_1} \text{ and } \mathrm{EA_2}$$

and

$$\pm\frac{2(F-F')^2\rho_{\mathrm{a}}{}^2P_{\mathrm{a}}{}^2}{(B-C)J(J+1)}[(1|p|1)+(0|p|0)]^2 \qquad \text{for EE,}$$

where + holds for $J_{1,J-1}$ and − for $J_{1,J}$. For $\mathrm{A_1E'}$ and $\mathrm{A_2E'}$ they are given by:

$$\pm\frac{4(F-F')^2\rho_{\mathrm{a}}{}^2P_{\mathrm{a}}{}^2}{(B-C)J(J+1)}[(1|p|1)+(0|p|0)]^2$$

which are $\pm(2\times0.07/J(J+1))P_{\mathrm{a}}{}^2$ at $s=83$. Thus, the Q-branches should show larger splittings than the R-branches. The observed splittings are, for example, 3.19 Mc/sec for 1_{11}—0_{00} and 3.28 Mc/sec for 1_{10}—1_{01} of the (+) state, and 3.70 Mc/sec for 1_{11}—0_{00} and 3.90 Mc/sec for 1_{10}—1_{01} of the (−) state (see Table 3). Thus, the difference is 0.09 for the (+) state and 0.20 Mc/sec for the (−) state; these values are in agreement with the $2\times0.07=0.14$ Mc/sec calculated above.

As is shown in Table 3, the averages of the splittings for the (+) and (−) states, corrected for the linear terms, were analyzed in order to obtain ΔA and ΔB, the differences in effective rotational contsants for AE′ and AA, which were determined to be 3.54_6 and 0.124_4 Mc/sec respectively. According to the results of the last section, these constants are independent of F' and V_3''. When the contribution of the V_3' term is neglected, ΔA and ΔB are given by:

$$\Delta A = F\rho_{\mathrm{a}}{}^2(W_{11}{}^{(2)} - W_{10}{}^{(2)} + W_{01}{}^{(2)} - W_{00}{}^{(2)}) \qquad (19\mathrm{a})$$

$$\Delta B = F\rho_{\mathrm{b}}{}^2(W_{11}{}^{(2)} - W_{10}{}^{(2)} + W_{01}{}^{(2)} - W_{00}{}^{(2)}) \qquad (19\mathrm{b})$$

where Eqs. (16) and (5) are used. From the observed values of ΔA and ΔB, the direction cosines of the CH_3 rotation axis were determined to be $\lambda_{\mathrm{a}}=0.839_3$ and $\lambda_{\mathrm{b}}=0.543_6$, and the angle between the top axes was found to be 114°8′±1°20′, which is in close agreement with the CCC angle determined by Lide.[1] Thus the conclusion of Lide ruling out a tilt of more than 2° or 3° is consistent with the present results. By assuming I_α to be 3.130 amuÅ² (obtained from the r_s structure of Lide), the barrier height was calculated to be 1163± 8 cm⁻¹, or 3325±20 cal/mol. The results are summarized in Table 5.

TABLE 5. ANALYSIS OF THE TRIPLET SPLITTINGS

$\Delta A=A(\mathrm{AE'})-A(\mathrm{AA})$	3.54_6 Mc/sec
$\Delta B=B(\mathrm{AE'})-B(\mathrm{AA})$	0.124 Mc/sec
λ_{a}	0.839_3
λ_{b}	0.543_6
Angle between two top axes	114°8′±1°20′
∠CCC[a]	112°24′±16′
s	80.8_2
V_3[b]	1163±8 cm⁻¹ 3325±20 cal/mol
V_3''[c]	−60±10 cm⁻¹ −170±30 cal/mol

a) From Ref. 1.

b) The error due to the inaccuracy of I_α, about ±3% or ±100 cal/mol, is not included. Also the contribution of the V_3' term was not corrected. See the text.

c) Allowance should be made for errors due to incompleteness of the present theory. They probably amount to ±(20−40) cal/mol. See the text.

The difference in splittings for the (+) and (−) states is −0.51 for 1_{11}—0_{00} and −0.62 Mc/sec for 1_{10}—1_{01}. The average, −0.56±0.10 Mc/sec, is taken to be the difference in the effective A rotational constant for the two states. When (18) was evaluated at s=80.82, the following relation was obtained (in Mc/sec):

$$-0.56 = 0.078 + 0.068\ (V_3''/F) \qquad (20)$$

Thus V_3'' was determined to be $-60\pm10\ \mathrm{cm}^{-1}$, or −170±30 cal/mol.

Discussion

The approximation made in the present paper is two-fold. The coupling of the internal rotation with the overall rotation, common to the one-top problem, was treated by the PAM method. Since the barrier height in propane was high, the observed splittings were explained by the second-order terms. The second point, typical of the two-top problem, is the coupling of the two tops, which is determined by the geometry and other physical properties of the molecule. For C_3H_8 the kinetic energy coupling parameter, F', is equal to $-0.1306\ F$; thus, the effect of the F'-dependent terms is appreciable. When such perturbation calculations as Eqs. (7) and (8) are not applicable, the wavefunction must be obtained by solving the secular determinant:

$$|V) = \sum_{V_0'} c(V_0'V)\,|V_0'),\quad \sum_{V_0'} |c(V_0'V)|^2 = 1 \qquad (21)$$

and the matrix elements in the effective rotational Hamiltonian, Eq. (9), must be calculated by using Eq. (21). For example,

$$(V'|p|V) = \sum_{V_0''}\sum_{V_0'} c^*(V_0''V')c(V_0'V)(V_0''|p|V_0')$$

Since the present treatment is valid only to the first-order in the coupling parameters, the potential constants, especially the value of V_3'', should be considered as preliminary. It is very difficult to estimate the uncertainty in the value of V_3'' in this regard, but errors are probably not larger than ±(20—40) cal/mol.

The barrier height, V_3, of 3325 cal/mol is in close agreement with the thermodynamic value (3100—3300 cal/mol)$^{2)}$ and with the value of Scharpen and Laurie (3550 cal/mol)$^{3)}$. It should be noted that this value includes the contribution of the V_3' term. The effect of the V_3' term is similar to that of V_6 in the one-top problem in that its determination makes it necessary to analyze the spectra in other torsional states.$^{10)}$ This is not possible with the propane molecule, since the second-excited states are too high and since, consequently, the spectra is too weak to be observed.

The error of V_3 shown in Table 5 is solely due to the errors in frequency measurements, but it should be remembered that I_α is accurate only to ±3%.

When all top-top couplings are neglected, the torsional frequency of the v=1—0 transition is calculated to be $243.4\ \mathrm{cm}^{-1}$, when V_3 is assumed to be 3325 cal/mol. This transition is split by the kinetic-energy coupling ($\pm16.2\ \mathrm{cm}^{-1}$) and also by the V_3'' terms ($\pm11.1\ \mathrm{cm}^{-1}$), resulting in two lines, at 216.1 and $270.7\ \mathrm{cm}^{-1}$ respectively. The former corresponds to the vibration of the A_2 symmetry (or the transition to the (+) state, in the present notation) and the latter to that of the B_2 symmetry (or the transition to the (−) state). Unfortunately, the effect of the V_3' terms could not be estimated. Gayles and King$^{11)}$ estimated the torsional frequencies from combination bands to be 208 (A_2) and $223.0\ \mathrm{cm}^{-1}$ (B_2).

When the two frequencies calculated above (216.1 and $270.7\ \mathrm{cm}^{-1}$) are used, the Boltzmann factors of the (+) and (−) states are 0.21 and 0.14 at dry-ice temperature. Thus, the (+)-state spectrum must be about 50% stronger than the (−)-state spectrum. Although the intensities of the vibrational satellites were, unfortunately, too weak to be measured quantitatively, it was definitely established that the (+)-state spectrum was stronger than the (−) one. This finding is consistent with the assignment of the (+) and (−) states made in Rotational Spectra.

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Appendix I. Evaluation of the Correction Terms, I_A, I_E, III_A, and III_E

In the following formulas the matrix elements, $(v'|p|v)$, and eigenvalues, E_v, are those in the one-top problem; the numerical calculation was carried out by using tables prepared by Hayashi and Pierce.$^{12)}$ The quantities in I_A and III_A are all of A symmetry, while all those in I_E and III_E are of E symmetry.

$$\begin{aligned}
I_\mathrm{A} = &-2F' \sum_{v=2,4,6,\cdots} |(1|p|v)|^2|(0|p|1)|^2/(E_1 - E_v)^2 \\
&-2F' \sum_{v=3,5,7,\cdots} |(0|p|v)|^2|(0|p|1)|^2/(E_0 - E_v)^2 \\
&+4F' \sum_{\substack{v'=2,4,6,\cdots \\ v''=3,5,7,\cdots}}\sum (0|p|v'')(v''|p|v')(v'|p|1)(1|p|0) \\
&\qquad\qquad /(E_1 - E_{v''})(E_1 - E_{v'}) \\
&+4F' \sum_{\substack{v'=3,5,7,\cdots \\ v''=2,4,6,\cdots}}\sum (1|p|v'')(v''|p|v')(v'|p|0)(0|p|1) \\
&\qquad\qquad /(E_0 - E_{v''})(E_0 - E_{v'})
\end{aligned}$$

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10) E. Hirota, *J. Chem. Phys.*, **45**, 1984 (1966).

11) J. N. Gayles, Jr., and W. T. King, *Spectrochim. Acta*, **21**, 543 (1965).

12) M. Hayashi and L. Pierce, Tables for the Internal Rotation Problem, University of Notre Dame, 1961.

$$+4F' \sum_{\substack{v'=2,4,6,\cdots \\ v'''=3,5,7,\cdots}} \sum (0|p|v''')(v'''|p|v')(v'|p|1)(1|p|0) /(E_1-E_{v'})(E_0-E_{v'''})$$

$$-V_3'' \sum_{v=2,4,6,\cdots} |(1|p|v)|^2 |(0|s|1)|^2/(E_1-E_v)^2$$

$$-V_3'' \sum_{v=3,5,7,\cdots} |(0|p|v)|^2 |(0|s|1)|^2/(E_0-E_v)^2$$

$$-(8V_3''/9s^2) \sum_{\substack{v'=2,4,6,\cdots \\ v''=3,5,7,\cdots}} \sum (0|p|v'')(v''|p|v')(v'|p|1)(1|p|0) \times (E_1-E_0)(E_0-E_{v''}) /(E_1-E_{v''})(E_1-E_{v'})$$

$$-(8V_3''/9s^2) \sum_{\substack{v'=3,5,7,\cdots \\ v''=2,4,6,\cdots}} \sum (1|p|v'')(v''|p|v')(v'|p|0)(0|p|1) \times (E_1-E_{v'})(E_0-E_1) /(E_0-E_{v''})(E_0-E_{v'})$$

$$-(8V_3''/9s^2) \sum_{\substack{v'=2,4,6,\cdots \\ v'''=3,5,7,\cdots}} \sum (0|p|v''')(v'''|p|v')(v'|p|1)(1|p|0) \times (E_{v'''}-E_{v'})(E_1-E_0) /(E_1-E_{v'})(E_0-E_{v'''}) \quad \text{(A. 1)}$$

$$III_{\mathrm{A}} = +16F'|(0|p|1)|^4/(E_0-E_1)^2$$

$$+8F' \sum_{v'=3,5,7,\cdots} |(0|p|1)|^2 |(0|p|v')|^2 /(E_0-E_1)(E_1-E_{v'})$$

$$-8F' \sum_{v'=2,4,6,\cdots} |(0|p|1)|^2 |(1|p|v')|^2 /(E_0-E_1)(E_0-E_{v'})$$

$$+8F' \sum_{v'=3,5,7,\cdots} |(0|p|1)|^2 |(0|p|v')|^2 /(E_0-E_1)(E_0-E_{v'})$$

$$-8F' \sum_{v'=2,4,6,\cdots} |(0|p|1)|^2 |(1|p|v')|^2 /(E_0-E_1)(E_1-E_{v'})$$

$$+(16V_3''/9s^2)(E_0-E_1)|(0|p|1)|^2 \sum_{v'=3,5,7,\cdots} |(0|p|v')|^2/(E_1-E_{v'})$$

$$-(16V_3''/9s^2)(E_0-E_1)|(0|p|1)|^2 \sum_{v'=2,4,6,\cdots} |(1|p|v')|^2/(E_0-E_{v'}) \quad \text{(A. 2)}$$

$$I_{\mathrm{E}} = -2F' \sum_{v=2,3,4,\cdots} |(1|p|v)|^2 |(0|p|1)|^2/(E_1-E_v)^2$$

$$-2F' \sum_{v=2,3,4,\cdots} |(0|p|v)|^2 |(0|p|1)|^2/(E_0-E_v)^2$$

$$+4F' \sum_{\substack{v'=2,3,4,\cdots \\ v''=2,3,4,\cdots}} \sum_{(v' \neq v'')} (0|p|v'')(v''|p|v')(v'|p|1)(1|p|0) /(E_1-E_{v'})(E_1-E_{v''})$$

$$+4F' \sum_{\substack{v'=2,3,4,\cdots \\ v''=2,3,4,\cdots}} \sum_{(v' \neq v'')} (1|p|v'')(v''|p|v')(v'|p|0)(0|p|1) /(E_0-E_{v''})(E_0-E_{v'})$$

$$+4F' \sum_{\substack{v'=2,3,4,\cdots \\ v'''=2,3,4,\cdots}} \sum (0|p|v''')(v'''|p|v')(v'|p|1)(1|p|0) /(E_1-E_{v'})(E_0-E_{v'''})$$

$$-V_3'' \sum_{v=2,3,4,\cdots} |(1|p|v)|^2 |(1|s|0)|^2/(E_1-E_v)^2$$

$$-V_3'' \sum_{v=2,3,4,\cdots} |(0|p|v)|^2 |(1|s|0)|^2/(E_0-E_v)^2$$

$$-(8V_3''/9s^2) \sum_{\substack{v'=2,3,4,\cdots \\ v''=2,3,4,\cdots}} \sum_{(v' \neq v'')} (0|p|v'')(v''|p|v')(v'|p|1)(1|p|0) \times (E_1-E_0)(E_0-E_{v''}) /(E_1-E_{v''})(E_1-E_{v'})$$

$$-(8V_3''/9s^2) \sum_{\substack{v'=2,3,4,\cdots \\ v''=2,3,4,\cdots}} \sum_{(v' \neq v'')} (1|p|v'')(v''|p|v')(v'|p|0)(0|p|1) \times (E_1-E_{v''})(E_0-E_1) /(E_0-E_{v''})(E_0-E_{v'})$$

$$-(8V_3''/9s^2) \sum_{\substack{v'=2,3,4,\cdots \\ v'''=2,3,4,\cdots}} \sum (0|p|v''')(v'''|p|v')(v'|p|1)(1|p|0) \times (E_{v'''}-E_{v'})(E_1-E_0) /(E_1-E_{v'})(E_0-E_{v'''}) \quad \text{(A. 3)}$$

$$III_{\mathrm{E}} = +16F'|(0|p|1)|^4/(E_0-E_1)^2$$

$$+8F' \sum_{v''=2,3,4,\cdots} |(0|p|v'')|^2 |(0|p|1)^2 /(E_1-E_{v''})(E_0-E_1)$$

$$-8F' \sum_{v''=2,3,4,\cdots} |(1|p|v'')|^2 |(0|p|1)|^2 /(E_0-E_{v''})(E_0-E_1)$$

$$+8F' \sum_{v'=2,3,4,\cdots} |(0|p|v')|^2 |(0|p|1)|^2 /(E_0-E_1)(E_0-E_{v'})$$

$$-8F' \sum_{v'=2,3,4,\cdots} |(1|p|v')|^2 |(0|p|1)|^2 /(E_0-E_1)(E_1-E_{v'})$$

$$+(16V_3''/9s^2)(E_0-E_1)|(0|p|1)|^2 \sum_{v'=2,3,4,\cdots} |(0|p|v')|^2/(E_1-E_{v'})$$

$$-(16V_3''/9s^2)(E_0-E_1)|(0|p|1)|^2 \sum_{v'=2,3,4,\cdots} |(1|p|v')|^2/(E_0-E_{v'}) \quad \text{(A. 4)}$$

where $(v|s|v')$ means $(v|\sin 3\alpha|v')$.