Infrared Absorption Intensities of Torsion-Rotation Transitions of Molecules with Symmetric Internal Rotor

Hiromu Sugeta and Tatsuo Miyazawa
Institute for Protein Research, Osaka University, Yamada-kami, Suita, Osaka 565

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The infrared absorption intensities of torsion-rotation transitions were theoretically derived on the basis of torsion-rotation interactions of molecules with symmetric internal rotor. The theoretical intensities depend upon molecular structure parameters and molecular dipole moment. Implications of the present theory are discussed on absolute intensities, orientations of dipole transition moment, band types (A, B, or C), and deuteration effects on absorption intensities of methyl torsional transitions. For propylene oxide and propylene sulfide, the far infrared spectra of the gaseous state were measured, and the experimental absorption intensities of methyl torsional vibrations were compared with theoretical intensities.

A number of investigations on internal-rotation barriers of symmetric internal rotors ($-CH_3$, $-SiH_3$, $-CF_3$ *etc.*) have been carried out by the microwave spectroscopy[1] and far-infrared spectroscopy.[2] Far infrared bands due to torsional vibrations often exhibit complicated contours due to torsion-rotation interactions.[2] For detailed analyses of torsional bands, it is necessary to elucidate the effects of torsion-rotation interactions not only on energy levels but also on absorption intensities of torsion-rotation transitions. The effects of these interactions on energy levels have been extensively studied for analysing microwave spectra of molecules with symmetric internal rotors.[3] In the present study, the infrared absorption intensities of torsion-rotation transitions have been worked out, taking account of torsion-rotation interactions.

Torsion-Rotation Wave Functions

The model used in the present study consists of a rigid frame and a symmetric internal rotor that performs torsional motion with respect to the frame. With the principal-axis-method, the Hamiltonian (H) for this model is given by[3]

$$H = H_r + H_t + H_{tr} \tag{1}$$

where H_r and H_t are the rotational and torsional Hamiltonian, respectively, and H_{tr} is the Hamiltonian for the torsion-rotation interactions. These Hamiltonians may be written as,

$$H_r = AP_a{}^2 + BP_b{}^2 + CP_c{}^2 + F\mathscr{P}^2 \tag{2}$$

$$H_t = Fp_\alpha{}^2 + V(\alpha) \tag{3}$$

$$H_{tr} = -F(p_\alpha\mathscr{P} + \mathscr{P}p_\alpha) = -2Fp_\alpha\mathscr{P} \tag{4}$$

and

$$A = \hbar^2/2I_a \text{ etc} \tag{5}$$

$$F = \hbar^2/2rI_\alpha \tag{6}$$

$$r = 1 - \sum\lambda_g{}^2I_\alpha/I_g \quad (g=\text{a, b, or c}) \tag{7}$$

where I_g is the principal moment of inertia of the entire molecule, I_α is the moment of inertia of the internal rotor about its symmetry axis, λ_g is the direction cosine between the principal axis (g) and the internal-rotation axis. P_g is the component of the total angular momentum (in unit of $\hbar$) along the principal axis g,

$$\tilde{P} = [P_a\ P_b\ P_c] \tag{8}$$

p_α is the angular momentum of the internal rotor along its symmetry axis and $V(\alpha)$ is the potential energy for the internal-rotation. The angular momentum $\mathscr{P}$ in Eqs. (2) and (4) is given as

$$\mathscr{P} = \sum_g(\lambda_gI_\alpha/I_g)P_g = \boldsymbol{\rho}\cdot\boldsymbol{P} \tag{9}$$

where

$$\tilde{\rho} = [\lambda_aI_\alpha/I_a\ \ \lambda_bI_\alpha/I_b\ \ \lambda_cI_\alpha/I_c] \tag{10}$$

In the present study, the torsion-rotation interaction H_{tr} [Eq. (4)] is treated as the perturbation term. The eigenvalues and wave functions of the rotational Hamiltonian H_r [Eq. (2)] are denoted as E_r and $|r\rangle$, respectively. The eigenvalues and wave functions of the torsional Hamiltonian H_t [Eq. (3)] are denoted as $E_{v\sigma}$ and $|v\sigma\rangle$, respectively, where v is the torsional quantum number and σ is the symmetry index ($\sigma=0$ for A and $\sigma=\pm1$ for E species). The unperturbed wave function is constructed as the product of the torsional and rotational parts, $|v\sigma\rangle|r\rangle$ and the matrix elements of the perturbation H_{tr} is given by

$$\begin{aligned}\langle r_2|\langle v_2\sigma_2|H_{tr}|v_1\sigma_1\rangle|r_1\rangle &= -2F\langle r_2|\langle v_2\sigma_2|p_\alpha\mathscr{P}|v_1\sigma_1\rangle|r_1\rangle \\ &= -2F\delta_{\sigma_1\sigma_2}\langle v_2\sigma_2|p_\alpha|v_1\sigma_1\rangle\langle r_2|\mathscr{P}|r_1\rangle\end{aligned} \tag{11}$$

Accordingly, with the first-order perturbation theory, the perturbed wave functions $|v\sigma,r\rangle$ are given by

$$|v\sigma, r\rangle = |v\sigma\rangle|r\rangle - 2F\sum_{v'}{}'\sum_{r'}\frac{\langle v'\sigma|p_\alpha|v\sigma\rangle\langle r'|\mathscr{P}|r\rangle}{(E_{v\sigma}+E_r)-(E_{v'\sigma}+E_{r'})}|v'\sigma\rangle|r'\rangle \tag{12}$$

Neglecting the rotational energy differences ($E_r-E_{r'}$) as compared with the torsional energy differences ($E_{v\sigma}-E_{v'\sigma}$), Eq. (12) may be rewritten as

$$|v\sigma, r\rangle = |v\sigma\rangle|r\rangle - 2F\left[\sum_{v'}{}'\frac{\langle v'\sigma|p_\alpha|v\sigma\rangle}{E_{v\sigma}-E_{v'\sigma}}|v'\sigma\rangle\right]\left[\sum_{r'}\langle r'|\mathscr{P}|r\rangle|r'\rangle\right] \tag{13}$$

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[1] W. Gordy and R. L. Cook, "Microwave Molecular Spectra", Interscience Publishers, New York, N. Y. (1970), Chap. 12, p. 423; J. E. Wollrab, "Rotational Spectra and Molecular Structure", Academic Press, New York, N. Y. (1967), Chap. 6, p. 145.

[2] K. D. Möller and W. G. Rothschild, "Far-Infrared Spectroscopy", Wiley-Interscience, New York, N. Y. (1971), Chap. 8, p. 256; A. Finch, P. N. Gates, K. Radcliffe, F. N. Dickson, and F. F. Bentley, "Chemical Applications of Far Infrared Spectroscopy", Academic Press, New York, N. Y. (1970), Chap. 4, p. 78.

[3] C. C. Lin and J. D. Swalen, *Rev. Mod. Phys.*, **31**, 841 (1959); D. R. Herschbach, *J. Chem. Phys.*, **31**, 91 (1959).

Line Strength of Torsion-Rotation Transition

The absorption intensity (I) for the transition between states A and B is given by[4)]

$$I = \frac{n}{z}\frac{8\pi^3\nu_{\mathrm{AB}}}{3hc}[\exp(-E_{\mathrm{A}}/kT)-\exp(-E_{\mathrm{B}}/kT)]S_{\mathrm{AB}} \tag{14}$$

where n is the number of molecules per unit volume, z is the partition function, E_{A} and E_{B} are the energy of the states A and B, respectively. ν_{AB} is the transition frequency

$$\nu_{\mathrm{AB}} = (E_{\mathrm{B}}-E_{\mathrm{A}})/h \tag{15}$$

and S_{AB} is the line strength given by

$$S_{\mathrm{AB}} = \sum_{\mathrm{a}}\sum_{\mathrm{b}}|\langle b|\bar{\boldsymbol{\mu}}|a\rangle|^2 = 3\sum_{\mathrm{a}}\sum_{\mathrm{b}}|\langle b|\bar{\mu}_{\mathrm{F}}|a\rangle|^2 \tag{16}$$

where a and b denote individual degenerate substates of A and B, respectively, $\bar{\boldsymbol{\mu}}$ is the electric dipole moment operator in the space-fixed coordinate system, and $\bar{\mu}_{\mathrm{F}}$ is the F component. The component $\bar{\mu}_{\mathrm{F}}$ is related to the molecule-fixed dipole moment operator μ_{g} by the direction cosine $\boldsymbol{\Phi}_{\mathrm{Fg}}$ between the space-fixed F axis and molecule-fixed g axis,

$$\bar{\mu}_{\mathrm{F}} = \boldsymbol{\Phi}_{\mathrm{F}}\cdot\boldsymbol{\mu} = \sum_{\mathrm{g}}\Phi_{\mathrm{Fg}}\mu_{\mathrm{g}} \tag{17}$$

$$\tilde{\boldsymbol{\Phi}}_{\mathrm{F}} = [\Phi_{\mathrm{Fa}}\ \Phi_{\mathrm{Fb}}\ \Phi_{\mathrm{Fc}}] \tag{18}$$

$$\tilde{\boldsymbol{\mu}} = [\mu_{\mathrm{a}}\ \mu_{\mathrm{b}}\ \mu_{\mathrm{c}}] \tag{19}$$

In general, the molecule-fixed dipole moment μ_{g} depends only upon vibrational coordinates whereas the direction cosines $\boldsymbol{\Phi}_{\mathrm{Fg}}$ depend only upon rotational coordinates. For a molecule with a rigid frame and a symmetric internal rotor, then, the transition moment for the unperturbed wave functions $|v\sigma\rangle|r\rangle$ may be written as

$$\begin{aligned}&\langle r_2|\langle v_2\sigma_2|\bar{\mu}_{\mathrm{F}}|v_1\sigma_1\rangle|r_1\rangle\\ &\quad= \langle v_2\sigma_2|\boldsymbol{\mu}|v_1\sigma_1\rangle\cdot\langle r_2|\boldsymbol{\Phi}_{\mathrm{F}}|r_1\rangle\\ &\quad= \sum_{\mathrm{g}}\langle v_2\sigma_2|\mu_{\mathrm{g}}|v_1\sigma_1\rangle\langle r_2|\Phi_{\mathrm{Fg}}|r_1\rangle\end{aligned} \tag{20}$$

Furthermore, with the present model, the molecule-fixed dipole moment $\boldsymbol{\mu}$ in Eq. (20) is independent of the internal rotation and is equal to the permanent dipole moment $\boldsymbol{\mu}^{\circ}$.

$$\tilde{\boldsymbol{\mu}} = \tilde{\boldsymbol{\mu}}^{\circ} = [\mu_{\mathrm{a}}^{\circ}\ \mu_{\mathrm{b}}^{\circ}\ \mu_{\mathrm{c}}^{\circ}] \tag{21}$$

Accordingly, for unperturbed wave functions,

$$\langle v_2\sigma_2|\mu_{\mathrm{g}}|v_1\sigma_1\rangle = \mu_{\mathrm{g}}^{\circ}\langle v_2\sigma_2|v_1\sigma_1\rangle = \mu_{\mathrm{g}}^{\circ}\delta_{v_1v_2}\delta_{\sigma_1\sigma_2} \tag{22}$$

and Eq. (20) may be rewritten as,

$$\begin{aligned}&\langle r_2|\langle v_2\sigma_2|\bar{\mu}_{\mathrm{F}}|v_1\sigma_1\rangle|r_1\rangle\\ &\quad= \langle r_2|\langle v_2\sigma_2|\boldsymbol{\mu}^{\circ}\cdot\boldsymbol{\Phi}_{\mathrm{F}}|v_1\sigma_1\rangle|r_1\rangle\\ &\quad= \delta_{v_1v_2}\delta_{\sigma_1\sigma_2}\boldsymbol{\mu}^{\circ}\cdot\langle r_2|\boldsymbol{\Phi}_{\mathrm{F}}|r_1\rangle\\ &\quad= \delta_{v_1v_2}\delta_{\sigma_1\sigma_2}\langle r_2|\bar{\mu}_{\mathrm{F}}|r_1\rangle\end{aligned} \tag{23}$$

The matrix element of the transition moment for $|v_2\sigma_2,r_2\rangle \leftarrow |v_1\sigma_1,r_1\rangle$ is now derived from the perturbed wave function $|v\sigma,r\rangle$ [Eq. (13)] and the transition moment for unperturbed wave functions $|v\sigma\rangle|r\rangle$ [Eq. 23)].

$$\begin{aligned}&\langle v_2\sigma_2, r_2|\bar{\mu}_{\mathrm{F}}|v_1\sigma_1, r_1\rangle = \langle r_2|\langle v_2\sigma_2|\bar{\mu}_{\mathrm{F}}|v_1\sigma_1\rangle|r_1\rangle\\ &\quad -2F\sum_v{}'\sum_r\frac{\langle v_2\sigma_2|p_\alpha|v\sigma_2\rangle}{E_{v_2\sigma_2}-E_{v\sigma_2}}\langle r_2|\mathscr{P}|r\rangle\langle r|\langle v\sigma_2|\bar{\mu}_{\mathrm{F}}|v_1\sigma_1\rangle|r_1\rangle\\ &\quad -2F\sum_v{}'\sum_r\langle r_2|\langle v_2\sigma_2|\bar{\mu}_{\mathrm{F}}|v\sigma_1\rangle|r\rangle\langle r|\mathscr{P}|r_1\rangle\frac{\langle v\sigma_1|p_\alpha|v_1\sigma_1\rangle}{E_{v_1\sigma_1}-E_{v\sigma_1}}\\ &= \delta_{v_1v_2}\delta_{\sigma_1\sigma_2}\langle r_2|\bar{\mu}_{\mathrm{F}}|r_1\rangle\\ &\quad -2F\sum_v{}'\sum_r\frac{\langle v_2\sigma_2|p_\alpha|v\sigma_2\rangle}{E_{v_2\sigma_2}-E_{v\sigma_2}}\langle r_2|\mathscr{P}|r\rangle\delta_{vv_1}\delta_{\sigma_2\sigma_1}\langle r|\bar{\mu}_{\mathrm{F}}|r_1\rangle\\ &\quad -2F\sum_v{}'\sum_r\delta_{v_2v}\delta_{\sigma_2\sigma_1}\langle r_2|\bar{\mu}_{\mathrm{F}}|r\rangle\langle r|\mathscr{P}|r_1\rangle\frac{\langle v\sigma_1|p_\alpha|v_1\sigma_1\rangle}{E_{v_1\sigma_1}-E_{v\sigma_1}}\end{aligned} \tag{24}$$

Here only for $\sigma_1=\sigma_2(=\sigma)$, the transition moments are nonvanishing. Furthermore, for torsion-rotation transitions ($v_1\neq v_2$), Eq. (24) may be rewritten as,

$$\begin{aligned}&\langle v_2\sigma, r_2|\bar{\mu}_{\mathrm{F}}|v_1\sigma, r_1\rangle\\ &\quad= -2F\sum_r\left[\frac{\langle v_2\sigma|p_\alpha|v_1\sigma\rangle}{E_{v_2\sigma}-E_{v_1\sigma}}\langle r_2|\mathscr{P}|r\rangle\langle r|\bar{\mu}_{\mathrm{F}}|r_1\rangle\right.\\ &\qquad\left.+\langle r_2|\bar{\mu}_{\mathrm{F}}|r\rangle\langle r|\mathscr{P}|r_1\rangle\frac{\langle v_2\sigma|p_\alpha|v_1\sigma\rangle}{E_{v_1\sigma}-E_{v_2\sigma}}\right]\\ &\quad= 2F\frac{\langle v_2\sigma|p_\alpha|v_1\sigma\rangle}{E_{v_2\sigma}-E_{v_1\sigma}}\langle r_2|\bar{\mu}_{\mathrm{F}}\mathscr{P}-\mathscr{P}\bar{\mu}_{\mathrm{F}}|r_1\rangle\\ &\quad= 2F\frac{\langle v_2\sigma|p_\alpha|v_1\sigma\rangle}{E_{v_2\sigma}-E_{v_1\sigma}}\langle r_2|[\bar{\mu}_{\mathrm{F}}, \mathscr{P}]|r_1\rangle\end{aligned} \tag{25}$$

The commutation $[\bar{\mu}_{\mathrm{F}},\mathscr{P}]$ in Eq. (25) may be derived from the commutation relations between the angular momentum P_{g} (g=x, y, or z) and the direction cosines $\boldsymbol{\Phi}_{\mathrm{Fg}}$,[5)]

$$[\Phi_{\mathrm{Fx}}, P_{\mathrm{x}}] = \Phi_{\mathrm{Fx}}P_{\mathrm{x}} - P_{\mathrm{x}}\Phi_{\mathrm{Fx}} = 0 \tag{26}$$

$$[\Phi_{\mathrm{Fx}}, P_{\mathrm{y}}] = [P_{\mathrm{x}}, \Phi_{\mathrm{Fy}}] = -i\Phi_{\mathrm{Fz}}\ etc. \tag{27}$$

From Eqs. (9), (17), and (21),

$$\begin{aligned}[\bar{\mu}_{\mathrm{F}}, \mathscr{P}] &= [(\boldsymbol{\mu}^{\circ}\cdot\boldsymbol{\Phi}_{\mathrm{F}}), (\boldsymbol{\rho}\cdot\boldsymbol{P})]\\ &= [(\mu_{\mathrm{x}}^{\circ}\Phi_{\mathrm{Fx}}+\mu_{\mathrm{y}}^{\circ}\Phi_{\mathrm{Fy}}+\mu_{\mathrm{z}}^{\circ}\Phi_{\mathrm{Fz}}), (\rho_{\mathrm{x}}P_{\mathrm{x}}+\rho_{\mathrm{y}}P_{\mathrm{y}}+\rho_{\mathrm{z}}P_{\mathrm{z}})]\\ &= -\mathrm{i}\{(\mu_{\mathrm{y}}^{\circ}\rho_{\mathrm{z}}-\mu_{\mathrm{z}}^{\circ}\rho_{\mathrm{y}})\Phi_{\mathrm{Fx}}+(\mu_{\mathrm{z}}^{\circ}\rho_{\mathrm{x}}-\mu_{\mathrm{x}}^{\circ}\rho_{\mathrm{z}})\Phi_{\mathrm{Fy}}\\ &\qquad+(\mu_{\mathrm{x}}^{\circ}\rho_{\mathrm{y}}-\mu_{\mathrm{y}}^{\circ}\rho_{\mathrm{x}})\Phi_{\mathrm{Fz}}\}\\ &= -\mathrm{i}(\boldsymbol{\mu}^{\circ}\times\boldsymbol{\rho})\cdot\boldsymbol{\Phi}_{\mathrm{F}}\end{aligned} \tag{28}$$

Substituting Eq. (28) into Eq. (25), the transition moment is finally expressed as the product of the vibrational part and rotational part.

$$\begin{aligned}&\langle v_2\sigma, r_2|\bar{\mu}_{\mathrm{F}}|v_1\sigma, r_1\rangle\\ &\quad= \underset{\text{[vibration]}}{\left\{-2\mathrm{i}F\frac{\langle v_2\sigma|p_\alpha|v_1\sigma\rangle}{E_{v_2\sigma}-E_{v_1\sigma}}(\boldsymbol{\mu}^{\circ}\times\boldsymbol{\rho})\right\}}\cdot\underset{\text{[rotation]}}{\{\langle r_2|\boldsymbol{\Phi}_{\mathrm{F}}|r_1\rangle\}}\end{aligned} \tag{29}$$

Absorption Intensity of Torsional Band

The vibrational part of the transition moment may be used for deriving the integrated absorption intensity of the torsional band. Thus, the molar absorption intensity of the torsional transitions $|v+1,\sigma\rangle \leftarrow |v,\sigma\rangle$ is given by

$$\begin{aligned}I_{v,\sigma;\,v+1,\sigma} &= \frac{N}{z}\frac{8\pi^3}{3h^2c}[\exp(-E_{v,\sigma}/kT)-\exp(-E_{v+1,\sigma}/kT)]\\ &\qquad\times 4F^2|\boldsymbol{\mu}^{\circ}\times\boldsymbol{\rho}|^2\frac{|\langle v_2\sigma|p_\alpha|v_1\sigma\rangle|^2}{E_{v+1,\sigma}-E_{v,\sigma}}\end{aligned} \tag{30}$$

[4)] B. L. Crawford, Jr. and H. L. Dinsmore, *J. Chem. Phys.*, **18**, 983 (1950).

[5)] P. C. Cross, R. M. Hainer, and G. W. King, *ibid.*, **12**, 210 (1944).

where N is the Avogadro number. The integrated absorption intensity of the torsional fundamental band is given by

$$\int_{\mathrm{band}} \alpha(\nu)\mathrm{d}\nu = \sum_{v,\sigma} I_{v+1,\sigma;\, v,\sigma} \tag{31}$$

where $\alpha(\nu)$ is the molar absorption coefficient for the absorption frequency ν.

For a high barrier case (see Appendix I), the energy levels $E_{v\sigma}$ and the integrals $<v+1,\sigma|p_\alpha|v,\sigma>$ are almost independent of the symmetry index σ, and from Eqs. (A3), (A7), and (A8),

$$|\langle v+1|p_\alpha|v\rangle|^2 = (N/2)^2[(v+1)s^{1/2}/2][1-(v+1)/2s^{1/2}] \tag{32}$$

$$E_{v+1}-E_v = (N/2)^2F[2s^{1/2}][1-(v+1)/2s^{1/2}] \tag{33}$$

so that

$$\frac{|\langle v+1|p_\alpha|v\rangle|^2}{E_{v+1}-E_v} = (v+1)/4F \tag{34}$$

Substituting Eq. (34) into Eq. (30),

$$I_{v,v+1} = \frac{N}{z}\,\frac{8\pi^3}{3h^2c}[\exp(-E_v/kT)-\exp(-E_{v+1}/kT)] \times |\boldsymbol{\mu}^\circ \times \boldsymbol{\rho}|^2 F(v+1) \tag{35}$$

Finally, with the harmonic oscillator approximation for energy levels, the integrated absorption intensity of the torsional band is obtained by substituting Eq. (35) into Eq. (31),

$$\int_{\mathrm{band}} \alpha(\nu)\mathrm{d}\nu \cong (8\pi^3N/3h^2c)F|\boldsymbol{\mu}^\circ \times \boldsymbol{\rho}|^2 \tag{36}$$

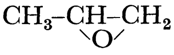
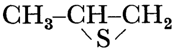
Discussion

Absolute Absorption Intensity. By the use of Eq. (30) [or (35)] and (31) [or (36)], the integrated intensity of the torsional band may be calculated from molecular structure parameters and molecular dipole moment. The theoretical intensity value is also useful for estimating the path length and sample pressure required for absorption measurements.

The absorption intensity is proportional to $F|\boldsymbol{\mu}^\circ \times \boldsymbol{\rho}|^2$ as shown in Eq. (30). Accordingly, the fundamental transition is forbidden for molecules in which the dipole moment $\boldsymbol{\mu}^\circ$ and the $\boldsymbol{\rho}$ vector are parallel to each other, for examples for CH_3–CX_3, CH_3–NO_2 *etc.* On the other hand, if the dipole moment $\boldsymbol{\mu}^\circ$ is nearly perpendicular to the $\boldsymbol{\rho}$ vector, the absorption intensity is strong. For a simple example, if the dipole moment is parallel to the a axis ($\mu^\circ=\mu^\circ{}_\mathrm{a}$, $\mu^\circ{}_\mathrm{b}=\mu^\circ{}_\mathrm{c}=0$) and the symmetry axis of the internal rotor is parallel to the b axis ($\lambda_\mathrm{a}=\lambda_\mathrm{c}=0$, $\rho_\mathrm{a}=\rho_\mathrm{c}=0$, $\lambda_\mathrm{b}=1$, $\rho_\mathrm{b}=I_\alpha/I_\mathrm{b}$), the absolute intensity of the torsional band is given by

$$\int_{\mathrm{band}} \alpha(\nu)\mathrm{d}\nu = \frac{8\pi^3N}{3h^2c}\,\frac{h^2I_\mathrm{b}}{8\pi^2I_\alpha(I_\mathrm{b}-I_\alpha)}\left(\mu^\circ\frac{I_\alpha}{I_\mathrm{b}}\right)^2 = (N\pi/3c)(\mu^\circ)^2I_\alpha/I_\mathrm{b}(I_\mathrm{b}-I_\alpha) \tag{37}$$

Thus, for this simple case, the absorption intensity is nearly proportional to the inversed square of the moment of inertia (I_b) of the entire molecule. In general, the absorption intensity of torsional vibrations is expected to be weaker for a molecule with a larger (heavier) frame than for a molecule with a smaller (lighter) frame.

As an experimental proof of the present intensity theory, the far infrared bands due to methyl torsional vibrations were studied. The far infrared spectra of propylene oxide  CH_3–CH–CH_2 ($\backslash O /$) and propylene sulfide  CH_3–CH–CH_2 ($\backslash S /$) have been reported previously by Fateley and Miller.[6] In the present study, however, the absorption intensities of the torsional bands of these molecules were remeasured with a Hitachi FIS-3 Far Infrared Spectrophotometer. It is experimentally difficult to determine the absolute values of the absorption intensities in the far infrared region. Therefore, the absorption intensities of these two molecules were measured with the same spectral conditions and were found to be 0.9_7 and $0.2_0\ \mathrm{cm^{-2}\cdot atm^{-1}}$ for propylene oxide and sulfide, respectively, at 300 K. On the other hand, the theoretical intensity was treated with Eqs. (30) and (31) and the intensity values were calculated as 1.76 and $0.45\ \mathrm{cm^{-2}\cdot atm^{-1}}$ for propylene oxide and sulfide, respectively, at 300 K, from the structure parameters and dipole moments as determined by the analyses of microwave spectra.[7,8] The experimental ratio of the absorption intensities of propylene oxide and sulfide is $4._9$: 1, in good agreement with the theoretical intensity ratio of 3.9: 1.

The theoretical intensity of propylene oxide and sulfide was also treated with the harmonic oscillator approximation [Eq. (36)]. Although the barriers were not extremely high ($s=\sim 69$ for oxide and ~ 89 for sulfide), the calculated intensity values of 2.03 and 0.47 agreed fairly well (especially for sulfide) with the intensity values calculated with Eqs. (30) and (31).

Orientation of Transition Moment. The band envelopes of absorption bands depend upon the direction of the transition dipole moment. The direction of the transition moment for the torsional vibration of the present model is given by the vector product of $\boldsymbol{\mu}^\circ \times \boldsymbol{\rho}$. This vector product is useful for predicting the type of the torsional bands of asymmetric-top molecules, since otherwise the direction of the transition dipole moment may not be determined from the molecular symmetry.

The molecules of propylene oxide and sulfide belong to the point group C_1 and the direction of the transition moment can not be determined from their molecular symmetry. However, from the present theory, the intensity ratio of the A, B, and C type transitions is calculated as 3: 18: 100 for propylene oxide and as 1: 16: 100 for propylene sulfide and accordingly both molecules are expected to exhibit prominent C-type band envelopes with sharp Q branches. In fact, as shown in Fig. 1, the far infrared spectra of propylene oxide and propylene sulfide exhibit Q-branch series primarily due to the C-type transitions.

Deuteration Effect of Methyl Group. The deuteration of a methyl group reduces the F value to about one half but approximately doubles the $\boldsymbol{\rho}$ vector.

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[6] W. G. Fateley and F. A. Miller, *Spectrochim. Acta*, **19**, 611 (1963).

[7] J. D. Swalen and D. R. Herschbach, *J. Chem. Phys.*, **27**, 100 (1957).

[8] S. S. Butcher, *ibid.*, **38**, 2310 (1963).

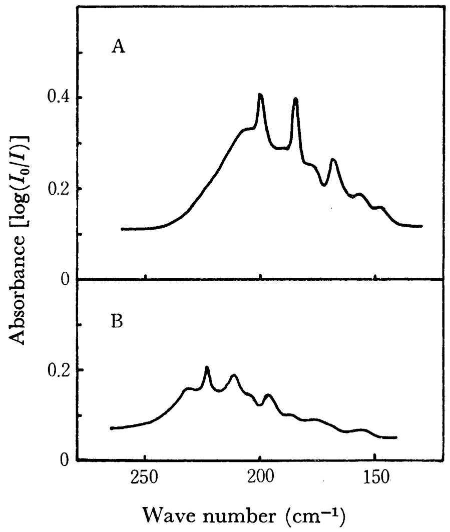

Fig. 1. Far infrared spectra of propylene oxide (path length of 4.9 m and sample pressure of 50 Torr) [A] and propylene sulfide (path length of 4.9 m and sample pressure of 96 Torr) [B].

Accordingly, the value of $F|\boldsymbol{\mu}^\circ \times \boldsymbol{\rho}|^2$ is increased nearly twice by the deuteration of the methyl group. For the simple example of Eq. (37), the absolute intensity of the torsional band is nearly proportional to I_α, the moment of inertia of the internal rotor, so that the intensity is nearly doubled on the deuteration of the methyl group. It is interesting to remark that the absorption intensities of the torsional vibration of the methyl group is expected to increase whereas the absorption intensities of the C–H stretching vibrations are decreased on deuteration of the methyl group. In fact, for ethyl fluoride, the absorption intensity of the torsional vibration of the methyl group was found to increase on deuteration of the methyl group.[9]

Appendix I High Barrier Approximation

The Hamiltonian and the wave equation for the internal rotation with the N-fold symmetry may be written as

$$H = Fp_\alpha^2 + V_N(1-\cos N\alpha)/2 \quad [p_\alpha = -i(\mathrm{d}/\mathrm{d}\alpha)] \qquad \text{(A1)}$$

$$H\Psi_{v\sigma}(\alpha) = E_{v\sigma}\Psi_{v\sigma}(\alpha) \qquad \text{(A2)}$$

where $E_{v\sigma}$ and $\Psi_{v\sigma}(\alpha)$ are the energy and wave function of the $v\sigma$ state (v: torsional quantum number, σ: symmetry index). Equations (A1) and (A2) may be transformed into a reduced form by the following transformations,

$$H = (N/2)^2F\eta$$

$$p_\alpha = (N/2)p_x \quad [p_x = -i(\mathrm{d}/\mathrm{d}x)]$$

$$V_N = (N/2)^2Fs$$

$$N\alpha = 2x$$

$$\Psi_{v\sigma}(\alpha) = \Phi_{v\sigma}(x)$$

$$E_{v\sigma} = (N/2)^2Fb_{v\sigma} \qquad \text{(A3)}$$

$$\eta = p_x^2 + s(1-\cos 2x)/2 \qquad \text{(A4)}$$

$$\eta\Phi_{v\sigma}(x) = b_{v\sigma}\Phi_{v\sigma}(x) \qquad \text{(A5)}$$

For a high barrier case ($s \gg 1$), Eq. (A4) may be expanded in the power series of x.

$$\eta = p_x^2 + sx^2 - (1/3)sx^4 + (2/45)sx^6 - \cdots \qquad \text{(A6)}$$

Equation (A6) may be treated as a perturbed harmonic oscillator Hamiltonian. The eigenvalues b_v for $b_v \ll s$ are derived by the second-order perturbation theory.

$$b_v = s^{1/2}(2v+1) - (1/2^3)[(2v+1)^2+1]$$
$$- (1/2^6)s^{-1/2}(2v+1)[(2v+1)^2+3] \qquad \text{(A7)}$$

The matrix elements of p_x, p_x^2, x, and x^2 are given, through first-order, as follows.

$$\langle v+1|p_x|v\rangle = is^{1/4}[(v+1)/2]^{1/2}[1-(1/4)s^{-1/2}(v+1)]$$
$$\langle v+3|p_x|v\rangle = -i(1/8)s^{-1/4}[(v+1)(v+2)(v+3)/2]^{1/2}$$
$$\langle v|p_x|v'\rangle = -\langle v'|p_x|v\rangle \qquad \text{(A8)}$$

$$\langle v|p_x^2|v\rangle = (1/2)s^{1/2}(2v+1)-(1/8)[(2v+1)^2+1]$$
$$\langle v+2|p_x^2|v\rangle = -(1/2)s^{1/2}[(v+1)(v+2)]^{1/2}$$
$$\times[1-(1/8)s^{-1/2}(2v+3)]$$
$$\langle v+4|p_x^2|v\rangle = (1/8)[(v+1)(v+2)(v+3)(v+4)]^{1/2}$$
$$\langle v|p_x^2|v'\rangle = \langle v'|p_x^2|v\rangle \qquad \text{(A9)}$$

$$\langle v+1|x|v\rangle = s^{-1/4}[(v+1)/2]^{1/2}[1+(1/4)s^{-1/2}(v+1)]$$
$$\langle v+3|x|v\rangle = -(1/24)s^{-3/4}[(v+1)(v+2)(v+3)/2]^{1/2}$$
$$\langle v|x|v'\rangle = \langle v'|x|v\rangle \qquad \text{(A10)}$$

$$\langle v|x^2|v\rangle = (1/2)s^{-1/2}(2v+1)+(1/8s)[(2v+1)^2+1]$$
$$\langle v+2|x^2|v\rangle = (1/2)s^{-1/2}[(v+1)(v+2)]^{1/2}$$
$$\times[1+(5/24)s^{-1/2}(2v+3)]$$
$$\langle v+4|x^2|v\rangle = -(1/24s)[(v+1)(v+2)(v+3)(v+4)]^{1/2}$$
$$\langle v|x^2|v'\rangle = \langle v'|x^2|v\rangle \qquad \text{(A11)}$$

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[9] H. Sugeta, Y. Adachi, and T. Miyazawa, The 28th Annual Meeting of the Chemical Society of Japan (1973), 2P05, p. 335.