

Calculated Raman Band Envelope of Formaldehyde

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Abstract The Raman band envelope of formaldehyde as an asymmetric rotor was calculated. The values of polarizability derivatives, which are required to calculate the Raman band envelope, were estimated by the aid of Wolkenstein's bond polarizability theory. The result of ν_2 and ν_3 bands is given.

Introduction

Many investigations of pure rotation or vib-rotation Raman spectra have been made on symmetric top molecules but little on asymmetric top molecules¹⁾. However, more information on the polarizability is contained in those of asymmetric top molecules. For the purpose of obtaining polarizability data, Raman spectra of gaseous formaldehyde which belongs to asymmetric top molecule are being studied in our laboratory. Formaldehyde was investigated in detail by microwave and infrared spectroscopy²⁻⁶⁾ and its rotational constants were obtained with accuracy but little by Raman spectroscopy.

Generally, the shape of Raman band envelope of a given molecule is determined by its polarizability if its rotational constants are known. Therefore, as one step of Raman study on formaldehyde, a program of computing a Raman band envelope was set up for the asymmetric top molecule. In order to apply the program to calculation for ν_2 and ν_3 bands of formaldehyde, the values of polarizability of formaldehyde were estimated from Raman intensity data⁷⁾ by the aid of the bond polarizability theory⁸⁾. Because experimental result with good quality has not been obtained yet, only the computed spectrum is shown in this report. The method adopted in our computing program is similar to that given for infrared spectra⁹⁾.

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Raman Intensity

The transition probability I from the (v, J, n) state of the lower vibrational level to the (v', J', n') state of the upper vibrational level is given by

$$I(\nu_{v'J'n'}^{vJn}) = \text{const} \cdot (\nu_i - \nu_{v'J'n'}^{vJn})^4 \frac{g_{J'n} \exp[-E(J, n)/kT]}{\sum_{J'n} g_{J'n} (2J+1) \exp[-E(J, n)/kT]} \\ \times \left| \frac{1}{3} (\alpha_0^0)_{v'}^v \sum_{kk'} T_k^{Jn} T_{k'}^{J'n'} \times {}^{(1)}B_{J'k'}^{Jk} + \frac{7}{30} \sum_i (\alpha_i^2)_{v'}^v \cdot \sum_{kk'} T_k^{Jn} T_{k'}^{J'n'} \times {}^{(2)}B_{J'k'}^{Jk} \right|^2$$

where the notations are the same as those in the previous papers^{9,10)} except for ${}^{(1)}B_{J'k'}^{Jk}$ and

$${}^{(1)}B_{J'k'}^{Jk} = \sqrt{(2J+1)(2J'+1)} (-1)^k \begin{bmatrix} J' & t & J \\ -k' & q & k \end{bmatrix}, \text{ where } t=0 \text{ or } 2 \text{ and } q=k'-k.$$

Polarizability

The values of the polarizability derivatives for formaldehyde with respect to normal coordinates Q_2 and Q_3 were obtained, by the aid of Wolkenstein's bond polarizability theory⁸⁾, from data on the absolute Raman intensities of CH_4 and CO_2 given by T. Yoshino and H. J. Bernstein⁷⁾.

For ν_2 bands of formaldehyde,

$$\frac{\partial \alpha_{xx}}{\partial Q_2} = 2[\alpha'_p(\text{CH}) \cdot (\cos \frac{\phi}{2})^2 + \alpha'_l(\text{CH}) \cdot (\sin \frac{\phi}{2})^2] \frac{\partial r_{\text{CH}}}{\partial Q_2} \\ + \alpha'_p(\text{CO}) \cdot \frac{\partial r_{\text{CO}}}{\partial Q_2} + [\alpha_l(\text{CH}) - \alpha_p(\text{CH})] \cdot \sin \phi \cdot \frac{\partial \phi}{\partial Q_2}$$

$$\frac{\partial \alpha_{yy}}{\partial Q_2} = 2 \cdot \alpha'_p(\text{CH}) \cdot \frac{\partial r_{\text{CH}}}{\partial Q_2} + \alpha'_p(\text{CH}) \cdot \frac{\partial r_{\text{CO}}}{\partial Q_2}$$

$$\frac{\partial \alpha_{zz}}{\partial Q_2} = 2[\alpha'_p(\text{CH}) \cdot (\sin \frac{\phi}{2})^2 + \alpha'_l(\text{CH}) \cdot (\cos \frac{\phi}{2})^2] \cdot \frac{\partial r_{\text{CH}}}{\partial Q_2} \\ + \alpha'_l(\text{CO}) \cdot \frac{\partial r_{\text{CO}}}{\partial Q_2} + [\alpha_p(\text{CH}) - \alpha_l(\text{CH})] \cdot \sin \phi \cdot \frac{\partial \phi}{\partial Q_2}$$

where coordinate axes were taken as shown in Fig. 1 and ϕ is given as $\phi_c = 116.5^\circ \pm 1.2^\circ$. $\alpha_p(\text{CH})$ and $\alpha_l(\text{CH})$ etc. are the perpendicular and longitudinal components of polarizability for CH bond etc. and $\alpha'_p = \frac{\partial \alpha_p}{\partial r}$.

From the data of T. Yoshino and H. J. Bernstein, $\alpha_l(\text{CH})$ and $\alpha_p(\text{CH})$ etc. are found as,

$$\begin{aligned} \alpha_l(\text{CH}) &= 0.858 \text{ A}^3, & \alpha_p(\text{CH}) &= 0.546 \text{ A}^3, \\ \alpha_l'(\text{CH}) &= 2.441 \text{ A}^2, & \alpha_p'(\text{CH}) &= 0.34 \text{ A}^2, \\ \alpha_l'(\text{CO}) &= 1.50 \text{ A}^2, & \alpha_c'(\text{CO}) &= 0.25 \text{ A}^2 \end{aligned}$$

Using above values and those of $\frac{\partial r_{\text{CH}}}{\partial Q_2}$ etc. given by T. Miyazawa¹¹⁾, the spherical tensor components of $\frac{\partial \alpha}{\partial Q_2}$ are obtained as follows :

$$\frac{\partial \alpha_0^0}{\partial Q_2} = 0.559 \text{ A}^2, \quad \frac{\partial \alpha_0^2}{\partial Q_2} = 0.018 \text{ A}^2, \quad \frac{\partial \alpha_2^2}{\partial Q_2} = \frac{\partial \alpha_{-2}^2}{\partial Q_2} = -0.070 \text{ A}^2 .$$

By the same process, these values for ν_3 band of formaldehyde are obtained as,

$$\frac{\partial \alpha_0^0}{\partial Q_3} = 0.046 \text{ A}^2, \quad \frac{\partial \alpha_0^2}{\partial Q_3} = -0.625 \text{ A}^2, \quad \frac{\partial \alpha_2^2}{\partial Q_3} = \frac{\partial \alpha_{-2}^2}{\partial Q_3} = 0.316 \text{ A}^2 .$$

Band Envelope

The band envelope was calculated on the basis of the rotational constants determined by microwave and infrared spectroscopy^{2,4)}, and the obtained rotational constants are :

$$\begin{aligned} A_0 &= 9.407473 \text{ cm}^{-1}, & B_0 &= 1.295405 \text{ cm}^{-1}, & C_0 &= 1.134223 \text{ cm}^{-1} \text{ for ground state,} \\ A_2 &= 9.39910 \text{ cm}^{-1}, & B_2 &= 1.287874 \text{ cm}^{-1}, & C_2 &= 1.125422 \text{ cm}^{-1} \text{ for } \nu_2 \text{ state,} \\ A_3 &= 9.46723 \text{ cm}^{-1}, & B_3 &= 1.30043 \text{ cm}^{-1}, & C_3 &= 1.129324 \text{ cm}^{-1} \text{ for } \nu_3 \text{ state.} \end{aligned}$$

The centrifugal distortion constants were also used but here those for the upper state were assumed to be equal to those for the ground state⁴⁾.

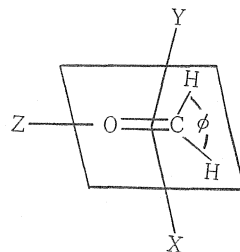
The process of calculating the envelope is similar to that previously used in infrared absorption⁹⁾. In our case, the intensity for the frequency ν_i is expressed by

$$R(\nu_i) = \int_{-\frac{a}{2}}^{\frac{a}{2}} \sum_m I(\nu_m) \frac{1}{2\pi^2\tau \cdot [(\nu - \nu_m)^2 + 1/(2\pi\tau)^2]} \cdot f(\nu - \nu_i, a) \cdot d\nu$$

where m is the transition from each rotational level and $1/(\pi\tau)$ is the half width of Lorentzian function (0.1 cm^{-1} in our case). $f(\nu - \nu_i, a)$ is the slit function of the monochromator (triangular function in our case), a being the slit width (0.4 cm^{-1} in our case). For the practical calculation, the values of $I(\nu_m)$ were summed up for the small range of frequency ($\Delta\nu = 0.1 \text{ cm}^{-1}$ in our case),

$$I'(\nu_m) = \sum_{\nu}^{\nu + \Delta\nu} I(\nu_m)$$

Fig. 1.

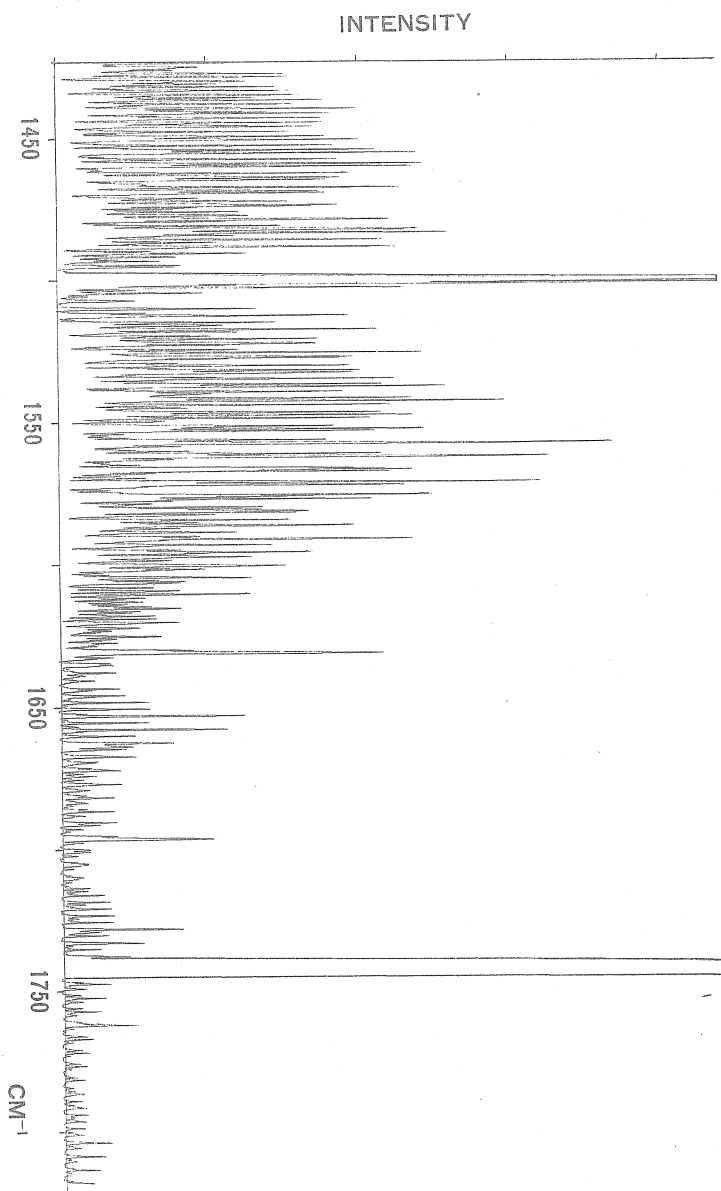


and $R(\nu_i)$ was calculated using $I'(\nu_m)$.

The calculation was made up to $J=26$ using Facom 230-35 of the computing center of Kanazawa University. The result is shown in Fig. 2.

In the paper of Davidson, Stoicheff and Bernstein¹²⁾, it was reported shortly that the ν_2 band was sharp and weak, and the ν_3 band was sharp and medium with the slit width of 5 cm^{-1} . This is inconsistent with our computing result in the point of relative intensities for ν_2 and ν_3 bands. This point will be made clear in our experimental research.

Fig. 2. Calculated Raman spectrum of ν_2 and ν_3 bands of formaldehyde



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Systematic Studies on the Conducting Tissue of the Gametophyte in Musci

(5) What is Expected of Systematics Regarding the Inner Structure of the Stem in Some Species of Thuidiaceae

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Abstract

It seems important for the phytotaxonomic study that every stage of the life cycle of mosses should be considered from every point of view, and that whether of the gametophyte generation or of the sporophyte, essential coordinations in the life cycle should be searched. In this paper we searched from this point of view for principles as to how the generation of gametophyte lives, and the inner structure of the stem was examined microscopically in the Thuidiaceae species. In view of the results so far achieved, (1) inner differential types of the stem (I-VI types), (2) comparison between thickness of cell walls of the central tissue and of the internal cortex (O, P and Q types), (3) comparison between the size of cells of the central tissue and that of cells of the internal cortex (L, M and N types), (4) distinction between the central tissue and the internal cortex (J and K types), and (5) cell-configuration of the central tissue (R and S types)—these items have to be made objects of investigation for taxonomic study. And the cross sections of the stem of the seven families, Fissidentaceae, Entodontaceae, Thuidiaceae, Mniaceae, Bartramiaceae, Dicranaceae and Polytrichaceae, hitherto observed, are studied as to the affinity regarding the anatomical characteristics. Many points of resemblance are found as in Thuidiaceae; that is, the above-stated five characteristics of the inner structure of the stem are quite common in many families.

Further, a systematic consideration was attempted making reference to the affinity among the anatomical characteristics of the stem. When the relationship among the genera of Thuidiaceae here observed is taxonomically considered as to the essential characters, it seems that one of the relationships among the genera of Thuidiaceae is as shown in Tab. 6, that is, the genera of Thuidiaceae are divided into Th- and An-groups. The genera of Th-group are classified into four groups, ThIIPKMIa-, ThIII PKMIb-, ThIIPJN1a- and ThIIPJN1b-groups, and the genera of An-group are classified into the three groups: AnIII PKM8a, AnIII PKM8b and AnIVQJN. But the

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