CHEMISTRY LETTERS, pp. 1147-1150, 1982. © The Chemical Society of Japan 1982

ON THE EFFECT OF THE TORSIONAL BARRIER IN TORSION-ROTATION-VIBRATION SPECTRA OF DIMETHYLACETYLENE-D_3

Jun NAKAGAWA* and Michiro HAYASHI
Department of Chemistry, Faculty of Science, Hiroshima University
Higashi-sendamachi, Nakaku, Hiroshima 730

Infrared specta of gaseous $CH_3C{\equiv}CCD_3$ were measured. With the aid of simulation spectra, torsional barrier in this molecule was evaluated to be 2±1 and 6±2 cm^{-1} from ν_9 (CH_3 degenerate stretching) and ν_{10} (CH_3 degenerate deformation) perpenducular bands, respectively. The dependence of the barrier height on the vibrational state was found.

In 1971, Olson and Papousek$^{1)}$ analyzed a high resolution infrared spectrum of perpendicular band of CH_3 degenerate stretching vibration in dimethylacetylene and reported the upper limit of the torsional barrier to be 4 cm^{-1}. Since then, there are some papers concerning this molecule, but no further discussions on the torsional barrier have been reported.

In the present paper, we deal with torsion-rotation-vibration spectra of dimethylacetylene-d_3, $CH_3C{\equiv}CCD_3$, in the hope of determining a somewhat more definite value for the barrier height of torsion from perpendicular bands. A merit of using the CD_3 partially substituted species instead of the parent species is in the fact that the Coriolis coupling term of the form $P_\gamma p_\gamma$, which is caused from the end-to-end coupling,$^{2,3)}$ can be safely neglected, since the degenerate normal vibrations do not occur in nearly degenerate pairs any more. The spectrometer used was a JEOL JIR-40X Fourier transform spectrometer with a maximum optical path difference of 8 cm.

Four perpendicular bands which can be resolved into successive Q-branches were observed in 2980, 2230, 1460 and 1040 cm^{-1} regions. The intensity alternation of the successive Q-branches due to statistical weights is clearly recognized in the 2980 and 1460 cm^{-1} bands as a similar manner to a perpendicular band of a CH_3X type molecule and these two bands are assigned to be CH_3 degenerate stretching (ν_9) and CH_3 degenerate deformation (ν_{10}) modes, respectively. On the other hand, the band near 2230 cm^{-1}, which is CD_3 degenerate stretching (ν_{13}) vibration, exhibits also the intensity alternation, but it is not so clear as that observed in the former two bands.

The assignment of the band near 1040 cm^{-1} is rather difficult, since CH_3 degenerate rocking (ν_{11}) and CD_3 degenerate deformation (ν_{14}) vibrations are expected to fall into this region. The spacings of the successive Q-branches, however, suggest this band is ν_{14}, since the corresponding band in $CD_3C{\equiv}CH^{4)}$ has almost the same Coriolis coupling constant. Thus, we assigned the 1040 cm^{-1} band as ν_{14}, but it is obvious that ν_{11} badly overlaps in this region.

The successive Q-branches of the above four bands are very broad (the half width of ~5 cm^{-1}) and nearly symmetric (see Figs. 1 and 2). Furthermore, for ν_{10} band, some of the successive Q-branches split into three or two lines as shown in Fig. 2. The central frequencies of the Q-branches can be fitted by the following polynomial of k;

$$\nu_9;\ \nu_k^Q = 2977.02 + 9.561\,k - 0.0237\,k^2, \qquad (1)$$

$$\nu_{10};\quad \nu_k^Q = 1463.55 + 14.077\ k - 0.0202\ k^2, \qquad (2)$$

$$\nu_{13};\quad \nu_k^Q = 2238.18 + 4.614\ k - 0.0477\ k^2, \qquad (3)$$

$$\nu_{14};\quad \nu_k^Q = 1035.85 + 7.498\ k + 0.0447\ k^2, \qquad (4)$$

Since the separation of the Q-branches are wide enough for ν_9 and ν_{10} bands, the effect of the torsional barrier to the spectrum was analyzed only for these two bands.

The $CH_3C{\equiv}CCD_3$ molecule belongs to the molecular symmetry group of G_{18} as long as vibrational wavefunctions and torsion-rotational wavefunctions are concerned$^{5)}$. The normal vibrations are divided into seven A_1, four E_1 and four E_2 species, where E_1 and E_2 are the degenerate vibrations mainly occuring in the CH_3C and CD_3C groups, respectively. As derived by Bunker,$^{5)}$ the energy levels assuming zero torsional barrier are written as;

$$E(A_1) = \nu + B[J(J+1)-K^2] + A_Hk_H^{\,2} + A_Dk_D^{\,2}, \qquad (5)$$

$$E(E_1) = \nu + B[J(J+1)-K^2] + A_H(k_H-\zeta l_H)^2 + A_Dk_D^{\,2}, \qquad (6)$$

were A_H and A_D represent the rotational constants around the molecular axis for the CH_3 and CD_3 groups, k_H and k_D are the quantum numbers associated with them, and $K=|k_H+k_D|\leqq J$. It should be noted that (k_H, k_D) and $(-k_H, -k_D)$ in the A_1 and (k_H, l_H, k_D) and $(-k_H, -l_H, -k_D)$ in the E_1 state are the degenerate pairs. Herafter we refer the levels by (k_H, k_D) and (k_H, l_H, k_D) in the A_1 and E_1 states, respectively.

The frequency of the Q-branch of the E_1 perpendicular band can be calculated using selection rules of $\Delta k_H=\Delta l_H=\pm1$, $\Delta k_D=0$ and $\Delta J=0$ to be;

$$\nu^Q_{k_H,\,k_D,\,J} = \nu_0 + A_H'(1-\zeta)^2 - B' \pm 2k_H[A_H'(1-\zeta)-B'] \mp 2B'k_D + [(A_H'-B')-(A_H''-B'')]k_H^{\,2}$$
$$+ [(A_D'-B')-(A_D''-B'')]k_D^{\,2} + (B'-B'')J(J+1), \qquad (7)$$

in which quantum numbers k_H and k_D are those in the ground state. From Eq. (7), it appears that the Q-branches occur in bunches, the separation of the bunches is approximately $2[A_H(1-\zeta)-B]$ and these bunches can be assigned k_H values. The Q-branches within each bunch separate 2B and they are assigned

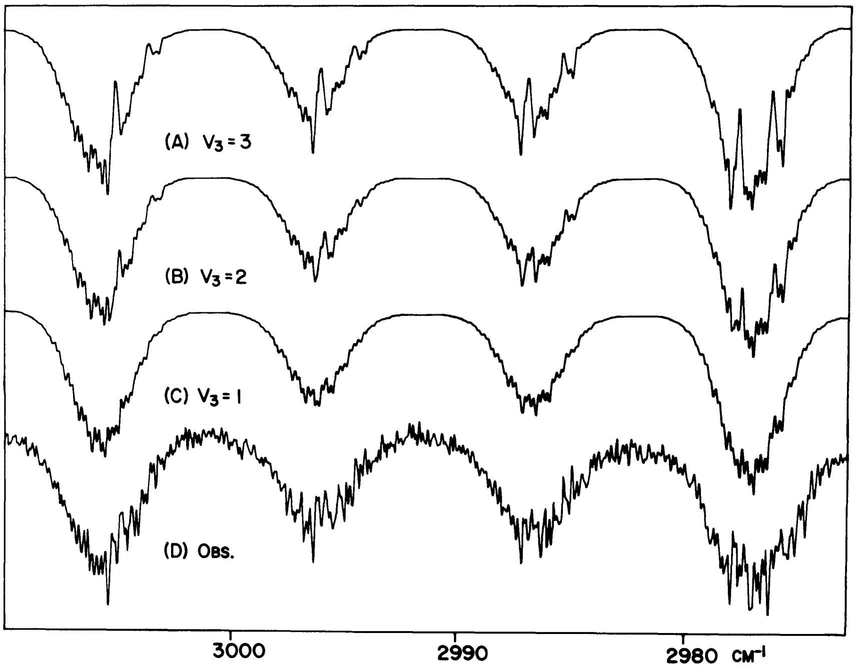

Fig. 1.
Observed and calculated spectra of ν_9 band in $CH_3C{\equiv}CCD_3$.

(A) Calculated spectrum, $V_3=3$, $\nu_0=2972.61$, $A_H''=5.300$, $A_H'=5.276$, $A_D''=A_D'=2.650$, $B''=0.1000$, $B'=0.1001$ cm^{-1}, and $\zeta=0.075$. Slit width 0.12 cm^{-1}.

(B) The same as (A) except $V_3=2$ cm^{-1}.

(C) The same as (A) except $V_3=1$ cm^{-1}.

(D) Observed spectrum, path length 1 m, pressure 10 mmHg.

k_D values.

Furthermore, from the statistical weights for CH_3, relative intensities of Q-branches with k_H=3n are twice stronger than those with k_H=3n±1. On the other hand, for CD_3, the ratio of the weights between k_D=3n and k_D=3n±1 is 11:8. Thus, the bunches of the Q-branches show clearly intensity alternation like a CH_3X type molecule and the Q-branches within the bunch exhibit intensity alternation of 11:8.

The obserbed spectrum of ν_9 band can be approximately explained by the feature of the free rotation described above, but a detailed examination shows some discrepancy in the spectrum (see Fig. 1). For example, the Q-branch at 3005.6 cm^{-1} shows a slight asymmetry and the higher frequency side is slightly dense. A more drastic discrepancy is found in ν_{10} band, where $^RQ_0$-branch at 1463.5 cm^{-1} splits into three lines, and some of other Q-branches also exhibit triplet or doublet (see Fig. 2).

These discrepancies can be explained by the effect of non-zero torsional barrier, since the torsional potential function, $V_3/2(1-\cos 3\theta)$, connects two levels in the same vibrational state whose k_H and k_D quantum number differ by ± 3 and ∓ 3 with each other.

For example, the effect on $^RQ_0$-branch is as following. Since (0, k_D) interact with (± 3, $k_D \mp 3$) and $A_H \simeq 2A_D$, the second order correction to the energy level of (0, k_D) is calculated to be $-6V/(81-4k_D^2)$, in which $V=(V_3/4)^2/A_D$. Thus, the levels with $|k_D| \geqq 5$ are lifted up and those with $|k_D| \leqq 4$ are pushed down. Similarly, (1, 1, k_D), to which the transition occurs from (0, k_D), has the correction term of $-6V/[81-4(2-2\zeta-k_D)^2]$ and ζ can be calculated from the fitting polynomial of Eqs.(1-4), assuming $A_H''=5.300$ and $A_D''=2.650$. From $\zeta_{10}=-0.352$, it is concluded that the levels with $k_D \leqq -2$ and $k_D \geqq 8$ are lifted up and those with $-1 \leqq k_D \leqq 7$ are pushed down.

From the above argument on the correction in the ground and ν_{10} states, the transition with k_D=-2 shifts to higher frequency while that with k_D=-1 shifts lower from their original positions. Since k_D=-1 transition occurs lower frequency side than k_D=-2 transition when the torsional barrier is zero, there occurs a dip between k_D=-1 and k_D=-2. Similarly, the spacing between k_D=4 and k_D=5 becomes wider.

On the other hand, the frequency shifts of transitions with k_D=8 and k_D=7, as well as k_D=-4

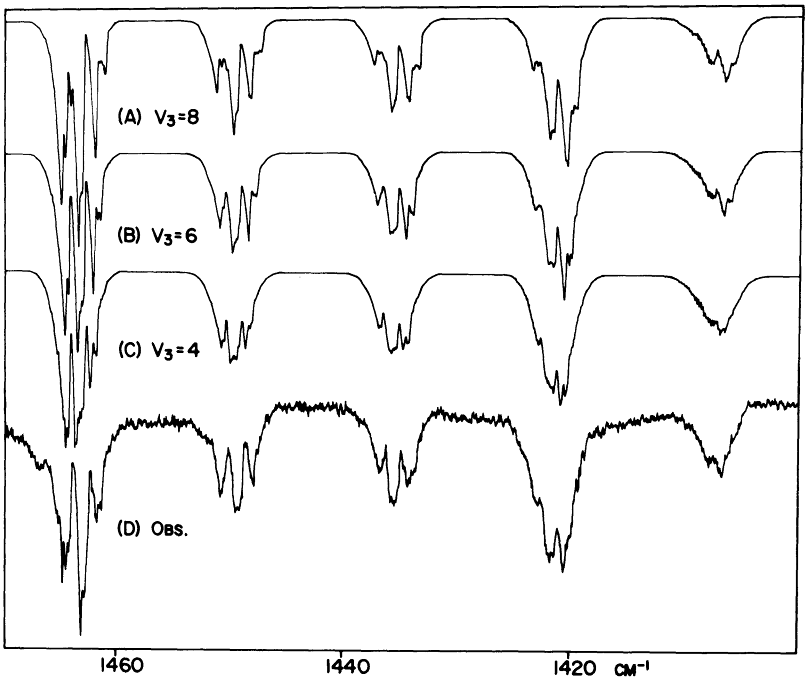

Fig. 2.
Observed and calculated spectra of ν_{10} band in $CH_3C\equiv CCD_3$.

(A) Calculated spectrum, V_3=8, ν_0=1454.10, A_H''=5.300, A_H'=5.280, $A_D''=A_D'$=2.650, B"=0.1000, B'=0.10015 cm^{-1} and ζ=-0.352. The parameters for the x,y-type Coriolis interaction with ν_4 are; ΔE=64.5 cm^{-1} and $|\zeta^x_{4,10}|$=0.55. Slit width 0.12 cm^{-1}.

(B) The same as (A) except V_3=6 cm^{-1}.

(C) The same as (A) except V_3=4 cm^{-1}.

(D) Observed spectrum, path length 16 cm^{-1}, pressure 25 mmHg.

and k_D=-5, make the spacing of these two transitions smaller, since k_D=8 transition has the correction to the higher frequency and k_D=7 transition to lower. These facts show that there are two holes in $^RQ_0$-branch if torsional barrier is small.

In order to determine the torsional barrier, computer simulations were carried out as shown in Fig. 1(ν_9) and Fig. 2(ν_{10}). The parameters used in the calculations are given in the figure captions and the J quantum numbers up to 80 were taken into consideration. Since these two bands are due to the vibrations occuring mainly in the CH_3 group, A_D' was assumed to equal to A_D''. V_3 value was also assumed to be common for the ground and excited states. We neglect all the contributions from hot bands which have intensity of roughly one third at room temperature. For intensity calculation, we took into account of the statistical weights, Boltzman factors and direction cosine matrix elements.

The difference, α^B=B"-B', is one of the important factors in the calculation, since the band width of a Q-branch depends on this value as well as the slit width. The later one was estimated to be 0.12 cm^{-1} from the optical path difference of the spectrometer. For ν_9 band, $\alpha_9{}^B$ was assumed to be -0.0001 cm^{-1}, since sharp lines were observed (see Fig. 1). In order to estimate $\alpha_{10}{}^B$, the x,y-type Coriolis interaction with ν_4 state should be taken into account, because this interaction makes the effective B rotational constants of the individual Q-branches different. The evidence of this interaction can be proved by the fact that $^PQ_5$-branch at 1394 cm^{-1}, which is slightly higher than ν_4 band at 1390 cm^{-1}, has a tail to higher frequency side, while $^PQ_6$ at 1378 cm^{-1} exhibits a tail to the reverse side. This interaction can also explain the fact that $^RQ_0$ at 1464 cm^{-1} has relatively sharp lines and the dip in $^PQ_4$ at 1408 cm^{-1} is much more shallow than in $^RQ_0$. Thus, the effect of this interaction to the rotational constant B was included in the calculation with $|\zeta_{4,10}{}^x|$=0.55 which was taken from the corresponding band system in $CH_3C{\equiv}CH$[6)] and $\alpha_{10}{}^B$ was assumed to be -0.00015 cm^{-1}.

From comparison of observed and calculated spectra in Fig. 1, the best fit spectrum is obtained when V_3=2 cm^{-1}. The spectrum with V_3=3 cm^{-1} has deeper dips compared to the observed spectrum. On the contrary, for V_3=1 cm^{-1}, the simulation spectrum shows relatively regular pattern. Consequently, V_3=2±1 cm^{-1} is determined form ν_9 band.

For ν_{10} band, Fig. 2 shows three simulation spectra with the V_3 values of 4, 6 and 8 cm^{-1}. If V_3=8 cm^{-1}, observed spectra should show clearler shoulder in $^RQ_0$, $^PQ_1$ and $^PQ_2$-branches. On the other hand, the spectrum with V_3=4 cm^{-1} does not exhibit such a clear deep dip observed in the actual spectrum. The simulation with V_3=6 cm^{-1} seems to be the best fit judging from over all agreement between the observed and calculated spectra. Thus, V_3 is determined to be 6±2 cm^{-1} from ν_{10} band.

We could not determine the torsional barriers in the ground and excited states independently, since the assignment of individual k_D value is not available from the present measurement. The fact, however, that the best fit values of the barrier in ν_9 and ν_{10} bands are different with each other indicates that the torsional barrier heights in ν_9 and ν_{10} excited states are different. The value in the ground state is not necessarily the same as in the excited state, but it is possibly around 2 cm^{-1}, since higher barrier makes the ν_9 perpendicular band more disturbed.

Referrences

1. W. B. Olson and D. Papousek, J. Mol. Spectrosc. 37, 527 (1971).
2. P. R. Bunker, J. Chem. Phys. 47, 718 (1967).
3. D. Papousek, J. Mol. Spectrosc. 28, 527 (1968).
4. J. L. Duncan, D. C. McKean, and G. D. Nivellini, J. Mol. Struct. 32, 255 (1976).
5. P. R. Bunker, Mol. Phys. 9, 257 (1965).
6. J. L. Duncan, I. J. Wright, and D. Ellis, J. Mol. Spectrosc. 37, 394 (1971).

(Received May 4, 1982)