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Vibration-rotation Spectrum of the Coriolis-interacting Band System ν_6 and ν_3 of Acetonitrile-d_3

Hiroatsu Matsuura* and Hiromu Murata

Department of Chemistry, Faculty of Science, Hiroshima University, Higashisenda-machi, Naka-ku, Hiroshima 730

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The vibration-rotation infrared spectrum of the Coriolis-interacting band system ν_6 and ν_3 was measured with a resolution of 0.08 cm^{-1}. The analysis of the spectrum gave values, more precise than before, of the parameters for these bands along with the interaction parameters. A close examination of the observed spectrum revealed a weak Fermi resonance between ν_6 and $\nu_4+\nu_8$. The parameters determined, in cm^{-1}, include: $(\nu_0)_6$ 1046.659, α_6^A 0.01550, α_6^B -0.000443, $(\nu_0)_3$ 1110.46, α_3^A -0.0078, and α_3^B 0.00092, where α_6^B and α_3^B do not involve the contribution of the Coriolis interaction between ν_6 and ν_3.

The vibration-rotation infrared spectra of acetonitrile-d_3 or methyl-d_3 cyanide, CD_3CN, have been studied previously by several investigators.[1—4] The resolution of these spectra was, however, not high enough to provide precise values for molecular parameters. In order to improve the spectroscopic data for CD_3CN, Fourier transform infrared spectrum with a higher resolution was measured and analyzed in the present work. We report in this paper the spectral analysis of the ν_6 band (CD_3 degenerate deformation) which is strongly coupled with the ν_3 band (CD_3 symmetrical deformation) through an *xy*-type Coriolis interaction.

Experimental

The sample of acetonitrile-d_3 was a product of CEA, France, with a stated isotope purity of 99.7% and was used for the spectral measurements without further purification. The infrared spectrum was recorded on a JEOL JIR-40X Fourier transform infrared spectrometer. Sample pressures of 7—20 Torr† in a 1-m cell were utilized in the measurements. The effective spectral resolution was 0.08 cm^{-1}. The observed wavenumbers were calibrated by using the IUPAC wavenumber data.[5]

Spectral Analysis

The vibration-rotation spectrum in the whole ν_6 band region and the expanded spectra of the ^{R}R and ^{P}P branches are shown in Figs. 1 and 2, respectively. The spectra exhibit a number of P- and R-branch lines together with Q branches, in contrast with the previous spectra[1,3,4] in which only the Q branches were resolved. The assignment of the quantum number K to the Q branches and the associated P and R branches was made straightforwardly by examining the intensity alternation and the starting positions of series of P- and R-branch lines (Fig. 2). The K assignment established in this work agrees with that in the previous analyses.[1,3,4] The $^{P}P_K$-branch lines with $K=1$—16 and the $^{R}R_K$-branch lines with $K=0$—15 were finally identified and assigned for the ν_6 band. Vibration-rotation lines assignable definitely to the ν_3 band were not identified because of much weaker intensities than those for the ν_6 band.

Subband Analysis of ν_6. In advance of the analysis of the whole band system, the subbands in ν_6 were analyzed, and the effective rotational constant B'_{eff} was obtained for each subband by using a formula

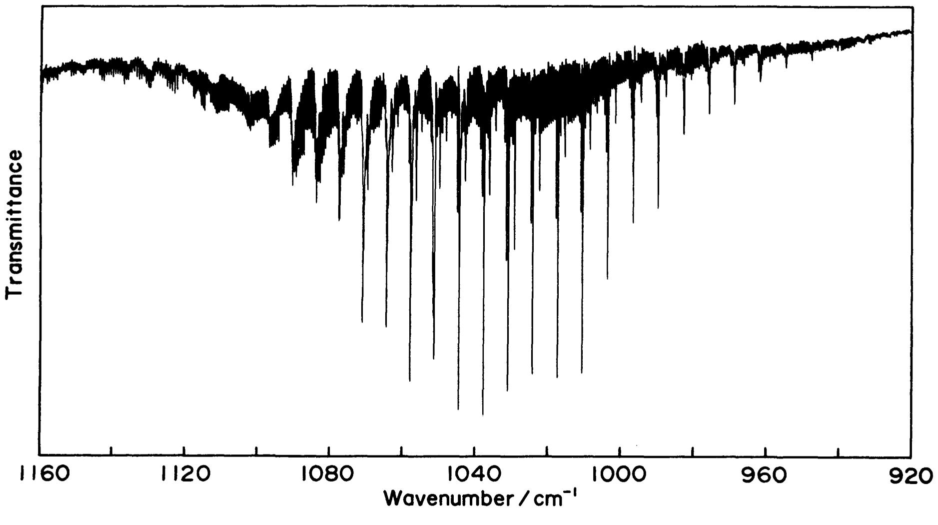

Fig. 1. Infrared spectrum of the ν_6 band region of gaseous CD_3CN.

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† 1 Torr = 133.322 Pa.

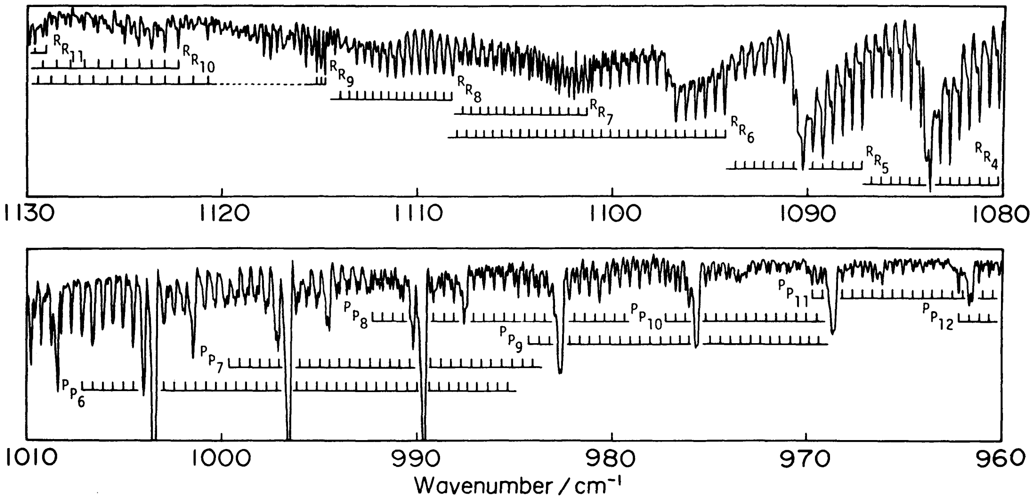

Fig. 2. Infrared spectra and assignments of the ^{R}R and ^{P}P branches of ν_6 of CD_3CN.

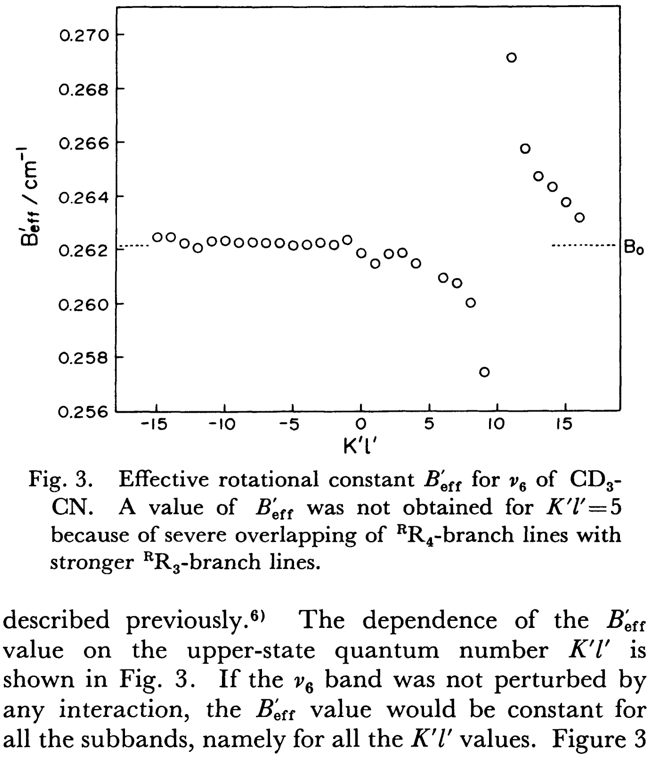

Fig. 3. Effective rotational constant B'_{eff} for ν_6 of CD_3-CN. A value of B'_{eff} was not obtained for $K'l'=5$ because of severe overlapping of $^{R}R_4$-branch lines with stronger $^{R}R_3$-branch lines.

described previously.[6] The dependence of the B'_{eff} value on the upper-state quantum number $K'l'$ is shown in Fig. 3. If the ν_6 band was not perturbed by any interaction, the B'_{eff} value would be constant for all the subbands, namely for all the $K'l'$ values. Figure 3 shows, however, a striking variation of B'_{eff} between $K'l'=9$ and 11, indicating that an energy-level crossing with another state occurs around $K'l'=10$.

An examination of the energy levels for CD_3CN indicates that the perturbation observed in the ν_6 band is due to the *xy*-type Coriolis interaction between the $v_6=1$ state (to be denoted by the ν_6 state or simply ν_6) and the $v_3=1$ state (the ν_3 state), which has been noted previously by Masri *et al.*[3] The variation fashion of the B'_{eff} value indicates that the vibration-rotation levels of ν_6 for $K'l'\leq 9$ are lower than the coupling ν_3 levels and, beyond the level crossing, the ν_6 levels are higher than the ν_3 levels. The vibration-rotation energy levels, finally determined in this work, of ν_6 (E), ν_3 (A_1), and $\nu_4+\nu_8$ (E) and the interactions coupling the levels are shown in Fig. 4. The $\nu_4+\nu_8$ state interacts weakly with the ν_6 state through a Fermi resonance, as will be mentioned later.

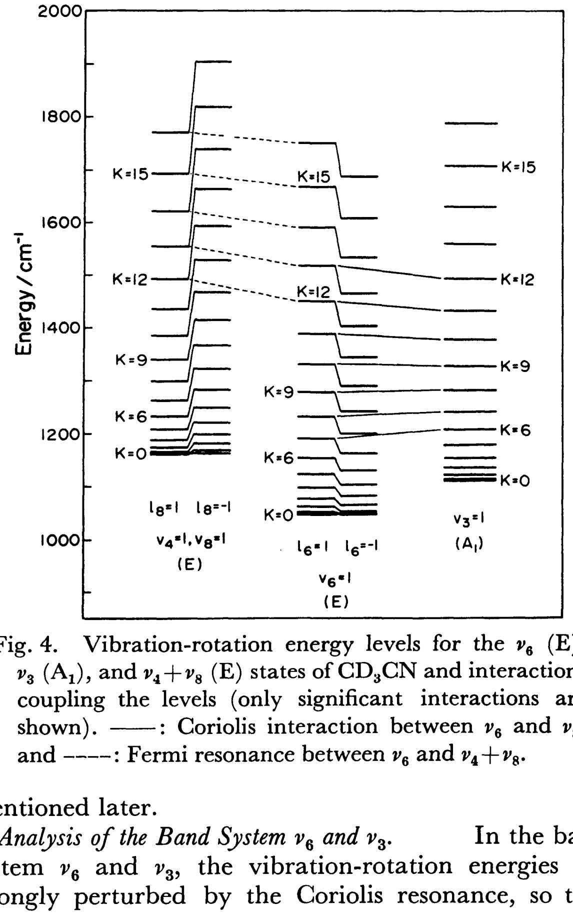

Fig. 4. Vibration-rotation energy levels for the ν_6 (E), ν_3 (A_1), and $\nu_4+\nu_8$ (E) states of CD_3CN and interactions coupling the levels (only significant interactions are shown). ——: Coriolis interaction between ν_6 and ν_3, and ----: Fermi resonance between ν_6 and $\nu_4+\nu_8$.

Analysis of the Band System ν_6 and ν_3. In the band system ν_6 and ν_3, the vibration-rotation energies are strongly perturbed by the Coriolis resonance, so that the treatment of the Coriolis interaction based on the second-order perturbation theory, known as a Van Vleck transformation, which is usually employed in off-resonance systems, is no longer valid. Accordingly, this interaction was explicitly taken into account in the analysis. The non-zero matrix element of the Hamiltonian for the *xy*-type Coriolis interaction between ν_6 (E) and ν_3 (A_1) is given by[6–8]

$$\begin{aligned}\langle v_3 = 1; J,K|H_{Cor}/hc|v_6 = 1,\ l_6 = \pm 1; J,K\pm 1\rangle \\ = \pm\, \xi^{(y)}_{3.6} f(J,K\pm 1),\end{aligned} \tag{1}$$

where

$$\xi^{(y)}_{3.6} = (1/\sqrt{2})[(\omega_6/\omega_3)^{1/2} + (\omega_3/\omega_6)^{1/2}](B\zeta^{(y)}_{3.6a}) \qquad (2)$$

and

$$f(J,K\pm1) = [J(J+1) - K(K\pm1)]^{1/2}. \qquad (3)$$

On the other hand, the vibration-rotation Hamiltonian gives the following unperturbed energy[9] with $|k|=K$:

$$\begin{aligned} E^0(v,l;J,k)/hc &= G(v,l) + B_v[J(J+1) - k^2] + A_vk^2 \\ &- \sum_t 2(A\zeta^{(z)}_{ta.tb})_vkl_t - (D_J)_vJ^2(J+1)^2 \\ &- (D_{JK})_vJ(J+1)k^2 - (D_K)_vk^4 \\ &+ \sum_t(\eta_{tJ})_vJ(J+1)kl_t + \sum_t(\eta_{tk})_vk^3l_t, \end{aligned} \qquad (4)$$

where $G(v,l)$ is the vibrational term and the index t refers to the doubly-degenerate modes. The vibrational term $G(v,l)$, and accordingly the band origin $(\nu_0)_v$ to be derived from the spectral analysis, include a term $A(\zeta^{(z)}_{ta.tb})^2$ which originates from the non-vibrational Hamiltonian.

The vibration-rotation transition wavenumbers were calculated by solving the energy matrix with elements given by Eqs. 1 and 4. The ground-state constants B_0, $(D_J)_0$, and $(D_{JK})_0$ were constrained to the well-determined microwave data[10] and the constants A_0 and $(D_K)_0$ were fixed to the estimated values.[3,11] The least-squares calculation gave satisfactory agreement between the observed and calculated wavenumbers with the exception of those for the ${}^RR_K(J)$ lines with $K\gtrsim12$.

The results of this preliminary calculation show that the perturbed ${}^RR_K(J)$ lines of ν_6 are shifted down more for larger K values, indicating that the perturbing vibration-rotation levels are higher than, but getting closer at higher levels to, those of the ν_6 levels. Possible interacting vibrational levels are $\nu_4+\nu_8$ and $\nu_7+\nu_8$ with estimated vibrational wavenumbers of about 1165 and 1180 cm^{-1}, respectively. Accordingly, the vibration-rotation energy levels for these combination bands were calculated by using the constants available. The results clarify that the levels of $\nu_4+\nu_8$ approach those of ν_6 within 40 cm^{-1} for $K'l'\geq13$ but an expected interaction between ν_6 and $\nu_7+\nu_8$ should be much less significant than between ν_6 and $\nu_4+\nu_8$. The minor perturbation observed in ν_6 is thus found to be due to the Fermi resonance between ν_6 (E) and $\nu_4+\nu_8$ (E).

The whole band system was analyzed by taking account of the Coriolis interaction between ν_6 and ν_3 and the Fermi resonance between ν_6 and $\nu_4+\nu_8$, as well as the $q^{(+)}_t$-type l-doubling interaction[9] in the degenerate vibrational state. Thus, in order to obtain perturbed energies, the following 5×5 energy matrix was set up and solved for $K\geq1$:

$$\left(\begin{array}{ccccc} E^0(v_6=1,\ l_6=-1;J,\ K-1), & W_{468} & -\xi^{(y)}_{3.6}f(J,\ K-1) & -q^{(+)}_6f(J,\ K+1)f(J,\ K-1)/2 & 0 \\ & E^0(v_4=1,\ v_8=1,\ l_8=-1;J,\ K-1) & 0 & 0 & -q^{(+)}_{4.8}f(J,\ K+1)f(J,K-1)/2 \\ & & E^0(v_3=1;J,\ K) & \xi^{(y)}_{3.6}f(J,\ K+1) & 0 \\ & \text{(Hermitian)} & & E^0(v_6=1,\ l_6=1;J,\ K+1) & W_{468} \\ & & & & E^0(v_4=1,v_8=1,\ l_8=1;\ J,K+1) \end{array}\right), \qquad (5)$$

where W_{468} is a parameter of the Fermi resonance between ν_6 and $\nu_4+\nu_8$ and is related to Mills' cubic force constant ϕ_{468} by $W_{468}=\phi_{468}/2\sqrt{2}.$ For $K=0$, on the other hand, the matrix is reduced to 3×3 and 2×2 matrices; for A_- species:[††]

$$\left[\begin{array}{ccc} E^0(v_3=1;\ J,\ K=0) & \sqrt{2}\ \xi^{(y)}_{3.6}[J(J+1)]^{1/2} & 0 \\ & E^0(v_6=1,\ l_6=1;\ J,\ K=1) + q^{(+)}_6J(J+1)/2 & W_{468} \\ \text{(Herimitian)} & & E^0(v_4=1,\ v_8=1,\ l_8=1;\ J,K=1) + q^{(+)}_{4.8}J(J+1)/2 \end{array}\right], \qquad (6)$$

and for A_+ species:

$$\left[\begin{array}{cc} E^0(v_6=1,\ l_6=1;\ J,K=1) - q^{(+)}_6J(J+1)/2 & W_{468} \\ \text{(Hermitian)} & E^0(v_4=1,\ v_8=1,\ l_8=1;\ J,K=1) - q^{(+)}_{4.8}J(J+1)/2 \end{array}\right]. \qquad (7)$$

The ${}^RR_0(J)$ and ${}^RP_0(J)$ transitions go to the A_- levels, while the ${}^RQ_0(J)$ transitions go to the A_+ levels.[7,12]

Wavenumbers for the vibration-rotation transitions of CD_3CN were obtained as differences between the perturbed energies in the excited vibrational states and those in the ground vibrational state. These wavenumbers were fitted to the observed wavenumbers by the least-squares adjustment of the spectroscopic parameters. In the calculation, some of the parameters for ν_3 and $\nu_4+\nu_8$ were assumed or set equal to those in the ground state; since pertinent experimental data to fix them were not available in the present work. Approximate values for the band origin of $\nu_4+\nu_8$ and the Fermi resonance parameter W_{468} were predetermined, in advance of the principal calculation, so as to reproduce the observed data most satisfactorily.

The parameters for the ν_6 and ν_3 bands and the interaction parameters were finally determined, as listed in Table 1, from a total of 517 vibration-rotation transition wavenumbers of ${}^PP_K(J)$ with $K=1$—16, ${}^RR_K(J)$ with $K=0$—15, and ${}^RP_0(J)$. The transition lines which were badly overlapped with others were not adopted in the calculation. The parameters in Table 1 reproduce the observed wavenumbers with a root-mean-square error of 0.014 cm^{-1}. A list of the observed transition wavenumbers has been deposited with the Chemical Society of Japan (Document No. 8257).

Results and Discussion

In the present work, the parameters have been

[††] In our earlier studies,[6,8] the different notation $A^{\pm}$ has been used; $A^{\pm}=A_{\mp}$.

TABLE 1. PARAMETERS FOR THE ν_6,ν_3, $\nu_4+\nu_8$ AND GROUND VIBRATIONAL STATES OF CD_3CN IN UNITS OF cm^{-1}

Parameter	ν_6	ν_3	$\nu_4+\nu_8$	Ground state
$(\nu_0)_v$	1046.659(7)[a]	1110.46(2)	1162[b]	0
A_v	2.61450(3)	2.6378(3)	$=A_0$	2.630[c]
B_v	0.262557(8)[d]	0.26119(4)[d]	0.26129[e]	0.26211407[f]
$(A\zeta^{(z)}_{ta.tb})_v$	−1.00068(7)	—	2.104[g]	—
$(D_J)_v$	$0.96(5)\times10^{-7}$	$=(D_J)_0$	$=(D_J)_0$	0.91567×10^{-7}[f]
$(D_{JK})_v$	$3.56(6)\times10^{-6}$	$=(D_{JK})_0$	$=(D_{JK})_0$	3.69125×10^{-6}[f]
$(D_K)_v$	$2.25(1)\times10^{-5}$	$=(D_K)_0$	$=(D_K)_0$	2.145×10^{-5}[h]
$(\eta_{tJ})_v$	$1.8(4)\times10^{-6}$	—	0	—
$(\eta_{tk})_v$	$-4.72(8)\times10^{-5}$	—	0	—
$q_t^{(+)}$	$1.3(2)\times10^{-4}$[d]	—	0	—
$\xi^{(y)}_{3.6}$	−0.1901(3)			
W_{468}	0.91[b,i]			

a) Standard deviations of the parameters, given in parentheses, apply to the last significant figure. b) Predetermined. c) Ref. 3. d) The value does not involve the contribution of the Coriolis interaction between ν_6 and ν_3. e) Derived from α_4^B and α_8^B (Ref. 16). f) Ref. 10. g) Derived from $\zeta^{(z)}_{8a.8b}$ (Ref. 11). h) Ref. 11. i) This value gives the cubic force constant $\phi_{468}=2\sqrt{2}\,W_{468}=2.6\ cm^{-1}$.

derived for the ν_6 and ν_3 bands along with the parameter of the Coriolis interaction between these vibrational states. The errors in the band origins $(\nu_0)_v$ have been estimated from the uncertainty in the standard wavenumbers[5] used for the calibration, that in the least-squares fitting of the calibration wavenumbers, and that in the least-squares determination of $(\nu_0)_v$.

The values determined in the present analysis for the rotational constants $B_6\equiv B_{v_6=1}$ and $B_3\equiv B_{v_3=1}$ do not involve the contribution of the Coriolis interaction between ν_6 and ν_3, since the perturbed energies for ν_6 and ν_3 were obtained by solving the energy matrix with the off-diagonal terms representing this Coriolis interaction and the diagonal terms representing the unperturbed energies without the contribution of this interaction. The constants α_6^B and α_3^B defined by

$$B_v = B_e - \sum_r \alpha_r^B(v_r+d_r/2), \tag{8}$$

where d_r is the degeneracy of the normal modes, are derived from the values for B_6, B_3, and B_0. The derived values for α_6^B and α_3^B therefore lack the contribution of the above-mentioned Coriolis interaction, and accordingly correspond to the expression for α_r^B in the second-order perturbation theory[13,14]††† with the term containing $\zeta^{(y)}_{3.6a}$ being dropped.

The spectral analysis gave a value for $(A\zeta^{(z)}_{6a.6b})_{v_6=1}$ which shows a vibrational dependence given by[9,15]

$$(A\zeta^{(z)}_{ta.tb})_v = (A\zeta^{(z)}_{ta.tb})_e - \sum_r \alpha_r^{A\zeta_t}(v_r+d_r/2). \tag{9}$$

The constant in the equilibrium state, $(A\zeta^{(z)}_{ta.tb})_e$, is separable into A_e and $\zeta^{(z)}_{ta.tb}$, namely

$$(A\zeta^{(z)}_{ta.tb})_e = A_e\zeta^{(z)}_{ta.tb}. \tag{10}$$

A combination of Eqs. 9 and 10 and an equation for A_v, similar to that for B_v in Eq. 8, gives an explicit relation between the constant $\zeta^{(z)}_{ta.tb}$ and the observable $(A\zeta^{(z)}_{ta.tb})_v$

$$\begin{aligned}\zeta^{(z)}_{ta.tb} &= [(A\zeta^{(z)}_{ta.tb})_v + \sum_r \alpha_r^{A\zeta_t}(v_r+d_r/2)]/A_e \\ &= [(A\zeta^{(z)}_{ta.tb})_v + \sum_r \alpha_r^{A\zeta_t}(v_r+d_r/2)]/ \\ &\quad [A_v+ \sum_r \alpha_r^A(v_r+d_r/2)].\end{aligned} \tag{11}$$

Since the determination of all of the constants $\alpha_r^{A\zeta_t}$ is practically impossible, a value for the Coriolis constant $\zeta^{(z)}_{ta.tb}$ with physical significance is never derived with a high precision.[9] In order to evaluate an effective value for $\zeta^{(z)}_{ta.tb}$, an approximation

$$(A\zeta^{(z)}_{ta.tb})_v \simeq A_v\zeta^{(z)}_{ta.tb} \tag{12}$$

has been conventionally used.[15] Physical meaning of the value thus derived is ambiguous and the resulting uncertainty in $\zeta^{(z)}_{ta.tb}$ is therefore unestimable. In the present analysis of ν_6 of CD_3CN, an effective value was derived for $\zeta^{(z)}_{6a.6b}$ by using Eq. 12. The value obtained is −0.3827 which may be compared with the value −0.374 calculated from the harmonic force constants.[11] These values agree with each other within 2.3%.

The parameter of the *xy*-type Coriolis interaction between ν_6 and ν_3, $\xi^{(y)}_{3.6}$ given by Eq. 2, involves the Coriolis constant $\zeta^{(y)}_{3.6a}$. This constant is, however, not separable from $\xi^{(y)}_{3.6}$, because the quantity $(B\zeta^{(y)}_{3.6a})$ shows a vibrational dependence as $(A\zeta^{(z)}_{ta.tb})_v$ does (Eq. 9). If an approximation

$$(B\zeta^{(y)}_{3.6a}) \simeq (B_3B_6)^{1/2}\zeta^{(y)}_{3.6a} \tag{13}$$

is made, an effective value for $\zeta^{(y)}_{3.6a}$ may be obtained from the $\xi^{(y)}_{3.6}$ value which was given by the spectral analysis. In doing this, the harmonic vibrational wavenumbers ω_6 and ω_3 are required, which are, in general, not easily derived. If, alternatively, the fundamental wavenumbers, not corrected for the vibrational anharmonicity, $(\nu_0)_6$ and $(\nu_0)_3$ are used for ω_6 and ω_3, possible errors may be involved in the derived value for $\zeta^{(y)}_{3.6a}$. To test the possibility of using the fundamental wavenumbers instead of the harmonic wavenumbers, calculations were made with Eq. 13 in two ways. The use of $(\nu_0)_6$ and $(\nu_0)_3$ determined in this work gave $|\zeta^{(y)}_{3.6a}|=0.505$, while the use of the harmonic wavenumbers,[11] $\omega_6=1061.7$ and $\omega_3=1128.0\ cm^{-1}$, ob-

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††† In Ref. 14, there is a typographic error; for 4/3 in the second term of the right side of Eq. 5, read 3/4.

tained by correcting for the anharmonicity by Dennison's rule, gave $|\zeta_{3,6a}^{(y)}|=0.513$. The difference between the two values is 1.5%. These values may be compared with 0.493 calculated from the harmonic force constants.[11] The experimentally derived values (0.505 and 0.513) are larger than the calculated one by 2 and 4%, respectively.

The *l*-doubling constant $q_6^{(+)}$ determined by the present analysis method does not have, similarly to α_6^B and α_3^B, the contribution of the Coriolis interaction between ν_6 and ν_3. The value obtained is thus explained by the second-order perturbation expression[12,14] for $q_6^{(+)}$ less the term containing $\zeta_{3,6a}^{(y)}$. Strictly speaking, the constant $q_t^{(+)}$ should show a vibrational dependence.[9] However, an estimation of its effect is practically quite difficult.

As seen from Eqs. 6 and 7, the effective rotational constant, not perturbed by the Coriolis and the Fermi interactions, for the $Kl_6=1$ levels of ν_6 is given by

$$B_{\mathrm{eff}}^0 = B_6 + q_6^{(+)}/2 \text{ for } {}^{\mathrm{R}}\mathrm{R}_0(J) \text{ and } {}^{\mathrm{R}}\mathrm{P}_0(J) \text{ transitions} \tag{14a}$$

$$B_{\mathrm{eff}}^0 = B_6 - q_6^{(+)}/2 \text{ for } {}^{\mathrm{R}}\mathrm{Q}_0(J) \text{ transitions,} \tag{14b}$$

B_{eff}^0 being the coefficient of $J(J+1)$ in the diagonal term of Eqs. 6 and 7 representing the $v_6=1$, $l_6=1$, $J,K=1$ state. The effective rotational constant B'_{eff} for $K'l'=1$, as given in Fig. 3, was derived from the ${}^{\mathrm{R}}\mathrm{R}_0(J)$ and ${}^{\mathrm{R}}\mathrm{P}_0(J)$ transitions. The value thus obtained involves the contributions of the *l*-doubling interaction mentioned above and the Coriolis interaction between ν_6 and ν_3. The smaller value for $K'l'=1$, as compared with those for the neighboring $K'l'$ values, is explained as follows. Although the *l*-doubling interaction with a positive $q_6^{(+)}$ value shifts up the energy levels associated with the ${}^{\mathrm{R}}\mathrm{R}_0(J)$ and ${}^{\mathrm{R}}\mathrm{P}_0(J)$ transitions (Eq. 14a), its effect is overwhelmed by the more dominant Coriolis interaction which shifts down the levels for $K'l'=1$ more largely than those for the neighboring $K'l'$ values (Eqs. 5 and 6). The constant B'_{eff}, if derived from the ${}^{\mathrm{R}}\mathrm{Q}_0(J)$ transitions, would be larger than that for the neighboring $K'l'$ values, since the levels associated with the ${}^{\mathrm{R}}\mathrm{Q}_0(J)$ transitions are completely free from the *xy*-type Coriolis interaction (Eq. 7), although the *l*-doubling interaction slightly shifts down the energy levels. The spectral observation in Fig. 1 that the contour of the ${}^{\mathrm{R}}\mathrm{Q}_0$ branch degrades to the higher wavenumber side, unlike the neighboring Q branches with sharper contours, is consistent with the expected B'_{eff} value.

The parameters $(\nu_0)_6\equiv(\nu_0)_{v_6=1}$, $(\nu_0)_3\equiv(\nu_0)_{v_3=1}$, α_6^A, α_3^A, α_6^B, α_3^B, $q_6^{(+)}$, $\zeta_{6a,6b}^{(z)}$, and $\zeta_{3,6a}^{(y)}$, determined explicitly or derived on assumptions in the present study are summarized in Table 2 in comparison with those reported previously. It is clearly shown that the precision of the parameters has been largely improved owing to the higher spectral resolution and the more legitimate procedure of the analysis in the present work. It should be noted, however, that the parameters for ν_3 were determined from the ν_6 transition lines through the Coriolis resonance between ν_3 ffnd ν_6. The transition lines associated intrinsically with ν_3 were not definitely identified because of their weak intensities.

TABLE 2. COMPARISON OF THE PARAMETERS FOR THE ν_6 AND ν_3 STATES[a)]

Parameter	Present work	Previous works	
		Masri *et al.*[b)]	Kondo and Person[c)]
$(\nu_0)_6$	1046.659(7)[d)]	1046.45	1047.0(1)
$(\nu_0)_3$	1110.46(2)	1110.0	1111.4(1)
α_6^A	0.01550(3)	0.0154	0.016(7)
α_3^A	−0.0078(3)	−0.0135[e)]	0[e)]
α_6^B	−0.000443(8)[f)]	0[e)]	0[e)]
α_3^B	0.00092(4)[f)]	0.0013[e)]	0[e)]
$q_6^{(+)}$	0.00013(2)[f)]	0[e)]	0[e)]
$\zeta_{6a,6b}^{(z)}$	−0.3827[g)]	−0.375[g)]	−0.408[g)]
$\lvert\zeta_{3,6a}^{(y)}\rvert$	0.513[h)]	0.47	0.484[e)]

a) The values are given in units of cm^{-1}, except for dimensionless $\zeta_{6a,6b}^{(z)}$ and $\zeta_{3,6a}^{(y)}$. b) Ref. 3. c) Ref. 4. d) Standard deviations of the parameters, given in parentheses, apply to the last significant figure. e) Assumed. f) The value does not involve the contribution of the Coriolis interaction between ν_6 and ν_3. g) Derived on the assumption that $(A\zeta_{6a,6b}^{(z)})_6=A_6\zeta_{6a,6b}^{(z)}$. See text. h) Derived from $\xi_{3,6}^{(y)}$ by using the harmonic wavenumbers (Ref. 11), on the assumption that $(B\zeta_{3,6a}^{(y)})=(B_3B_6)^{1/2}\zeta_{3,6a}^{(y)}$. See text.

The microwave spectra of CD_3CN in the excited vibrational states have been reported by Matsumura *et al.*[16] The observed spectral lines were complicated and they did not make definite assignments of the transitions for the ν_6 and ν_3 states. We therefore refrain from further discussion on their spectroscopic data.

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