Vibration-Rotation Spectrum of Methyl Fluoride II. Analysis of $\nu_3+\nu_6$ Band

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The $\nu_3+\nu_6$ band of methyl fluoride has been measured with a high-resolution infrared spectrometer. The molecular constants are obtained with the least-squares method. The effect of the x,y-type Coriolis interaction is discussed and the theoretical spectra are compared with the observed spectrum.

In a previous paper[1] (hereafter referred to as I), we have reported the analysis of the $2\nu_3$ band of CH_3F under high resolution. As mentioned in I, the $2\nu_3$ band is expected to have the x,y-type Coriolis interaction with the $\nu_3+\nu_6$ band similar to that observed in the ν_3 and ν_6 fundamentals.[2,3] The effect of this interaction may be seen more clearly in the weaker $\nu_3+\nu_6$ band and the result of the analysis is reported in the present paper.

Since the vibration-rotation energy levels for both the $2\nu_3$ and $\nu_3+\nu_6$ bands have been accurately determined, more precise scheme may be drawn for the x,y-type Coriolis interaction between the two levels. As mentioned in I, the band centers of these two bands are separated by about 140 cm^{-1}; the shifts of vibration-rotation levels are relatively small and may be treated in the conventional way. The effect of the perturbation would be more profound in the intensity of the $\nu_3+\nu_6$ band. The $\nu_3+\nu_6$ band may further couple with the $(2\nu_6)^0$ and $(2\nu_6)^2$ bands through the same ζ^y_{36} term. These bands occur at higher frequency side of the $\nu_3+\nu_6$ band and are extremely weak, and their effects on the $\nu_3+\nu_6$ band are negligible for the intensity wise.

Experimental

The sample was purchased from PCR Inc. of USA with the stated purity of 99% and used without further purification.

The spectra were measured with a 2500 mm focal length Littrow-McCubbin type instrument at the University of Tokyo,[1,4] in the 12th and 13th orders of a 31.6 lines/mm grating. An InSb detector was used at liquid nitrogen temperature. A White type long-path cell was used and its path length was kept 6 m. The sample pressure was *ca.* 45 mmHg and the resolving power was better than 0.06 cm^{-1}.

The frequencies of the observed lines were calibrated against the standard lines of CO.[5] In the region where the CO lines overlap with CH_3F lines, the suitable lines of $D^{35}Cl$ and $D^{37}Cl$ were used as the secondary standard, the frequencies of which had been calibrated against the CO lines. The standard deviation of the fitted lines was 0.007 cm^{-1} and, therefore, the accuracy of the observed lines was believed to be better than $\pm$0.01 cm^{-1}.

Spectral Features and Assignment of the Observed Bands

The rapidly scanned spectra ($\Delta\nu\simeq$0.10 cm^{-1}) of P- and R-branch sides are shown in Figs. 1 and 2, the 12th and 13th orders of grating being used respectively. Since each Q-branch is resolved into its J-components, the Q-branches cannot be distinguished from P- and R-branches. Near the band center, however, the Q-branches appear fairly clearly, because there is no overlapping with the strong ^RR- and ^PP-branches. Many of the P- and R-branch lines in the subbands are seen to be resolved into the individual components. Furthermore, the spectrum of R-branch side shows the clear series of the ^RR-branches which begin by about 2270 and 2291 cm^{-1}, while no obvious series are found in the P-branch side.

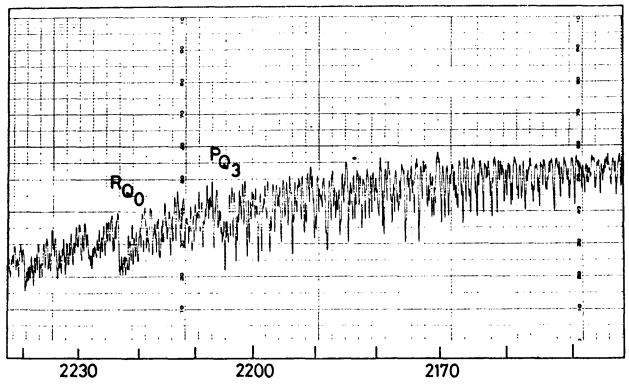

Fig. 1. The rapid scan spectrum of the $\nu_3+\nu_6$ band of CH_3F. P-branch side. Grating order=12th. Path length=6 m. Pressure=45 mmHg. Resolution= 0.10 cm^{-1}.

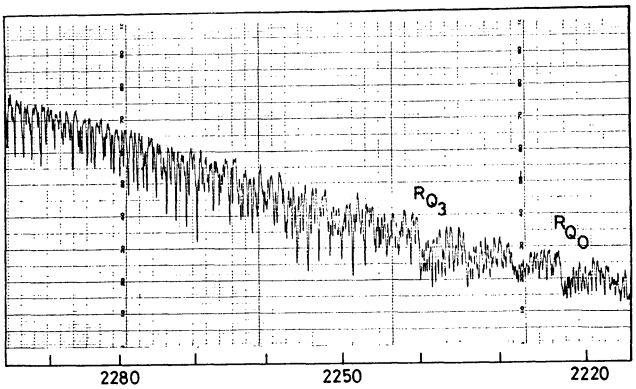

Fig. 2. The rapid scan spectrum of the $\nu_3+\nu_6$ band of CH_3F. R-branch side. Grating order=13th. Path length=6 m. Pressure=45 mmHg. Resolution= 0.10 cm^{-1}.

Although the assignment of the observed lines is complicated by the fact that the Q-branches are resolved into its J-components, we can assign the lines by the following way.

(1) Since no strong ^{R}R-branch and ^{P}P-branch lines occur near the band center, the most prominent Q-branch line can be assigned to the $^{R}Q_0$. (2) The lines of the $^{R}Q_1$, $^{R}Q_2$, $^{R}Q_3$, $^{P}Q_1$, $^{P}Q_2$, and $^{P}Q_3$ branches are easily identified, because they show usual intensity alternation due to the three fold symmetry. The J-components of each Q-branch are determined graphically. (3) ^{R}R-branches are assigned in consideration of the statistical weights and the missing lines ($J \geqq K$).

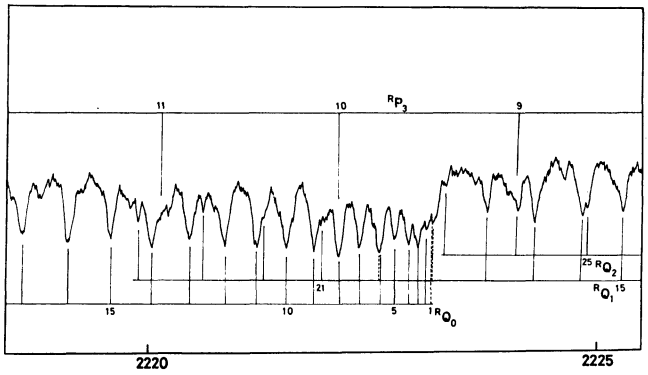

Fig. 3. The band center of the $\nu_3+\nu_6$ band. The $^{R}Q_0$-branch is mainly seen. Resolution=0.06 cm^{-1}.

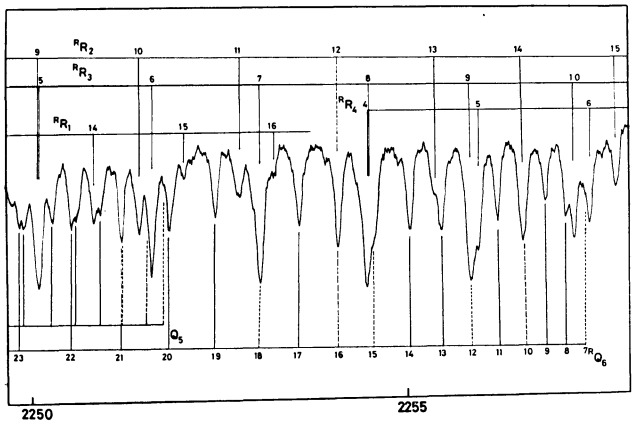

Fig. 4. The $^{P}Q_6$-branch of the $\nu_3+\nu_6$ band. Unassigned stronger bands are mainly from $^{P}P_1$- and $^{P}P_2$-branches.

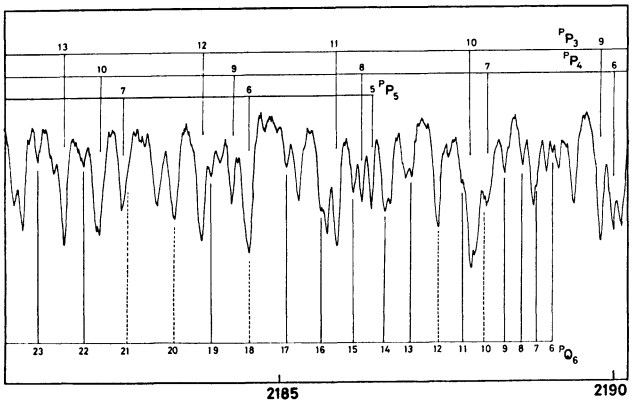

Fig. 5. The $^{R}Q_6$-branch of the $\nu_3+\nu_6$ band.

(4) The assignments of the ^{P}P-branches are made by the use of the parameters obtained from the analysis of the ^{R}R-branches and from the microwave study.[6] A few of the ^{R}P- and ^{P}R-branches are observed.

In Fig. 3 the spectrum of $^{R}Q_0$ branch is shown with the assignment of several lines. The spectra near the $^{P}Q_6$- and $^{R}Q_6$-branches are shown in Figs. 4 and 5, respectively; the P-branch side is more complex and less intense.

Determination of the Molecular Constants

The vibration-rotation energy of a symmetric top in an E-vibrational state can be written in the form

$$\begin{aligned} T_{v,l}(J,k) = {} & G(v,l) + B_v J(J+1) + (A_v - B_v)k^2 \\ & - 2A_v\zeta_v kl - D_J{}^v[J(J+1)]^2 \\ & - D_{JK}^v J(J+1)k^2 - D_K{}^v \cdot k^4 \\ & + \eta_J{}^v J(J+1)kl + \mu_K{}^v k^3 l, \end{aligned} \tag{1}$$

where $G(v,l)$ is the vibrational energy, A_v and B_v are the rotational constants, and $D_J{}^v$, $D_{JK}{}^v$, $D_K{}^v$, $\eta_J{}^v$, and $\eta_K{}^v$ are the centrifugal distorsion constants and ζ_v is Coriolis coupling constant.

From the selection rules for a perpendicular band ($\Delta k=+1$, $\Delta l=+1$, and $\Delta J=0, \pm 1$, or $\Delta k=-1$, $\Delta l=-1$, and $\Delta J=0, \pm 1$), the transition frequencies can be calculated as the differences between the energy levels of the upper and lower states. Some of the parameters, however, cannot be determined from the analysis of this band alone. The A'' value is obtained from the ζ-sum rule,[2] the D_k'' value is calculated from the harmonic force field,[7] and the D_{JK}'' value is obtained by the microwave study.[6] The molecular constants which are obtained from the least-squares method are listed in Table 1 together with the microwave values. A part of the observed frequencies are listed in Table 2 with their assignments and the calculated frequencies.[8] The lines which are not fully resolved are given zero or smaller weights.

Table 1. Molecular constants obtained from $\nu_3+\nu_6$ band of CH_3F (cm^{-1} except ζ)

	$\nu_3+\nu_6$ Present work	Ground state	
		Present work	Winton[6]
ν_0	2221.705 (12)[a]		
A	5.0879 (2)	5.081[b]	
B	0.83657 (13)	0.85170 (12)	0.851794
α^A	−0.0069 (2)		
α^B	0.01513 (3)		
ζ	0.274 (1)		
D_J	1.84×10^{-6} (15)	1.91×10^{-6} (14)	1.997×10^{-6}
D_{JK}	1.76×10^{-5} (2)	1.47×10^{-5}[b]	1.47×10^{-5}
D_K	7.9×10^{-5} (1)	8.0×10^{-5}[b]	
η_J	3.4×10^{-5} (2)		
η_K	1.3×10^{-4} (1)		

a) The numbers in parentheses represent twice of the standard errors to be attached to the last significant figures. b) Assumed.

TABLE 2. ^{R}R-BRANCH OF THE $\nu_3+\nu_6$ BAND OF CH_3F (cm^{-1})

$J\backslash K$	1		2		3		4	
	Obsd	$\Delta\nu$	Obsd	$\Delta\nu$	Obsd	$\Delta\nu$	Obsd	$\Delta\nu$
1	2232.178[a]	−40						
2	2233.829	−2	2239.642[a]	34				
3	2235.404	−9	2241.203	13	2247.014	5		
4	2236.958	−7	2242.746	4	2248.577	17	2254.432	13
5	2238.506	20	2244.272	9	2250.080	−1	2255.920	−19
6	2239.987	10	2245.748	−6	2251.579	8	2257.423	−6
7	2241.442	5	2247.210	−4	2253.011	−20	2258.875	−13
8	2242.860	−7	2248.677[a]	34	2254.432	−28	2260.299	−18
9	2244.272	5	2250.080[a]	37	2255.840	−19	2261.719	4
10	2245.652	17	2251.416	5	2257.205	−22	2263.088	6

$\Delta\nu$: (Obsd−Calcd) × 1000 cm^{-1}. a) blended lines, weight zero.

x,y-Type Coriolis Interaction

As mentioned earlier, the $\nu_3+\nu_6$ band has Coriolis interaction with $2\nu_3$, $(2\nu_6)^0$ and $(2\nu_6)^2$ bands. In this section, the influence of this interaction to the $\nu_3+\nu_6$ band will be discussed.

Since the selection rules for this type of interaction is $\Delta J=0$, $\Delta k=+1$, and $\Delta l=+1$ or $\Delta J=0$, $\Delta k=-1$, and $\Delta l=-1$, the analyses of the $2\nu_3$ and $\nu_3+\nu_6$ bands show that the levels which interact with each other are closest at $k=26$ or 27 and the effects are hardly observed for the levels of relatively small k values. In this work, assignment can be done to the $k=12$ lines for R-branch and the $k=10$ lines for P-branch. If there is any strong local interaction, the effect will be seen as the difference of the effective rotational constant $B'_{\rm eff}$ for each subband. In Fig. 6, the $B'_{\rm eff}$ values are plotted against the upper state quantum numbers $k'l'$. These $B'_{\rm eff}$ values agree each other within the experimental errors and no systematic variations are found. This means the interaction does not affect any particular rotational levels strongly, but the contribution of the interaction will be included as a whole in the parameters of Eq. (1).

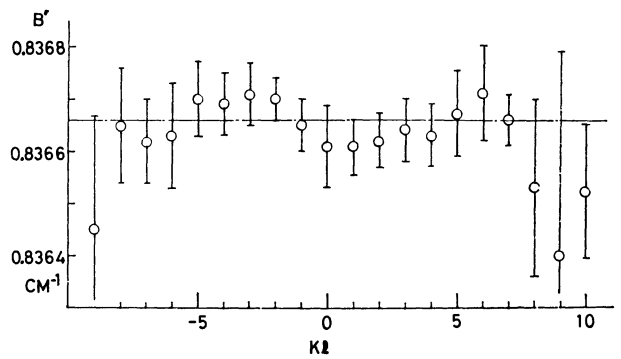

Fig. 6. The effective rotational constants plotted against the upper state quantum number $k'l'$.

The influence to the intensity is qualitatively shown in the fact that the R-branch structure is much simpler than that of the P-branch and the series of lines can be seen more clearly in the R-branch. The maximum J-values which we can assign are about 35 for the P-branch and 25 for the R-branch. For Q-branches, the ^{R}Q-branch is stronger than the ^{P}Q-branch. If the influence of the x,y-type Coriolis interaction is only seen as the anomaly of the intensity, the contribution from the weak $2\nu_6$ band can safely be neglected. Then we consider only the interaction between the $2\nu_3$ and $\nu_3+\nu_6$ bands.

The calculation of the intensity perturbation was given by di Lauro and Mills[3] in detail, the Hamiltonian matrix of this interaction can be written as

$$\begin{array}{lll} |1,1^{+1};J,k+1\rangle & |2,0;J,k\rangle & |1,1^{-1};J,k-1\rangle \\ \begin{bmatrix} \nu_{36}+F'(J,k,l) & +2B_e\Omega\zeta^{y}_{36}f(J,k) & 0 \\ & \nu_{33}+F''(J,k) & -2B_e\Omega\zeta^{y}_{36}f(J,k-1) \\ \text{(Hermitian)} & & \nu_{36}+F'(J,k-1,-l) \end{bmatrix} \end{array} \quad (2)$$

where ν_{36} and ν_{33} denote the vibrational energies of the $\nu_3+\nu_6$ and $2\nu_3$ levels, respectively. $F'(J,k,l)$ and $F''(J,k)$ are the rotational energy levels $T_{v,l}(J,k)-G(v,l)$ in Eq. (1),

$$\Omega = \frac{1}{2}[(\omega_3/\omega_6)^{1/2}+(\omega_6/\omega_3)^{1/2}]$$

and $$f(J,k) = [J(J+1)-k(k+1)]^{1/2} \quad (3)$$

Perturbed energy can be obtained by diagonalizing the Hamiltonian matrix (2). Perturbed line intensities depend upon the mixing of the wave functions and the vibrational transition moments of these two bands, M_{33} and M_{36}. According to the calculations of di Lauro and Mills,[3] the enhancement or the depletion of the particular line intensity depends upon the sign of the product of $M_{33}\times M_{36}\times\zeta^{y}_{36}$. If this sign is positive, ^{P}P-, ^{R}P-, and ^{R}Q-branches of $\nu_3+\nu_6$ band are enhanced and ^{R}R-, ^{P}R-, and ^{R}Q-branches are depleted. This is called as 'positive' perturbation. The situation is reversed when the sign of the above product is negative.

If the unperturbed energy of the interaction levels, the intensity ratio M_{33}/M_{36}, and the Coriolis coupling constant, ζ^{y}_{36} are known, the theoretical spectrum can be calculated. A computer program for x,y-Coriolis interaction is written in Fortran IV for a HITAC 8800/8700 system in the University of Tokyo, and simulated spectra may be obtained with the aid of a Calcomp x,y-plotter. This program is used to judge whether the perturbation is 'positive' or 'negative'.

Discussion

The analysis of the ν_6 fundamental band[2] gave the Coriolis coupling constant ζ_6^z as 0.284, which agrees fairly well with our present result, 0.274. The vibration-rotation constants for this band are given as $(B_0-B_{36})=0.0151$ and $(A_0-A_{36})=-0.0069$ cm^{-1}. From the preceding analyses, the vibration-rotation constants of the fundamental bands have been obtained as $\alpha_3^B=0.01134$,[2] $\alpha_6^B=0.0043$,[2] $\alpha_3^A=0.00977$,[1] and $\alpha_6^A=-0.013$ cm^{-1}.[2] From these constants, the rotational constants of $\nu_3+\nu_6$ band are expected to be $(B_0-B_{36})=0.0156$ and $(A_0-A_{36})=-0.0033$ cm^{-1}. The constant for B agrees well with the observed value, while for A the agreement is poor. This is almost certainly due to the rather large experimental error of the α_6^A constant, since the unresolved ^{P}P-branches and the ambiguities of the J-values of Q-branch maxima make the subband origins of the ν_6 band uncertain. We believe that the value of the $2\nu_3$ and $\nu_3+\nu_6$ bands is more reliable. Since the ^{R}R-branches were fully resolved, the α_6^B value was obtained with smaller experimental errors.

Table 3. 'Corrected' molecular constants of $2\nu_3$ and $\nu_3+\nu_6$ bands of CH_3F (in cm^{-1} except ζ)

	$2\nu_3$ band	$\nu_3+\nu_6$ band	Ground state[6]
ν_0	2081.382	2221.705	
A	5.06170	5.08779	5.081[b]
B	0.83553	0.83369	0.851794
D_J	1.96×10^{-6}	1.82×10^{-6}	1.997×10^{-6}
D_{JK}	1.0×10^{-5}	2.26×10^{-5}	1.47×10^{-5}
D_K	8.2×10^{-5}	7.91×10^{-5}	8.0×10^{-5} [a]
ζ		0.274	
η_J		1.34×10^{-4}	
η_K		1.0×10^{-5}	
	$\lvert\zeta_{36}^y\rvert=0.38$[a]		
	$[M_{36}/M_{33}]^2=0.05$.[b]		

a) Calculated from the Harmonic force field.[7]
b) Assumed.

Since the vibration-rotation levels of both the $2\nu_3$ and $\nu_3+\nu_6$ bands are known, we can estimate the rotational and centrifugal distortion constants corrected for the perturbation between these two levels. If the value of $|\zeta_{36}^y|$ is fixed to 0.38 which has been obtained from the harmonic force field in Ref. 7, we obtain the 'corrected' constants listed in Table 3. Recently Betrencourt[9] reported the analysis of the $2\nu_3$ band which is consistent with our previous results (I). He also gave the unperturbed constants for the $2\nu_3$ level which are slightly different from ours. The differences arise mainly from the fact that somewhat different values are used for the energy levels of the $\nu_3+\nu_6$ band and for ζ_{36}^y.

If the ratio of the transition moments, M_{36}/M_{33}, is further assumed, the simulated spectra can be drawn by the program mentioned earlier. In Fig. 7, the calculated spectra are shown for the cases of the positive and negative perturbations. From the comparison with the observed spectrum, the Coriolis perturbation between the $2\nu_3$ and $\nu_3+\nu_6$ bands is concluded to be 'positive'.

So far we have ignored the effect of the $(2\nu_6)^0$ or $(2\nu_6)^2$ band. The consideration of these two bands would hardly affect the spectroscopic constants in the $2\nu_3$ band from which they are apart by about 280 cm^{-1}, but the effect may be significant on the $\nu_3+\nu_6$ band. It was shown[3] that the x,y-Coriolis interaction affects in different way on the $^RQ_0$-branch, on $^RR_0$- and $^RP_0$-branches, and on the remaining other branches, and that there are three effective rotational constants B'_{eff}. In our measurement, the effective rotational constant which is obtained from $^RQ_0$-branch is 0.83672 ± 0.00007 and the constant obtained from $^RR_0$- and $^RP_0$-branches is 0.83661 ± 0.00005, while the constant obtained from the remaining branches is 0.83667 ± 0.00002 cm^{-1}. In these calculations, the ground state constants are fixed to the microwave values, and for the calculation of $^RQ_0$- and $^RR,P_0$-branches, the upper state constants except B' and D_J' are assumed to be the same as the values obtained from

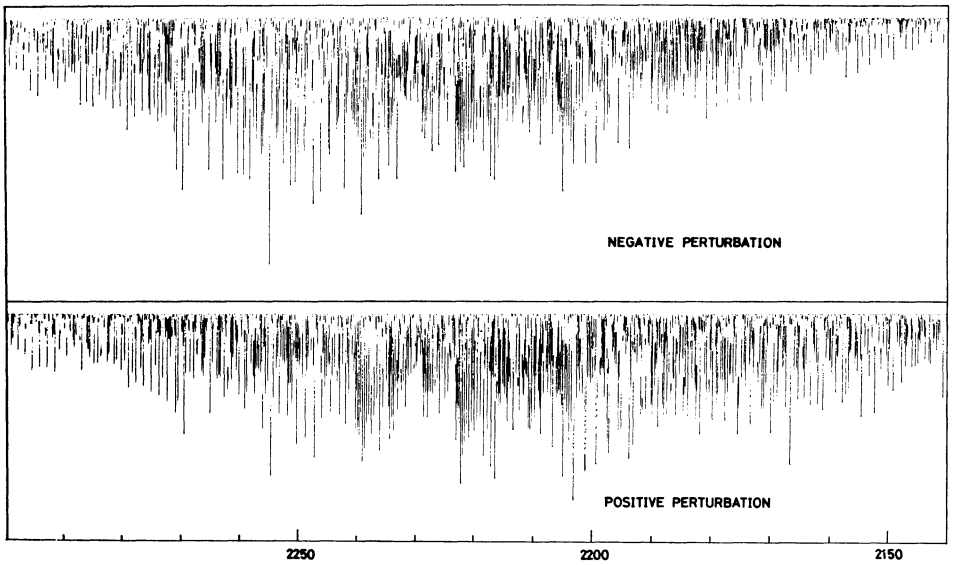

Fig. 7. Simulated spectra of the $\nu_3+\nu_6$ band.

all the other data.

If we consider the four way Coriolis interaction among the $2\nu_3$, $\nu_3+\nu_6$, $(2\nu_6)^0$, and $(2\nu_6)^2$ bands as well as the l-type doubling, the effective rotational constants of the $\nu_3+\nu_6$ band are given as

$$B'_{\text{eff}} = B'_{\text{unp}} - 4B_e^2\zeta^2\Omega^2/\Delta E'' - q/2 \quad (\text{for } {}^{R}Q_0\text{-branch}) \tag{4}$$

$$B'_{\text{eff}} = B'_{\text{unp}} + 8B_e^2\zeta^2\Omega^2/\Delta E - 4B_e^2\zeta^2\Omega^2/\Delta E' - 4B_e^2\zeta^2\Omega^2/\Delta E'' + q/2 \quad (\text{for } {}^{R}R,P_0\text{-branches}) \tag{5}$$

$$B'_{\text{eff}} = B'_{\text{unp}} + 4B_e^2\zeta^2\Omega^2/\Delta E - 2B_e^2\zeta^2\Omega^2/\Delta E' - 4B_e^2\zeta^2\Omega^2/\Delta E'' \quad (\text{for other branches}) \tag{6}$$

where $\Delta E=(\nu_3+\nu_6)-2\nu_3$, $\Delta E'=(2\nu_6)^0-(\nu_3+\nu_6)$, $\Delta E''=(2\nu_6)^2-(\nu_3+\nu_6)$, and q denotes the l-type doubling constant. The above equations are further reduced, if we assume $\Delta E=\Delta E'=\Delta E''$.

$$B'_{\text{eff}} = B'_{\text{unp}} - 4B_e^2\zeta^2\Omega^2/\Delta E - q/2 \quad (\text{for } {}^{R}Q_0\text{-branch}) \tag{7}$$

$$B'_{\text{eff}} = B'_{\text{unp}} + q/2 \quad (\text{for } {}^{R}R,P_0\text{-branches}) \tag{8}$$

$$B'_{\text{eff}} = B'_{\text{unp}} - 2B_e^2\zeta^2\Omega^2/\Delta E \quad (\text{for other branches}) \tag{9}$$

It is interesting to note that B'_{eff} for the ${}^{R}R_0$- and ${}^{R}P_0$-branches is *unperturbed* in contrast to the case of the two way Coriolis interaction originally treated by di Lauro and Mills.[3] If we use $|\zeta_{35}^{y}|=0.38$, $B_e=0.8518\ \text{cm}^{-1}$, and $\Delta E=140\ \text{cm}^{-1}$, these corrections are calculated as -0.00298, 0, and $-0.00149\ \text{cm}^{-1}$ for the above three kinds of branches. From the experimental value, l-type doubling constant can be roughly estimated as $-0.003\ \text{cm}^{-1}$.

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