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The Microwave Spectrum of Methyl Iodide in Excited Vibrational States. Fermi and Coriolis Interactions among v_3+v_6, v_5, and v_2 Vibrations

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The $J=2\leftarrow 1$ transitions of methyl iodide in the v_3, v_6, $2v_3$, v_2, v_3+v_6, and v_5 vibrationally-excited states are observed. In v_3+v_6, the central component, $\nu_{36}{}^0$, of the $J=2\leftarrow 1$, $K=1\leftarrow 1$ transition is observed at 14.6 MHz, higher than the $\nu_{36}{}^+$ of the l-type doubling. This is interpreted by the fact that the E state with $K=-l=\pm 1$ is affected more strongly by the Fermi resonance through k_{356} than is the A state with $K=l=\pm 1$. The Fermi resonance through k_{356} causes the Coriolis coupling between v_2 and v_5 through $\zeta_{25}^{(y)}$ to be transferred to v_3+v_6. As a result, the l-type doubling constant, q_6, is determined to be -5.8 MHz. The Stark effect in the presence of the l-type doubling and nuclear quadrupole splitting is formulated and used in the analysis.

The vibration-rotation bands of CH_3I were studied by Jones and Thompson, who determined the vibration-rotation constants, $\alpha_v{}^B$, for several vibrational modes.[1] Further studies by Morino *et al.* by infrared[2] and microwave spectroscopy[3] made clear that the Fermi resonance was present through k_{356} between the v_3+v_6 and v_5 states. According to a recent study of the vibration-rotation spectra by Matsuura *et al.*,[4] the Coriolis interactions through $\zeta_{25}^{(y)}$ and a higher-order term $\xi_{356}^{(y)}$ should also be taken into account to make the infrared and microwave spectra consistent with each other. With their results at hand, the $J=2\leftarrow 1$ microwave transitions have been observed in the present study, and the effect of the Fermi resonance on the l-type doubling has been analyzed. Buckingham and Stephens analyzed the Stark effect of CH_3I by taking into account cross-product terms between the molecular Stark effect, H_E, and the electric quadrupole coupling, H_Q, of the iodine atom as H_EH_Q and $H_E{}^2H_Q$ in order to get a more accurate dipole moment.[5] Their formulation has been extended in the present study to include the effect of the l-type doubling used in the assignment of the spectra.

Experimental

The sample of CH_3I was distilled before use. The microwave spectrometer used was of a conventional 100-kHz Stark-modulation type. The absorption cell was made of an X-band waveguide 3 m long. In order to increase the intensities for higher vibrational levels, the absorption cell was heated to about 60—80 °C. The $J=2\leftarrow 1$ transitions were observed with an Oki 30V10 klystron.

Assignment of the Spectra

The Stark effect of the $J=2\leftarrow 1$ and $K=1\leftarrow 1$ transitions is of the first order, whereas that of the $J=2\leftarrow 1$ and $K=0\leftarrow 0$ transitions is of the second order. The $K=1\leftarrow 1$ transitions were observed at the relatively low Stark field of about 15 V/cm.

The observed transition frequencies of the lines for v_3, v_6, $2v_3$, and v_2 coincided with those predicted from the constants obtained from the measurement of the $J=1\leftarrow 0$ transitions.[3] The satellite lines which appeared equally spaced at the upper- and lower-frequency sides of the v_6 spectra, $\nu_6{}^0$, were identified as the $\nu_6{}^+$ and $\nu_6{}^-$ components of the l-type doubling. The $\nu_v{}^+$ and $\nu_v{}^-$ notations refer, respectively, to the transitions between the upper and lower levels of the l-type doubling, *i.e.*, the transitions between the levels with $K=l=\pm 1$, the A symmetry, and $\nu_v{}^0$ corresponds to the transition between the levels with $K=-l=\pm 1$, the E symmetry.

The spectra for v_5 and v_3+v_6 were assigned by the use of their Stark effects. The Stark effects of the $\nu_v{}^+$ and $\nu_v{}^-$ lines are different from that of the $\nu_v{}^0$ line because a nonvanishing matrix element of the Stark effect is present between the l-type doublets. The Stark effect in the presence of both nuclear quadrupole coupling and l-type doubling has been formulated; it will be described in the Appendix. The calculated Stark effects for the $F=7/2\leftarrow 5/2$, $J=2\leftarrow 1$, and $K=1\leftarrow 1$ transitions are shown in Figs. 1a and 2a. The observed Stark effects of the candidate lines, which were not resolved into M_F components, are shown in Figs. 3 and 4. To make a better comparison between the observed and calculated Stark patterns, the line shape of the merged spectrum was calculated on the assumption of the Lorentzian line shapes, with the half-width at the half-height of $\Delta\nu=0.5$ MHz. The peak frequencies of the resultant curves at various strengths of the Stark field are plotted in Figs. 1b and 2b for the transitions in v_6 and v_3+v_6 respectively. The value of 0.5 MHz for $\Delta\nu$ was estimated from the zero-field line width of the square-wave modulated spectra. From Figs. 1b and 3, $\nu_6{}^-$, $\nu_6{}^0$, and $\nu_6{}^+$ were assigned to the lines appearing from the lower to higher frequencies. A similar comparison of Figs. 2b and 4 established that $\nu_{36}{}^0$ was observed at a frequency higher than $\nu_{36}{}^+$. The $\nu_5{}^0$ was not observed for some unknown reason, but $\nu_5{}^+$ and $\nu_5{}^-$ were assigned on similar grounds.

The observed frequencies for v_3, $2v_3$, and v_2 are summarized in Table 1. The deviations were calculated by means of the rotational constant and eQq, which were derived from the least-squares fitting of the ob-

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[1] E. W. Jones and H. W. Thompson, *Proc. Roy. Soc. Ser. A*, **288**, 50 (1965).

[2] Y. Morino, J. Nakamura, and S. Yamamoto, *J. Mol. Spectrosc.*, **22**, 34 (1967).

[3] Y. Morino and C. Hirose, *ibid.*, **22**, 99 (1967).

[4] H. Matsuura, T. Nakagawa, and J. Overend, *J. Chem. Phys.*, **59**, 1449 (1973).

[5] A. D. Buckingham and P. J. Stephens, *Mol. Phys.*, **7**, 481 (1964).

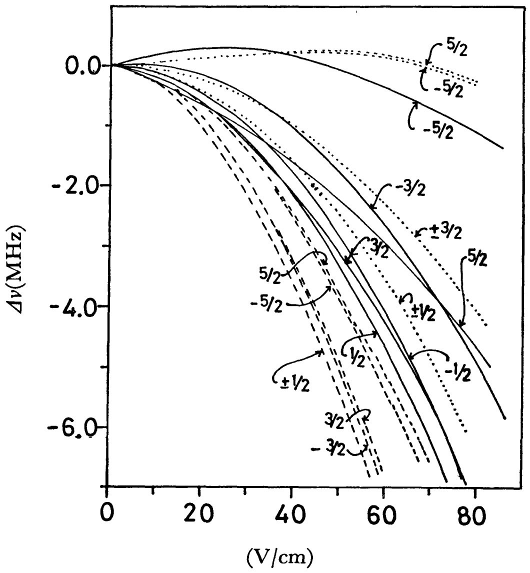

Fig. 1a. Calculated Stark shifts of ν_6^+, ν_6^0, and ν_6^- lines; J=2←1, F=7/2←5/2, K=1←1. M_F values are shown in the figure. Relative intensities of M_F components are 3 : 5 : 6 for M_F=5/2 : 3/2 : 1/2. Broken, solid, and dotted lines indicate the M_F components of ν_6^+, ν_6^0, and ν_6^-.

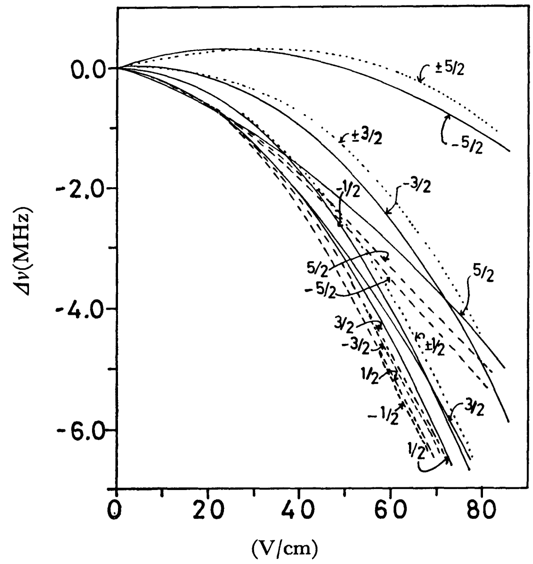

Fig. 2a. Calculated Stark shifts of ν_{36}^+, ν_{36}^0, and ν_{36}^- lines; J=2←1, F=7/2←5/2, K=1←1. The relative intensities of M_F structures are 3 : 5 : 6 for M_F=5/2 : 3/2 : 1/2. Broken, solid, and dotted lines indicate the M_F components of ν_{36}^+, ν_{36}^0, and ν_{36}^-.

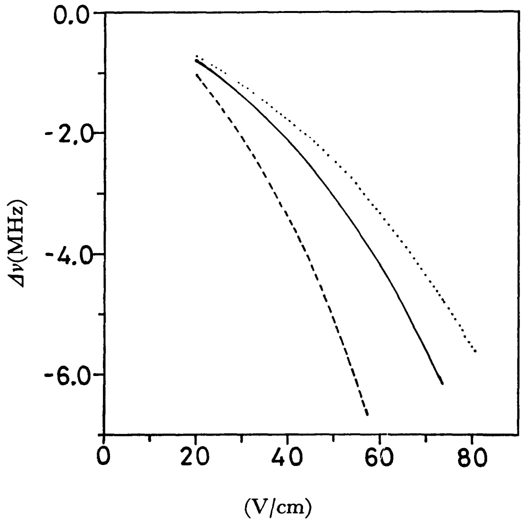

Fig. 1b. Calculated peak frequency *vs.* the Stark field.

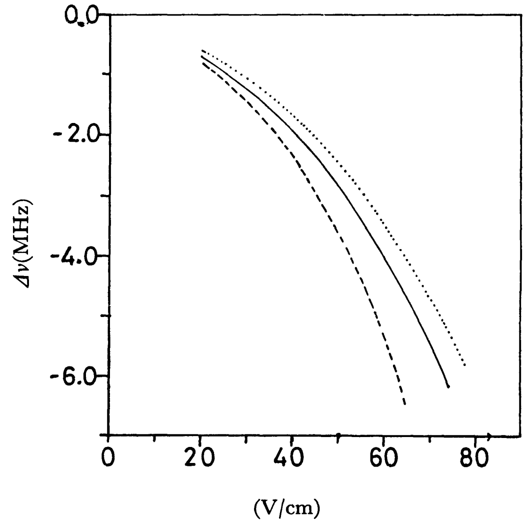

Fig. 2b. Calculated peak frequency *vs.* Stark field.

served frequencies of the J=2←1 and K=±1,0 transitions for v_3, $2v_3$, and v_2. The second-order correction on eQq was made by the procedure Gordy *et al.*[6] used in their analysis of the rotational spectra of the ground vibrational state of CH_3I. Table 2 lists the vibration-rotation constants, defined as $\alpha_v = B_0 - B_v$, and eQq.

The transitions, ν_v^+, ν_v^-, or ν_v^0, listed in Table 3 were analyzed in terms of the effective rotational constants, B_v^+, B_v^-, and B_v^0, and in terms of eQq separately from the other set; the differences in the effective rotational constants, $B_v^+ - B_v^-$, were taken as $|q_v|$. They are listed in Table 4.

Kuczkowski showed that, for CD_3I[7], the effects of asymmetry in eQq, which is induced by the degenerate vibrations on transition frequencies, were not more than 0.7 MHz. Therefore, these effects were neglected in the present study.

Discussion

Table II shows that the values of α_v^B are in good agreement with those obtained from the J=1←0 transitions[3] and infrared spectroscopy.[1,4,8] From this it is clear that there is no significant perturbation working on these vibrational states. However, v_2 is perturbed by the $\zeta_{25}^{(y)}$ Coriolis coupling, as will be discussed below.

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[6] W. Gordy, J. W. Simmons, and A. G. Smith, *Phys. Rev.*, **74**, 243 (1948).

[7] R. L. Kuczkowski, *J. Mol. Spectrosc.*, **45**, 261 (1973).

[8] H. Matsuura and J. Overend, *J. Chem. Phys.*, **56**, 5725 (1972).

TABLE 1. OBSERVED FREQUENCIES AND THEIR DEVIATIONS FROM THE CALCULATED VALUES OF THE $J=2\leftarrow1$ TRANSITIONS (in MHz)

v_3 state	K	$F'\leftarrow F$		$\nu_{\rm obsd}^{\rm a)}$	$\Delta\nu^{\rm b)}$
	0	3/2	3/2	29654.75*	−0.09
	0	5/2	3/2	29380.85*	−0.25
	0	3/2	5/2	30235.71*	−0.19
	0	5/2	5/2	29962.05*	−0.11
	0	7/2	5/2	29862.07*	0.02
	0	5/2	7/2	29556.76*	0.39
	0	7/2	7/2	29456.49*	0.23
	1	3/2	3/2	29999.23*	0.44
	1	5/2	3/2	29858.0	0.21
	1	3/2	5/2	29705.90*	−0.44
	1	5/2	5/2	29564.90*	−0.44
	1	7/2	5/2	29518.45*	0.15
	1	5/2	7/2	29769.72*	0.02
	1	7/2	7/2	29723.0	0.34
	1	9/2	7/2	29905.98*	−0.27
$2v_3$ statc	K	$F'\leftarrow F$		$\nu_{\rm obsd}^{\rm a)}$	$\Delta\nu^{\rm b)}$
	0	3/2	3/2	29437.2	0.30
	0	5/2	3/2	29163.7	0.55
	0	7/2	5/2	29644.48*	0.34
	0	7/2	7/2	29238.3	0.00
	0	9/2	7/2	29611.97*	0.58
	1	3/2	5/2	29488.3	−0.14
	1	5/2	5/2	29347.0	−0.40
	1	7/2	5/2	29300.0	−0.37
	1	5/2	7/2	29551.0	−0.80
	1	7/2	7/2	29504.7	−0.06
v_2 state	K	$F'\leftarrow F$		$\nu_{\rm obsd}^{\rm a)}$	$\Delta\nu^{\rm b)}$
	0	5/2	3/2	29433.6	0.24
	0	3/2	5/2	30290.2	0.08
	0	5/2	5/2	30016.31*	0.56
	0	7/2	7/2	29509.0	0.31
	1	1/2	3/2	30173.6	−0.20
	1	3/2	3/2	30052.2	−0.26
	1	3/2	5/2	29759.4	0.06
	1	5/2	5/2	29617.8	−0.22
	1	7/2	5/2	29570.42*	−0.45
	1	7/2	7/2	29775.5	−0.20
	1	9/2	7/2	29959.8	0.08

a) Estimated error limits are ±0.2 MHz and, for transitions with asterisk, ±0.1 MHz.
b) $\Delta\nu=\nu_{\rm obsd}-\nu_{\rm calcd}$.

TABLE 2. VIBRATION-ROTATION CONSTANTS AND *eQq* IN THE VIBRATIONALLY-EXCITED STATES OF CH_3I (in MHz)

	Present study		M. W. value[c)]	I. R. value[d)]
	$\alpha_{\rm V}^{\rm B}$ a)	eQq	$\alpha_{\rm V}^{\rm B}$	$\alpha_{\rm V}^{\rm B}$
v_3	54.42±0.04[b)]	−1934.3±0.7[b)]	54.2_8±0.1	54.8_6
$2v_3$	108.90±0.12	−1934.5±1.9	108.8_3±0.05	109.7_2
v_2	41.13±0.04	−1938.7±0.7	40.9_7±0.1	40.1_7

a) Vibration-rotation constants $\alpha_{\rm V}^{\rm B}$ is defined here as $\alpha_{\rm V}^{\rm B}=B_0-B_{\rm V}$, where $B_0=7501.25$ MHz.
b) 2.5 times variance. c) Reference 3. d) Reference 1.

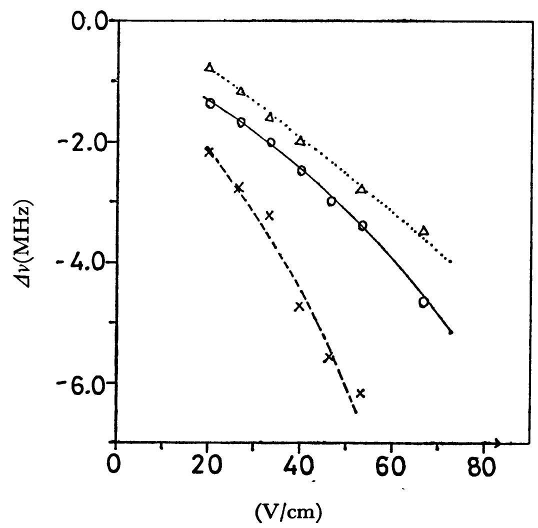

Fig. 3. Observed Stark shifts in v_6 state; $J=2\leftarrow1$, $F=7/2\leftarrow5/2$, $K=1\leftarrow1$. Points denoted as ×, ○, and △ indicate the observations for ν_6^+, ν_6^0, and ν_6^-, respectively.

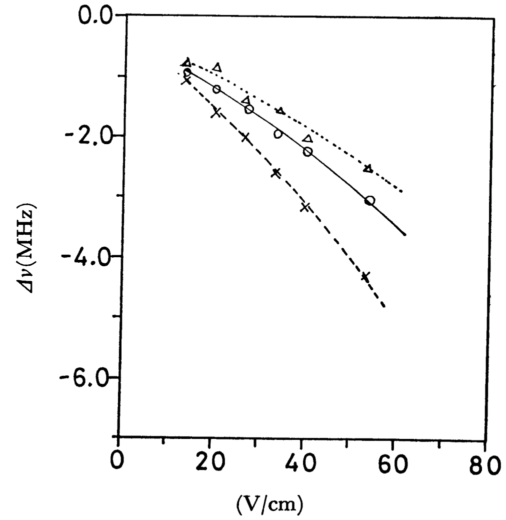

Fig. 4. Observed Stark shifts in the v_3+v_6 state; $J=2\leftarrow1$, $F=7/2\leftarrow5/2$, $K=1\leftarrow1$. Points denoted as ×, ○, and △ indicate the observations for ν_{36}^+, ν_{36}^0, and ν_{36}^-, respectively.

l-Type Doubling Affected by Coriolis Coupling. As has been pointed out by Morino and Hirose, who studied CH_3Br and CD_3Br,[9)] the rotational levels in v_5 are remarkably affected by the Coriolis coupling with v_2, while the effective rotational constants for v_2 are essentially unchanged.

The application of their formula to CH_3I indicates that the Coriolis coupling between v_2 and v_5 should be taken into account, but the higher-order interaction through $\xi_{356}^{(y)}$, which was reported by Matsuura *et al.*, was found to be negligible in the present case. Thus, the present problem is to solve the Fermi resonance through k_{356} and the Coriolis coupling through $\zeta_{25}^{(y)}$ as principal perturbers of the rotational levels in v_3+v_6, v_5, and v_2.

l-Type Doubling Affected by Fermi Resonance. The degenerate Coriolis coupling constant, $\zeta_5^{(z)}$, has a negative value, whereas $\zeta_6^{(z)}$, which should apply to

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9) Y. Morino and C. Hirose, *J. Mol. Spectrosc.*, **24**, 204 (1967).

TABLE 3. OBSERVED FREQUENCIES OF THE J=2←1 K=1←1 TRANSITIONS IN THE DEGENERATE VIBRATIONAL STATES (in MHz)

v_6 state F′←F		$\nu^{+\,a)}$	$\Delta\nu^{b)}$	$\nu^{0\,a)}$	$\Delta\nu^{b)}$	$\nu^{-\,a)}$	$\Delta\nu^{b)}$
1/2	3/2	30256.0	−0.16	30242.9	−0.11	30233.3	0.48
3/2	3/2	3.135.13*	0.47	—		30110.89*	−0.49
5/2	3/2	29993.22*	0.06	29980.3	0.24	29969.8	−0.15
3/2	5/2	29840.2	−0.96	29827.8	−0.30	29818.89*	0.87
5/2	5/2	29699.69*	0.02	—		29676.8	0.21
7/2	5/2	29652.95*	0.49	29639.49*	0.06	29629.47*	0.07
5/2	7/2	—		29891.8	0.12	29881.1	−0.48
7/2	7/2	—		29844.40*	−0.08	29833.6	−0.80
9/2	7/2	30041.88*	0.08	30028.76*	0.07	30018.85*	0.29

v_3+v_6 state F′←F		$\nu^{+\,a)}$	$\Delta\nu^{b)}$	$\nu^{0\,a)}$	$\Delta\nu^{b)}$	$\nu^{-\,a)}$	$\Delta\nu^{b)}$
1/2	3/2	—		—		30056.0	0.22
5/2	5/2	29512.0	0.10	29527.5	0.19	29500.4	0.03
7/2	5/2	29464.5	−0.08	29480.0	−0.17	29453.9	0.64
7/2	7/2	29670.2	−0.02	—		29656.8	−1.15
9/2	7/2	—		29869.0	−0.02	29842.1	0.27

v_5 state F′←F		$\nu^{+\,a)}$	$\Delta\nu^{b)}$	$\nu^{0\,a)}$	$\Delta\nu^{b)}$	$\nu^{-\,a)}$	$\Delta\nu^{b)}$
3/2	3/2	30233.3	0.48	—		30181.7	−0.91
5/2	5/2	29799.4	0.09	—		29749.0	−0.26
7/2	5/2	29752.3	0.05	—		—	
9/2	7/2	30139.7	−0.61	—		30091.3	1.17

a, b) See a, b) in Table 1.

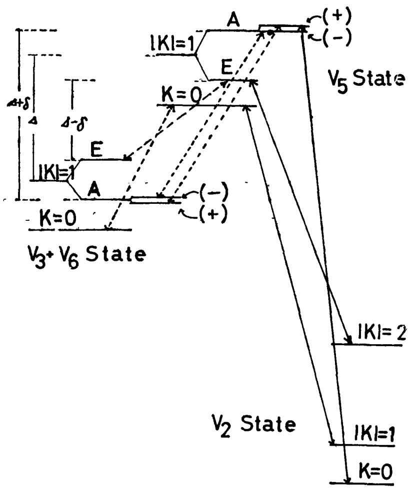

Fig. 5. Schematic interaction diagram of the Fermi resonance and Coriolis coupling among the rotational levels of v_2, v_3+v_6, and v_5. Broken lines indicate the levels interacting with each other by the Fermi resonance, and dotted lines indicate the levels coupled by the Coriolis interaction.

v_3+v_6, is positive.[1,4,10] The energy levels with $K\neq0$ are split by the degenerate Coriolis coupling into doublets with A and E symmetries by the separation of $-4A_vKl_v\zeta_v^{(z)}$; one of the levels with $K=l_v=\pm1$, which has the A symmetry, is further split by the l-type doubling. A schematic diagram is shown in Fig. 5. If we take Δ as the vibrational separation of the unperturbed levels, v_3+v_6 and v_5, the separation between the E levels ($K=\pm1$) is smaller than Δ by $-2\times(A_5^0\zeta_5^{(z)}-A_{36}^0\zeta_6^{(z)})+(A_5^0-A_{36}^0)$, while that between the A levels ($K=\pm1$) is larger by the same amount. Substituting the values of $A_5^0=5.127\ \mathrm{cm}^{-1}$, $A_{36}^0=5.2116\ \mathrm{cm}^{-1}$,

TABLE 4. EFFECTIVE ROTATIONAL CONSTANTS, eQq, AND l-TYPE DOUBLING CONSTANTS IN THE DEGENERATE VIBRATIONAL STATES OF CH_3I (in MHz)

		B_v(obsd)	eQq(obsd)	$\|q_v\|$(obsd)
v_6 state	ν^+	7480.61±0.12[a]	−1941.2±1.9[a]	5.80±0.20[a]
	ν^0	7477.34±0.05	−1940.8±0.8	
	ν^-	7474.81±0.12	−1940.3±2.0	
v_3+v_6 state	ν^+	7433.81±0.10	−1946.3±1.6	
	ν^0	7437.45±0.12	−1938.8±1.6	
	ν^-	7430.67±0.20	−1937.4±3.1	
v_5 state	ν^+	7505.34±0.15	−1934.7±2.6	12.5±0.6
	ν^-	7492.80±0.45	−1934.0±9.0	

a) 2.5 times variance.

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10) Y. Morino and J. Nakamura, This Bulletin **38**, 443 (1965).

$\zeta^{(z)}_5=-0.2444$, and $\zeta^{(z)}_6=0.2019$,[4] we get 4.611 cm^{-1} for $-2({}^{0}_{5}A\zeta^{(z)}_5-A^0_{36}\zeta^{(z)}_6)+(A^0_5-A^0_{36})$, which is as much as 20% of the vibrational difference, Δ, of about 24.0 cm^{-1}.

The basic formulas to be applied to the Fermi resonance in the present case were given in a preceding paper.[3] When the corrections for the above-mentioned term are included, we get the following equations for the effective (perturbed) rotational constants:

$$B_5(\mathrm{K}=0) = \{(1+\Delta/[\Delta^2+4W^2]^{1/2})B^0_5 + (1-\Delta/[\Delta^2+4W^2]^{1/2})B^0_{36}\}/2, \tag{1}$$

$$B_{36}(\mathrm{K}=0) = \{(1-\Delta/[\Delta^2+4W^2]^{1/2})B^0_5 + (1+\Delta/[\Delta^2+4W^2]^{1/2})B^0_{36}\}/2, \tag{2}$$

$$B_5(\mathrm{K}=1,\ \mathrm{E}) = [\{1+(\Delta-\delta)/[(\Delta-\delta)^2+4W^2]^{1/2}\}B^0_5 + \{1-(\Delta-\delta)/[(\Delta-\delta)^2+4W^2]^{1/2}\}B^0_{36}]/2, \tag{3}$$

$$B_{36}(\mathrm{K}=1,\ \mathrm{E}) = [\{1-(\Delta-\delta)/[(\Delta-\delta)^2+4W^2]^{1/2}\}B^0_5 + \{1+(\Delta-\delta)/[(\Delta-\delta)^2+4W^2]^{1/2}\}B^0_{36}]/2, \tag{4}$$

$$B^{\pm}_5(\mathrm{K}=1,\ \mathrm{A}) = [\{1+(\Delta+\delta)/[(\Delta+\delta)^2+4W^2]^{1/2}\}(B^0_5\pm q_5/2) + \{1-(\Delta+\delta)/[(\Delta+\delta)^2+4W^2]^{1/2}\} \times (B^0_{36}\pm q_6/2)]/2, \tag{5}$$

and

$$B^{\pm}_{36}(\mathrm{K}=1,\ \mathrm{A}) = [\{1-(\Delta+\delta)/[(\Delta+\delta)^2+4W^2]^{1/2}\} + (B^0_5\pm q_5/2) + \{1+(\Delta+\delta)/[(\Delta+\delta)^2+4W^2]^{1/2}\} \times (B^0_{36}\pm q_6/2)]/2, \tag{6}$$

where:

$$\Delta = v^0_5 - v^0_{36} + A^0_5(\zeta^{(z)}_5)^2 - A^0_{36}(\zeta^{(z)}_6)^2, \tag{7}$$

$$W = k_{356}/2\sqrt{2}, \tag{8}$$

$$\delta = -2(A^0_5\zeta^{(z)}_5 - A^0_{36}\zeta^{(z)}_6) + (A^0_5 - A^0_{36}), \tag{9}$$

where A^0_5, A^0_3, B^0_5, and B^0_{36} denote the rotational constants for the unperturbed v_5 and v_3+v_6 states respectively, and where q_5 and q_6 are the l-type doubling constants. The constants, $\zeta^{(z)}_{36}$ and q_{36}, are set equal to $\zeta^{(z)}_6$ and q_6 respectively in the above equations. Equations (1) and (2) are identical with Eqs. (2) and (3) of Ref. 3. Thus, the J=2←1 and K=0←0 transitions can be predicted from the results given in Ref. 3.

Using the results reported in Refs. 3 and 4, we get the values listed in Table 5. The results show that the central line, $\nu_{36}{}^0$, which gives B_{36}(K=1,E), is shifted up by 12.6 MHz from the K=0 line, in agreement with the predicted value. The $\nu_{36}{}^0$ frequency can exceed that of the $\nu_{36}{}^+$ line; the assignment we have given indicates that this is the case for CH_3I.

The analysis of the spectra in v_6 has given $|q_6|=$ 5.8 MHz (Table 4),[11] and q_5 can not be very different from the calculated value of 13.4 MHz.[12] Furthermore, the substitution of the above-mentioned values of q_6 and q_5 into Eq. (6) gives $B^+{}_{36}-B^-{}_{36}=3.9\pm0.2$ MHz, significantly different from the observed value, 3.1±0.2 MHz. This difference can be accounted for by taking account of both the Fermi resonance and the Coriolis coupling, as will be discussed below.

TABLE 5. EFFECTIVE ROTATIONAL CONSTANTS AND ENERGY DIFFERENCES[a]

$B_5(\mathrm{K}=0)$[a]	7498.10 MHz	$B_5(\mathrm{K}=1,\ \mathrm{E})$[a]	7495.01 MHz
$B_{36}(\mathrm{K}=0)$[a]	7433.88 MHz	$B_{36}(\mathrm{K}=1,\ \mathrm{E})$[a]	7436.96 MHz
$B_5\pm(\mathrm{K}=1,\ \mathrm{A})$[a]	$7500.34\pm\lvert 0.4515q_5+0.0485q_6\rvert$ MHz		
$B_{36}\pm(\mathrm{K}=1,\ \mathrm{A})$[a]	$7431.64\pm\lvert 0.0485q_5+0.4515q_6\rvert$ MHz		
Δ[b]	23.997 cm^{-1}	B^0_5[d]	7508.61 MHz
W[b]	10.470 cm^{-1}	B^0_{36}[d]	7423.37 MHz
δ[c]	4.522 cm^{-1}		

a) Rotational constants perturbed by the Fermi resonance through k_{356}. b) Ref. 4. c) $\delta=-2(A^0_5\zeta^{(z)}_5-A^0_{36}\zeta^{(z)}_6)+(A^0_5-A^0_{36})$. d) Ref. 3.

l-Types Doubling Affected by Both Fermi and Coriolis Interactions. The Fermi resonance causes the rotational levels in v_5 and v_3+v_6 to be mixed up considerably. Since the Coriolis coupling through $\zeta^{(y)}_{25}$ is expected to be significant, the two perturbations should be solved simultaneously in order to make a more complete analysis of the spectra.

One of the two levels of the (K=1,A) state, designated as (−) in Ref. 9, is not coupled by the Coriolis interaction to any rotational level of v_2, while the (+) state is coupled to the (J,K=0) level of v_2 through $\zeta^{(y)}_{25}$ (see case I(a) of Ref. 9). The present case can be reduced to two problems. One is for the (−) state, where only the Fermi resonance is present, and the secular equation is expressed by:

$$\begin{vmatrix} E_1-\lambda & W \\ W & E_2-\lambda \end{vmatrix} = 0 \tag{10}$$

where

$$E_1 = v^0_3 + v^0_6 + B^0_{36}\mathrm{J}(\mathrm{J}+1) + A^0_{36} - B^0_{36} - 2A^0_{36}\zeta^{(z)}_6 - q_6\mathrm{J}(\mathrm{J}+1)/2 + A^0_{36}(\zeta^{(z)}_6)^2,$$

$$E_2 = v^0_5 + B^0_5\mathrm{J}(\mathrm{J}+1) + A^0_5 - B^0_5 - 2A^0_5\zeta^{(z)}_5 - q_5{}^*\mathrm{J}(\mathrm{J}+1)/2 + A^0_5(\zeta^{(z)}_5)^2,$$

$$W = k_{356}/2\sqrt{2}$$

and $q_5{}^*$ is the unperturbed l-type doubling constant for the v_5 state, −0.66 MHz.[4] The other is for the (+) state, (K=1,E), and K=0, where the Fermi resonance between v_5 and v_3+v_6 and the Coriolis coupling between v_5 and v_2 have to be taken into account simultaneously; the secular equation to be solved is expressed by Eq. (11)[13]:

$$\begin{vmatrix} E_1-\lambda & W & 0 \\ W & E_2-\lambda & C \\ 0 & C & E_3-\lambda \end{vmatrix} = 0. \tag{11}$$

The expressions for the E_i and C elements are for the K=0 level:

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[11] Evidence for a negative sign of q_6 is given in the Discussion part.

[12] The harmonic term of the l-type doubling constant q_5 for CD_3I, CH_3Br, and CD_3Br are calculated to be 15.5, 26.0 and 32.0 MHz, respectively, while the corresponding observed values are 15.2, 26.3 and 32.2 MHz.

[13] Equations (10) and (11) do not apply to the K=±1 levels of v_2, since they are further connected to the K=±2 levels of v_5 through $\zeta^{(y)}_{25}$. Thus the solution of Eq. (11) obtained from Eq. (12) is not exact for λ_3.

$$\begin{aligned}
E_1 &= v_3^0 + v_6^0 + B_{36}^0\mathrm{J}(\mathrm{J}+1) + A_{36}^0(\zeta_6^{(z)})^2,\\
E_2 &= v_5^0 + B_5^0\mathrm{J}(\mathrm{J}+1) + A_5^0(\zeta_5^{(z)})^2,\\
E_3 &= v_2^0 + B_2^0\mathrm{J}(\mathrm{J}+1) + A_2^0 - B_2^0, \qquad (12)\\
C &= \{(v_2^0/v_5^0)^{1/2} + (v_5^0/v_2^0)^{1/2}\}[\mathrm{J}(\mathrm{J}+1)/2]^{1/2}B_e\zeta_{25}^{(y)},
\end{aligned}$$

for the (K=1,E) level:

$$\begin{aligned}
E_1 &= v_3^0+v_6^0+B_{36}^0\mathrm{J}(\mathrm{J}+1)+A_{36}^0-B_{36}^0+2A_{36}^0\zeta_6^{(z)}+A_{36}^0(\zeta_6^{(z)})^2,\\
E_2 &= v_5^0 + B_5^0\mathrm{J}(\mathrm{J}+1) + A_5^0 - B_5^0 + 2A_5^0\zeta_5^{(z)} + A_5^0(\zeta_5^{(3)})^2,\\
E_3 &= v_2^0 + B_2^0\mathrm{J}(\mathrm{J}+1) + 4(A_2^0-B_2^0), \qquad (13)\\
C &= \{(v_2^0/v_5^0)^{1/2} + (v_5^0/v_2^0)^{1/2}\}[(\mathrm{J}-1)(\mathrm{J}+2)/2]^{1/2}B_e\zeta_{25}^{(y)},
\end{aligned}$$

and for the (+) level:

$$\begin{aligned}
E_1 &= v_3^0 + v_6^0 + B_{36}^0\mathrm{J}(\mathrm{J}+1) + A_{36}^0 - B_{36}^0 - 2A_{36}^0\zeta_6^{(z)}\\
&\quad + q_6\mathrm{J}(\mathrm{J}+1)/2 + A_{36}^0(\zeta_6^{(z)})^2,\\
E_2 &= v_5^0 + B_5^0\mathrm{J}(\mathrm{J}+1) + A_5^0 - B_5^0 - 2A_5^0\zeta_5^{(z)} + q_5^*\mathrm{J}(\mathrm{J}+1)/\\
&\quad 2 + A_5^0(\zeta_6^{(z)})^2,\\
E_3 &= v_2^0 + B_2^0\mathrm{J}(\mathrm{J}+1), \qquad (14)\\
C &= \{(v_2^0/v_5^0)^{1/2} + (v_5^0/v_2^0)^{1/2}\}[\mathrm{J}(\mathrm{J}+1)]^{1/2}B_e\zeta_{25}^{(y)},
\end{aligned}$$

where the equilibrium rotational constant, B_e, is set equal to the ground-state rotational constant, B_0, 7501.25 MHz.³⁾

A computer calculation was performed by using the values reported in Refs. 3 and 4; the results are listed in Table VI. The Coriolis interaction through $\zeta_{25}^{(y)}$ was corrected for the $B_5{}^0$ listed in Table V; 7500.16 MHz was used in the calculation. The agreement with the observed values confirms the reported values.

TABLE 6. EFFECTIVE ROTATIONAL CONSTANTS FOR $\mathrm{v}_3+\mathrm{v}_6$ AND v_5 (in MHz)

		B_v(obsd)ᵃ⁾	B_v(calcd)
$\mathrm{v}_3+\mathrm{v}_6$ state	ν^+	7433.81±0.10	7433.49
	ν^0	7437.45±0.12	7437.44
	ν^-	7430.67±0.20	7429.97
v_5 state	ν^+	7505.34±0.15	7505.91
	ν^-	7492.80±0.45	7493.54

a) 2.5 times variance.

Determination of the Sign of q_6. The combined effect of the Fermi and Coriolis interactions enables us to determine the sign of the *l*-type doubling constant, q_6, by microwave spectroscopy. The effect on B_{36}^+ is different from that on B_{36}^-; the difference between B_{36}^+ and B_{36}^- is 1.7 MHz, even when we assume q_6=0.0 MHz. This difference can be interpreted as indications that the $\zeta_{25}^{(y)}$ term, which is dominant in the *l*-type doubling of v_5, is transferred to $\mathrm{v}_3+\mathrm{v}_6$ through the Fermi resonance. We have to add the normal *l*-type doubling in $\mathrm{v}_3+\mathrm{v}_6$, which is supposedly the same as in v_6, to make the resultant B_{36}^+ and B_{36}^- values agree with the observed values. The dotted lines and broken lines in Fig. 6 show the predicted rotational constants *vs.* the absolute value of q_6 for the cases of $q_6>0$ and $q_6<0$, respectively, while the solid lines are the observed rotational constants. For the $|q_6|$=5.8 MHz value, the broken lines are closer to the observed values than the dotted lines, the latter difference being too large to be accounted for the higher-order terms ignored in the present analysis. Therefore, the negative sign of q_6, that is, $q_6=-5.8$ MHz, is preferred. This is in agreement with the conclusion of Matsuura *et al.*⁴⁾

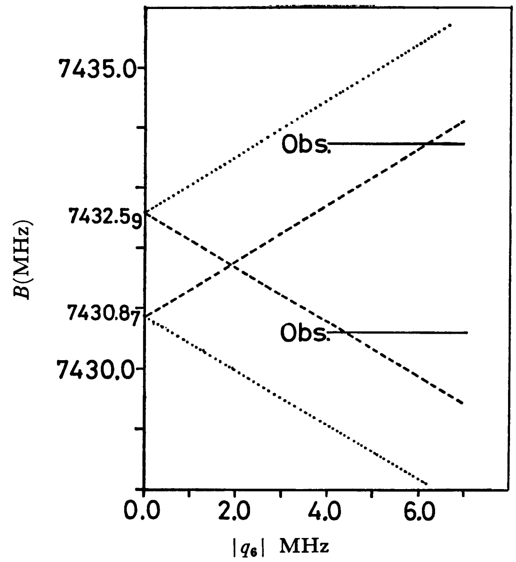

Fig. 6. Predicted rotational constants of the *l*-type doubling in $\mathrm{v}_3+\mathrm{v}_6$, $\nu_{36}{}^+$ and $\nu_{36}{}^-$, *vs.* $|q_6|$. Dotted and broken lines correspond to the prediction for $q_6>0$ and for $q_6<0$, respectively, and the solid lines indicate the observed rotational constants.

Appendix

Stark effect in the degenerate vibrational states of CH_3I.

The effective Hamiltonian which has to be solved is expressed as:

$$\mathrm{H} = \mathrm{H}_\mathrm{rot} + \mathrm{H}_\mathrm{Q} + \mathrm{H}_l + \mathrm{H}_\mathrm{E}, \qquad \text{(A1)}$$

where H_rot, H_Q, H_l, and H_E are the Hamiltonian operators for the rotation, the nuclear quadrupole coupling caused by the iodine nucleus, the *l*-type doubling, and the Stark effect respectively.

Since the differences in energy for different J values (more than 15 GHz) are much larger than those among the splittings caused by H_Q or H_l, only the terms which are diagonal in J need to be considered for the present purpose; the off-diagonal terms can be treated as second-order perturbations. Furthermore, an appropriate representation for the present case of a weak-field case is $|\mathrm{v}_t,l_t\rangle|\mathrm{F},\mathrm{M_F},\mathrm{J},\mathrm{K},\mathrm{M_J}\rangle$. We set another restriction: The degenerate vibration is singly excited, *i.e.* $\mathrm{v}_t=1$, $l_t=\pm1$. However, combination tones of the $\mathrm{v}_3+\mathrm{v}_6$ type are not excluded from the present considerations, since the degenerate vibration is still singly-excited.

The nonvanishing matrix elements of H_Q and H_E for the $|\mathrm{F},\mathrm{M_F},\mathrm{J},\mathrm{K},\mathrm{M_J}\rangle$ wave function have been given in textbooks¹⁴,¹⁵⁾ or papers.¹⁶,¹⁷⁾ We still have to consider H_l. Since H_l is of no significance when K=0, $|\mathrm{K}|\geqq2$, or K=

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14) C. H. Townes and A. L. Shawlow, "Microwave Spectroscopy", Chap. 10. McGraw-Hill, New York, 1955.

15) W. Gordy and R. L. Cook, "Microwave Molecular Spectra", Chap. 10. Interscience Publishers, New York, 1970.

16) W. Low and C. H. Townes, *Phys. Rev.*, **76**, 1295 (1949).

17) F. Coester, *ibid.*, **77**, 454 (1950).

$-l_t=\pm 1$,[18] the Stark effect is essentially equal to that in the ground-vibrational state. The effect of H_l is significant only when $K=l_t=\pm 1$, where the proper representations are expressed as:

$$\begin{aligned}&|v_t, 1, F, M_F, J, 1, M_J; +\rangle\\ &\quad=\{|v_t, 1, F, M_F, J, 1, M_J\rangle\\ &\qquad+|v_t, -1, F, M_F, J, -1, M_J\rangle\}/\sqrt{2}\end{aligned}\tag{A2}$$

and:

$$\begin{aligned}&|v_t, 1, F, M_F, J, 1, M_J; -\rangle\\ &\quad=\{|v_t, 1, F, M_F, J, 1, M_J\rangle\\ &\qquad-|v_t, -1, F, M_F, J, -1, M_J\rangle\}/\sqrt{2}.\end{aligned}\tag{A3}$$

The functions expressed in Eqs. (A2) and (A3) diagonalize both H_{rot} and H_l. The nonvanishing matrix elements of H_Q and H_E in the above representations are:

$$\begin{aligned}&\langle v_t, 1, F, M_F, J, 1, M_J; +|H_Q|v_t, 1, F, M_F, J, 1, M_J; +\rangle\\ &=\langle v_t, 1, F, M_F, J, 1, M_J; -|H_Q|v_t, 1, F, M_F, J, 1, M_J; -\rangle\\ &=\langle F, M_F, J, K=1, M_J|H_Q|F, M_F, J, K=1, M_J\rangle\\ &=(eQq/2)\{3K^2-J(J+1)\}\{3C(C+1)/4-I(I+1)J(J+1)\}/\\ &\quad\{I(2I-1)J(2J-1)(J+1)(2J+3)\},\end{aligned}\tag{A4}$$

where:

$$\begin{aligned}&C=F(F+1)-I(I+1)-J(J+1),\\ &\langle v_t, 1, F, M_F, J, 1, M_J; +|H_E|v_t, 1, F, M_F, J, 1, M_J; -\rangle\\ &=\langle F, M_F, I, K=1, M_J|H_E|F, M_F, J, K=1, M_J\rangle\\ &=-\mu E M_F\{J(J+1)+F(F+1)-I(I+1)\}/\\ &\quad\{2J(J+1)F(F+1)\},\end{aligned}\tag{A5}$$

and where:

$$\begin{aligned}&\langle v_t, 1, F, M_F, J, 1, M_J; +|H_E|v_t, 1, F+1, M_F, J, 1, M_J; -\rangle\\ &=\langle v_t, 1, F+1, M_F, J, 1, M_J; +\\ &\quad|H_E|v_t, 1, F, M_F, J, 1, M_J; -\rangle\\ &=\langle F, M_F, J, K=1, M_J|H_E|F+1, M_F, J, K=1, M_J\rangle\\ &=\langle F+1, M_F, J, K=1, M_J|H_E|F, M_F, J, K=1, M_J\rangle\\ &=-\mu E[\{(F+1)^2-M_F{}^2\}\{(F+1)^2-(I-J)^2\}\\ &\quad\times\{(I+J+1)^2-(F+1)^2\}]^{1/2}/\\ &\quad[2J(J+1)(F+1)\{(2F+1)(2F+3)\}^{1/2}],\end{aligned}\tag{A6}$$

where eQq is the electric quadrupole coupling constant of the iodine atom, μ is the electric dipole moment, and E is the applied electric field.

Since H_E is nonvanishing only between the (+) and (−) levels which are split by the *l*-type doubling, the secular equation to be solved is twice as large as that in the case of $K=-l_t=\pm 1$. These off-diagonal elements, in combination with the relatively small splitting caused by H_l (about a few tens of MHz in contrast to about a hundred MHz of splittings among different F levels), can complicate the Stark effect. Especially, the F levels lying in between the other F levels can be severely perturbed.

In the actual analysis, a computer was used in both cases, and the shifts in transition frequencies due to the Stark field were derived for the $J=2\leftarrow 1$, $F=7/2\leftarrow 5/2$, and $K=1\leftarrow 1$ transitions of the v_6 and v_3+v_6 vibrational states in order to compare them with the observations.

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[18] The energy levels for $K\geqq 2$, which consists of four levels, are not in strict degeneracy; for $|K-l_t|=3n\pm 1$ ($n=0,1,2,\cdots$), they are split into two doubly degenerate levels, and for $|K-l_t|=3n$ ($n=0,1,2,\cdots$), there are three levels with A_1, A_2, and E symmetries. Since the splittings among the levels interrelated by H_E are negligible for CH$_3$I, we can treat them as though the levels were degenerate. It should be noted, however, that H_E has an off-diagonal element between A_1 and A_2 levels in contrast to the diagonal element for the E levels.