Vibration-Rotation Interaction Constants, *l*-Type Doubling Constants and Cubic Force Constants of CH_3I and CD_3I

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The harmonic parts of the vibration-rotation interaction constants and the *l*-type doubling constants were calculated for CH_3I and CD_3I from the harmonic force field. The harmonic parts were subtracted from the experimental values to obtain the anharmonic parts which give relations among the cubic normal-coordinate force constants. Some of the individual values for the cubic force constants associated with the bending modes were obtained by using the derived relations and the previously estimated values for the stretch-stretch-stretch cubic force constants of the methyl group.

Spectroscopic data for CH_3I and CD_3I have been accumulated by the systematic studies of high-resolution infrared spectra and microwave spectra. The observed values of rotational constants in the ground vibrational state and a knowledge of the dependence of these rotational constants on each of the normal modes of vibration made it possible to determine accurately the equilibrium geometry of the methyl iodide molecule.[1] From the experimental values of the vibration-rotation interaction constants (α) and the *l*-type doubling constants (q), supplemented by the calculation of the harmonic contributions to these constants, relations among the cubic normal-coordinate force constants may be derived.[2,3] Although the determination of the individual force constants is not possible for this molecule,[4] these relations are still important in the estimation and discussion of vibrational anharmonicity in the methyl iodide molecule. In the present study, we have derived such relations for CH_3I and CD_3I from the α and q constants, and have used the relations together with the previously estimated cubic force constants of the CH stretching modes[5] to obtain some of the individual cubic force constants associated with the bending modes.

Vibration-Rotation Interaction Constants

The vibration-rotation interaction constants α_s^B and α_s^A are defined according to the relations[6]

$$B_{[v]} = B_e - \sum_s \alpha_s^B(v_s + d_s/2), \tag{1}$$

and

$$A_{[v]} = A_e - \sum_s \alpha_s^A(v_s + d_s/2). \tag{2}$$

The α_s^B and α_s^A constants consist of harmonic and anharmonic parts, namely

$$\alpha_s^B = \alpha_s^B(\text{harm}) + \alpha_s^B(\text{anharm}), \tag{3}$$

and

$$\alpha_s^A = \alpha_s^A(\text{harm}) + \alpha_s^A(\text{anharm}). \tag{4}$$

$\alpha_s^B(\text{harm})$ and $\alpha_s^B(\text{anharm})$ are given by the following general expressions[7]

$$\alpha_s^B(\text{harm}) = -\frac{2B_e^2}{d_s\omega_s} \times \sum_\sigma \left[\sum_{\substack{s'\sigma' \\ (s'\neq s)}} \frac{3\omega_s^2+\omega_{s'}^2}{\omega_s^2-\omega_{s'}^2} (\zeta_{s\sigma,s'\sigma'}^{(y)})^2 + \frac{4}{3}\sum_\xi \frac{(a_{s\sigma}^{(y\xi)})^2}{I_{\xi\xi}^{(e)}} \right], \tag{5}$$

and

$$\alpha_s^B(\text{anharm}) = -4\pi\frac{B_e^2}{d_s}\left(\frac{c}{h}\right)^{1/2} \times \sum_\sigma \left[\frac{3k_{sss}a_{s\sigma}^{(yy)}}{\omega_s^{3/2}} + \sum_{\substack{s'\sigma' \\ (s'\neq s)}} \frac{k_{sss'}a_{s'\sigma'}^{(yy)}}{\omega_{s'}^{3/2}} \right]. \tag{6}$$

$\alpha_s^A(\text{harm})$ and $\alpha_s^A(\text{anharm})$ are given by the corresponding expressions with A_e and z, in place of B_e and y, respectively. The harmonic parts of α_s^B and α_s^A may be rewritten into forms more convenient for the present case, as will be given below. k_{sss} and $k_{sss'}$ appearing in the anharmonic parts are the cubic force constants when the potential function of a molecule is expanded in terms of dimensionless normal coordinates q_s:

$$V(q)/hc = \frac{1}{2}\sum_s \omega_s q_s^2 + \sum_{s\le s'\le s''}\sum\sum k_{ss's''}q_s q_{s'} q_{s''} + \sum_{s\le s'\le s''\le s'''}\sum\sum\sum k_{ss's''s'''}q_s q_{s'} q_{s''} q_{s'''} + \cdots\cdots \tag{7}$$

For the non-degenerate modes, $\alpha_s^B(\text{harm})$ and $\alpha_s^B(\text{anharm})$ are given by

$$\alpha_s^B(\text{harm}) = -\frac{2B_e^2}{\omega_s} \times \left[\sum_{t\subset E} \frac{4\omega_t^2}{\omega_s^2-\omega_t^2} (\zeta_{s,ta}^{(y)})^2 + 3\{1-\sum_i (l_{i,s}^{(y)})^2\} \right], \tag{8}$$

and

$$\alpha_s^B(\text{anharm}) = -4\pi B_e^2\left(\frac{c}{h}\right)^{1/2} \times \left[\frac{3k_{sss}a_s^{(yy)}}{\omega_s^{3/2}} + \sum_{\substack{s'\subset A_1 \\ (s'\neq s)}} \frac{k_{sss'}a_{s'}^{(yy)}}{\omega_{s'}^{3/2}} \right], \tag{9}$$

1) H. Matsuura and J. Overend, *J. Chem. Phys.*, **56**, 5725 (1972).

2) Y. Morino, K. Kuchitsu, and S. Yamamoto, *Spectrochim. Acta*, **24A**, 335 (1968).

3) T. Oka, *J. Chem. Phys.*, **47**, 5410 (1967).

4) For molecules with more than three atoms, all of the independent cubic force constants cannot be determined from the experimental values of the α and q constants, since the experimental data are insufficient.

5) J. Overend and K. Machida, *Spectrochim. Acta*, **26A**, 1225 (1970).

6) G. Herzberg, "Molecular Spectra and Molecular Structure, II. Infrared and Raman Spectra of Polyatomic Molecules," D. Van Nostrand Co., Inc., New York (1945), p. 370.

7) For symbols and notation in the forthcoming expressions, see H. H. Nielsen, "Handbuch der Physik," Vol. 37, ed. by S. Flügge, Springer-Verlag, Berlin (1959), p. 173.

and for the doubly-degenerate modes

$$\alpha_t^B(\text{harm}) = -\frac{2B_e^2}{\omega_t}\left[\sum_{s\subset A_1}\frac{2\omega_s^2}{\omega_t^2-\omega_s^2}(\zeta_{s,ta}{}^{(y)})^2 + \sum_{\substack{t'\subset E\\(t'\neq t)}}\frac{4\omega_{t'}{}^2}{\omega_t^2-\omega_{t'}{}^2}(\zeta_{ta,t'a}{}^{(y)})^2 + 3\left\{1-\frac{1}{2}\sum_i[(l_{i,ta}{}^{(y)})^2+(l_{i,tb}{}^{(y)})^2]\right\}\right], \quad (10)$$

and

$$\alpha_t^B(\text{anharm}) = -4\pi B_e^2\left(\frac{c}{h}\right)^{1/2}\sum_{s\subset A_1}\frac{k_{tatas}a_s{}^{(yy)}}{\omega_s{}^{3/2}}. \quad (11)$$

Similarly for α_s^A(harm) and α_s^A(anharm); for the non-degenerate modes

$$\alpha_s^A(\text{harm}) = -\frac{2A_e^2}{\omega_s}\cdot 3[1-\sum_i(l_{i,s}{}^{(z)})^2], \quad (12)$$

and

$$\alpha_s^A(\text{anharm}) = -4\pi A_e^2\left(\frac{c}{h}\right)^{1/2} \times\left[\frac{3k_{sss}a_s{}^{(zz)}}{\omega_s{}^{3/2}}+\sum_{\substack{s'\subset A_1\\(s'\neq s)}}\frac{k_{sss'}a_{s'}{}^{(zz)}}{\omega_s{}^{3/2}}\right], \quad (13)$$

and for the doubly-degenerate modes

$$\alpha_t^A(\text{harm}) = -\frac{2A_e^2}{\omega_t}\left[\sum_{\substack{t'\subset E\\(t'\neq t)}}\frac{4\omega_{t'}{}^2}{\omega_t^2-\omega_{t'}{}^2}(\zeta_{ta,t'b}{}^{(z)})^2 - 3(\zeta_{ta,tb}{}^{(z)})^2 + 3\{1-\sum_i(l_{i,ta}{}^{(z)})^2\}\right], \quad (14)$$

and

$$\alpha_t^A(\text{anharm}) = -4\pi A_e^2\left(\frac{c}{h}\right)^{1/2}\sum_{s\subset A_1}\frac{k_{tatas}a_s{}^{(zz)}}{\omega_s{}^{3/2}}. \quad (15)$$

Since the harmonic parts, α_s^B(harm) and α_s^A(harm), are determined by only the quadratic force constants, we may calculate their values from the harmonic force field. That of methyl iodide is reasonably well known,[8-10] and we have used in the present calculations the hybrid-orbital force field determined by Russell, Needham and Overend.[9] The anharmonic parts, α_s^B(anharm) and α_s^A(anharm), are then obtained by subtracting the calculated values of α_s^B(harm) and α_s^A(harm) from the experimental values of α_s^B and α_s^A. The experimental values of α_s^B and α_s^A, the calculated values of α_s^B(harm) and α_s^A(harm), and α_s^B(anharm) and α_s^A(anharm) are listed in Tables 1 and 2.

Table 1. α_s^B and α_s^A for CH_3I, in cm^{-1}

s	α_s^B(obs)[a]	α_s^B(harm)	α_s^B(anharm)
1	0.00017	−0.000075	0.00024
2	0.000849[b]	0.000066[b]	0.000783
3	0.001811	−0.000657	0.002468
4	−0.000122	−0.000078	−0.000044
5	0.000058[b]	−0.000095[b]	0.000153
6	0.000787	0.000105	0.000682
s	α_s^A(obs)[a]	α_s^A(harm)	α_s^A(anharm)
1	0.0514	−0.0450	0.0964
2	−0.0222	−0.0137	−0.0085
3	−0.0038	−0.0003	−0.0035
4	0.0311	−0.0588	0.0899
5	0.0460	0.0504	−0.0044
6	−0.0347	0.0128	−0.0475

a) For sources, see Table I of Ref. 1.
b) Not affected by the Coriolis interaction between ν_2 and ν_5. In Table I of Ref. 1, footnote k should be given to the figures $+0.000849\pm0.000003$ and $+0.000058\pm0.000002$, but not to α_2^B and α_5^B.

Table 2. α_s^B and α_s^A for CD_3I, in cm^{-1}

s	α_s^B(obs)[a]	α_s^B(harm)	α_s^B(anharm)
1	0.000135	−0.000062	0.000197
2	0.00103	0.000605	0.00043
3	0.00126	−0.000425	0.00168
4	0.000086	−0.000070	0.000156
5	−0.000403	−0.000366	−0.000037
6	0.000494	0.000089	0.000405
s	α_s^A(obs)[a]	α_s^A(harm)	α_s^A(anharm)
1	0.0232	−0.0151	0.0383
2	−0.0078	−0.0058	−0.0020
3		−0.0000	
4	0.0135	−0.0192	0.0327
5	0.0148	0.0174	−0.0026
6	−0.0135	0.0025	−0.0160

a) For sources, see Table I of Ref. 1. Recently microwave spectra of CD_3I in the excited vibrational states have been measured and values for α_2^B, α_3^B, α_5^B, and α_6^B have been obtained (Y. Kawashima and K. Kozima, Symposium on Molecular Structure, Sendai, 1972).

The observed values of α_2^B and α_5^B for CH_3I have been corrected for the Coriolis interaction between ν_2 and ν_5[11]; we use the symbols $\alpha_2^{B'}$ and $\alpha_5^{B'}$ for these corrected quantities. Thus $\alpha_2^{B'}$ and $\alpha_5^{B'}$ are given by

$$\alpha_s^{B'} = \alpha_s^{B'}(\text{harm}) + \alpha_s^B(\text{anharm}) \quad (s=2 \text{ or } 5) \quad (16)$$

and $\alpha_s^{B'}$(harm) corresponds to the quantity obtained by dropping the term containing $\zeta_{2,5a}{}^{(y)}$ from the expression in Eq. (5).

l-Type Doubling Constants

The *l*-type doubling constant q_t consists of harmonic and anharmonic parts[3] like α_s^B and α_s^A;

$$q_t = q_t(\text{harm}) + q_t(\text{anharm}). \quad (17)$$

For CH_3X type molecules, q_t(harm) and q_t(anharm) are given by

$$q_t(\text{harm}) = \frac{2B_e^2}{\omega_t}\left[\sum_{s\subset A_1}\frac{3\omega_t^2+\omega_s^2}{\omega_t^2-\omega_s^2}(\zeta_{s,ta}{}^{(y)})^2 - \frac{3}{4}\frac{(a_{tb}{}^{(yz)})^2}{I_{zz}{}^{(e)}}\right], \quad (18)$$

which may be rewritten into

8) J. Aldous and I. M. Mills, *Spectrochim. Acta*, **19**, 1567 (1963).
9) J. W. Russell, C. D. Needham, and J. Overend, *J. Chem. Phys.*, **45**, 3383 (1966).
10) J. L. Duncan, A. Allan, and D. C. McKean, *Mol. Phys.*, **18**, 289 (1970).

$$q_t(\text{harm}) = \frac{2B_e^2}{\omega_t}\left[\sum_{s\subset A_1}\frac{4\omega_s^2}{\omega_t^2-\omega_s^2}(\zeta_{s,ta}^{(y)})^2 + 3\sum_i\{(l_{i,tb}^{(y)})^2-(l_{i,ta}^{(y)})^2\}\right], \quad (19)$$

and

$$q_t(\text{anharm}) = 8\pi B_e^2\left(\frac{c}{h}\right)^{1/2} \times\left[\frac{3k_{tatata}a_{ta}^{(yy)}}{\omega_t^{3/2}}+\sum_{\substack{t'\subset E\\(t'\neq t)}}\frac{k_{tatat'a}a_{t'a}^{(yy)}}{\omega_{t'}^{3/2}}\right]. \quad (20)$$

The observed value of q_5 for CH_3I does not include the effect of the Coriolis interaction between ν_2 and ν_5,[11] and its harmonic part, q_5'(harm), is obtained by dropping the term containing $\zeta_{2,5a}^{(y)}$ from the expression in Eq. (18), which is then rewritten as

$$q_5'(\text{harm}) = \frac{2B_e^2}{\omega_5}\left[\frac{4\omega_1^2}{\omega_5^2-\omega_1^2}(\zeta_{1,5a}^{(y)})^2 + \frac{4\omega_3^2}{\omega_5^2-\omega_3^2}(\zeta_{3,5a}^{(y)})^2 - 3(\zeta_{2,5a}^{(y)})^2 + 3\sum_i\{(l_{i,5b}^{(y)})^2-(l_{i,5a}^{(y)})^2\}\right]. \quad (21)$$

The harmonic parts of the l-type doubling constants were calculated from the harmonic force field of Russell *et al.*[9] and were subtracted from the observed values[12] to obtain the anharmonic parts of the l-type doubling constants, q_t (anharm) (Table 3).

TABLE 3. q_t FOR CH_3I AND CD_3I, IN cm^{-1}

	t	q_t(obs)	q_t(harm)	q_t(anharm)
	4		0.000073	
CH_3I	5	−0.000022[a,b]	−0.000012[b]	−0.000010
	6	−0.000200[c]	−0.000266	0.000066
	4		0.000078	
CD_3I	5	0.000580[d]	0.000516	−0.000064
	6	−0.000126[d]	−0.000204	0.000078

a) Ref. 11. b) Not affected by the Coriolis interaction between ν_2 and ν_5. c) H. Matsuura and J. Overend, *Spectrochim. Acta*, **27A**, 2165 (1971); see also footnote 18 of Ref. 11. d) D. R. Anderson and J. Overend, *Spectrochim. Acta*, **28A**, 1231 (1972). The signs of q_5 and q_6 of CD_3I listed in this table are opposite to and the values are twice those reported by Anderson and Overend, because of different definitions of the q_t constant used. The values in this table are in accord with Mills' sign convention[13] and Eqs. (18)—(20).

Cubic Force Constants

From the anharmonic parts of the α_s^B, α_s^A and q_t constants, we obtain relations among the cubic normal-coordinate force constants through Eqs. (9), (11), (13), (15) and (20). α_s^B(anharm) and α_s^A(anharm) relate the cubic constants k_{ss1}, k_{ss2} and k_{ss3}, and q_t(anharm) relates k_{tt4}, k_{tt5} and k_{tt6}. Thus α_s^B and α_s^A, and q_t are complementary in the anharmonic information they provide. Making use of the harmonic potential function[9] incalculating the $a_s^{(\xi\eta)}$ coefficients appearing in the equations, we obtain the following explicit relations[14] for CH_3I from the α_s^B constants:

$$\begin{aligned}
-0.08k_{111}+0.08k_{112}-2.83k_{113} &= 24\ cm^{-1},\\
-0.03k_{221}+0.23k_{222}-2.83k_{223} &= 78\ cm^{-1},\\
-0.03k_{331}+0.08k_{332}-8.50k_{333} &= 247\ cm^{-1},\\
-0.03k_{441}+0.08k_{442}-2.83k_{443} &= -4\ cm^{-1},\\
-0.03k_{551}+0.08k_{552}-2.83k_{553} &= 15\ cm^{-1},
\end{aligned}$$

and

$$-0.03k_{661}+0.08k_{662}-2.83k_{663} = 68\ cm^{-1}, \quad (22)$$

from the α_s^A constants:

$$\begin{aligned}
-0.54k_{111}-0.24k_{112}-0.08k_{113} &= 96\ cm^{-1},\\
-0.18k_{221}-0.71k_{222}-0.08k_{223} &= -9\ cm^{-1},\\
-0.18k_{331}-0.24k_{332}-0.24k_{333} &= -4\ cm^{-1},\\
-0.18k_{441}-0.24k_{442}-0.08k_{443} &= 90\ cm^{-1},\\
-0.18k_{551}-0.24k_{552}-0.08k_{553} &= -4\ cm^{-1},
\end{aligned}$$

and

$$-0.18k_{661}-0.24k_{662}-0.08k_{663} = -48\ cm^{-1}, \quad (23)$$

and from the q_t constants:

$$0.28k_{554}-3.04k_{555}+0.15k_{556} = -10\ cm^{-1},$$

and

$$0.28k_{664}-1.01k_{665}+0.44k_{666} = 66\ cm^{-1}. \quad (24)$$

Similar relations are obtained for CD_3I:

$$\begin{aligned}
-0.11k_{111}+0.03k_{112}-2.23k_{113} &= 20\ cm^{-1},\\
-0.04k_{221}+0.09k_{222}-2.23k_{223} &= 43\ cm^{-1},\\
-0.04k_{331}+0.03k_{332}-6.69k_{333} &= 168\ cm^{-1},\\
-0.04k_{441}+0.03k_{442}-2.23k_{443} &= 16\ cm^{-1},\\
-0.04k_{551}+0.03k_{552}-2.23k_{553} &= -4\ cm^{-1},
\end{aligned}$$

and

$$-0.04k_{661}+0.03k_{662}-2.23k_{663} = 41\ cm^{-1}, \quad (25)$$

$$\begin{aligned}
-0.31k_{111}-0.14k_{112}-0.02k_{113} &= 38\ cm^{-1},\\
-0.10k_{221}-0.43k_{222}-0.02k_{223} &= -2\ cm^{-1},\\
-0.10k_{441}-0.14k_{442}-0.02k_{443} &= 33\ cm^{-1},\\
-0.10k_{551}-0.14k_{552}-0.02k_{553} &= -3\ cm^{-1},
\end{aligned}$$

and

$$-0.10k_{661}-0.14k_{662}-0.02k_{663} = -16\ cm^{-1}, \quad (26)$$

$$0.38k_{554}-4.79k_{555}+0.10k_{556} = -64\ cm^{-1},$$

and

$$0.38k_{664}-1.60k_{665}+0.31k_{666} = 78\ cm^{-1}. \quad (27)$$

The signs of the k constants are in accord with those of the $\boldsymbol{L}$ matrix elements given in Table 4.[15]

11) H. Matsuura, T. Nakagawa, and J. Overend, *J. Chem. Phys.*, to be published. Detailed analysis of ν_5 of CH_3I.

12) The signs of the observed values for q_t, listed in Table 3, are in accord with Mills' sign convention[13] and are consistent with Eqs. (18)—(20).

13) I. M. Mills, *Pure Appl. Chem.*, **18**, 285 (1969); G. J. Cartwright and I. M. Mills, *J. Mol. Spectrosc.*, **34**, 415 (1970).

14) $k_{tts}=k_{tatas}=k_{tbtbs}$, $k_{ttt}=k_{tatata}=-(1/3)k_{tatbtb}$ and $k_{ttt'}=k_{tatat'a}=-k_{tbtbt'a}=-(1/2)k_{tatbt'b}$.

15) The geometry of the molecule and the internal-symmetry coordinates used in this study are the same as those of Russell *et al.*[9]

Table 4. Elements of the L matrix, in $amu^{-1/2}$

	L_{11}	L_{12}	L_{13}	L_{21}	L_{22}	L_{23}
CH_3I	1.007	0.011	0.004	−0.102	1.356	0.109
CD_3I	0.720	0.020	0.007	−0.150	1.040	0.023
	L_{31}	L_{32}	L_{33}	L_{44}	L_{45}	L_{46}
CH_3I	−0.045	0.100	0.282	1.051	0.026	−0.025
CD_3I	−0.066	0.149	0.255	0.781	0.006	−0.012
	L_{54}	L_{55}	L_{56}	L_{64}	L_{65}	L_{66}
CH_3I	0.106	1.522	−0.133	−0.068	0.254	0.910
CD_3I	0.188	1.113	−0.051	−0.103	0.111	0.679

The determination of individual values for the k constants is not possible from the above relations; the combination of Eqs. (22) and (23), or Eqs. (25) and (26) gives only relations between two k constants. For planar or pyramidal XY_3 molecules, the k constants appearing in the relations similar to Eqs. (22), (23), (25) and (26) can be determined uniquely, and some of the k constants have, in fact, been obtained from observed α_s^B and α_s^C for NH_3 and ND_3.[2]

Overend and Machida[5] have made a simple calculation of the anharmonic force constants of the CH stretching modes for the methyl group, assuming a Morse function for a CH bond. Their estimation of the cubic force constants may be used to obtain other force constants, making use of the relations derived in this study. While the stretch-stretch-stretch cubic force constants may be estimated relatively easily,[5] the estimation of the constants involving bending modes is not so simple, and the relations among the k constants are useful in estimating the latter. In Table 5 are listed the force constants estimated by Overend and Machida[5] and the new force constants of CH_3I and CD_3I determined in the present work. They are compared with the corresponding constants for NH_3 and ND_3. The values of k_{111}, k_{444}, and k_{441} (the CD stretch-stretch-stretch force constants) for CD_3I were derived from the corresponding values for CH_3I by multiplying by the factor $[(\mu_D+\mu_C)/(\mu_H+\mu_C)]^{3/4}\simeq 0.63$, where μ_H, μ_D, and μ_C are the reciprocals of the masses of H, D, and C atoms.

Table 5. Estimates of the cubic normal-coordinate force constants, in cm^{-1}, for CH_3I and CD_3I and corresponding constants for NH_3 and ND_3

	k_{111}	k_{112}	k_{113}	k_{441}	k_{442}	k_{443}
CH_3I	−173[a]	−10	−4	−518[a]	13	7
CD_3I	−109[b]	−33	−4	−326[b]	5	−2
NH_3[c]	−228	4		−603	136	
ND_3[c]	−153	−77		−382	89	
	k_{444}	k_{551}	k_{552}	k_{553}	k_{356}	
CH_3I	−122[a]	61	−26	−7	29.614[d]	
CD_3I	−77[b]					
NH_3[c]	−142	87	−36			
ND_3[c]	−89	22	−17			

a) Ref. 5. b) See text. c) Ref. 2. d) Absolute value.[11]

Duncan *et al.*[10] have estimated the interaction terms of the Fermi resonance between ν_1 and $2\nu_5$ of CH_3I from the intensities of these parallel bands. From the interaction term, the value of $|k_{551}|$ is found to be 61 cm^{-1}. By comparing with the corresponding value (+87 cm^{-1}) for NH_3,[2] it seems reasonable to take a positive sign for k_{551}. The values for k_{552} and k_{553} derived through the relations in Eqs. (22) and (23) are listed in Table 5. A value for k_{356} of CH_3I is also listed. This was obtained by the detailed analyses of the Fermi doublet, ν_5 and $\nu_3+\nu_6$.[11,16,17]

Discussion

There are 38 independent cubic normal-coordinate force constants for CH_3I or CD_3I. Of these, we have estimated or observed 11 constants for the former and 7 for the latter, as shown in Table 5. The stretch-stretch-stretch constants (k_{111}, k_{444} and k_{441}) previously estimated for the CH_3 and CD_3 groups[5] are of the reasonable magnitudes, compared with those of NH_3 and ND_3, and the systematic variations of the values from those of the ammonia molecule are related closely to the values of the quadratic internal-coordinate force constants (*i.e.*, 5.5 mdyn/Å for the methyl group and 7 mdyn/Å for ammonia).

In the present study, we have been able to estimate two stretch-stretch-bend interaction constants (k_{112} and k_{442}) of the CH_3 or CD_3 group. The values obtained for k_{442} for CH_3I and CD_3I are found to be about ten times smaller than the corresponding values for NH_3 and ND_3. This difference may be real and may reflect structural differences between the CH_3 group and ammonia. Alternatively it may stem from approximation made in our analysis and, with this possibility in mind, we refrain from further comments. It is interesting to note, on the other hand, that the bend-bend-stretch constant (k_{551}) and the bend-bend-bend constant (k_{552}) of CH_3I have magnitudes similar to those for NH_3.

The cubic constant k_{356} for CH_3I has been determined experimentally from the analyses of the perpendicular bands, ν_5 and $\nu_3+\nu_6$.[11,16,17] The value obtained is only an absolute one, but is very accurate, *i.e.*, $|k_{356}|=29.6144\pm0.0007$ cm^{-1}.[11] The same force constant has also been determined from the Fermi doublets, $\nu_5+\nu_6$ and $\nu_3+2\nu_6$, and $\nu_2+\nu_5$ and $\nu_2+\nu_3+\nu_6$, to be 29.572 ± 0.002 cm^{-1} and 29.1 ± 0.2 cm^{-1}, respectively.[18]

At the present time, we do not have individual values for the cubic force constants other than those listed in Table 5. However, the relations among the cubic force constants derived in the present study are useful in estimating other force constants and in discussing the vibrational anharmonicity in the methyl

16) Y. Morino, J. Nakamura, and S. Yamamoto, *J. Mol. Spectrosc.*, **22**, 34 (1967).
17) H. Matsuura and J. Overend, *J. Chem. Phys.*, **55**, 1787 (1971).
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halide molecules.

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