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Infrared Intensities in Methyl Chloride. II. Binary Overtone and Combination Bands

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Infrared intensities of binary overtones and combinations of CH_3Cl and CD_3Cl molecules have been measured by the pressure broadening technique. Simplified formulas for the intensities of binary overtone and combination bands of symmetric top molecules were given. Contribution from the mechanical anharmonicity was calculated by use of these equations. Contribution from the electric anharmonicity was estimated by *ab initio* MO method (4-31 G*). The calculated intensities were compared with the observed values and discussed.

In Part I, we have analyzed the fundamental band intensities of CH_3Cl and CD_3Cl molecules to determine the values of the first derivatives of the dipole moment with respect to the normal coordinates ($\partial \boldsymbol{P}/\partial Q_j$).[1] The result of Part I is applied in the present study to analyze the intensities of binary overtone and combination bands of this molecule. The general expressions have been developed for the absorption intensities of two quantumn transitions in polyatomic molecules using the contact transformation method.[2-4] Up to the second order of approximation, the transition moments of the binary overtone and combination bands can be calculated if both the first and second partial derivatives of the molecular dipole moment with respect to the normal coordinates together with the cubic normal coordinate force constants are known. In Part I, we have determined the values of the first derivatives of the dipole moment including their signs. Furthermore the cubic force constants have also been obtained by the present authors[5] through the analysis of the vibration-rotation interaction constants. Therefore, it may be possible to gain some information on the values of the second derivatives of the dipole moment from the intensities of the two quantumn transitions.

The present paper reports the result of such analysis for methyl chloride molecule.

Theoretical

The dipole moment function of a molecule is expanded as a Taylor series in the dimensionless normal coordinates and is written as,

$$\boldsymbol{P} = \boldsymbol{P}_0 + \sum_r \boldsymbol{P}_r q_r + (1/2) \sum_{rs} \boldsymbol{P}_{rs} q_r q_s + \cdots, \tag{1}$$

where $\boldsymbol{P}_r$ stands for $(\partial \boldsymbol{P}/\partial q_r)$, $\boldsymbol{P}_{rs}$ for $(\partial^2 \boldsymbol{P}/\partial q_r \partial q_s)$, *etc.*[3] On the other hand, the potential function may also be expanded in dimensionless normal coordinates to give:

$$V/hc = (1/2) \sum_r \omega_r q_r^2 + (1/6) \sum_{rst} \varphi_{rst} q_r q_s q_t + \cdots, \tag{2}$$

where ω_r is rth normal frequency and φ_{rst} is a cubic force constant.[6]

In order to evaluate matrix elements of the dipole moment operator for anharmonic vibrational wave functions, we may use a contact transformation, T, to obtain,

$$\boldsymbol{P}' = T\boldsymbol{P}T^{-1}, \tag{3}$$

where

$$T = \exp(\mathrm{i}\lambda S). \tag{4}$$

All details of the contact transformation calculations are given in Refs. 2, 3, and 4, and are not repeated here.

Then, according to Overend,[4] the integrated intensities of binary combination bands may be expressed by the following equation:

$$A_{ss'} = (8\pi^3 N/3hc)(\omega_s + \omega_{s'}) d_f (Q_{ss'})^2 \times Z_s Z_{s'} [1 - \exp\{-\beta(\omega_s + \omega_{s'})\}], \tag{5a}$$

where

$$Q_{ss'} = |<v_s = v_{s'} = 0|\boldsymbol{P}'|v_s = v_{s'} = 1>|. \tag{5b}$$

Similarly, for binary overtone bands,

$$A_{ss} = (8\pi^3 N/3hc)(2\omega_s) d_f (Q_{ss})^2 Z_s^2 \{1 - \exp(-2\beta\omega_s)\}, \tag{6a}$$

where

$$Q_{ss} = |<v_s = 0|\boldsymbol{P}'|v_s = 2>|. \tag{6b}$$

Here, N is Avogadro's number, c is the velocity of light, h is Plank's constant, ω_s is the sth normal frequency, d_f is the degeneracy of the upper vibrational state, β is $1/kT$, Z_s is the partition function for the sth normal vibration, $Z_s = 1/\{1 - \exp(-\beta\omega_s)\}$, and $\boldsymbol{P}'$ is the transformed molecular dipole moment.

By substituting appropriate expressions for the transition moments, Q_{ss} and $Q_{ss'}$, we can also use these equations for the absorption intensities of different kind of two quantumn transitions of symmetric top molecules. The method of evaluating the transition moments was shown by Overend.[7] The result is as follows:

$$Q^z_{ss} = (1/2\sqrt{2})[P^z_{ss} + \sum_{s'} P^z_{s'} \varphi_{sss'} \omega_{s'}/(4\omega_s^2 - \omega_{s'}^2)], \tag{7}$$

$$Q^z_{ss'} = (1/2)[P^z_{ss'} + \sum_{s''} P^z_{s''} \varphi_{ss's''} \omega_{s''}/\{(\omega_s + \omega_{s'})^2 - \omega_{s''}^2\}], \tag{8}$$

$$Q^x_{st} = (1/2)[P^x_{st} + \sum_{t'} P^x_{t'} \varphi_{stt'} \omega_{t'}/\{(\omega_s + \omega_t)^2 - \omega_{t'}^2\}], \tag{9}$$

$$Q^z_{tt} = (1/2)[P^z_{tt} + \sum_{s} P^z_{s} \varphi_{tts} \omega_s/(4\omega_t^2 - \omega_s^2)], \tag{10}$$

$$Q^x_{tt} = (1/2)[P^x_{tt} + \sum_{t'} P^x_{t'} \varphi_{ttt'} \omega_{t'}/(4\omega_t^2 - \omega_{t'}^2)], \tag{11}$$

$$Q^z_{tt'} = (1/\sqrt{2})[P^z_{tt'} + \sum_{s} P_s^z \varphi_{tt's} \omega_s/\{(\omega_t + \omega_{t'})^2 - \omega_s^2\}], \tag{12}$$

$$Q^{x}_{tt'} = (1/\sqrt{2})[P^{x}_{tt'} + \sum_{t''} P^{x}_{t''}\varphi_{tt't''}\omega_{t''}/ \{(\omega_t+\omega_{t'})^2-\omega_{t''}^2\}]. \quad (13)$$

In these equations, all of the summations are unrestricted, so that $\Sigma_{s'}$ includes the term with $s'=s$ and $\Sigma_{t'}$ includes the term with $t'=t$, *etc.* However, the index s runs only over nondegenerate modes and the index t runs only over degenerate modes. The numerical subscripts on t for the other dipole moment expansion coefficients are as follows; $P^{x}_{t}=P^{x}_{t\mathrm{a}}=P^{y}_{t\mathrm{b}}$, $P^{z}_{tt'}=P^{z}_{t\mathrm{a}t'\mathrm{a}}=P^{z}_{t\mathrm{b}t'\mathrm{b}}$, and $P^{x}_{tt'}=P^{x}_{t\mathrm{a}t'\mathrm{a}}=-P^{x}_{t\mathrm{b}t'\mathrm{b}}=-P^{y}_{t\mathrm{a}t'\mathrm{b}}=-P^{y}_{t\mathrm{b}t'\mathrm{a}}$.[7] Similarly, the numerical subscripts on t for the other cubic anharmonic force constants are as follows; $\varphi_{stt'}=\varphi_{st\mathrm{a}t'\mathrm{a}}=\varphi_{st\mathrm{b}t'\mathrm{b}}$; $\varphi_{tt't''}=\varphi_{t\mathrm{a}t'\mathrm{a}t''\mathrm{a}}=-\varphi_{t\mathrm{a}t'\mathrm{b}t''\mathrm{b}}=-\varphi_{t\mathrm{b}t'\mathrm{a}t''\mathrm{b}}=-\varphi_{t\mathrm{b}t'\mathrm{b}t''\mathrm{a}}$.[8]

These equations are by no means new but have a definite advantage over the previous ones[7] in that the expressions are given for the individual cases in much simpler forms.

Experimental Results

The sample gases of CH_3Cl and CD_3Cl are the same as those used in Part I which were purchased from Takachiho Chemical Co. and Merck Sharp & Dohme Co. Canada, respectively. The purity of CH_3Cl was stated as 99.5% and that of CD_3Cl was 99 atom%. As will be described later inspection of full region of the infrared spectra of these gases well guaranteed the stated sample purities.

Spectra were all observed with a Nicolet model 7199 FT-IR spectrophotometer accomodated with a mercury-cadmium telluride detector. Optical resolution of 0.25 cm^{-1} was used (maximum path difference of 4 cm, with Happ-Genzel apodization). For intensity measurements, a 6 cm high pressure cell with KBr windows was used under a total pressure of 1.11×10^6 Pa. In order to investigate rotational fine structure of the bands, a conventional 10 cm glass body cell was used. The sample pressure was measured with an MKS baratron type 220, which covers a pressure range of 1.333×10^5 to 1.333×10^2 Pa with a stated accuracy of 0.25% of reading.

Integration of the "isolated" band area were carried out in a manner similar to the one described in Ref. 9 according to the following equation:

$$B_i = (1/nl)\int_{\mathrm{band}\ i} \ln (T_0/T)\mathrm{d}\nu, \quad (14)$$

where n is the sample concentration (mol m^{-3}), l is the optical path length (m), T and T_0 are the transmittance values of the cell with and without the sample gas, respectively. The band intensity is given by units of km mol^{-1}

In many places in the spectra of both CH_3Cl and CD_3Cl, overtone and combination bands were observed to be overlapping with each other. Therefore, whenever possible use was made of a simulation technique to obtain individual band intensities. As usual, the simulation calculation was carried out for the spectra taken under the pressurized sample condition.[1,9] In the calculations, the ground state values of the rotational constants A and B were assumed for the excited vibrational states unless otherwise described. On the other hand, the values of the band centers ν^0 and Coriolis zeta constants ζ^z were obtained from the analysis of the spectra when they were not available in the literature.

For CH_3Cl molecule, the spectral region from 6300 through 500 cm^{-1} has been investigated. There are several things to be noticed in the spectrum. One is a fact that strongly absorbing bands are all due to the fundamentals. Only exception is a parallel component of the $2\nu_5$ band. The fact that the intensity of this particular band is by far the largest among the (binary) overtones and combinations strongly suggests that it is due to the Fermi resonance with the neighboring ν_1 band. This is in accord with the conclusion obtained by Bensari-Zizi and Alamichel.[10] Secondly, as regards the remaining bands, the large majority of them can be assigned to binary overtones and combinations. Also we can find a few of the ternary combinations such as $(\nu_2+2\nu_5^0)$, $(2\nu_2+\nu_5)$, $(\nu_6+2\nu_5^0)$, and $(\nu_3+2\nu_5^0)$.[11] It is most probable that their intensities are borrowed from the neighboring binary combinations through the Fermi resonances. Almost nothing is left to be assigned to impurity bands.

In the 6200—5800 cm^{-1} region, $2\nu_4$, $(\nu_1+\nu_4)$, and $2\nu_1$ bands are expected. The parallel component of the $2\nu_4$ band is clearly observed at 6015.1 cm^{-1}. The band center of the perpendicular component, $2\nu_4(\perp)$, was tentatively located at 6062 cm^{-1}. Since the $2\nu_4(\perp)$ band is strongly perturbed by the Fermi resonance with $(\nu_4+3\nu_6)$ band, the intensity of the $2\nu_4(//)$ was first determined by a simulation calculation for the spectral region of 6050—5980 cm^{-1}. And then the $2\nu_4(\perp)$ intensity was determined by subtracting the parallel component from the total area for these two bands. On the other hand, $(\nu_1+\nu_4)$ band is distributed over obscured $2\nu_1$ band, and the intensities for these two bands were not determined separately.

In a large bush observed between 4600 and 4300 cm^{-1}, $(\nu_4+\nu_5)$, $(\nu_1+\nu_5)$, $(\nu_2+\nu_4)$, and $(\nu_1+\nu_2)$ bands are expected. Since the spectrum of this region is so complicated that their individual intensities were not obtained separately. Towards the lower frequency skirts of this complicated structure, $(\nu_2+2\nu_5^0)$ band is observed.[11]

$(\nu_4+\nu_6)(\perp)$ and $(\nu_4+\nu_6)(//)$ bands are distributed over a region of 4120—4000 cm^{-1}. For these bands, since peaks of the $(\nu_4+\nu_6)(\perp)$ band are not apparent, only the total absorption area was determined from the spectrum. On the other hand, $(\nu_1+\nu_6)$ band appears with a neat band contour at 3979.66 cm^{-1}.[12] The $(\nu_1+\nu_6)$ intensity was obtained through simulating the spectrum from 3990 to 3910 cm^{-1}, by use of the molecular parameters reported in Ref. 12. Also the intensity of $(\nu_3+\nu_4)$ band was obtained through simulation calculation for the spectrum from 3830 to 3730 cm^{-1}. $(\nu_1+\nu_3)$ band is located at 3700.67 cm^{-1}.[12] The intensity of this band was obtained through calculation of the spectrum between 3730 and 3650 cm^{-1}.

The strong $2\nu_5^0$ band is located at 2879.25 cm^{-1},[10] and $(\nu_2+\nu_5)$ band is found at 2803.39 cm^{-1}.[13] Separation of the $(\nu_2+\nu_5)$ intensity from the $2\nu_5^0$ absorption was carried out through comparison of the observed and calculated areas for both 2920—2820 and 2820—2720 cm^{-1} regions.

For the ($\nu_5+\nu_6$) and ($\nu_2+\nu_6$) region, a rotational analysis has been carried out by DiLauro and Alamichel.[14] Therefore, the molecular constants determined by them have been utilized to make simulation analysis of the spectrum. ($\nu_2+\nu_3$) band was observed independently from other bands,[15] and its intensity was obtained in a straightforward manner. Due to the weakness of the absorptions, none of the intensities of the ($\nu_3+\nu_5$),[15] ($\nu_3+\nu_6$), and $2\nu_6$ bands were determined accurately. The observed intensities for CH_3Cl are summarized in Table 1.

For CD_3Cl molecule, the spectral region from 4800 through 500 cm^{-1} has been investigated. The general feature of the spectrum is very similar to that for CH_3Cl. However, in this case, we have observed three distinct bands at 3012,1300, and 1250 cm^{-1}, respectively. These bands seems to be due to CHD_2Cl species. From their intensities, the concentration of CHD_2Cl can be considered to be less than 1%.

The perpendicular component of $2\nu_4$ band is located at 4550.9 cm^{-1}, and the parallel one at 4515.5 cm^{-1}. The

TABLE 1. OBSERVED BAND INTENSITIES FOR $CH_3Cl^{a)}$

Band	ν_i / cm^{-1}	ζ_i	$B_i^{b)}$ / km mol^{-1}	Band	ν_i / cm^{-1}	ζ_i	$B_i^{b)}$ / km mol^{-1}
$2\nu_4(//)$	6015.1	—	0.290(15)	$2\nu_5(//)$	$2879.25^{e)}$	—	$4.16(34)^{a)}$
$2\nu_4(\perp)$	6062	−0.10	0.429(43)	$2\nu_5(\perp)$	2892.33	?	
$\nu_1+\nu_4$	5923.7	0.11	0.92(18)	$\nu_2+\nu_5$	$2803.39^{f)}$	$-0.262^{f)}$	0.316(32)
$2\nu_1$	?	—		$2\nu_2$	?	—	$0.0^{c)}$
$\nu_4+\nu_5(//,\perp)$	?	?	3.02(30)	$\nu_5+\nu_6(//)$	$2466.26^{g)}$	$0.518^{g)}$	0.004(4)
$\nu_1+\nu_5$	?	?		$\nu_5+\nu_6(\perp)$	$2461.88^{g)}$	$-0.012^{g)}$	0.433(43)
$\nu_2+\nu_4$	?	?		$\nu_2+\nu_6$	$2367.72^{g)}$	$0.242^{g)}$	0.255(13)
$\nu_1+\nu_2$	?	—		$\nu_3+\nu_5$	$2182.38^{h)}$	$-0.247^{h)}$	$0.0^{c)}$
$\nu_4+\nu_6(//)$	4042	?	0.369(37)	$\nu_2+\nu_3$	$2080.54_{h)}$	—	0.087(5)
$\nu_4+\nu_6(\perp)$	?	?		$2\nu_6(//,\perp)$	?	?	$0.0^{c)}$
$\nu_1+\nu_6$	$3979.66^{d)}$	$0.252^{d)}$	0.134(7)	$\nu_3+\nu_6$	?	?	$0.0^{c)}$
$\nu_3+\nu_4$	3773.6	0.08	0.164(8)	$2\nu_3$	?	—	?
$\nu_1+\nu_3$	$3700.67^{d)}$	—	0.205(10)	ν_5	1452.12	—	$11.38(78)^{a)}$
ν_4	3038.91	—	$10.77(120)^{a)}$	ν_2	1354.95	—	$8.41(68)^{a)}$
ν_1	2967.76	—	$19.15(144)^{a)}$	ν_6	1017.26	—	$3.85(42)^{a)}$
				ν_3	732.88	—	$23.69(94)^{a)}$

a): For the fundamental bands, see Ref. 1. b): Numbers in parentheses are estimated errors. c): These bands were not observed because of the noise level; althought the noise level was dependent on the spectral region, their intensities may not utmost exceed 0.1 km mol^{-1}. d): Ref. 12. e): Ref. 10. f): Ref. 13. g): Ref. 14. h): Ref. 15.

TABLE 2. OBSERVED BAND INTENSITIES FOR $CD_3Cl^{a)}$

Band	ν_i / cm^{-1}	ζ_i	$B_i^{b)}$ / km mol^{-1}	Band	ν_i / cm^{-1}	ζ_i	$B_i^{b)}$ / km mol^{-1}
$2\nu_4(//)$	4515.5	—	0.202(10)	$2\nu_5(//)$	2104.0	—	$2.56(13)^{a)}$
$2\nu_4(\perp)$	4550.9	−0.33	0.284(14)	$2\nu_5(\perp)$	?	?	
$\nu_1+\nu_4$	4405.3	0.17	0.224(45)	$\nu_2+\nu_5$	?	?	?
$2\nu_1$	?	—		$2\nu_2$	2034.4	—	$1.29(10)^{a)}$
$\nu_4+\nu_5(//)$	3322	?	0.91(9)	$\nu_5+\nu_6(//)$	1813	?	0.384(38)
$\nu_4+\nu_5(\perp)$	3310?	0.10		$\nu_5+\nu_6(\perp)$	1801	0.08	
$\nu_2+\nu_4$	?	?		$\nu_3+\nu_5$	?	?	
$\nu_1+\nu_5$	?	?		$\nu_2+\nu_6$	?	?	?
$\nu_1+\nu_2$	?	—	$0.0^{c)}$	$\nu_2+\nu_3$	1725.7	—	0.125(13)
$\nu_4+\nu_6(//)$	3046	?	?	$2\nu_6(//,\perp)$	?	?	$0.0^{c)}$
$\nu_4+\nu_6(\perp)$	?	?	?	$\nu_3+\nu_6$	?	?	$0.0^{c)}$
$\nu_3+\nu_4$	?	?	$0.0^{c)}$	$2\nu_3$	1394.9	—	0.124(12)
$\nu_1+\nu_6$	?	?	$0.0^{c)}$	ν_5	1059.97	—	$5.76(46)^{a)}$
$\nu_1+\nu_3$	2859.2	—	0.119(6)	ν_2	1028.67	—	$12.37(37)^{a)}$
ν_4	2283.29	—	$5.42(12)^{a)}$	ν_6	767.61	—	$0.57(10)^{a)}$
ν_1	2160.24	—	$1.96(24)^{a)}$	ν_3	701.36	—	$17.70(35)^{a)}$

a): For the fundamental bands, see Ref. 1 b): Numbers in parentheses are estimated errors. c): These bands were not observed because of the noise level; although the noise level was dependent on the spectral region, their intensities may not utmost exceed 0.1 km mol^{-1}

Table 3. Values of the cubic force constants φ_{rst} for methyl chloride [a] (Units are cm^{-1})

rst	CH_3Cl	CD_3Cl	*rst*	CH_3Cl	CD_3Cl
A group[b]			255	−60.7	−5.1
111	−1106.3	−669.9	256	−203.5	−150.5
112	−7.1	−11.8	266	−176.1	−152.5
113	17.6	−2.4	344	19.5	2.8
122	−102.6	−68.6	345	−6.6	14.9
123	−14.2	15.5	346	−70.5	−25.2
133	48.5	52.7	355	−49.4	6.7
222	204.2	104.5	356	−242.6	−144.5
223	−20.9	−55.6	366	−84.3	−64.2
233	−21.9	−61.6	C group[b]		
333	−260.5	−221.3	444	−820.4	−532.1
B group[b]			445	−58.9	−43.8
144	−1035.5	−648.6	446	9.6	−5.7
145	−11.9	18.5	455	−183.5	−128.4
146	−18.8	−34.5	456	156.3	63.7
155	95.5	62.8	466	166.3	99.0
156	−2.2	−19.8	555	−460.6	−204.6
166	623.8	372.5	556	−295.8	−208.0
244	50.6	28.2	566	−19.4	−47.9
245	−79.6	−26.4	666	86.3	55.4
246	−281.6	−180.9			

a): Calculated from the cubic symmetry force constants in Ref. 5. b): See Ref. 5 for the classification of the force constants.

individual intensities of these two bands were easily obtained by the simulation method. The feature of the $(\nu_1+\nu_4)$ and $2\nu_1$ band region is quite similar to that in CH_3Cl, and the intensities of these bands were not separately determined. Also the spectral region for $(\nu_4+\nu_5)$, $(\nu_2+\nu_4)$, and $(\nu_1+\nu_5)$ shows a very complicated appearance, and the individual intensities were not determined either.

Althogh $(\nu_4+\nu_6)(/\!/)$ band appears with an appreciable intensity,peaks due to the perpendicular component were not identified, as in the case of CH_3Cl. Instead, there was an extra parallel type band at 3011.6 cm^{-1}, presumably due to CHD_2Cl molecule. In fact, we have also observed a structure which seemed to be due to the "perpendicular" component of the same band. Due to the weakness, neither of $(\nu_3+\nu_4)$ and $(\nu_1+\nu_6)$ bands were clearly identified.

The parallel band of $(\nu_1+\nu_3)$ is clearly observed at 2861.6 cm^{-1}, which is accompanied by $(2\nu_2+\nu_3)$ and $(\nu_3+2\nu_5{}^0)$ bands. Intensities for $2\nu_5(/\!/)$ and $2\nu_2$ have already been determined in Part I.[1] In this case however the intensity value for the $2\nu_5$ band should be considered as to include contributions both from $2\nu_5{}^0$ and $2\nu_5{}^2$.

Peaks due to the perpendicular component of $(\nu_5+\nu_6)$ band are apparent in the region between 1900 and 1750 cm^{-1}. However, the individual band intensities contributing to this region can not separately be obtained because of the spectral complexity. The $(\nu_2+\nu_3)$ band is clearly seen at 1725.7 cm^{-1}. Also $2\nu_3$ band is apparent at 1394.9 cm^{-1}, although we did not find clearly the $2\nu_6$ band anywhere. As mentioned above, a pair of parallel and perpendicular type bands appear at 1300 and 1250 cm^{-1}, respectively, which may

Table 4. Calculated values of the second derivatives of the transformed dipole moment for CH_3Cl (in 1 D$\approx$3.3356$\times$10^{-30} C m)

rs(*α*)	Calcd I[a]	Calcd II[b]	Calcd III[c]
11(z)	0.0094	−0.0099	−0.0005
12(z)	−0.0005	−0.0017	−0.0022
13(z)	−0.0005	0.0074	0.0069
22(z)	−0.0105	−0.0329	−0.0434
23(z)	−0.0021	0.0185	0.0164
33(z)	−0.0247	0.0193	−0.0054
14(x)	0.0042	−0.0191	−0.0149
15(x)	0.0006	−0.0143	−0.0137
16(x)	−0.0013	0.0078	0.0065
24(x)	−0.0003	0.0172	0.0169
25(x)	−0.0048	−0.0077	−0.0125
26(x)	−0.0110	0.0179	0.0069
34(x)	−0.0003	0.0093	0.0090
35(x)	0.0009	−0.0001	0.0008
36(x)	−0.0202	0.0005	−0.0197
44(z)	0.0083	−0.0223	−0.0140
44(x)	0.0030	−0.0182	−0.0152
45(z)	−0.0002	−0.0030	−0.0032
45(x)	−0.0005	−0.0130	−0.0135
46(z)	−0.0017	0.0106	0.0089
46(x)	0.0003	0.0028	0.0031
55(z)	0.0326	0.0055	0.0381
55(x)	−0.0214	0.0069	−0.0145
56(z)	−0.0095	−0.0065	−0.0160
56(x)	−0.0007	−0.0121	−0.0128
66(z)	0.0193	−0.0240	−0.0047
66(x)	0.0016	0.0002	0.0018

a): Contribution from the mechanical anharmonicity. b): The electrical anharmonicity. c): Calcd I+II.

be due to CHD_2Cl.

The observed band intensities for the CD_3Cl molecule are summarized in Table 2.

Numerical Calculations and Discussion

As is apparent in the equations shown in a previous section, the intensities of binary overtone and combination bands contain contributions both from electrical and mechanical anharmonicities. If the second derivatives of the dipole moment are neglected, we can calculate the intensities of these bands by using the values of $(\partial \boldsymbol{P}/\partial Q_r)$ and cubic force constants. The former has been determined in Part I, and the latter can be calculated from the cubic symmetry force field determined in Ref. 5. The cubic force constants obtained from the symmetry force constants are shown in Table 3. Calcd I in Tables 4 and 5 shows thus derived mechanical anharmonicity correction to the second derivatives of the dipole moment. Calcd I in Tables 6 and 7 shows the calculated intensities from these values. However, comparison of these values with the observed ones reveals that the agreement is not so good. Indeed, this is not surprising because we did not consider the second derivatives themselves to obtain the calculated intensities.

In order to obtain some estimates of the dipole moment derivatives, *ab initio* calculations may be useful. In fact, Scanlon *et al.* have calculated the second derivatives of the dipole moment for CH_4[16] and SF_6[17] with some success. In the following, a similar calculation will be carried out to obtain the values of the second derivatives of the dipole moment for methyl chloride.

The calculations were carried out by using the HONDO program[18] (IMS version) with the 4-31 G* basis set, where d-functions with α=0.80 were used for both C and Cl atoms. The dipole moment derivatives were calculated with the experimental normal coordinates[19,21] for the optimized molecular geometry: CH=1.0775 Å, CCl=1.7775 Å, and ∠HCH=110.29°. The displacements for the second derivatives were obtained by addition of the simple harmonic motion of the two normal coordinates involved. Distorsions of 0.02 $u^{1/2}$ Å were employed in each case.

Calcd II in Tables 4 and 5 shows the resulting *ab initio* values of the second derivatives of the dipole moment. The numbers for Calcd III in the same tables are the sums of the numbers for Calcd I and II. On the other hand, Calcd II in Tables 6 and 7 shows the calculated intensities for the overtones and combinations using

Table 5. Calculated values of the second derivatives of the transformed dipole moment for CD_3Cl (in 1 D≈3.3356×10^{-30} C m)

$rs(\alpha)$	Calcd I[a]	Calcd II[b]	Calcd III[c]
11(z)	0.0076	−0.0075	0.0001
12(z)	−0.0002	−0.0002	−0.0004
13(z)	0.0010	0.0045	0.0055
22(z)	−0.0199	−0.0142	−0.0341
23(z)	−0.0038	0.0225	0.0187
33(z)	−0.0185	0.0124	−0.0061
14(x)	0.0031	−0.0154	−0.0123
15(x)	0.0001	−0.0051	−0.0050
16(x)	0.0000	0.0033	0.0033
24(x)	−0.0002	0.0125	0.0123
25(x)	−0.0014	−0.0011	−0.0025
26(x)	−0.0085	0.0136	0.0051
34(x)	0.0001	0.0052	0.0053
35(x)	0.0014	0.0087	0.0101
36(x)	−0.0068	−0.0008	−0.0076
44(z)	0.0064	−0.0177	−0.0113
44(x)	0.0022	−0.0148	−0.0126
45(z)	−0.0006	−0.0017	−0.0023
45(x)	−0.0002	−0.0038	−0.0040
46(z)	−0.0012	0.0077	0.0065
46(x)	0.0003	0.0002	0.0005
55(z)	0.0396	0.0056	0.0452
55(x)	−0.0123	0.0208	0.0085
56(z)	−0.0137	−0.0039	−0.0176
56(x)	−0.0021	−0.0006	−0.0027
66(z)	0.0104	−0.0160	−0.0056
66(x)	0.0000	−0.0008	−0.0008

a): Contribution from the mechanical anharimonicity. b): The electrical anharmonicity. c): Calcd I+II.

Table 6. Comparison of the observed band intensities with the calculated values for CH_3Cl (Units are km mol^{-1})

Band	Obsd	Calcd I[a]	Calcd II[b]
$2\nu_4$(//)	0.290(15)	0.260	0.750
$2\nu_4$(⊥)	0.429(43)	0.070	1.751
$\nu_1+\nu_4$	0.92(18)	0.131	1.679
$2\nu_1$		0.163	0.001
$\nu_4+\nu_5$(//,⊥)	3.02(30)	0.003	2.106
$\nu_1+\nu_5$		0.002	1.047
$\nu_2+\nu_4$		0.001	1.568
$\nu_1+\nu_2$		0.001	0.013
$\nu_4+\nu_6$(//)	0.369(37)	0.014	0.409
$\nu_4+\nu_6$(⊥)		0.001	0.097
$\nu_1+\nu_6$	0.134(7)	0.008	0.215
$\nu_3+\nu_4$	0.164(8)	0.000	0.396
$\nu_1+\nu_3$	0.205(10)	0.001	0.113
$2\nu_5$(//)	4.16(34)	1.934	2.642
$2\nu_5$(⊥)		1.677	0.771
$\nu_2+\nu_5$	0.316(32)	0.081	0.550
$2\nu_2$	0.0[c]	0.094	1.605
$\nu_5+\nu_6$(//)	0.004(4)	0.283	0.801
$\nu_5+\nu_6$(⊥)	0.433(43)	0.003	1.029
$\nu_2+\nu_6$	0.255(13)	0.361	0.144
$\nu_3+\nu_5$	0.0[c]	0.002	0.002
$\nu_2+\nu_3$	0.087(5)	0.006	0.361
$2\nu_6$(//,⊥)	0.0[c]	0.487	0.037
$\nu_3+\nu_6$	0.0[c]	0.926	0.881
$2\nu_3$	?	0.296	0.014

a): Contribution from mechanical anharmonicity only was taken into account. b): The second derivatives of the dipole moment estimated through *ab initio* method (4-31 G*) were also taken into consideration. c): See footnote c) to Table 1.

TABLE 7. COMPARISON OF THE OBSERVED BAND INTENSITIES WITH THE CALCULATED VALUES FOR CD_3Cl (UNITS ARE km mol^{-1})

Band	Obsd	Calcd I a)	Calcd II b)
$2\nu_4(//)$	0.202(10)	0.118	0.364
$2\nu_4(\perp)$	0.284(14)	0.027	0.911
$\nu_1+\nu_4$	0.224(45)	0.053	0.844
$2\nu_1$		0.077	0.000
$\nu_4+\nu_5(//)$	0.91(9)	0.001	0.022
$\nu_4+\nu_5(\perp)$		0.000	0.133
$\nu_2+\nu_4$		0.000	0.628
$\nu_1+\nu_5$		0.000	0.102
$\nu_1+\nu_2$	0.0 c)	0.000	0.000
$\nu_4+\nu_6(//)$	?	0.006	0.165
$\nu_4+\nu_6(\perp)$	?	0.001	0.002
$\nu_3+\nu_4$	0.0 c)	0.000	0.108
$\nu_1+\nu_6$	0.0 c)	0.000	0.041
$\nu_1+\nu_3$	0.119(6)	0.002	0.056
$2\nu_5(//)$	2.56(13)	2.103	2.740
$2\nu_5(\perp)$		0.404	0.196
$\nu_2+\nu_5$	?	0.005	0.016
$2\nu_2$	1.29(10)	0.258	0.759
$\nu_5+\nu_6(//)$	0.384(38)	0.442	0.730
$\nu_5+\nu_6(\perp)$		0.022	0.035
$\nu_3+\nu_5$		0.004	0.232
$\nu_2+\nu_6$	?	0.168	0.060
$\nu_2+\nu_3$	0.125(13)	0.016	0.393
$2\nu_6(//,\perp)$	0.0 c)	0.109	0.033
$\nu_3+\nu_6$	0.0 c)	0.090	0.113
$2\nu_3$	0.124(12)	0.160	0.017

a): Contribution from mechanical anharmonicity only was taken into account. b): The second derivatives of the dipole moment estimated by 4-31 G* were also taken into consideration. c): See footnote c) Table 2.

these estimated values of the dipole derivatives. On the whole, agreement of the calculated intensities with the observed ones improved much by the inclusion of the *ab initio* values of the second derivatives. The agreement is almost semi-quantitative for all bands expect $2\nu_2$, $(\nu_5+\nu_6)(//)$, and $(\nu_3+\nu_6)$ of CH_3Cl molecule. Therefore, the *ab initio* values of the second derivatives should at least be of correct orders of magnitude.

However, the discrepancies are still much larger than we expected. In this concern, it should be noted that the effect of Fermi resonance has not been taken into account exactly in the expressions given in this paper. The intensity values calculated from these equations may contain large errors when there are close resonances. For example, in the case of $2\nu_5(//)$ band of CH_3Cl and CD_3Cl, a part of discrepancy between the observed and calculated intensities must be due to Fermi resonance with the respective ν_1 band. Discrepancies are, however, also noted for some of those which are free from such resonances. It is possible that a considerable part of the discrepancy is due to the errors in the normal coordinate force constants used here. In fact, in order to determine the force constants through the least-squares calculation, we were forced to constrain some of the 38 independent force constants.5) Moreover, the resulting errors for many of the force constants were more or less of the same magnitudes as or even larger than the derived values of the constants themselves.5)

At any rate, it is clear that a further effort to refine the cubic force field is required before definite values are obtained for the second derivatives of the dipole moment of this molecule.

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References

1) S. Kondo, Y. Koga, T. Nakanaga, and S. Saëki, *Bu. Chem. Soc. Jpn.*, **56**, 416 (1983).

2) C. Secroun, A. Barbe, and P. Jouve, *J. Mol. Spectrosc.* **45**, 1 (1973).

3) S. J. Yao and J. Overend, *Spectrochim. Acta, Part A*, **32**, 1059 (1976).

4) J. Overend, *J. Chem. Phys.*, **64**, 2878 (1976).

5) S. Kondo, Y. Koga, T. Nakanaga, and S. Saëki, *J. Mol. Spectrosc.*, **100**, 332 (1983).

6) A. R. Hoy, I. M. Mills, and G. Strey, *Mol. Phys.*, **24**, 1265 (1972).

7) J. Overend, "Vibrational Intensities in Infrared and Raman Spectroscopy," ed by W. B. Person and G. Zerbi, Elsevier, Amsterdam (1982), p. 203.

8) I. M. Mills, "Molecular Spectroscopy: Modern Research," ed by K. N. Rao and C. W. Mathews, Academic Press, New York (1972), p. 115.

9) For example, see S. Kondo and S. Saëki, *J. Chem. Phys.*, **74**, 6603 (1981).

10) N. Bensari-Zizi and C. Alamichel, *Mol. Phys.*, **43**, 1255 (1981).

11) N. Bensari-Zizi, C. Alamichel, and G. Guelachvili, *Spectrochim. Acta, Part A*, **37**, 773 (1981).

12) N. Bensari-Zizi, C. Alamichel, and G. Guelachvili, *Can. J. Phy.*, **59**, 994 (1981).

13) M. Morillon-Chapey, G. Graner, C. Alamichel, C. Betrencourt-Stirnemann, M. Betrencourt, and J. Pinard, *J. Phys. (Paris)*, **31**, 519 (1970).

14) C. DiLauro and C. Alamichel, *J. Mol. Spectrosc.*, **81**, 390 (1980).

15) N. Bensari-Zizi, C. Alamichel, and G. Guelachvili, *Mol. Phys.*, **46**, 171 (1982); **34**, 1131 (1977).

16) K. Scanlon, R. A. Eades, D. A. Dixon, and J. Overend, *J. Phys. Chem.*, **85**, 2878 (1981).

17) K. Scanlon, R. A. Eades, and D. A. Dixon, *Spectrochim. Acta, Part A*, **38**, 849 (1982).

18) M. Dupuis and H. F. King, *J. Chem. Phys.*, **68**, 3998 (1978).

19) In part I, the harmonic force field of Duncan, Allan, and McKean20) was used. In the present work, a slightly modified one by Duncan, McKean, and Speirs21) is utilized. See Ref. 5.

20) J. L. Duncan, A. Allan, and D. C. Mckean, *Mol. Phys.*, **18**, 289 (1970).

21) J. L. Duncan, D. C. McKean, and G. K. Speirs, *Mol. Phys.*, **24**, 553 (1972).