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Infrared Intensities in Methyl Chloride. I. The Fundamental Bands

Shigeo Kondo,* Yoshinori Koga, Taisuke Nakanaga, and Shinnosuke Saëki
National Chemical Laboratory for Industry, Tsukuba Research Center, Yatabe, Ibaraki 305

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The integrated intensities of the fundamental bands of CH_3Cl and CD_3Cl molecules have been measured by the pressure broadening technique. The Coriolis intensity perturbation between ν_3 and ν_6 bands of CD_3Cl has been analysed to determine the sign to be negative. The intensity analysis has been carried out to determine the correct signs of $(\partial p/\partial Q_i)$. The resulting signs are $(-++)$ for A_1 and $(-+-)$ for E species. The $(\partial p/\partial S_j^R)$ values as well as the atomic polar tensors have been obtained.

Recently, several investigations have been carried out on the infrared intensities of a series of methyl halide molecules.[1–4] This is not only because these molecules are fundamental ones from a spectroscopic viewpoint, but because there has been a well known sign ambiguity problem which was described in a very clearcut manner by Abbate and Gussoni.[3]

A first study on the subject made by Barrow and McKean[5] did not give any definite answer to this question, for they only measured intensities of the parent molecules, and had nothing but chemical intuition to determine the correct sign combination for $(\partial p/\partial Q_i)$, which can not be enough to solve this tough problem in the infrared intensity studies. On the other hand, Dickson *et al.*[6] have measured the fundamental band intensities for both CH_3X and CD_3X molecules, where X=Cl, Br, and I. Their measurements were carried out very carefully, and reasonably accurate intensity values have been obtained except those which are badly overlapped with each other. In fact, they have almost succeeded in determining the signs of $(\partial p/\partial Q_i)$ simply by comparing the values of the intensity parameters obtained for the two isotopic molecules for various sign combinations. Their best sign choice was $(-++)$ for A_1 and $(-+-)$ for E species.[6] However, Russell *et al.*[1] have pointed out that a number of other sign combinations become possible when the intensity errors due to overlappings and also the force field errors are taken into account.

On the other hand, Newton and Person[2] have selected a sign combination of $(\partial p/\partial Q_i)$ of methyl fluoride on the basis of the CNDO/2 method, and extended that particular choice to the methyl chloride molecule. Their signs are $(-++)$ both for A_1 and E species.[2] Later, however, Abbate and Gussoni[3] have pointed out that the choice for methyl fluoride made by Newton and Person[2] is definitely against the isotopic invariance rule.

In a previous paper,[4] we have shown that this confusion on the sign problem of methyl fluoride was completely due to an erroneous intensity value of ν_6 band of CD_3F molecule. The final answer was found to be $(-++)$ both for A_1 and E species of this molecule. Then, a question arises whether we can still extend the same sign combination to the methyl chloride molecule.

Considering the experimental results reported thus far, there seems little doubt that the signs for A_1 species are $(-++)$. However, the signs for E species are still debatable. Therefore, the current question is whether the recently improved technique for the infrared intensity measurement and analysis can give a definite answer for the E species signs. For that purpose, we have carefully remeasured all the fundamental band intensities of CH_3Cl and CD_3Cl molecules. We have also determined the sign of the Coriolis interaction between ν_3 and ν_6 of CD_3Cl molecule. Then, a least squares calculation has been carried out to determine definitely the correct signs of $(\partial p/\partial Q_i)$.

Experimental

The CH_3Cl gas was purchased from Takachiho Chemical Co. and CD_3Cl gas from Merck Sharp and Dohme Co. Canada. The purity of CH_3Cl was stated as 99.5% and that of CD_3Cl was 99 atom%. Inspection of full region of the infrared spectra of these gases well guaranteed the stated sample purities.[7]

Spectra were all observed with a resolution of 0.25 cm^{-1} (optical path length of 4 cm, with Happ-Genzel apodization). A Nicolet model 7199 FT-IR spectrophotometer was used with a mercury-cadmium telluride detector. For intensity measurements, a 6 cm high pressure cell accommodated 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 also 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%. Integration of the "isolated" band area were carried out in a manner similar to the one described in Ref. 8. Separation of the overlapping bands was done by the simulation technique as usual.[4,9]

Results

Fundamental Band Intensities. In the CH stretching region of CH_3Cl molecule, ν_1 and ν_4 overlap with each other. Also $2\nu_5$ band appears with a fairly high intensity presumably due to the Fermi resonance with the ν_1 band. Separation of the ν_1 and ν_4 bands was made by a simulation calculation taking account of the Fermi resonance between ν_4 and $3\nu_6$ bands, by using the molecular parameters in Refs. 10 and 11. The result is shown in Fig. 1. The $2\nu_5$ intensity was obtained simply by integrating the absorption area from 2920 through 2820 cm^{-1}. The integrated band intensity is defined by

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

where n is the sample concentration (mol/m^3), l is the optical path length (m), T and T_0 are the transmittance

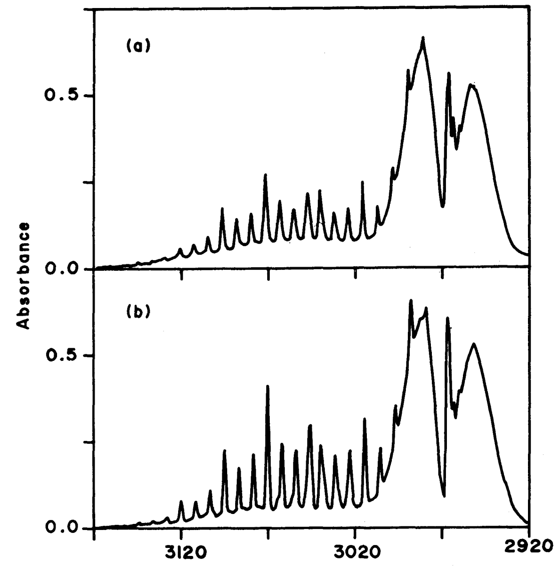

Fig. 1. Observed and calculated spectra of ν_1 and ν_4 region of CH_3Cl. (a) Observed spectrum with a sample pressure of 1.245×10^4 Pa in a 6 cm cell under a total presure of 1.11×10^6 Pa of nitrogen. Resolution of 0.25 cm^{-1} was used. (b) Calculated spectrum with the molecular parameters in Refs. 10 and 11.

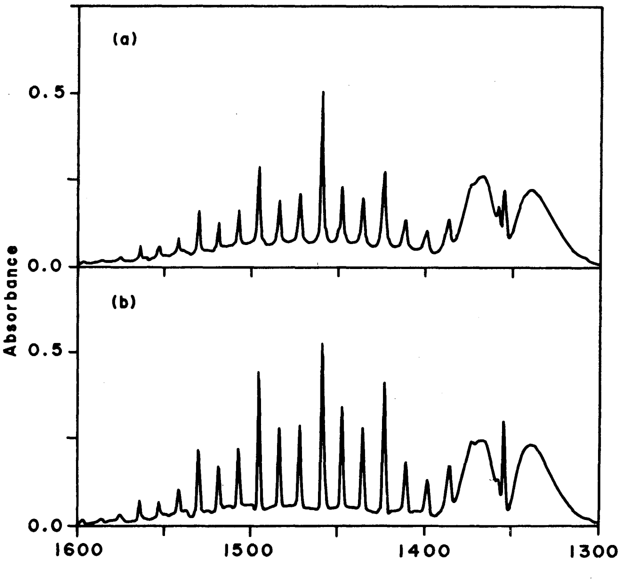

Fig. 2. Observed and calculated spectra of ν_2 and ν_5 region of CH_3Cl. (a) Observed spectrum with a sample pressure of 1.245×10^4 Pa in a 6 cm cell under a total pressure of 1.11×10^6 Pa of nitrogen. Resolution of 0.25 cm^{-1} was used. (b) Calculated spectrum for a negative Coriolis perturbation between ν_2 and ν_5. The molecular constants in Ref. 14 were utilized.

TABLE 1. OBSERVED BAND INTENSITIES OF METHYL CHLORIDE (km/mol)

Band		ν_i[a)]/cm^{-1}	This work[b)]	Ref. 2	Ref. 1
CH_3Cl	ν_4	3038.91[c)]	10.77(120)	9.69	9.70
	ν_1	2967.76[d)]	19.15(144)	17.56	20.17
	$2\nu_5(a_1)$	2879	4.16(34)	3.86	7.46
	ν_5	1452.12[e)]	11.38(78)	12.31	9.72
	ν_2	1354.95[e)]	8.41(68)	6.80	8.97
	ν_6	1017.26[e)]	3.85(42)	4.02	4.19
	ν_3	732.88[e)]	23.69(94)	23.19	20.94
CD_3Cl	ν_4	2283.29[e)]	5.42(12)	5.12	
	ν_1	2160.24[e)]	11.96(24)	11.39	
	$2\nu_5(a_1)$	2104	2.56(13)	3.34	
	$2\nu_2$	2034.39[e)]	1.29(10)	···	
	ν_5	1059.970[f)]	5.76(46)	6.91	
	ν_2	1028.673[f)]	12.37(37)	10.76	
	ν_6	767.61[e)]	0.57(10)	1.11	
	ν_3	701.36[e)]	17.70(35)	15.36	

a) Frequencies for ^{35}Cl molecules. b) Numbers in parentheses are the uncertainties to be used in the intensity calculation, which are the largest of 0.10 km/mol, 2 % of the band intensity and the estimated error for the band. The estimated error is twice the standard error from the Beer's law plot plus something due to the overlappings, where necessary. c) Ref. 10. d) Ref. 11. e) Ref. 12. f) Ref. 14.

values of the cell with and without the sample gas, respectively. The band intensity is given by units of km/mol. In the CH deformation region, ν_2 and ν_5 bands overlap with each other. Band separation was made by using the molecular parameters reported in the literature,[12–14)] taking into account the Coriolis interaction between ν_2 and ν_5. The result is shown in Fig. 2. On the other hand, the ν_3 and ν_6 bands are well isolated from other bands, and their intensities were obtained by simply integrating the respective band area. The result is summarized in Table 1.

In the CD stretching region of CD_3Cl, ν_4 band is well isolated from other bands. As for the ν_1 band, which is the symmetric CD_3 stretching mode, there are two neighboring overtone bands, $2\nu_5$ and $2\nu_2$. However, since their band contours are all similar (parallel bands), and overlappings are not so serious, separation of these bands is by no means difficult.

On the other hand, in the CD deformation region ν_2 and ν_5 bands are mutually heavily overlapped, and furthermore, they are in strong Coriolis resonance as well. Their separation was carried out by simulation method by using the parameters reported in Ref. 14, and is shown in Fig. 3.

ν_3 band is the strongest fundamental band of the CD_3Cl molecule, near which a weak perpendicular band of ν_6 is observed. Since the ν_6 band is very much weaker than the ν_3 band, it is quite possible that the former suffers a considerable intensity perturbation from the latter. By using the molecular parameters in Refs. 12 and 14, together with the calculated value for the zeta constant $\zeta_{3,6a}{}^{y}$ (+0.276), simulation calculations have been carried out for different signs of the perturbation. If the sign is negative, the higher frequency region of ν_6 band is such that partly obscured Q branch peaks are distributed over a rather thick back ground which is composed of the degraded R and P branches, and in the lower frequency region rather sharp Q branches are located against a relatively thin back ground. On the other hand, if the sign is positive,

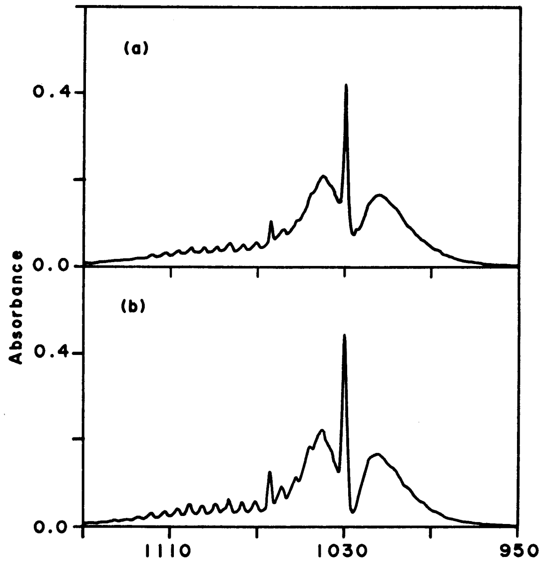

Fig. 3. Observed and calculated spectra of ν_2 and ν_5 region of CD_3Cl. (a) Observed spectrum with a sample pressure of 6.64×10^3 Pa in a 6 cm cell under a total presure of 1.11×10^6 Pa of nitrogen. Resolution of 0.25 cm^{-1} was used. (b) Calculated spectrum for a negative Coriolis perturbation between ν_2 and ν_5. The molecular constants in Ref. 14 were employed.

Table 2. Symmetry coordinates of methyl chloride

A_1: $S_1=(\Delta r_1+\Delta r_2+\Delta r_3)/\sqrt{3}$

$S_2=[K(\Delta\alpha_1+\Delta\alpha_2+\Delta\alpha_3)-(\Delta\beta_1+\Delta\beta_2+\Delta\beta_3)]/\sqrt{3(1+K^2)}$ [a]

$S_3=\Delta R$

E: $S_{4a}=(2\Delta r_1-\Delta r_2-\Delta r_3)/\sqrt{6}$

$S_{5a}=(2\Delta\alpha_1-\Delta\alpha_2-\Delta\alpha_3)/\sqrt{6}$

$S_{6a}=(2\Delta\beta_1-\Delta\beta_2-\Delta\beta_3)/\sqrt{6}$

$S_{4b}=(\Delta r_2-\Delta r_3)/\sqrt{2}$

$S_{5b}=(\Delta\alpha_2-\Delta\alpha_3)/\sqrt{2}$

$S_{6b}=(\Delta\beta_2-\Delta\beta_3)/\sqrt{2}$

a) $K=-3\sin\beta\cos\beta/\sin\alpha$.

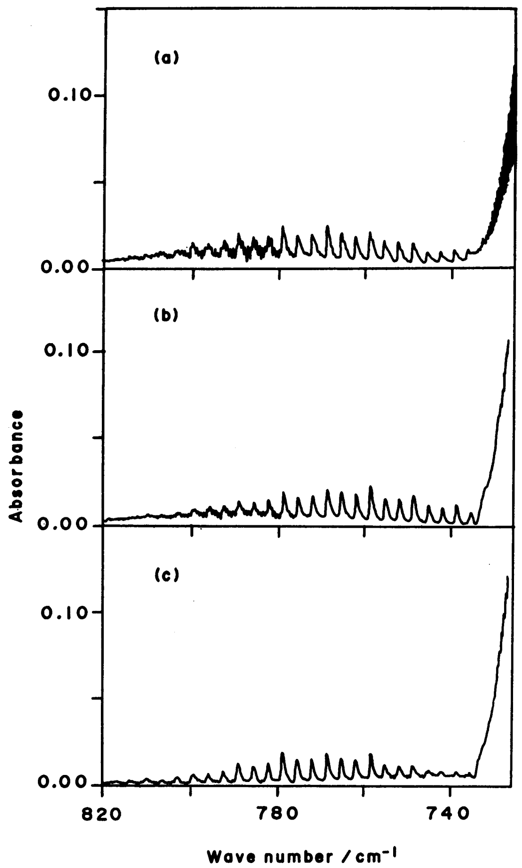

Fig. 4. Observed and calculated spectra of ν_6 region of CD_3Cl. (a) Observed spectrum with sample pressure of 4.95×10^3 Pa in a 10 cm cell.Resolution of 0.25 cm^{-1} was used, and calculated spectra (b) with a negative Coriolis perturbation between ν_6 and ν_3, and (c) with a positive interaction. The molecular constants reported in Ref. 14 were used.

completely the reverse is true. These features are exactly what are expected from the theory by DiLauro and Mills.[15] The observed spectrum definitely agrees better with the one calculated for a negative sign, as shown in Fig. 4. Thus, the sign of the ν_3-ν_6 interaction in CD_3Cl molecule has been determined as negative. The ν_6 band intensity was obtained through simulation calculation for a pressurized spectrum of this region.

Intensity Calculation. If the pressure broadening effect is sufficiently large compared with the employed spectral resolving power,[16] the integrated band intensity B_i can be taken as the absolute intensity A_i which is expressed by,[17]

$$A_i=(N\pi/3c^2)(\partial p/\partial Q_i)^2, \tag{2}$$

where N is Avogadro's number, c is the light velocity, p is the molecular dipole moment, and Q_i is the ith normal coordinate. Further, $(\partial p/\partial Q_i)$ is expressed by a linear combination of $(\partial p/\partial S_j)$, where S_j is the jth symmetry coordinate, namely,

$$(\partial p/\partial Q_i)=\Sigma(\partial p/\partial S_j)L_{ji}, \tag{3}$$

where L_{ji} is the L matrix element.

As usual, the intensity parameter is defined by the following equation,[18]

$$p_j=(\partial p/\partial S_j^R)=(\partial p/\partial S_j)+p^0K_j, \tag{4}$$

where p^0 is the permanent dipole moment and K_j is the rotational correction coefficient. The symmetry coordinates were defined the same as in Ref. 4, and are shown in Table 2. The molecular coordinate system and the internal coordinates are shown in Fig. 5. As usual, we have preferred to set up the whole molecular system so that we may have a positive permanent dipole moment. (The positive dipole moment is defined to be directed from the negative to the positive end of the molecule. There may be little doubt that the chlorine atom is the negative end of the methyl chloride molecule.) The absolute value of p^0 has been determined as 1.869(10) D by Shulman *et al.*[19]

Table 3 shows the L matrices for CH_3Cl and CD_3Cl molecules, which are obtained by using the harmonic force field reported by Duncan *et al.*[20] Definition of the symmetry coordinates in reference molecule S_j^R

Table 3. L matrices of methyl chloride[a)]

CH_3Cl	A_1:	1.008	−0.012	0.001	E:	1.051	0.021	−0.001
		−0.075	1.376	0.168		0.112	1.499	−0.222
		−0.044	0.084	0.321		−0.101	0.315	0.906
CD_3Cl	A_1:	0.722	0.003	0.009	E:	0.781	0.000	0.010
		−0.133	1.060	0.022		0.192	1.100	−0.085
		−0.066	0.148	0.292		−0.137	0.135	0.693

a) Calculated for the ^{35}Cl species from the force field and molecular geometry in Ref. 19. Units are either $u^{-1/2}$ or rad $u^{-1/2}$Å^{-1} depending on whether S_j is the bond stretching or angle bending coordinate.

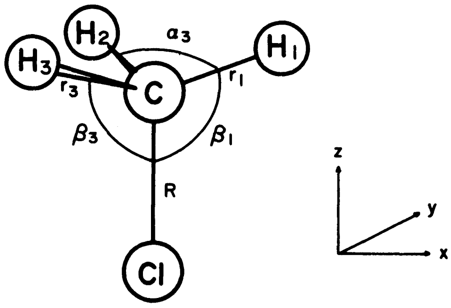

Fig. 5. The methyl chloride molecule, molecular axis, and the internal coordinates.

Table 4. Symmetry coordinates of reference molecule S_j^R and the rotational correction coefficients K_j in methyl chloride[a)]

S_j^R	Fixed atoms	CH_3Cl	CD_3Cl
4a	C, Cl	+0.038	+0.057
5a	C, Cl	+0.037	+0.056
6a	C, Cl	−0.070	−0.111

a) Units are Å^{-1} for S_{4a} and rad^{-1} for S_{5a} and S_{6a}.

Table 5. Residual values from the least squares calculations for the intensities varying the signs of $(\partial p/\partial Q_i)$[a)]

A_1 species $(123)^H(123)^D$	Res.	E species $(456)^H(456)^D$	Res.
(+++)(+++)	91	(+++)(+++)	236
(−++)(−++)	2.0	(−++)(−++)	220
(+−+)(+−+)	689	(+−+)(+−+)	159
(−−+)(−−+)	608	(−−+)(−−+)	156
(++−)(++−)	608	(++−)(++−)	0.8
(−+−)(−+−)	689	(−+−)(−+−)	1.5
(+−−)(+−−)	2.0	(+−−)(+−−)	20
(−−−)(−−−)	91	(−−−)(−−−)	34

a) The residual is defined in the text; Eq. 5.

Table 6. Comparison of the observed values of the intensity parameters with the *ab initio* values

Parameter	Obsd[a)]		*ab initio*[b)]
	$(-++)(-+-)^H$	$(-++)(++-)^H$	
p_1/D Å^{-1}	−0.610(12)[c)]	−0.610	−0.78
p_2/D rad^{-1}	0.197(13)	0.197	0.40
p_3/D Å^{-1}	2.224(29)	2.224	2.97
p_4/D Å^{-1}	−0.294(6)	0.356	−0.43
p_5/D rad^{-1}	0.353(9)	0.348	0.34
p_6/D rad^{-1}	−0.293(12)	−0.299	−0.38

a) The preferred combination is $(-++)(-+-)^H$. b) Calculated with the 6-31G* basis set; Ref. 20. c) Numbers in parentheses are the standard errors from least squares calculations.

and the values of the rotational correction coefficients are listed in Table 4.

Intensity calculations were carried out by a least squares method varying the signs of $(\partial p/\partial Q_i)$ for A_1 and E species separately. For the calculation, the residual value was defined as,

$$\text{Res.} = \Sigma (X_i^{\text{obsd}} - X_i^{\text{calcd}})^2 / (\Delta X_i^{\text{obsd}})^2, \qquad (5)$$

where X_i denotes the dipole moment derivatives $(\partial p/\partial Q_i)$ for the parent molecule and the band intensity A_i for the isotopic species. The signs of $(\partial p/\partial Q_i)$ for the parent molecule are actually examined in that calculation. The residual value was used to examine the propriety of the sign combination postulated in the calculation.[18)] Since there are three normal vibrations both for A_1 and E species, eight sign combinations are possible for each of them. In Table 5, residual values have been obtained from the least squares calculations for eight sign combinations of both symmetry species.

In A_1 species, considering that the number of the intensity data is six, possibility is limited either to (−++) or to (+−−) set, for these are only sets whose residuals are less than the data number of six, while those of other sets are by far larger than that. Similarly, in E species, the residual values for (++−) and (−+−) sets are much smaller than the others. Therefore, we may pick up these two sets as possible ones. But for the sake of security, we also included (+−−) and (−−−) sets together to go to further checking.

Now, we can further restrict possibility by the Coriolis sign information. According to DiLauro and Mills,[15)] the sign of ν_2-ν_5 Coriolis interaction in CD_3Cl molecule is negative. Since the zeta constant $\zeta_{2,5a}^y$ is calculated as negative (−0.596) from the present L matrices, which are shown in Table 3, the sign of the product $(\partial p/\partial Q_2)(\partial p/\partial Q_5)$ must be positive, *i.e.* $(\partial p/\partial Q_2)^D$ and $(\partial p/\partial Q_5)^D$ are of the same sign. Further, as described in a previous section, the sign of the ν_3-ν_6 Coriolis perturbation of CD_3Cl has been found to be negative. Since the zeta constant $\zeta_{3,6a}^y$ is calculated to be +0.276 from the L matrix, the sign of $(\partial p/\partial Q_3)(\partial p/\partial Q_6)^D$ must be negative. Therefore, inspection of the (−++) and (+−−) sets of A_1 species together with the (++−), (−+−), (+−−), and (−−−) sets of E species reveals that only possible combinations are (−++) set from A_1 together with either (++−) or (−+−) set from E species.

Finally, of the two sets preferred in E species, there is at present no experimental preference of one to the other. We need additional information to determine the final choice. For that purpose, the CNDO/2 method[2] or ab initio calculation[21] may be helpful. Table 6 shows a comparison of the resulting parameter values for the $(-++)(-+-)^{\mathrm{H}}$ and $(-++)(++-)^{\mathrm{H}}$ sets with the *ab initio* values. As is seen in the table, the obtained values of the parameters other than p_4 agree well with the *ab initio* result. As for the parameter p_4, the sign is different in the two sets while the magnitude is obtained almost the same. The *ab initio* calculation predicts it to be negative. Therefore, the $(-++)(-+-)$ set may be the correct signs of $(\partial p/\partial Q_i)$ for methyl chloride. Table 7 shows a comparison of the observed band intensities with the calculated. The polar tensor[22] calculated from these parameter values is shown in Table 8.

TABLE 7. OBSERVED AND CALCULATED INTENSITIES OF THE FUNDAMENTAL BANDS OF METHYL CHLORIDE (km/mol)

Band		Obsd[a]	Calcd[b]
CH_3Cl	ν_1	23.31(148)[c]	22.40
	ν_2	8.41(68)	9.13
	ν_3	23.69(94)	23.55
	ν_4	10.77(120)	9.50
	ν_5	11.38(78)	11.46
	ν_6	3.85(42)	3.71
CD_3Cl	ν_1	15.82(32)[d]	15.92
	ν_2	12.37(37)	12.13
	ν_3	17.70(35)	17.77
	ν_4	5.42(12)	5.44
	ν_5	5.76(46)	5.76
	ν_6	0.57(10)	0.60

a) Numbers in parentheses are the uncertainty indicators, reciprocal squares of which were utilized as the weighting factors in the least squares calculation. See Table 1. b) Calculated with the parameter values obtained for the $(-++)(-+-)^{\mathrm{H}}$ signs. c) Sum of the intensities for ν_1 and $2\nu_5$ in Table 1. d) Sum of the intensities for ν_1, $2\nu_5$, and $2\nu_2$ in Table 1.

Discussion

As was discussed by Russell *et al.*,[1] major contributions to the errors in the resulting intensity parameters are from the uncertainties in the intensity data and force constants. For the experimental data utilized in Ref. 1, the latter was shown to be much smaller than the former. Furthermore, the errors in the force field utilized in the present study have been reduced much (on the average, a factor of ten for A_1 and of about three for E species[20]). Therefore, in the present case, contribution from the force error should be negligible and the intensity factor only remains effective, which has also been reduced much, indeed. Besides that, we have been able to use two pieces of definite information on the relative signs of $(\partial p/\partial Q_i)$. These were obtained from the Coriolis intensity analyses in Ref. 15 (for ν_2-ν_5) and in the present study (for ν_3-ν_6) for the CD_3Cl molecule. Considering these conditions, it is a natural consequence that the correct sign combination has definitely been determined in this study.

It has become widely known that *ab initio* calculations can be critically checked by use of the experimentally determined values and signs of the molecular dipole moment and its derivatives. Wiberg[21] has carried out *ab initio* calculations to predict that the correct signs of $(\partial p/\partial Q_i)$ for methyl fluoride is $(-++)(-++)$, which perfectly agreed with the result in Ref. 4. He has also calculated the dipole derivatives of methyl chloride, and expected that the signs may be $(-++)$ for A_1 and $(-+-)$ for E species. In the present study this prediction has certainly been confirmed to be correct. Moreover, the sign of $(\partial p/\partial Q_4)$ was so determined that the resulting sign of p_4 agrees with the *ab initio* result.

We are planning in a subsequent paper[7] to analyze the intensities of the overtones and combinations of this molecule, utilizing the result obtained here for the fundamentals.

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TABLE 8. ATOMIC POLAR TENSORS $\boldsymbol{P}_x$ IN METHYL CHLORIDE[a] (in D/Å)

			$H_1(D_1)$[b]			C			Cl		
CH_3Cl	e_a	$-+-$	−0.215	0	−0.171	0.565	0	0	−0.847	0	0
	e_b	$-+-$	0	0.402	0	0	0.565	0	0	−0.847	0
	a_1	$-++$	−0.302	0	−0.238	0	0	2.955	0	0	−2.242
CD_3Cl	e_a	$-+-$	−0.198	0	−0.161	0.547	0	0	−0.851	0	0
	e_b	$-+-$	0	0.401	0	0	0.547	0	0	−0.851	0
	a_1	$-++$	−0.288	0	−0.248	0	0	2.960	0	0	−2.216

a) For the coordinate system in Fig. 5. b) H_1 atom in Fig. 5.

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16) In the present study, the measurement was carried out under the pressure of 1.11×10^6 Pa, which means that the true width of individual vibration-rotation lines is expected to be about 2 cm^{-1}. On the other hand, the resolution used was 0.25 cm^{-1}. Considering the fact that the absorption bands are composed of many overlapping vibration-rotation lines, the present combination of line width and resolution should indeed be sufficient to obtain the absolute band intensities.

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