January, 1985] © 1985 The Chemical Society of Japan Bull. Chem. Soc. Jpn., 58, 65—72 (1985)

Infrared Intensities in Methyl Chloride. III. Improvement of the Anharmonic Force Field and the Analysis of the Overtone and Combination Band Intensities

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(Received August 3, 1984)

A recently obtained anharmonic *ab initio* force field of methyl chloride has been improved by the method of "predicate observations" using the observed values of the spectroscopic constants. The newly obtained force field was used to make re-analysis of the absorption intensities of the binary overtone and combination bands for CH_3Cl and CD_3Cl. Contribution from the electrical anharmonicity to the band intensities was estimated and compared with the *ab initio* result.

In Part II of the present series, we have analyzed the binary overtone and combination band intensities of CH_3Cl and CD_3Cl attempting to determine the values of the second derivatives of the dipole moment with respect to the normal coordinates $(\partial^2 P/\partial q_r \partial q_s)$.[1] However, for some of the observed bands the predicted intensities were markedly different from the observed ones, where *ab initio* values were used for the second derivatives of the dipole moment. It seemed that some of the cubic force constants then available[2] contained relatively large errors. Therefore, we did not show the values of the second derivatives of the dipole moment derived therefrom.

Recently, the present authors have calculated the anharmonic potential function for methyl chloride as well as for methyl fluoride by *ab initio* MO method. Certainly, these theoretical force fields were obtained without any procedure of fitting to the observed values of the spectroscopic constants. Still, their values have been shown to remarkably well reproduce the observed values of the molecular constants such as the vibration-rotation constants, 1-doubling constants, and the vibrational anharmonicity constants.[3] This means that if the calculations are made with well selected basis functions, the individual values of the theoretical (cubic) force constants are really close to the true values.

Furthermore, in a separate paper[4] we have shown for methyl fluoride that thus obtained anharmonic *ab initio* force field can be further refined by fitting the calculated values of the molecular constants still better to the observed values. In this manner, we have obtained a set of anharmonic force constants for methyl fluoride, which are able to estimate the mechanical contribution to the effective dipole moment in the excited vibrational states to an accuracy of at least a few thousandths of a Debye unit.[4]

Therefore, also in the case of methyl chloride since we have full cubic terms of the anharmonic force field derived from *ab initio* MO method, we expect that an improved set of anharmonic force constants be obtained through a similar analysis as adopted in methyl fluoride. And then, it will be possible to make a quantitative estimation of the values of the second derivatives of dipole moment from the analysis of the absorption band intensities of the two quantum transitions of this molecule.

Results

(1) Refinement of the Cubic Force Constants. In a previous paper,[3] the anharmonic force field of methyl chloride has been derived *ab initio* with Pople's 4-31G* basis set[5,6] and also Dunning's double zeta basis set augmented with the polarization functions for H, C, and Cl atoms (DZP).[7] The effect of the configuration interaction was also examined by using the Møller-Plesset second-order perturbation theory (abbreviated as MP2).[8] The anharmonic force field was also calculated by adopting the MP2/DZP geometry as the reference geometry for the SCF calculations with 4-31G* and DZP basis sets. The five sets in total of the anharmonic force field thus obtained were found to be very similar to each other.

Furthermore, in order to moderate a systematic trend observed among these anharmonic force fields that the diagonal force constants for the bond stretching modes become smaller on going from lower levels of theoretical calculation to higher levels, and become closer to the observed values,[3] each set of the theoretical force constants was scaled by the observed quadratic force constants. For the scaling, the harmonic force field derived by Duncan *et al.*[9] was utilized. The scaled values of the force constants are summarized in Table 1.

In order to refine further the theoretical force constants thus obtained the method of "predicate observations" was utilized.[10] In this method, a parameter is tied to a "predicate" value by a spring whose strength can be adjusted arbitrarily. It was emphasized that the fitting procedure to the observed values of the molecular constants should not be too strict particularly when the concerned vibrational levels are involved in intramolecular resonances.[4]

In the actual calculation, the least-squares method was used, where in stead of the usual residual value the following quantity was minimized;

TABLE 1. SCALED VALUES OF THE *ab initio* CUBIC SYMMETRY FORCE CONSTANTS OF METHYL CHLORIDE[a,b)]

F_{ijk}	I	II	III	IV	V	F_{ijk}	I	II	III	IV	V
111	−16.89	−17.49	−16.71	−17.33	−17.73	255	−0.37	−0.39	−0.35	−0.34	−0.33
112	−0.11	−0.18	−0.11	−0.10	−0.11	256	0.12	0.11	0.05	0.12	0.12
113	0.22	0.25	0.16	0.17	0.19	266	0.12	0.02	0.09	0.17	0.15
122	−0.09	−0.11	−0.09	−0.08	−0.07	344	0.33	0.38	0.34	0.35	0.31
123	0.04	−0.05	0.13	0.12	0.10	345	0.02	0.01	0.04	0.04	0.00
133	−0.48	−0.52	−0.52	−0.53	−0.52	346	−0.10	−0.11	−0.02	−0.03	−0.04
222	0.63	0.51	0.62	0.70	0.69	355	−0.01	0.00	−0.05	−0.05	−0.04
223	−0.57	−0.61	−0.67	−0.59	−0.60	356	0.01	0.01	0.02	0.05	0.06
233	0.67	0.64	0.44	0.54	0.75	366	−0.80	−0.82	−0.76	−0.75	−0.81
333	−16.88	−17.40	−16.51	−16.34	−16.88	444	−12.47	−13.00	−12.08	−12.62	−12.55
144	−17.34	−18.04	−17.02	−17.75	−17.67	445	−0.23	−0.27	−0.33	−0.36	−0.26
145	0.08	0.08	−0.01	0.00	0.06	446	0.10	0.11	−0.11	−0.11	−0.08
146	0.16	0.17	0.05	0.06	0.12	455	0.07	0.06	0.06	0.06	0.07
155	−0.25	−0.23	−0.19	−0.21	−0.24	456	0.02	0.02	0.18	0.20	0.08
156	0.05	0.02	−0.06	−0.01	−0.01	466	0.01	0.01	−0.04	−0.03	−0.03
166	−0.10	−0.11	−0.03	−0.04	−0.02	555	−0.07	−0.05	−0.04	−0.05	−0.04
244	0.10	0.12	0.07	0.10	0.07	556	−0.05	−0.08	−0.06	−0.05	−0.04
245	0.12	0.11	0.13	0.16	0.12	566	0.24	0.26	0.21	0.21	0.21
246	−0.03	−0.08	0.02	0.03	0.04	666	−0.45	−0.47	−0.43	−0.44	−0.41

a) Units are 10^{12} N m^{-2} for stretching, 10^{2} N m^{-1} rad^{-1} for stretch-stretch-bend, 10^{-8} N rad^{-2} for stretch-bend-bend, and 10^{-18}N m rad^{-3} for bending force constants. b) Set I is for 4-31G* at the consistent geometry, II for 4-31G* at MP2/DZP geometry, III for DZP at the consistent geometry, IV for DZP at MP2/DZP geometry, and V for MP2/DZP at the consistent geometry.

TABLE 2. OBSERVED AND CALCULATED VALUES OF x'S, g'S, α'S, AND q'S FOR $CH_3{}^{35}Cl$
UNITS ARE cm^{-1} FOR x AND g, AND 10^{-5} cm^{-1} FOR α AND q

	Obsd	Calcd[a)]				
		I	II	III	IV	V
$x_{44}+3g_{44}$	15.3 (—) [b)]	12.8	16.5	10.3	14.0	12.8
$x_{55}+3g_{55}$	−7.6 (10) [c)]	−7.2	−7.3	−7.2	−7.2	−7.2
$x_{66}+3g_{66}$	5.7 (10) [c)]	5.5	5.6	6.0	5.9	5.7
g_{45}	—	−11.3	−11.0	−11.1	−11.4	−11.0
g_{46}	—	1.5	2.1	0.6	0.5	1.0
g_{56}	−2.2 (10) [c)]	−2.4	−2.5	−2.6	−2.6	−2.4
$\lvert\varphi_{122}\rvert$	57.0 (—) [d)]	277.0	277.7	280.2	273.8	276.2
$\lvert\varphi_{155}\rvert$	99.8 (140) [d),e)]	97.4	98.5	97.0	96.2	96.0
$\alpha_1{}^{A}$	5538 (500) [f)]	5117	5405	5064	5285	5450
$\alpha_2{}^{A}$	−2297 (10) [g)]	−2295	−2295	−2294	−2294	−2295
$\alpha_3{}^{A}$	850 (50) [h)]	911	914	956	943	902
$\alpha_4{}^{A}$	2590 (100) [i)]	2746	2780	2730	2760	2756
$\alpha_5{}^{A}$	4586 (10) [g)]	4585	4585	4585	4584	4585
$\alpha_6{}^{A}$	−2536 (20) [j)]	−2536	−2535	−2536	−2537	−2537
$\alpha_1{}^{B}$	−6 (500) [f)]	1	−1	7	5	3
$\alpha_2{}^{B*}$	124 (500) [g)]	124	114	133	127	135
$\alpha_3{}^{B}$	384 (5) [h),k)]	384	385	385	384	384
$\alpha_4{}^{B}$	−18 (5) [i)]	−22	−25	−22	−24	−23
$\alpha_5{}^{B*}$	−14 (500) [g)]	−27	−30	−14	−18	−17
$\alpha_6{}^{B}$	163 (5) [j),k)]	162	163	163	163	163
$q_4{}^{(+)}$	0 (10) [i)]	5	5	9	8	6
$q_5{}^{(+)*}$	[0] (500) [g)]	−3	−4	−5	−4	−5
$q_6{}^{(+)}$	−49 (10) [k)]	−45	−45	−44	−44	−44

a) Calculated values for I, II, III, IV, and V are obtained from the force fields I, II, III, IV, and V in Table 4, respectively. b) Ref. 1. c) Ref. 12. d) Ref. 2. e) Ref. 13. f) Ref. 14. g) Ref. 15. h) Ref. 16. i) Ref. 17. j) Ref. 18. k) Ref. 19.

TABLE 3. OBSERVED AND CALCULATED VALUES OF x's, g's, α's, AND q's FOR $CD_3{}^{35}Cl$
UNITS ARE cm^{-1} FOR x AND g, AND $10^{-5}\,cm^{-1}$ FOR α AND q

	Obsd	Calcd[a]				
		I	II	III	IV	V
$x_{44}+3g_{44}$	9.8(—)[b]	9.8	12.0	8.6	10.9	9.8
$x_{55}+3g_{55}$	—	−1.1	−0.8	−0.8	−1.1	−1.0
$x_{66}+3g_{66}$	—	2.3	2.4	2.5	2.4	2.4
g_{45}	−5.8(—)[b]	−5.2	−4.9	−5.0	−5.2	−5.0
g_{46}	—	1.7	2.0	1.2	1.2	1.4
g_{56}	−6.0(—)[b]	−1.0	−0.9	−1.0	−1.0	−0.9
$\lvert\varphi_{122}\rvert$	115.2(—)[c]	199.1	196.9	204.8	199.4	200.3
$\lvert\varphi_{155}\rvert$	63.4(—)[c]	65.5	66.8	68.1	67.1	65.9
$\alpha_1{}^A$	1950(500)[d]	2084	2185	2070	2149	2210
$\alpha_2{}^A$	−915(20)[e]	−937	−936	−940	−942	−934
$\alpha_3{}^A$	300(500)[f]	405	407	427	423	397
$\alpha_4{}^A$	1253(20)[g]	1248	1251	1247	1251	1251
$\alpha_5{}^A$	1537(10)[e]	1541	1540	1539	1541	1541
$\alpha_6{}^A$	−900(500)[d],[h]	−1007	−1003	−1008	−1007	−1008
$\alpha_1{}^B$	29(500)[i]	21	19	25	25	24
$\alpha_2{}^{B*}$	122(500)[e],[j]	90	84	98	94	95
$\alpha_3{}^B$	298(5)[j]	296	298	293	294	297
$\alpha_4{}^B$	11(5)[g]	12	13	12	13	13
$\alpha_5{}^{B*}$	−61(500)[e],[j]	−52	−54	−44	−46	−46
$\alpha_6{}^B$	93(5)[j]	93	93	91	92	92
$q_4{}^{(+)}$	—	12	12	16	16	13
$q_5{}^{(+)*}$	31(500)[e],[j]	−1	−2	−3	−2	−3
$q_6{}^{(+)}$	3(10)[j]	3	2	3	3	3

a) Calculated values for I, II, III, IV, and V are obtained from the force fields I, II, III. IV, and V in Table 4, respectively. b) Ref. 1. c) Ref. 2. d) Ref. 20. e) Ref. 21. f) Ref. 22. g) Ref. 23. h) Ref. 24. i) Ref. 25. j) Ref. 19.

$$\chi_0 = \chi_1 + \chi_2, \tag{1a}$$

where

$$\chi_1 = \sum_i W_i(E_i^{\text{obsd}} - E_i^{\text{calcd}})^2, \tag{1b}$$

and

$$\chi_2 = \sum_j w_j(p_j^{\text{pred}} - p_j)^2. \tag{1c}$$

Here, p_j^{pred} is the "predicate" value and p_j the current value of the jth force constant, and w_j is a weight factor.

As usual, the weight W_i for the ith observed constant E_i was determined as $1/(\Delta E_i)^2$, where ΔE_i is the estimated "error" in E_i.[2] It is to be noted, however, that the values ΔE_i employed here are in general much larger than the experimental uncertainties reported in the literature,[11–25] for they should also include uncertainties due to approximations used for the theoretical expressions of the constants.[26] The actual values for ΔE_i were rather arbitrarily chosen as listed in Tables 2 and 3.

On the other hand, in order to choose appropriate values for w_j, trial calculations were carried out a number of times, in each of which different values were adopted for w_j as in the case of methyl fluoride. Eventually, the value of 0.1 in the respective units, which are given in the footnote to Table 1, in general and the value of 0.3 for the diagonal stretching force constants were adopted for Δp_j, where $w_j=1/(\Delta p_j)^2$. These values are the same as those used in Ref. 4.

Once the values of ΔE_i and Δp_j are determined, the procedure for refining the force constants is straightforward. The calculation was carried out for the above mentioned five sets of anharmonic force field (Table 1). For example, in the case of 4-31G* with the consistent geometry, the original value of residual was $\chi_1=3270$. Through the refinement, the value has been altered to be $\chi_1=11.0$ ($\chi_2=25.7$). Thus, the degree of agreement between the observed and calculated constants became better by more than two orders of magnitude in the residual value. Similarly, for the MP2/DZP case, through the refinement calculation, the residual value changed from $\chi_1=3860$ to $\chi_1=10.2$ ($\chi_2=28.2$).

Table 4 shows the result of the refinement calculations. Comparison of the numbers listed in Tables 1 and 4 reveals that the changes in the individual cubic force constants are by no means large. Apart from the

TABLE 4. IMPROVED VALUES OF THE CUBIC SYMMETRY FORCE CONSTANTS OF METHYL CHLORIDE[a),b)]

F_{ijk}	I	II	III	IV	V
111	−17.03 (43)	−17.52 (38)	−16.87 (44)	−17.40 (39)	−17.73 (38)
112	−0.16 (15)	−0.20 (13)	−0.17 (15)	−0.13 (14)	−0.12 (13)
113	0.21 (14)	0.24 (14)	0.15 (14)	0.16 (14)	0.19 (14)
122	−0.08 (13)	−0.07 (16)	−0.08 (13)	−0.10 (13)	−0.09 (13)
123	0.01 (14)	−0.07 (13)	0.13 (13)	0.10 (14)	0.07 (14)
133	−0.44 (15)	−0.47 (15)	−0.43 (18)	−0.46 (17)	−0.49 (14)
222	0.69 (06)	0.69 (07)	0.69 (06)	0.70 (06)	0.71 (05)
223	−0.62 (10)	−0.59 (10)	−0.63 (12)	−0.62 (11)	−0.66 (10)
233	0.78 (14)	0.79 (16)	0.66 (21)	0.69 (17)	0.83 (12)
333	−16.93 (17)	−17.00 (20)	−16.77 (23)	−16.80 (22)	−16.97 (16)
144	−16.68 (53)	−17.02 (76)	−16.50 (45)	−16.86 (68)	−16.78 (68)
145	0.08 (14)	0.09 (14)	−0.01 (14)	0.00 (14)	0.07 (14)
146	0.15 (14)	0.14 (14)	0.04 (14)	0.04 (14)	0.10 (14)
155	−0.37 (10)	−0.35 (10)	−0.34 (10)	−0.35 (10)	−0.36 (10)
156	−0.10 (19)	−0.12 (19)	−0.17 (17)	−0.15 (19)	−0.13 (18)
166	−0.07 (12)	−0.05 (14)	−0.04 (12)	−0.08 (12)	−0.04 (12)
244	0.21 (19)	0.30 (26)	0.16 (16)	0.27 (24)	0.24 (24)
245	0.11 (14)	0.13 (16)	0.12 (14)	0.16 (15)	0.13 (15)
246	−0.05 (14)	−0.12 (15)	0.01 (14)	0.00 (15)	0.00 (15)
255	−0.30 (05)	−0.31 (05)	−0.31 (04)	−0.30 (05)	−0.30 (04)
256	0.00 (09)	0.01 (08)	0.02 (07)	0.01 (12)	0.01 (08)
266	0.18 (05)	0.17 (06)	0.16 (05)	0.18 (05)	0.16 (05)
344	0.13 (12)	0.13 (15)	0.15 (12)	0.13 (13)	0.13 (12)
345	−0.03 (15)	−0.04 (16)	0.00 (15)	0.00 (15)	−0.03 (15)
346	−0.06 (15)	−0.07 (16)	0.02 (15)	0.00 (15)	−0.01 (14)
355	−0.01 (14)	0.01 (14)	−0.05 (14)	−0.05 (14)	−0.04 (14)
356	0.05 (13)	0.05 (12)	0.07 (13)	0.09 (13)	0.07 (12)
366	−0.90 (06)	−0.90 (06)	−0.88 (06)	−0.88 (06)	−0.88 (06)
444	−12.48 (41)	−13.01 (41)	−12.10 (41)	−12.64 (41)	−12.56 (41)
445	−0.23 (14)	−0.26 (14)	−0.31 (14)	−0.35 (14)	−0.25 (14)
446	0.10 (14)	0.10 (14)	−0.11 (14)	−0.11 (14)	−0.08 (14)
455	−0.13 (09)	−0.12 (09)	−0.15 (10)	0.16 (10)	−0.13 (09)
456	−0.10 (16)	−0.11 (17)	0.00 (19)	0.02 (20)	−0.05 (17)
466	−0.03 (14)	−0.02 (14)	−0.07 (14)	−0.06 (14)	−0.06 (14)
555	−0.04 (15)	−0.02 (15)	−0.02 (15)	−0.03 (15)	−0.02 (15)
556	0.00 (12)	−0.02 (13)	0.00 (14)	0.02 (13)	0.00 (12)
566	0.27 (10)	0.27 (10)	0.25 (10)	0.25 (10)	0.25 (10)
666	−0.48 (12)	−0.49 (12)	−0.43 (13)	−0.44 (13)	−0.42 (13)

a) For the units, see footnote a) to Table 1. b) The results for I, II, III, IV, and V have been derived by adopting I, II, III, IV, and V in Table 1, respectively, as the "predicate" values. See text.

diagonal stretching force constants, most of them show changes less than 0.1 of the respective units. The numbers in the parentheses are one standard deviation resulting from the least-squares calculation under the present condition. It is to be noted that they can not simply be considered as the errors involved in their values.[4)] The calculated values of the spectroscopic constants from these force constants are listed in Tables 2 and 3. Certainly, a very good agreement is obtained between the calculated and observed constants.

The obtained values of the force constants for the five cases are all very similar to each other; they actually agree with each other within the "standard errors" resulting from the present calculations.

(2) Binary Overtone and Combination Band Intensities. It is well known that the integrated intensity of a binary combination band is expressed by the following equation:[1,27)]

$$A_{ss'} = 2.5066\times(\omega_s+\omega_{s'})d_f\,|Q_{ss'}|^2 Z_s Z_{s'}\{1-\mathrm{e}^{-\beta(\omega_s+\omega_s')}\}. \tag{2}$$

Similarly, for a binary overtone band,

$$A_{ss} = 2.5066\times(2\omega_s)d_f\,|Q_{ss}|^2 Z_s^2(1-\mathrm{e}^{-2\beta\omega_s}). \tag{3}$$

Here, 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 Q_{ss} and $Q_{ss'}$ are the transition moments calculated from the contact transformed dipole moment operator.[27] The numerical coefficient used in these equations is for the case where ω_s and φ_{rst} are given in cm^{-1}, P_r and P_{rs} in Debye units, and A_{ss} and $A_{ss'}$ in $\mathrm{km\,mol}^{-1}$.

The actual expressions for the transition moments, Q_{ss} and $Q_{ss'}$, are given in Ref. 1 for different kinds of two quantum transitions of symmetric top molecules. They are given by the effective values of the second derivatives of the transformed dipole moment $\Omega_{ss'}{}^{\alpha}$ multiplied by different numerical factors as follows:[1] $Q_{ss}{}^{z}=\Omega_{ss}{}^{z}/2\sqrt{2}$, $Q_{ss'}{}^{z}=\Omega_{ss'}{}^{z}/2$, $Q_{st}{}^{x}=\Omega_{st}{}^{x}/2$, $Q_{tt}{}^{z}=\Omega_{tt}{}^{z}/2$, $Q_{tt}{}^{x}=\Omega_{tt}{}^{x}/2$, $Q_{tt'}{}^{z}=\Omega_{\tau\tau'}{}^{z}/\sqrt{2}$, and $Q_{tt'}{}^{x}=\Omega_{tt'}{}^{x}/\sqrt{2}$, where the index s denotes a nondegenerate mode and t denotes a degenerate mode.

The intensities of binary overtone and combination bands contain contributions both from electrical and mechanical anharmonicities. The mechanical contribution to the intensities may be obtainable if the normal coordinate cubic force constants and the values for $(\partial P/\partial q_r)$ are known. The former can be calculated from the anharmonic symmetry force field determined in the present study. They were calculated from the force field in Table 4 (case V) and are shown in Table 5. The phases of the normal coordinates used here is the same as in Part I of the present series.[11] On the other hand, the P_r values have also been determined in Part I and the actual values expressed in Debye units are summarized in Table 6.

TABLE 5. NORMAL COORDINATE CUBIC FORCE CONSTANTS φ_{rst} FOR METHYL CHLORIDE.[a] UNITS ARE cm^{-1}

φ_{rst}	CH_3Cl	CD_3Cl	φ_{rst}	CH_3Cl	CD_3Cl
111	−1047.0	−627.6	255	−29.4	−7.8
112	−46.4	−64.7	256	−62.0	−42.8
113	6.2	−4.1	266	40.3	4.6
122	276.2	200.3	344	22.6	2.3
123	73.1	29.8	345	−17.9	−5.0
133	20.3	17.1	346	−65.0	−12.8
222	−119.4	−102.3	355	−15.2	−3.0
223	−71.1	−53.6	356	−34.4	−12.1
233	−30.0	−61.8	366	−67.0	−53.4
333	−259.5	−220.7	444	−815.5	−532.4
144	−1050.7	−659.9	445	−95.9	−65.5
145	0.5	25.6	446	7.6	−8.9
146	4.8	−10.4	455	−156.0	−112.6
155	96.0	65.9	456	152.0	75.1
156	−33.6	−34.3	466	169.3	105.9
166	398.9	220.0	555	−41.8	−24.2
244	47.3	29.0	556	31.2	19.1
245	−53.8	−17.8	566	−75.3	−37.6
246	−298.3	−192.1	666	−28.6	−22.5

a) Calculated from the cubic symmetry force constants V in Table 4.

TABLE 6. SUMMARY OF $P_r{}^{\alpha}$ VALUES (Debye UNITS)

$P_r{}^{\alpha}$	CH_3Cl		CD_3Cl	
	Obsd[a]	Calcd[b]	Obsd[a]	Calcd[b]
$P_1{}^{z}$	−0.0778 (25)	−0.0920	−0.0756 (8)	−0.0936
$P_2{}^{z}$	0.0696 (28)	0.1107	0.0972 (15)	0.1420
$P_3{}^{z}$	0.1599 (32)	0.2177	0.1412 (28)	0.1923
$P_4{}^{x}$	−0.0368 (21)	−0.0605	−0.0303 (3)	−0.0534
$P_5{}^{x}$	0.0554 (19)	0.0504	0.0462 (18)	0.0406
$P_6{}^{x}$	−0.0384 (21)	−0.0400	−0.0171 (15)	−0.0189

a) Ref. 11. b) From 4-31G* calculation.

TABLE 7. OBSERVED AND CALCULATED INTENSITIES FOR THE OVERTONES AND COMBINATIONS OF CH_3Cl. UNITS ARE km/mol

Band	Obsd[a]	Calcd[b]		
		I[c]	II[d]	III[e]
$2\nu_4$(//)	0.290 (15)	0.750	0.694	0.735
$2\nu_4$(⊥)	0.429 (43)	1.751	1.773	1.772
$\nu_1+\nu_4$	0.92 (18)	1.679	1.617	1.665
$2\nu_1$		0.001	0.003	0.003
$\nu_4+\nu_5$(//, ⊥)	3.02 (30)	2.106	1.888	1.966
$\nu_1+\nu_5$		1.047	1.028	1.058
$\nu_2+\nu_4$		1.568	1.642	1.603
$\nu_1+\nu_2$		0.013	0.005	0.005
$\nu_4+\nu_6$(//)	0.369 (37)	0.409	0.340	0.343
$\nu_4+\nu_6$(⊥)		0.097	0.102	0.097
$\nu_1+\nu_6$	0.134 (7)	0.215	0.217	0.214
$\nu_3+\nu_4$	0.164 (8)	0.396	0.375	0.382
$\nu_1+\nu_3$	0.205 (10)	0.113	0.147	0.147
$2\nu_5$(//)	4.16 (34)	2.642	5.688	2.726
$2\nu_5$(⊥)		0.771	0.010	0.264
$\nu_2+\nu_5$	0.316 (32)	0.550	0.473	0.445
$2\nu_2$	0.0	1.605	0.002	0.001
$\nu_5+\nu_6$(//)	0.004 (4)	0.801	0.237	0.387
$\nu_5+\nu_6$(⊥)	0.433 (43)	1.029	0.214	0.230
$\nu_2+\nu_6$	0.255 (13)	0.144	0.256	0.182
$\nu_3+\nu_5$	0.0	0.002	0.001	0.001
$\nu_2+\nu_3$	0.087 (5)	0.361	0.479	0.461
$2\nu_6$(//, ⊥)	0.0	0.037	0.060	0.048
$\nu_3+\nu_6$	0.0	0.881	0.006	0.011
$2\nu_3$	?	0.014	0.049	0.045

a) Ref. 1. b) Second derivatives of the dipole moment by *ab initio* MO method (4-31G*) are taken into consideration. c) Mechanical contribution is from the force field in Ref. 2. d) Mechanical contribution is from the force field of V in Table 1. e) Mechanical contribution is from the force field of V in Table 4.

Tables 7 and 8 show the observed and calculated values of the absorption intensities of binary overtone and combination bands. In these tables, calculated intensities are shown for three cases; the first one is from

TABLE 8. OBSERVED AND CALCULATED INTENSITIES FOR THE OVERTONES AND COMBINATIONS OF CD_3Cl. UNITS ARE km/mol

Band	Obsd[a)]	Calcd[b)]		
		I[c)]	II[d)]	III[e)]
$2\nu_4(//)$	0.202(10)	0.364	0.339	0.357
$2\nu_4(\perp)$	0.284(14)	0.911	0.916	0.917
$\nu_1+\nu_4$	0.224(45)	0.844	0.812	0.834
$2\nu_1$		0.000	0.001	0.001
$\nu_4+\nu_5(//)$	0.91(9)	0.022	0.028	0.027
$\nu_4+\nu_5(\perp)$		0.133	0.105	0.113
$\nu_2+\nu_4$		0.628	0.648	0.633
$\nu_1+\nu_5$		0.102	0.099	0.104
$\nu_1+\nu_2$	0.0	0.000	0.035	0.035
$\nu_4+\nu_6(//)$	?	0.165	0.127	0.126
$\nu_4+\nu_6(\perp)$	?	0.002	0.003	0.003
$\nu_3+\nu_4$	0.0	0.108	0.099	0.102
$\nu_1+\nu_6$	0.0	0.041	0.033	0.033
$\nu_1+\nu_3$	0.119(6)	0.056	0.053	0.052
$2\nu_5(//)$	2.56(13)	2.740	6.136	3.287
$2\nu_5(\perp)$		0.196	0.593	0.366
$\nu_2+\nu_5$	?	0.016	0.019	0.014
$2\nu_2$	1.29(10)	0.759	1.543	1.460
$\nu_5+\nu_6(//)$	0.384(38)	0.730	0.133	0.245
$\nu_5+\nu_6(\perp)$		0.035	0.038	0.031
$\nu_3+\nu_5$		0.232	0.169	0.167
$\nu_2+\nu_6$	?	0.060	0.126	0.094
$\nu_2+\nu_3$	0.125(13)	0.393	0.468	0.456
$2\nu_6(//, \perp)$	0.0	0.033	0.012	0.010
$\nu_3+\nu_6$	0.0	0.113	0.003	0.003
$2\nu_3$	0.124(12)	0.017	0.033	0.031

a) Ref. 1. b) Second derivatives of the dipole moment by *ab initio* MO method (4-31G*) are taken into consideration. c) Mechanical contribution is from the force field in Ref. 2. d) Mechanical contribution is from the force field of V in Table 1. e) Mechanical contribution is from the force field of V in Table 4.

TABLE 9. ANALYSIS OF THE TRANSITION DIPOLE MOMENT FOR CH_3Cl (IN $10^{-4}\times D$)

rs(α)	I[a)]	II[b)]	III[c)]	IV[d)]
11(z)		87		−99
12(z)		30		−17
13(z)	+94(3)	4	90(−98)	74
22(z)	0(109)	337	−337	−329
23(z)	+82(3)	0	82(−82)	185
33(z)		−289		193
14(x)		42		−191
15(x)		5		−143
16(x)	+52(2)	−13	65(−39)	78
24(x)		−1		172
25(x)	−95(5)	−35	−60(130)	−77
26(x)	+93(3)	−101	194(8)	179
34(x)	+59(2)	−4	63(−55)	93
35(x)	0(61)	−5	5	−1
36(x)	0(68)	−27	27	5
44(z)	−88(3)	84	−172(4)	−223
44(x)	−75(4)	29	−104(46)	−182
45(z)		−4		−30
45(x)		0		−130
46(z)		−24		106
46(x)		3		28
55(z)	+480(20)	332	148(−812)	55
55(x)		−154		69
56(z)	−11(11)	−46	35(57)	−65
56(x)	−84(5)	60	−144(24)	−121
66(z)	0(89)	181	−181	−240
66(x)	0(63)	9	−9	2

a) Observed values of $\Omega_{rs}{}^{\alpha}$. Numbers in parentheses are the estimated errors. Their signs were so chosen that the resulting value of P_{rs} (see III) may agree better with the *ab initio* value (see IV). b) Mechanical anharmonicity obtained from set V of Table 4. c) Estimated values of P_{rs}; I—II. The numbers in parentheses are for the alternative signs of $\Omega_{rs}{}^{\alpha}$ in column I. d) *Ab initio* values of P_{rs} (Ref. 1).

the cubic force field in Ref. 2, the second from the scaled force field initially obtained with the MP2/DZP calculation (case V in Table 1), and the third one from the final force field (case V in Table 4). In all these calculations, the P_{rs} values obtained in Ref. 1 from *ab initio* MO calculation with 4-31G* basis set were utilized. Marked differences are observed between the first case and the other two cases, particularly in the values for $2\nu_2$, $\nu_5+\nu_6$, and $\nu_3+\nu_6$ of CH_3Cl, and $2\nu_2$ and $\nu_5+\nu_6$ of CD_3Cl. Certainly, this is due to the difference in the employed anharmonic force fields. If the values of the normal coordinate force constants listed in Table 5 are compared with those in Table 3 of Ref. 1, those concerned mainly with ν_2, ν_5, and ν_6 are markedly different between the two results. In fact, the values for the cubic force constants such as φ_{122}, φ_{222}, φ_{166}, φ_{256}, φ_{266}, φ_{356}, φ_{555}, φ_{556}, and φ_{666} have been improved very much.

On the other hand, the difference between the second and third cases is not so large. This is expected because the actual changes in the individual force constants were not large, although there was remarkable improvement on the agreement between the observed and calculated molecular constants. Also the latter improvement of the force field has yielded considerable changes in the calculated intensities of $2\nu_5$, $\nu_5+\nu_6$, and $\nu_2+\nu_6$ of both CH_3Cl and CD_3Cl molecules.

Tables 9 and 10 show the results of the analysis of the observed values of the transition dipole moment. In these tables, the column I shows the observed values of $\Omega_{rs}{}^{\alpha}$. These numbers are given with the signs. They were chosen as follows; at first, the contribution from the mechanical anharmonicity to $\Omega_{rs}{}^{\alpha}$ has been obtained by using the force constants for case V in Table 4 and is shown in column II. Then, the values of P_{rs} have been obtained by subtracting the numbers listed in column II from those in column I (and are shown in column III).

TABLE 10. ANALYSIS OF THE TRANSITION DIPOLE MOMENT FOR CD_3Cl (IN $10^{-4}\times D$)

$rs(\alpha)$	I[a)]	II[b)]	III[c)]	IV[d)]
11 (z)		68		−75
12 (z)	0 (100)	43	−43	−2
13 (z)	+82 (3)	8	74 (−90)	45
22 (z)	+450 (18)	615	−165 (−1065)	−142
23 (z)	+108 (6)	−24	132 (−84)	225
33 (z)	−168 (9)	−206	38 (374)	124
14 (x)		32		−154
15 (x)		0		−51
16 (x)	0 (52)	−4	4	33
24 (x)		−2		125
25 (x)		−12		−11
26 (x)		−72		136
34 (x)	0 (53)	−1	1	52
35 (x)		−2		87
36 (x)	0 (74)	−4	4	−8
44 (z)	−85 (3)	65	−150 (20)	−177
44 (x)	−71 (2)	21	−92 (50)	−148
45 (z)		−8		−17
45 (x)		1		−38
46 (z)		−20		77
46 (x)		4		2
55 (z)	+441 (12)	439	2 (−880)	56
55 (x)		−91		208
56 (z)		−63		−39
56 (x)		32		−6
66 (z)	0 (102)	128	−128	−160
66 (x)	0 (72)	12	−12	−8

a) Observed values of $\Omega_{rs}{}^{\alpha}$. Numbers in parentheses are the estimated errors. Their signs were so chosen that the resulting value of P_{rs} (see III) may agree better with the *ab initio* value (see IV). b) Mechanical anharmonicity obtained from set V of Table 4. c) Estimated values of P_{rs}; I—II. The numbers in parentheses are for the alternative signs of $\Omega_{rs}{}^{\alpha}$ in column I. d) *Ab initio* values of P_{rs} (Ref. 1).

The resulting values of P_{rs} for the two possible signs of $\Omega_{rs}{}^{\alpha}$ were compared with the theoretical values in column IV, the latter being obtained with Pople's 4-31G* basis set.[1)] The signs given to the numbers in column I were so chosen that the resulting values of P_{rs} may agree better with the theoretical ones. In fact, if they are chosen in this manner, agreement between the observed and calculated values of P_{rs} is very good, *i.e.*, there is almost no doubt about the correctness of the present sign choice of $\Omega_{rs}{}^{\alpha}$. The numbers in parentheses in column III are those for the alternative signs of the transition moment.

Discussion

We did not show actual values of the errors involved in P_{rs} in Tables 9 and 10. This is because the errors involved in the force constants themselves are, as stated above, not well known. However, from comparison of the observed values of P_{rs} with the *ab initio* values listed in the same tables, the magnitudes of the errors may be on the average a few thousandths of a Debye unit.

On the other hand, it is well known that information on P_{rs} is also obtainable through observation of the dipole moment in the excited vibrational states.[28)] By vibrationally averaging the transformed dipole moment operator[27)] with a harmonic oscillator wave function, we obtain the expression for the dipole moment in each vibrational state;

$$\langle P\rangle_v = P_0 + \sum_a \delta P_a(v_a + d_a/2), \tag{4a}$$

where

$$\delta P_a = (1/2)\{P_{aa} - \sum_m P_m\varphi_{aam}/\omega_m\}. \tag{4b}$$

For CD_3Cl, Yamada and Hirota have measured the dipole moment in the ν_2 and ν_5 states; they obtained $\langle P\rangle_2=1.90741(33)$, $\langle P\rangle_5=1.90607(36)$, and $\langle P\rangle_0=1.90597(33)$ D.[21)] Eq. (6) shows that from comparison of the dipole moment in the ν_2 and ν_5 states, respectively, with that of the ground state, we obtain the following quantities;

$$\delta P_2 = (1/2)\{P_{22} - P_1\varphi_{122}/\omega_1 - P_2\varphi_{222}/\omega_2 - P_3\phi_{223}/\omega_3\}, \tag{5}$$

and

$$\delta P_5{}^z = (1/2)\{P_{55}{}^z - P_1\varphi_{155}/\omega_1 - P_2\varphi_{255}/\omega_2 - P_3\varphi_{355}/\omega_3\}. \tag{6}$$

By substituting in these equations the above data for the dipole moment,[21)] the observed values for the first derivatives (Table 6),[1)] and the cubic force constants in Table 5, we obtain the values of $P_{22}=-0.0243$ D and $P_{55}{}^z=-0.0034$ D. If these values are compared with those resulting from the band intensities, *i.e.* $P_{22}=-0.0165$ D and $P_{55}{}^z=0.0002$ D (Table 10), the agreement between the two sets of data is about the magnitude we expected in the above for the errors in P_{rs}.

In this concern, it should be remembered that the expressions used for the intensity analysis has been derived through the contact transformation method.[1,27)] The contribution of the mechanical anharmonicity calculated by using these equations may, therefore, contain large errors when there are close resonances. In the case of CD_3Cl, the values of P_{22} and $P_{55}{}^z$ derived from the intensity analysis may have suffered from the effect of this approximation. Considering this, the above discrepancy of the two sets of data could indicate the upper limit of the errors involved in the values of P_{rs} obtained in the present analysis.

Now a study on the infrared intensities of binary overtone and combination bands of methyl fluoride is in progress in our laboratory. Also we are planning to extend similar studies on various molecules, *e.g.*, methyl bromide, formaldehyde, ethylene, and so forth.

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