Calculation of Infrared Band Intensities of Various Chlorinated Ethanes

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Infrared absorption intensities of fundamental bands of three molecular species, CH_3CCl_3, CD_3CCl_3 in the vapor phase, and C_2Cl_6 in dilute solution in carbon disulfide have been measured. From the intensity data of four kinds of chlorinated ethanes C_2H_6, C_2D_6, CH_3CCl_3, CD_3CCl_3, the least number of common intensity parameters has been determined using the least squares method. Intensities of C_2Cl_6 calculated using the determined values of intensity parameters have been compared with the observed intensities in solution. It has proved that for almost all electro-optical parameters, it is possible to determine values commonly applicable to various chlorinated ethanes, while for μ_{CH} and $\delta\mu_{CH}/\delta r_{CH}$, it is not possible to find commonly applicable values, as in the case of chlorinated methanes.

In our previous paper,[1] infrared band intensity data of thirteen kinds of chlorinated methanes, from methane to carbon tetrachloride, were interpreted in terms of common intensity parameters as few as possible. The least squares method was applied to determine values of those parameters to obtain the best fit between observed and calculated intensities. As a result, for most of the electro-optical parameters, values commonly applicable to all chlorinated methanes could be determined, while for the two parameters μ_{CH} and $\delta\mu_{CH}/\delta r_{CH}$, it was not possible to find commonly applicable values.

In this study, in order to examine whether similar trends are also found in other cases, the molecular series of chlorinated ethane have been investigated, using the same technique as in the previous study. Molecular species treated in this study are C_2H_6, C_2D_6; CH_3CCl_3, CD_3CCl_3; C_2Cl_6, all having three-fold symmetry axis.

As compared with the case of chlorinated methanes, the treatment of ethane series requires many more electro-optical parameters in calculation. For example, several parameters associated with C–C bonds such as μ_{CC} or $\delta\mu_{CC}/\delta r_{CC}$ have to be taken into account, from the intensity expression based on the theory. Consequently, computative process is more complex and more time-consuming. However, it is of much interest to examine how the values of parameters change from chlorinated methanes to ethanes.

Experimental

Infrared absorption intensities of fundamental bands of three molecular species CH_3CCl_3, CD_3CCl_3 in the vapor phase and C_2Cl_6 in dilute carbon disulfide solution were measured in a range 4000—600 cm^{-1} using a Perkin-Elmer Model 421 grating spectrophotometer combined with a digital data recorder.[2] Intensities for bands below 600 cm^{-1} were roughly estimated by inspection from observed spectra measured using Perkin-Elmer Model 225 and 180 spectrophotometers. Deuterated methyl chloroform CD_3CCl_3, supplied from Merk Sharp & Dohm of Canada Limited, was used without further purification. Observed spectra of CH_3CCl_3 and CD_3CCl_3 in the vapor phase are shown in Figs. 1 and 2. Methods and instrumental conditions were almost the same as described in the previous papers.[1,3]

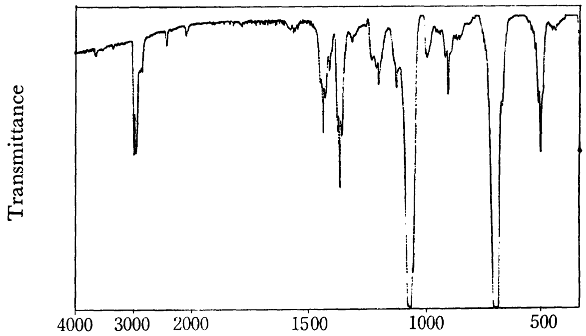

Fig. 1. Vapor phase spectrum of CH_3CCl_3.

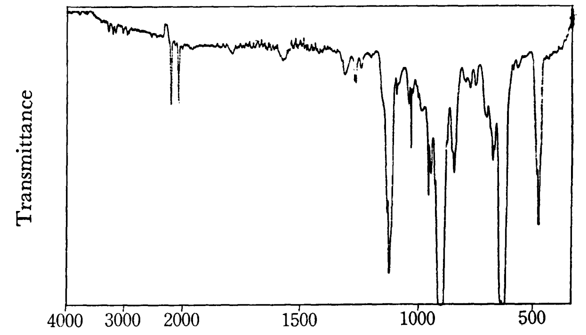

Fig. 2. Vapor phase spectrum of CD_3CCl_3.

Results and Discussion

In order to estimate the absolute band intensity, and to obtain the **L**-matrix necessary for computing the band intensity, the assignment of fundamental bands has to be determined definitely. Concerning the ethane species, C_2H_6 and C_2D_6, the frequency and intensity data are all obtained from literatures[4-13]

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[1] K. Tanabe and S. Saëki, *Spectrochim. Acta*, **26A**, 1469 (1970).

[2] K. Tanabe, S. Saëki, and M. Mizuno, *Japan Analyst*, **18**, 1347 (1969).

[3] S. Saëki and K. Tanabe, *Spectrochim. Acta*, **25A**, 1325 (1969).

[4] F. Stitt, *J. Chem. Phys.*, **7**, 297 (1939).

[5] A. M. Thorndike, *J. Chem. Phys.*, **15**, 868 (1947).

[6] L. F. Smith, *ibid.*, **17**, 139 (1949).

[7] G. E. Hansen and D. M. Dennison, *ibid.*. **20**, 313 (1952).

[8] J. Romanko, T. Feldman, and H. L. Welsh, *Can. J. Chem.*, **33**, 588 (1955).

[9] I. M. Nyquist, I. M. Mills, W. B. Person, and B. Crawford, *J. Chem. Phys.*, **26**, 552 (1957).

[10] D. W. Lepard, D. M. C. Sweeney, and H. L. Welsh, *Can. J. Chem.*, **40**, 1567 (1962).

[11] J. L. Duncan, *Spectrochim. Acta*, **20**, 1197 (1964).

[12] D. W. Lepard, D. E. Shaw, and H. L. Welsh, *Can. J. Chem.*, **44**, 2353 (1966).

[13] D. E. Shaw and H. L. Welsh, *ibid.*, **45**, 3823 (1967).

Table 1. Frequencies and intensities of ethane

Species		ν_{obsd} a)	A_{obsd} b)
CH_3CH_3			
A_{1g}	1	2954	—
	2	1388	—
	3	995	—
A_{1u}	4	289	—
A_{2u}	5	2954	4780 ± 280
	6	1379	400 ± 40
E_u	7	2996	12320 ± 370
	8	1486	1340 ± 130
	9	820	610 ± 10
E_g	10	2969	—
	11	1460	—
	12	1190	—
CD_3CD_3			
A_{1g}	1	2100	—
	2	1155	—
	3	843	—
A_{1u}	4	200	—
A_{2u}	5	2095	2420 ± 140
	6	1077	290 ± 30
E_u	7	2236	6440 ± 360
	8	1081	910 ± 90
	9	594	330 ± 20
E_g	10	2225	—
	11	1055	—
	12	970	—

a) ν_{obsd} (cm^{-1}) taken from Refs. 4—13.
b) A_{obsd} ($l \cdot mol^{-1} \cdot cm^{-2}$) from Ref. 9.

where band assignments are correctly made. These data are summarized in Table 1.

As for methyl chloroform CH_3CCl_3, several authors reported frequency data and made a tentative assignment of fundamental bands. The observed bands are considered to be correctly assigned therein, except for the C–C stretching vibration. To this mode, diffrent frequencies, 1075,14) 1068,15) 1012,16) 1007,17) 977,18) 867,19) and 714 cm^{-1},20) were assigned by different authors. The last two values seem inappropriately low as compared with the C–C stretching frequencies in similar molecules: 995 in C_2H_6, 972 in CH_3CH_2Cl, 1052 in *trans*-CH_2ClCH_2Cl, 1027 in *gauche*-CH_2ClCH_2Cl, and 975 in C_2Cl_6. In particular, the band at 714 cm^{-1} should be assigned to the C–Cl degenerate stretching mode.

The vapor phase spectrum observed in the region 1500—400 cm^{-1} is shown in Fig. 3. The strongest band at 1100—1070 cm^{-1} shows a very complex band envelope, which is undoubtedly assigned to the CH_3 rocking vibration (species E). On the other hand, the C–C stretching mode is expected to show a P, Q, R band envelope similar to the CH_3 symmetric stretching (at 2951 cm^{-1}) or symmetric deformation band (at 1386 cm^{-1}) of the same symmetry species A_1. Although no observed band may be assigned to the C–C stretching mode with certainty, the band observed at about 1010 cm^{-1} has been tentatively assigned to this mode, after Cleveland *et al.* (1012 cm^{-1}),16) or Karplus and Halford (1007 cm^{-1}).17)

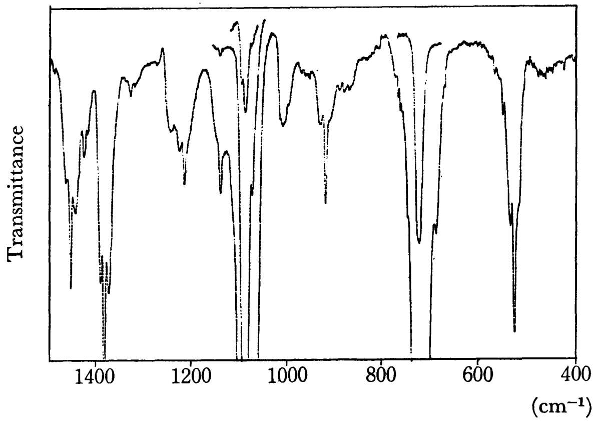

Fig. 3. Vapor phase spectrum of CH_3CCl_3 in a region 1500—400 cm^{-1}.

As for deuterated methyl chloroform CD_3CCl_3, no previous data on vibrational frequencies and intensities have been reported. Most of fundamental bands for this molecule have been assigned by referring to those of CH_3CCl_3, or taking into account band profiles observed in the vapor phase. The C–C stretching frequency could not be determined in like manner, hence its band has been assigned by referring to the frequency product rule for the isotopic species CH_3CCl_3 and CD_3CCl_3, as given in Table 2. Although there may be some ambiguity in assigning the fundamental frequencies only on the basis of observed spectrum, the observed values listed in Table 3 have been adopted as the tentative assignment. Taking into account the fact that not the harmonic frequencies but the observed frequencies are employed for the product rule in Table 2, the observed values listed are considred to satisfy the rule, hence the band assignment for these species might be correctly made.

Table 2. Frequency product rule for CH_3CCl_3 and CD_3CCl_3

	Theoretical	Observed
A_1	$\left(\frac{m_H{}^2 \times M_D}{m_D{}^2 \times M_H}\right)^{1/2} = 0.5060$	$\prod_{i=1}^{5} \frac{\nu^i_{\text{obsd}}(D)}{\nu^i_{\text{obsd}}(H)} = 0.5233$
E	$\left(\frac{m_H{}^3 \times M_D \times I_D}{m_D{}^3 \times M_H \times I_H}\right)^{1/2} = 0.3725$	$\prod_{i=7}^{12} \frac{\nu^i_{\text{obsd}}(D)}{\nu^i_{\text{obsd}}(H)} = 0.3812$

m: atomic weight, $m_H = 1.0078$, $m_D = 2.0141$
M: molecular weight, $M_H = 133.405$, $M_D = 136.424$
I : moment of inertia, $I_H = 213.175$, $I_D = 229.075$.

The calculation of normal vibrations, necessary for determining the **L**-matrix to evaluate the band intensity as well as for confirming the above band assignment, has been carried out using the local symmetry force field (LSFF). Force constants based on this field, being considered to be mutually transferable among

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14) D. C. Smith and G. F. Brown, *J. Chem. Phys.*, **20**, 473 (1952).

15) G. Allen and H. J. Bernstein, *Can. J. Chem.*, **32**, 2124 (1954).

16) M. Z. El-Sabban, A. G. Meister, and F. F. Cleveland, *J. Chem. Phys.*, **19**, 855 (1951).

17) R. Karplus and R. S. Halford, *ibid.*, **18**, 910 (1950).

18) T. R. Rubin, B. H. Levedahl, and D. M. Yost, *J. Amer. Chem. Soc.*, **66**, 279 (1944).

19) P. Venkateswarlu, *J. Chem. Phys.*, **19**, 298 (1951).

20) G. F. Hull Jr., *ibid.*, **3**, 534 (1935).

TABLE 3. OBSERVED AND CALCULATED NORMAL FREQUENCIES (cm^{-1})

Species	A ν_{obsd}	A ν_{calcd}	E ν_{obsd}	E ν_{calcd}
CH_3CH_3	2954	2951	2996	3001
	1388	1395	1486	1476
	995	1005	820	823
	2954	2953	2969	2971
	1379	1399	1460	1455
			1190	1188
CD_3CD_3	2100	2140	2236	2237
	1155	1155	1081	1063
			594	594
	2095	2127	2225	2230
	1077	1065	1055	1033
			970	948
CH_3CCl_3	2951	2945	3013	3002
	1386	1383	1455	1499
	1010	1006	1088	1090
	526	524	724	721
	344	333	303	319
			239	234
CD_3CCl_3	2146	2122	2264	2255
	1140	1120	1045	1077
	950	920	925	924
	510	507	660	652
	330	327	300	306
			220	218
CCl_3CCl_3	978	998	780	783
	432	432	278	280
	169	170	115	116
	679	683	858	862
	375	387	341	332
			224	211

the chlorinated ethanes treated here, have been determined using the least squares method from fifty-five observed frequencies. Calculated normal frequencies are given in Table 3, compared with the observed values, and the converged values of the LSFF constants are in Table 4, where asterisks indicate the constants fixed at zero in the least squares calculation.

Agreement between calculated and observed frequencies is satisfactory on the whole, and the converged values of the LSFF constants seem appropriate. The frequencies assigned tentatively for the C–C stretching vibration of methyl chloroforms CH_3CCl_3 and CD_3CCl_3 are represented with the above LSFF constants to a reasonable extent, thus the above band assignment could be considered acceptable.

Infrared band intensities of fundamental bands of three molecular species CH_3CCl_3, CD_3CCl_3, and C_2Cl_6, estimated on the basis of such band assignment, are listed in Table 5. The intensity sum rule proposed by Crawford[21] gives the results shown in the same table. It can be deduced from this result that these intensity data are reliable and accurate for calculation.

For computing the band intensity of chlorinated ethanes, parameters other than those used for chlorinated

TABLE 4. CONVERGED VALUES AND THEIR DEVIATIONS OF THE LSFF CONSTANTS (md/Å, md, or md·Å)

f(CC)	4.52 (0.08)	f(ds)	4.71 (0.05)
f(ss)	4.99 (0.02)	f(dd)	0.58 (0.03)
f(sd)	0.57 (0.01)	f(dr)	0.68 (0.03)
f(ss,sd)	0.00*	f(ds,dd)	0.09 (0.10)
f(ss,CC)	0.00*	f(ds, dr)	0.00*
f(sd, CC)	−0.31 (0.01)	f(dd, dr)	−0.01 (0.04)
f(ss, ss)	−0.01 (0.04)	f(ds, ds)	−0.06 (0·01)
f(sd, sd)	0.02 (0.01)	f(dd, dd)	−0.01 (0.01)
		f(dr, dr)	0.13 (0.01)
f(SS)	4.52 (0.05)	f(DS)	2.33 (0.46)
f(SD)	1.09 (0.05)	f(DD)	2.10 (0.58)
f(SS, SD)	0.67 (0.05)	f(DR)	0.80 (0.10)
f(SS, CC)	0.00*	f(DS, DD)	0.00*
f(SD, CC)	−0.91 (0.05)	f(DS, DR)	0.69 (0.15)
f(SS, SS)	0.00*	f(DD, DR)	0.00*
f(SD, SD)	−0.03 (0.05)	f(DS, DS)	0.55 (0.14)
		f(DD, DD)	0.00*
		f(DR, DR)	−0.17 (0.07)
f(ss, SS)	0.00*	f(ds, DS)	−1.23 (0.20)
f(sd, SD)	0.06 (0.10)	f(dd, DD)	0.00*
		f(dr, DR)	0.07 (0.02)

SS : symmetric stretching SD : symmetric deformation
DS : degenerate stretching DD: degenerate deformation
DR: degenerate rocking

Small and capital letters are referred to the LSFF coordinates for the C–H and the C–Cl bonds, respectively.

Asterisks indicate the force constants fixed at zero in the least squares calculation.

TABLE 5. OBSERVED INTENSITIES AND THEIR SUM RULE

Species			ν_{obsd} (cm^{-1})	A_{obsd} $\left(\frac{l}{mol \cdot cm^2}\right)$	$\frac{A_{obsd}}{\nu^2_{obsd}} \times 10^3$
CH_3CCl_3	A_1	1	2951	550± 50	6.99±0.36
		2	1386	770± 30	
		3	1010	260± 20	
		4	526	800± 100	
		5	344	400± 50	
	E	7	3013	660± 30	43.7±2.7
		8	1455	750± 70	
		9	1088	10000±1000	
		10	724	17500±1400	
		11	303	50± 20	
		12	239	50± 20	
CD_3CCl_3	A_1	1	2146	150± 50	7.06±0.92
		2	1145	1500± 300	
		3	950	50± 40	
		4	510	800± 100	
		5	330	300± 100	
	E	7	2264	200± 50	41.1±1.6
		8	1045	170± 50	
		9	925	14500±1000	
		10	660	9500±700	
		11	300	100± 50	
		12	220	50± 20	
C_2Cl_6	A_{2u}	5	679	4000± 300	
		6	375	100± 50	
	E_u	7	780	39400±3500	
		8	278	100± 50	
		9	115	(100)	

A_{obsd} in CH_3CCl_3, CD_3CCl_3 is in the vapor phase, and A_{obsd} in C_2Cl_6 is in dilute solution of carbon disulfide.

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[21] B. Crawford Jr., *J. Chem. Phys.*, **20**, 977 (1952).

methanes have to be introduced into the calculation based on the valence-optical theory.[22,23] These parameters are for example, the ones associated with the C–C bond, such as μ_{CC}, or $\delta\mu_{CC}/\delta r_{CC}$. Furthermore, if parameters due to the long-range methyl-methyl group interaction such as $\delta\mu_{CH}/\delta r_{CH}$ (where μ_{CH} and r_{CH} are attached to different carbon atoms, respectively) are taken into account, the total number of the electro-optical parameters becomes too large as compared with the number of available intensity data. In order to determine values for intensity parameters from the observed data, reduction of the unknown parameters is necessary, and for this purpose, those parameters which might be expected to have rather small values, such as the above $\delta\mu_{CH}/\delta r_{CH}$, are neglected.

Intensity parameters determined in calculation based on these considerations are twenty-four as follows:

(a) for C–H bond; μ_{CH}, $\delta\mu_{CH}/\delta r_{CH}$, $\delta\mu_{CH}/\delta r'_{CH}$, $\delta\mu_{CH}/\delta r_{CC}$, $\delta\mu_{CH}/\delta\alpha_{HCH}$, $\delta\mu_{CH}/\delta\alpha'_{HCH}$, $\alpha\mu_{CH}/\delta\alpha_{HCC}$, $\alpha\mu_{CH}/\delta\alpha'_{HCC}$,

(b) for C–Cl bond; μ_{CCl}, $\delta\mu_{CCl}/\delta r_{CCl}$, $\delta\mu_{CCl}/\delta r'_{CCl}$, $\delta\mu_{CCl}/\delta r_{CC}$, $\delta\mu_{CCl}/\delta\alpha_{ClCCl}$, $\delta\mu_{CCl}/\delta\alpha'_{ClCCl}$,, $\delta\mu_{CCl}/\delta\alpha_{ClCC}$, $\delta\mu_{CCl}/\delta\alpha'_{ClCC}$,

(c) for C–C bond; μ_{CC}, $\delta\mu_{CC}/\delta r_{CC}$, $\delta\mu_{CC}/\delta r_{CH}$, $\delta\mu_{CC}/\delta r_{CCl}$, $\delta\mu_{CC}/\alpha_{HCH}$, $\delta\mu_{CC}/\delta\alpha_{HCC}$, $\delta\mu_{CC}/\delta\alpha_{ClCCl}$, $\delta\mu_{CC}/\delta r_{ClCC}$.

These twenty-four parameters have been adjusted using the least squares method from the thirty-three data, that is, the thirty-two intensity data of C_2H_6, C_2D_6, CH_3CCl_3, CD_3CCl_3, and the permanent dipole moment of the methyl chloroform molecule.[24] The computative process is the same as in the previous papers, and the molecular constants used are given in Table 6.

TALEB 6. MOLECULAR CONSTANTS

	CH_3CH_3 CD_3CD_3	CH_3CCl_3 CD_3CCl_3	C_2Cl_6
C–H	1.1068	1.09	
C–Cl		1.76	1.763
C–C	1.5324	1.54	1.499
∠HCH	107°55′	109°28′	
∠ClCCl		109°	108°14′

Bond lengths are in (Å).

Because of the sign ambiguity inherent in intensity studies, several converged sets of intensity parameters are obtained, as in our previous cases. Although it is desirable to repeat the least squares calculation by changing the starting values of parameters in various ways to find out the most acceptable set with the smallest residual, such repetative computations are time-consuming and could not be carried out. Hence, first, the parameters were classified into the following three groups: (1) these common to chlorinated methanes, (2) those considered to be less important and to have small values, and (3) those considered to be more important and to have significant values. And as the starting values of the parameters, the values already determined were adopted for the first group, zero values were assumed for the second group, and various with changes of signs were tested for the third group. After more than fifteen starting sets of parameters have been tested, several sets have been obtained for converged values of the least squares calculation, and the set with the smallest residual among those has been considered to be most acceptable.

TABLE 7. CALCULATED INTENSITIES (l mol^{-1} cm^{-2})

Species		i	A_{obsd}	A_{calcd}		Mode
				(I)	(II)	
CH_3CH_3	A_{1u}	5	4780	4690	4696	CH_3 ss
		6	400	447	445	CH_3 sd
	E_u	7	12320	1420	12266	CH_3 ds
		8	1340	648	1495	CH_3 dd
		9	610	611	611	CH_3 dr
CD_3CD_3	A_{1u}	5	2420	2459	2462	CD_3 ss
		6	290	243	242	CD_3 sd
	E_u	7	6440	762	6547	CD_3 ds
		8	910	318	811	CD_3 dd
		9	330	327	325	CD_3 dr
CH_3CCl_3	A_1	1	550	411	411	CH_3 ss
		2	770	760	760	CH_3 sd
		3	260	265	265	CC
		4	800	860	863	CCl_3 SS
		5	400	399	395	CCl_3 SD
	E	7	660	827	667	CH_3 ds
		8	750	953	737	CH_3 dd
		9	10000	2653	6741	CH_3 dr
		10	17500	12081	15233	CCl_3 DS
		11	50	280	17	CCl_3 DD
		12	50	403	26	CCl_3 DR
CD_3CCl_3	A_1	1	150	362	362	CD_3 ss
		2	1500	487	488	CD_3 sd
		3	50	42	42	CC
		4	800	728	731	CCl_3 SS
		5	300	348	345	CCl_3 SD
	E	7	200	196	244	CD_3 ds
		8	170	397	127	CD_3 dd
		9	14500	7446	13804	CD_3 dr
		10	9500	8304	8413	CCl_3 DS
		11	100	70	190	CCl_3 DD
		12	50	134	36	CCl_3 DR
CCl_3CCl_3[a]	A_{1u}	5	(4000)	4000	3972	CCl_3 SS
		6	(100)	100	98	CCl_3 SD
	E_u	7	(39400)	45496	47375	CCl_3 DS
		8	(100)	10	27	CCl_3 DD
		9	(100)	64	287	CCl_3 DR
$\mu(CH_3CCl_3)$	(Debye)		1.78	1.78	1.78	
Residual				1416	93	

a) For C_2Cl_6, A_{obsd} is measured in solution of carbon disulfide, and should not be compared directly with A_{calcd}.

Band intensities thus calculated in terms of twenty-four parameters (Calcd I) are listed in Table 7, compared with the observed values, where intensities of C_2Cl_6 have been calculated using the determined values of parameters as described above. Agreement between calculated and observed values is satisfactory on the whole, but considerable disagreement is found in several bands,

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[22] L. A. Gribov and E. M. Popov, *Opt. Spectry.*, **12**, 304 (1962).

[23] L. A. Gribov, "Intensity Theory for Infrared Spectra of Polyatomic Molecules," Consultants Bureau (1964).

[24] R. H. Wiswall and C. P. Smyth, *J. Chem. Phys.*, **9**, 356 (1941).

This is the same situation as in the case of the chlorinated methanes reported in our previous paper.[1] That is, intensities for bands associated with the C–Cl bonds are well represented in terms of the above parameters, while in some bands associated with the C–H or C–D bonds, the calculated intensities are very much lower than the observed values. The disagreement in the CH_3 or CD_3 degenerate stretching in ethanes and rocking bands in methyl chloroforms is especially remarkable.

In order to revise such deficiency, it will be necessary to adjust some parameters separately for each molecules. In the case of chlorinated methanes treated in our previous paper,[1] similar disagreements in calculated intensities of some bands were encountered, and in order to get over such difficulties, two parameters μ_{CH} and $\delta\mu_{CH}/\delta r_{CH}$ were separately adjusted for each molecule. As a result, it has been proved that these two parameters may really be effective and sensitive in interpreting the observed intensities. And it has also been found that the adjustment of parameters other than μ_{CH} or $\delta\mu_{CH}/\delta r_{CH}$ was not effective for the satisfactory explanation of observed intensities. Therefore, in order to fit the calculated intensities of the $CH_3(CD_3)$ degenerate rocking bands of CH_3CCl_3 (CD_3CCl_3) to the observed values, it is considered effective to assign different values to μ_{CH} for ethanes and methyl chloroforms, and in order to resolve large discrepancies in the $CH_3(CD_3)$ degenerate stretching band intensities of ethanes, it is considered effective to assign different values to $\delta\mu_{CH}/\delta r_{CH}$. It may be considered less effective to adjust other parameters for resolving the discrepancies in intensities.

Hence, next calculation based on these considerations has been carried out using the least squares method to adjust the twenty-six parameters, of which μ_{CH} and $\delta\mu_{CH}/\delta r_{CH}$ are assumed to take different values for ethanes and methyl chloroforms (Calcd II). The calculated intensities are given in Table 7, compared with the observed values and the calculated values obtained in Calcd I. It is seen that the agreement is much improved and large discrepancies in the CH_3 (CD_3) degenerate stretching and rocking band intensities are successfully resolved in this calculation. The value 93 of the residual, sum of weighted deviations, in Calcd II is much smaller than the value 1416 in Calcd I. This shows that the average difference between observed and calculated intensities in Calcd II is about twice as large as the experimental errors of the intensity measurement.

As mentioned in Experimental, since the vapor phase spectrum of C_2Cl_6 was not observed because of its very low pressure, the band intensities were measured in solution of carbon disulfide. Therefore, the calculated intensities for C_2Cl_6 listed in Table 7 correspond to the intensities to be measured in the vapor phase, and should not be compared with the intensities observed in solution which are also shown in parentheses in Table 7 only as the information.

TABLE 8. CONVERGED VALUES AND THEIR DEVIATIONS OF INTENSITY PARAMETERS (D, or D/Å)

Parameter	Calcd (I)	Calcd (II)
μ_{CH} (C_2H_6) (CH_3CCl_3)	0.28 (0.04)	0.35 (0.02) 0.49 (0.05)
μ_{CCl}	−1.47 (0.05)	−0.93 (0.98)
μ_{CC}(CH_3CCl_3)	0.00*	0.00*
$\delta\mu_{CH}/\delta r_{CH}$ (C_2H_6) (CH_3CCl_3)	0.57 (0.06)	0.88 (0.01) 0.28 (0.04)
$\delta\mu_{CH}/\delta r'_{CH}$	0.33 (0.03)	0.17 (0.01)
$\delta\mu_{CH}/\delta r_{CC}$	0.00*	0.00*
$\delta\mu_{CH}/\delta\alpha_{HCH}$	0.27 (0.06)	0.38 (0.02)
$\delta\mu_{CH}/\delta\alpha'_{HCH}$	0.00*	0.00*
$\delta\mu_{CH}/\delta\alpha_{HCC}$	−0.00 (0.03)	0.04 (0.01)
$\delta\mu_{CH}/\delta\alpha'_{HCC}$	0.00*	0.00*
$\delta\mu_{CCl}/\delta r_{CCl}$	−2.33 (0.30)	−2.28 (0.25)
$\delta\mu_{CCl}/\delta r'_{CCl}$	−0.16 (0.22)	−0.19 (0.20)
$\delta\mu_{CCl}/\delta r_{CC}$	0.00*	0.00*
$\delta\mu_{CCl}/\delta\alpha_{ClCCl}$	1.36 (0.46)	1.85 (0.66)
$\delta\mu_{CCl}/\delta\alpha'_{ClCCl}$	0.00*	0.00*
$\delta\mu_{CCl}/\delta\alpha_{ClCC}$	0.70 (0.67)	1.24 (0.39)
$\delta\mu_{CCl}/\delta\alpha'_{ClCC}$	1.97 (0.39)	1.50 (0.65)
$\delta\mu_{CC}/\delta r_{CC}$	0.86 (0.10)	0.86 (0.09)
$\delta\mu_{CC}/\delta r_{CH}$	−0.18 (0.04)	0.02 (0.04)
$\delta\mu_{CC}/\delta r_{CCl}$	−0.15 (0.22)	−0.15 (0.22)
$\delta\mu_{CC}/\delta\alpha_{HCH}$	0.00*	0.00*
$\delta\mu_{CC}/\delta\alpha_{HCC}$	0.20 (0.02)	0.06 (0.04)
$\delta\mu_{CC}/\delta\alpha_{ClCCl}$	0.00*	−0.00 (0.00)
$\delta\mu_{CC}/\delta\alpha_{ClCC}$	0.30 (0.20)	0.33 (0.21)

Asterisks indicate the parameters fixed at zero in the least squares calculation.

In Table 8, converged values and their standard deviations in most acceptable sets are given for intensity parameters for Calcd I and II. Parameters with asterisks in the table are fixed at zero in the least squares calculation. Among these parameters, μ_{CC} may probably have some finite value especially in the case of CH_3CCl_3. However, its value can by no means be determined here because too many parameters are taken in this case. Therefore the values determined for the other parameters should be considered to be valid only under the postulation of negligence of μ_{CC}. Although this is indeed a very disagreable ambiguity, this is inevitable at the present stage of such intensity studies. In the treatment of many other molecules, it will be probable to obtain experimental facts which give us a clearer knowlegde about μ_{CC}.

It can be deduced that in Calcd II, a slight difference in converged values for μ_{CH} of ethanes and of methyl chloroforms is found but this is the very reason for the successful explanation of the CH_3 (CD_3) degenerate rocking band intensities in these molecules. That is, μ_{CH} is a very sensitive parameter to interpret the band intensity, and consequently, it has proved that it is not possible to find out a value commonly applicable to ethanes and methyl chloroforms for this parameter.

A similar situation is also found in the derivative $\delta\mu_{CH}/\delta r_{CH}$. The fact that some difference in $\delta\mu_{CH}/\delta r_{CH}$ for ethane and methyl chloroform obtained in Calcd II is quite similar to the chlorinated methanes,[1] hence, assigning different values to this parameter for each molecule is necessary for a successful explanation of the CH_3 (CD_3) degenerate stretching band intensities of these molecules.

Some comment has to be made here with respect to the significance of the converged values of the intensity parameters as listed in Table 8. As mentioned in our previous papers[1,3] as well as pointed out by Gribov himself,[25] the valence-optical theory used here has an essential disadvantage which seems to be almost fatal. Too many electro-optical parameters have to be taken into account, and furthermore, due to the fact that they always appear in forms of linear combinations in intensity expressions, individual value of each parameter can not be determined. This is attributed to an assumption that a molecular dipole moment is decomposed as a vector sum of bond dipole moments, in interpreting the band intensity data in terms of intensity parameters.

If one takes a viewpoint in which significant or meaningful quantities are derived from the infrared intensity data, such decomposition is certainly broken down, and one relies upon the treatment as in the serial works by Crawford and his collaborators. In their treatment, the infrared intensity data are interpreted in terms of parameters which are derivatives of the molecular dipole moment with respect to various symmetry coordinates. However, analyses in their studies are restricted within different isotopic species of a certain molecule, and infrared intensity data of various molecules can not be interpreted with their approach. Because the intensity parameters used in their analysis are chracteristic of a molecule as a whole and cannot be transferred among various molecules since both μ and S_i in $(\delta\mu/\delta S_i)$ (where μ is a molecular dipole moment and S_i is the i-th molecular symmetry coordinate) are quantities inherent to a framework of a molecule as a whole.

If one attempts to interpret the intensity data of different molecules in terms of the least number of common parameters, such parameters have to be associated with the bond property. Because the conception of "bond" is most natural and general for chemists in considering some properties of various kinds of different molecular species. In the classical "bond moment hypothesis" used in the previous infrared studies, all bond moments are assumed to depend only on the variation of their own bond lengths. On this basis, many calculations have been carried out for bond moments and their derivatives with respect to the stretching of their bonds, using the experimental results of the band intensities. However, with this approximation, it was very often encountered that different sets of values were obtained for bond moments and/or bond derivatives from sets of the band intensities belonging to different symmetry species, and that the vector sum of bond moments was not equal to the total permanent dipole of the molecule. This fact suggests that this approximation is too rough to explain the observed intensities.

Taking into account the dependence of a bond dipole on the variation of its neighboring internal coordinates, Gribov *et al.* pointed out the necessity of introducing the moment derivatives with respect to some neighboring internal coordinates. This improvement is quite reasonable from the viewpoint of the necessary variation in electron distribution with the displacements of atoms in vibration. This valence-optical theory is an extension of the classical bond moment hypothesis which is designated as the zero-order approximation of the valence-optical theory according to Gribov. That is, in addition μ_i and $\delta\mu_i/\delta r_i$ determined in the classical theory, more electro-optical parameters $\delta\mu_i/\delta r_j$ and $\delta\mu_i/\delta\alpha_{jkl}$ are to be determined using the observed band intensity data. As mentioned above, those parameters cannot be obtained individually, but merely their linear combinations can be determined from the intensity calculations as a disadvantage of this theory.

The form of the linear combinations in which the parameters take part, is dependent on the framework of the molecule as a whole, and is different from molecule to molecule. Hence, if the assumption that the electro-optical parameters may take the same values independent of the molecular species is accepted, some of the parameters are to be determined by solving simultaneous equations of linear combinations of the parameters. Values thus determined for the parameters are qualified to explain the observed intensity data of various different molecules. The converged values given in Table 8 implies such significance, although they still depend on values at which undeterminable parameters should be fixed. Since no unambiguous answer can be given to the question which parameters among several undeterminable parameters should be fixed at what values, it is reasonable to fix less important parameters at zero, using some chemical intuition or taking into account the potential energy matrix element.[1,3] Therefore it is concluded that the converged values in Table 8 are necessary and sufficient to interpret the infrared intensity data of ethanes and methyl chloroforms. And, even though the above parameters μ_{CH} and $\delta\mu_{\mathrm{CH}}/\delta r_{\mathrm{CH}}$ may also be linearly combined with some other parameters and only values of those linear combinations may be determined definitely, it is considered to be very probable that these two parameters may really be effective and sensitive in interpreting the band intensity data, as was already experienced in the case of chlorinated methanes.[1]

For several parameters common to the chlorinated methanes and ethanes, results are summarized in Table 9. This shows clearly the above conclusion that in

TABLE 9. PARAMETERS COMMON TO CHLORINATED METHANES AND ETHANES (D, or D/Å)

Species	μ_{CH}	$\dfrac{\delta\mu_{\mathrm{CH}}}{\delta r_{\mathrm{CH}}}$	μ_{CCl}	$\dfrac{\delta\mu_{\mathrm{CCl}}}{\delta r_{\mathrm{CCl}}}$
CH_4	0.95	0.54		
CH_3Cl	0.59	0.34	−1.32	−2.86
CH_2Cl_2	0.13	0.10		
$CHCl_3$	0.09	−0.06		
CCl_4				
C_2H_6	0.35	0.88	−0.93	−2.28
CH_3CCl_3	0.49	0.28		
C_2Cl_6				

Results for chlorinated methanes are taken from Set (A) in Table 9 of Ref. 1, and for ethanes, from Calcd II in Table 8 of this paper.

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[25] L. A. Gribov, *Opt. Spectry.*, **25**, 53 (1968).

order to explain the band intensity data of various chlorinated ethanes as well as methanes in terms of as few common intensity parameters as possible,, most parameters may take common values transferable to various molecular species, but it is not possible to find out commonly applicable values for the two parameters μ_{CH} and $\delta\mu_{CH}/\delta r_{CH}$ for the various chlorinated methanes and ethanes. Furthermore, this may suggest that bond properties in the C–H bonds in these molecules vary from one to another much more than in C–Cl bonds. These conclusions might be confirmed by the quantum-chemical approach such as the CNDO techniques.