Infrared Absorption Intensities of *trans*- and *cis*-Dichloroethylene

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Infrared absorption intensities of *trans*- and *cis*-dichloroethylene were measured in the vapor phase, and interpreted in terms of intensity parameters common to the isomers. In order to obtain L matrices, force constants common to the isomers were determined so as to attain the best fit between the observed and calculated frequencies of CHCl=CHCl, CDCl=CDCl and CHCl=CDCl. Using the L matrices thus obtained, intensity parameters were determined so as to attain the best fit between the observed and calculated intensities of CHCl=CHCl. As a result, the observed frequencies and intensities were satisfactorily represented in terms of the force constants and the intensity parameters common to the isomers.

In our serial studies on rotational isomerism,[1-3] the energy differences between the rotational isomers were evaluated by applying the absolute intensity method. This is quite a unique method, not requiring any temperature variation in experiment, hence it may give a very reliable value for an energy difference. But it has a great disadvantage that intensity parameters are assumed to be transferable between the rotational isomers concerned. The validity of this assumption can by no means be confirmed by any direct method.

In our serial studies on infrared absorption intensities,[4-6] intensity data were interpreted in terms of intensity parameters common to some molecular groups or molecular series. At least as far as the molecular series treated so far are concerned, it was concluded that intensity parameters are transferable among some molecular groups.

In this investigation, in order to confirm the transferability of intensity parameters in molecules containing double bonds, infrared absorption intensities of *trans*- and *cis*-dichloroethylene CHCl=CHCl measured in the vapor phase have been interpreted in terms of intensity parameters assumed as transferable between the isomeric molecules.

Experimental

Infrared absorption intensities of fundamental bands of *trans*- and *cis*-dichloroethylene CHCl=CHCl were measured in the vapor phase using Perkin-Elmer Model 421 grating spectrophotometer combined with a digital recorder.[7] The vapor phase spectra recorded are shown in Figs. 1(a) and 1(b). The commercial material of the extra pure grade was used without further purification. The observed spectrum of *trans* isomer shows that it contains at most 1% of *cis* isomer.

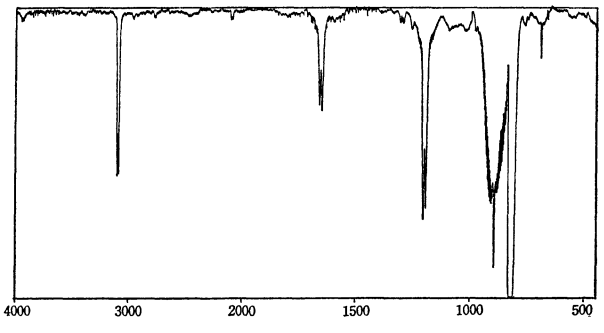


Fig. 1(a). Vapor phase spectrum of *trans*-dichloroethylene.

Gas cells 5 or 10 cm thick with KBr or polyethylene windows were used, and measurements were made at least ten times at different sample pressures ranging from 5 to 100 mmHg. Since vibration-rotation fine structures were observed for some absorption bands, dry air was introduced as foreign gas into gas cells in order to pressurize up to 1 atm, and absolute band intensities were evaluated by applying the Wilson-Wells extrapolation technique. The plots of intensities against pressures for some absorption bands are shown in Fig. 2.

In order to integrate absorbance curves for obtaining absolute band intensities, encoded paper tapes punched out from the digital recorder were processed by using a FACOM

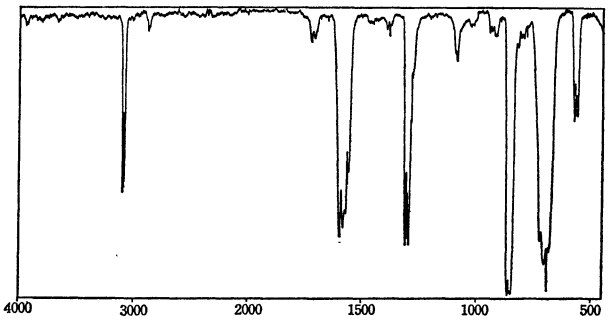


Fig. 1(b). Vapor phase spectrum of *cis*-dichloroethylene.

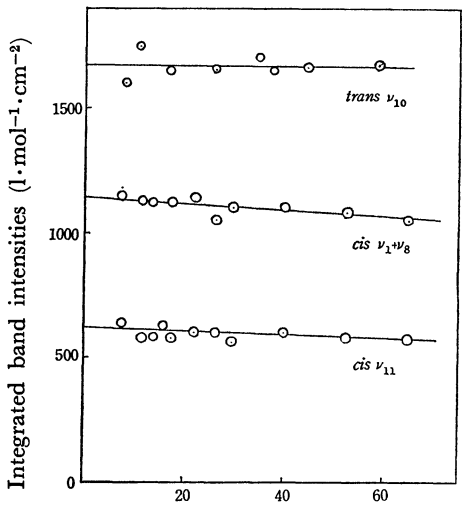


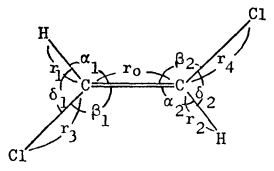
Fig. 2. The Wilson-Wells extrapolation plot.

TABLE 1. OBSERVED AND CALCULATED INTENSITIES OF DICHLOROETHYLENE
(Unit: l·mol^{-1}·cm^{-2})

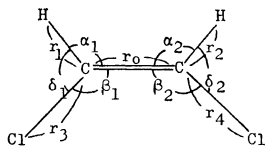
		ν_{obsd} (cm^{-1})	A_{obsd}	Shimozawa, Wilson[8]		Dervil[9]		A_{calcd}
				A_{soln}[a]	A_{P-W}[b]	A_{soln}	A_{P-W}[b]	
trans	ν_9	3097	1200± 50	1632	1246			1183
	ν_{10}	1201	1700± 50	1452	1106			1862
	ν_6	898	4900±100	6620	5060			4881
	ν_{11}	826	9600±200			14000[c]	9470	8712
	ν_{12}	250	10± 5					25
	ν_7	227	100± 50					6
cis	ν_8	3087	1100± 50	1990	1524			1018
	ν_1	3086						123
	ν_2	1592	2200±300[d]					2656
	ν_9	1303	1800±100	2420	1850			310
	ν_3	1179	10± 5					23
	ν_{10}	857	5800±200			7150[e]	5845	5740
	ν_4	721	5700±200					2475
	ν_{12}	695						4569
	ν_{11}	569	600± 50					684
	ν_5	173	10± 5					21

a) Carbon tetrachloride solution. b) Gaseous intensities estimated by applying the Polo-Wilson's equation. c) Carbon disulfide solution. d) Owing to the overlapping with a combination band, the error is fairly large. e) *n*-Hexane solution.

TABLE 2. INTERNAL COORDINATES OF DICHLOROETHYLENE



trans



cis

r_0	CC stretching
r_1, r_2	CH stretching
r_3, r_4	CCl stretching
$(\alpha_1-\delta_1)/\sqrt{2}$, $(\alpha_2-\delta_2)/\sqrt{2}$	CCH bending
$(2\beta_1-\alpha_1-\delta_1)/\sqrt{6}$, $(2\beta_2-\alpha_2-\delta_2)/\sqrt{6}$	CCCl bending
π_1, π_2	Out-of-plane bending
τ	Torsion

TABLE 3. CONVERGED VALUES AND STANDARD DEVIATIONS OF FORCE CONSTANTS
(Unit: mdyn/Å, mdyn, or mdyn·Å)

F(CH)	5.15(0.03)
F(CC)	9.28(0.31)
F(CCl)	3.97(0.03)
E(CCH)	0.50(0.01)
F(CCCl)	0.88(0.02)
F(π)	0.25(0.00)
F(to)	0.62(0.01)
F(CH, CH')	−0.06(0.02)
F(CH, CC)	−0.16(0.10)
F(CH, CCH)	0.26(0.07)
F(CC, CCH)	0.28(0.08)
F(CC, CCCl)	0.20(0.12)
F(CCl, CCl')	0.12(0.03)
F(CCl, CCH)	−0.30(0.02)
F(CCl, CCCl)	0.39(0.02)
F(CCH, CCH')	0.00(0.01)
F(CCH, CCCl)	−0.04(0.02)
F(CCCl, CCCl')	−0.01(0.02)
F(π, π')	0.03(0.00)
F(π, to)	−0.07(0.00)

Model 270—30 electronic computer system. For the absorption bands below 500 cm^{-1}, the digital recording was not available, and their absorption intensities were estimated by using a planimeter.

Other experimental conditions for the intensity measurement are the same as described in our previous papers.[1-7]

Results and Discussion

The absolute intensities of fundamental bands of *trans*- and *cis*-dichloroethylene CHCl=CHCl measured in the vapor phase are listed in Table 1 with experimental errors. Although several papers were published on the vibrational frequencies of dichloroethylene, the absorption intensities for these isomeric molecules have received little attention.

Shimozawa and Wilson[8] measured the infrared absorption intensities of several fundamental bands of *trans*- and *cis*-dichloroethylene in carbon tetrachloride or carbon disulfide solution, and evaluated the gaseous band intensities by applying the Polo-Wilson's equation. The values estimated by them are in rather good accordance with the intensities obtained in this study, except for the ν_{10} band of *trans* isomer.

Dervil[9] measured the infrared absorption intensities of the *trans* ν_{11} and *cis* ν_{10} bands of dichloroethylene in hexane or carbon disulfide solution. The gaseous

Table 4. Observed and calculated frequencies of dichloroethylene (cm^{-1})

			CHCl=CHCl			CDCl=CDCl				CHCl=CDCl		
			ν_{obsd}	ν_{calcd}	$\delta\nu$[a]	ν_{obsd}	ν_{calcd}	$\delta\nu$		ν_{obsd}	ν_{calcd}	$\delta\nu$
trans	1	A_g	3073	3082	9	2325	2319	−6	A′	3087	3090	3
	2		1585	1596	11	1570	1557	−13		2310	2301	−9
	3		1274	1260	−14	992	998	6		1574	1576	2
	4		852	858	6	765	752	−13		1241	1237	−4
	5		349	354	5	346	350	4		964	970	6
	6	A_u	898	898	0	660	655	−5		830	831	1
	7		227	224	−3	227	220	−7		776	774	−2
	8	B_g	763	765	2	657	656	−1		348	352	4
	9	B_u	3097	3098	1	2290	2282	−8		250	265	15
	10		1201	1218	17	916	913	−3	A″	830	834	4
	11		826	826	0	791	797	6		660	656	−5
	12		250	271	21	250	260	10		227	222	−5
cis	1	A_1	3086	3089	3	2325	2320	−5	A′	3078	3090	12
	2		1592	1602	10	1576	1563	−14		2306	2300	−6
	3		1179	1192	13	850	849	−1		1591	1582	−9
	4		721	720	−1	700	699	−1		1253	1251	−2
	5		173	160	−13	171	160	−11		957	966	9
	6	A_2	876	880	4	695	681	−14		788	780	−8
	7		406	405	−1	368	373	5		710	710	0
	8	B_1	3087	3091	4	2280	2280	−0		558	556	−2
	9		1303	1289	−14	1051	1052	1		175	160	−15
	10		857	859	2	766	755	−11	A″	817	819	2
	11		569	562	−7	540	550	10		584	584	−0
	12	B_2	695	701	6	558	541	−17		387	388	1

a) $\delta\nu = \nu_{calcd} - \nu_{obsd}$.

intensities estimated from her values by applying the Polo-Wilson's equation agree well with the present results. Hence the observed intensity data obtained in this study can be considered as reliable enough for the intensity computation.

In order to interpret these intensity data, it is necessary to obtain L matrices by the normal mode analysis. Concerning the vibrational frequencies of dichloroethylene, Bernstein *et al.*[10,11] pointed out the errors for the band assignments made by Wu,[12,13] Trumpy,[14] Herzberg,[15] or Pitzer *et al.*,[16] and reported the correct band assignment for *trans*- and *cis*-dichloroethylene CHCl=CHCl, CDCl=CDCl and CHCl=CDCl. However, the determination of force constants in dichloroethylene has received little attention, except for the out-of-plane vibrations studied by Pitzer *et al.*[16] or Dowling.[17]

In order to obtain L matrices as accurate as possible, force constants have been determined by the least-squares method so as to attain the best fit between the observed and calculated frequencies of *trans*- and *cis*-dichloroethylene CHCl=CHCl, CDCl=CDCl and CHCl=CDCl. Twenty force constants based on the internal coordinates given in Table 2 have been assumed as common to the *trans* and *cis* isomer, and their values have been refined from total seventy-two frequency data. As for the torsional coordinate, not τ(Cl–C–C–Cl), but the coordinate of the internal rotation type has been taken.

Previous authors pointed out that for substituted ethane or ethylene, it is necessary to introduce the *trans* interaction constant. Such an interaction constant may be required in the present case. However, since in this study, we examine whether we can explain the observed frequencies and intensities in terms of the force constants and the intensity parameters common to the isomeric molecules, the *trans* interaction constant has not been taken into account, and the determination of the common force constants has been carried out.

Converged values and standard deviations of the force constants are listed in Table 3, and the calculated normal frequencies are compared in Table 4 with the observed fundamental frequencies. The agreement between the observed and calculated frequencies is satisfactory on the whole, and the converged values of the force constants are all quite acceptable as compared with those of related molecules. A rather good agreement between the observed and calculated frequencies for the CCH bending vibrations may suggest that the *trans* interaction constant takes less significant role in representing the normal frequencies of dichloroethylene. Thus the L matrices obtained by this normal mode analysis can be considered as suitable enough for the intensity computation described below.

Using the L matrix data thus obtained, the intensity data given in Table 1 have been interpreted in terms of intensity parameters on the basis of the Gribov's valence-optical theory.[18,19] As for the intensity parameters for interpreting the intensity data of *trans*- and *cis*-dichloroethylene, the following assumption has been

TABLE 5. CONVERGED VALUES AND STANDARD DEVIATIONS OF INTENSITY PARAMETERS
(Unit : D, or D/Å)

μ_{CH}	0.80(0.01)
μ_{CCl}	−0.29(0.01)
$\delta\mu_{CH}/\delta r_{CH}$	0.14(0.04)
$\delta\mu_{CH}/\delta r_{CCl}$	−1.00(0.41)
$\delta\mu_{CH}/\delta\alpha_{CCH}$	0.12(0.05)
$\delta\mu_{CH}/\delta\beta_{CCCl}$	0.52(0.23)
$\delta\mu_{CCCl}/\delta r_{CCl}$	−3.57(0.21)
$\delta\mu_{CCCl}/\delta r_{CH}$	0.26(0.02)
$\delta\mu_{CCl}/\delta r_{CC}$	0.14(0.26)
$\delta\mu_{CCl}/\delta\beta_{CCCl}$	−0.26(0.14)
$\delta\mu_{CCCl}/\delta\alpha_{CCH}$	−0.28(0.07)

taken. That is, only bond moment derivatives have been taken where the bond moments and the internal coordinates are associated with the same carbon atoms, and the other bond moment derivatives have all been neglected.

The intensity parameters based on this assumption, as listed in Table 5, have been considered to take equal values between the *trans* and *cis* isomers, that is, they have been assumed as transferable. The values of these parameters have been refined by the least-squares method so as to attain the best fit between the observed and calculated band intensities and molecular dipole moment. Converged values and standard deviations of the intensity parameters are given in Table 5, and the calculated band intensities are compared in Table 1 with the observed intensities.

The agreement between the observed and calculated band intensities is rather satisfactory except for the ν_9 band of *cis*-dichloroethylene. The average difference between the calculated and observed intensities is about four times larger than the expreimental errors of the observed intensities. The accordance to such an extent is acceptable, taking into account the assumptions placed on the determination of the intensity parameters.

The converged values of the intensity parameters listed in Table 5 are all acceptable as compared with those of related molecules treated previously. Moreover, the determined values of the bond moments μ_{CH} and μ_{CCl} can well explain the observed molecular dipole moment of *cis*-dichloroethylene measured in the gaseous state ($\mu_{obsd}=1.90$ D, $\mu_{calcd}=1.899$ D). However, a comment has to be made on the values of μ_{CH} and μ_{CCl}.

In the case of chlorinated methanes[4,5] or ethanes,[6] μ_{CH} was converged to the values near 0.5 D, while μ_{CCl} was converged to −1.0 D. On the other hand, in the present case, μ_{CH} is relatively large, but the absolute value of μ_{CCl} is fairly small. The value of μ_{CH} is in rather good agreement with the one for ethylene (0.7 D).[20] The small value of μ_{CCl} might suggest that the non-bonded electron cloud on chlorine atoms in dichloroethylene may be attracted into π-electron cloud of the double bond.[21] Such a result will be confirmed by a quantum-chemical approach such as a CNDO technique.

In conclusion, the transferability of the intensity parameters in dichloroethylene may confirm that intensity parameters might be transferable in related molecules, and thus the absolute intensity method may reasonably be applied to the determination of an energy difference between the rotational isomers.

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