

Infrared intensity analysis of CH_2Cl_2 and CD_2Cl_2 in vapour and liquid states*

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Abstract. In the infrared spectra of molecules with more than one C-H bond the symmetric and antisymmetric stretching bands often overlap, causing uncertainty in the intensity analysis. For CH_2Cl_2 and CD_2Cl_2 in the vapour state, the two bands overlap to such an extent that Straley who takes it as one band attributes it to anti-symmetric stretching while Saeki *et al* assign it to the symmetric stretching. Following the method of analysis initiated in this laboratory, we have solved this problem by ultimately obtaining intensities separately for A_1 and B_2 species. The band is mostly due to the symmetric stretching, 0.06 out of the total of 0.31 contributing to B_2 . Thus, this gives a method of separating the intensities of bands which are highly overlapping.

Keywords. Infrared intensity analysis; dipole moments.

1. Introduction

Infrared intensity analysis carried out for a variety of molecules has been reported by Buddha *et al* (1976), Wahegaonkar *et al* (1977) and Pratibha *et al* (1978). It has been possible to determine the dipole moments and derivatives of a number of bands C-H, C=O, C-Cl, etc. While carrying out this analysis, it has been observed that for molecules with two or more C-H bonds, the symmetric and antisymmetric stretch bands overlap introducing errors in separating them. For many of the molecules worked so far, this separation was done with some success. But the spectra of CH_2Cl_2 taken by Straley (1955), Robinson *et al* (1962) and then by Saeki and Tanabe (1969) have presented a serious difficulty. The intensity due to $\nu_1=2997\text{ cm}^{-1}$ was attributed to CH symmetric stretching by Tanabe and Saeki and to the anti-symmetric stretching by Straley. The separation of the bands was found to be so difficult that the above authors regarded it as a single band. Intensity analysis presents a serious difficulty in such cases. This problem is studied in this paper.

The infrared absorption spectra of CH_2Cl_2 and CD_2Cl_2 were taken in the liquid and vapour states by Tanabe and Saeki. The frequency distribution, the assignments and intensities of the various bands, as given by various workers, are shown in table 1. It is seen that in the vapour phase, the intensity due to 2997 cm^{-1} is assigned to A_1 by Saeki and Tanabe and to B_2 by Straley. But for the liquid state, the bands are sufficiently distinguishable.

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Table 1. Frequencies, assignments and $\delta P/\delta Q$ values

Species	Frequency (cm ⁻¹)	Saeki and Tanabe (1969) ±	($\delta P/\delta Q$)† vapour Straley (1955)	($\delta P/\delta Q$)† liquid Tanabe and Saeki (1969) ±	($\delta P/\delta Q$) liquid present method	
<i>A</i> ₁	<i>v</i> ₁	714	0.337799	—	0.358289	—
	<i>v</i> ₂	2997	0.313717	—	0.256149	0.3079
	<i>v</i> ₃	1430	0.092510	—	0.173070	—
CH ₂ Cl ₂	<i>v</i> ₄	283	0.092510	—	0.09251	—
	<i>B</i> ₁	<i>v</i> ₆	757	1.164000	123	1.280742
<i>v</i> ₇		1268	0.615960	63.1	0.620576	—
<i>B</i> ₂	<i>v</i> ₈	3055	—	22.6	0.192575	-0.0602
	CD ₂ CL ₂	<i>v</i> ₉	896	0.130828	11.7	0.206859
<i>A</i> ₁	<i>v</i> ₁	687	0.337799	—	0.348195	—
	<i>v</i> ₂	2275	0.247660	—	0.216955	-0.2436
	<i>v</i> ₃	1050	0.053410	—	0.168899	—
	<i>v</i> ₄	281	0.092510	—	0.09251	—
<i>B</i> ₁	<i>v</i> ₆	727	0.977580	—	1.094593	—
	<i>v</i> ₇	960	0.844500	—	0.893732	—
<i>B</i> ₂	<i>v</i> ₈	2374	—	—	0.106821	-0.000462
	<i>v</i> ₉	713	0.08445	—	—	-0.0446

†Large number of figures are shown against each value for the sake of computational consistency.

2. Intensity formulae

The intensity formulae are derived for this molecule in the usual manner, on the same lines as described by Buddha *et al* (1976) and are given below. ΣI_i^2 equations explained by the above authors are also given. Another equation relating the molecular dipole moment to bond dipole moments is also given. These data are taken from dielectric constant measurements from the literature, (Robert Weast 1968-69).

*A*₁ type

$$\begin{aligned}
 I_i &= \frac{\delta P_z}{\delta Q_i} \\
 &= \sqrt{2} \cos \alpha/2 [\epsilon_3 L_{1i} - \epsilon_1 L_{2i}] - \frac{1}{\sqrt{2}} \sin \alpha/2 (\mu_1 + \mu_3) L_{3i} \\
 &\quad + \frac{\sqrt{3}}{2} \sin \alpha/2 \cdot \left[\frac{\cos \alpha/2}{R} + 1 \right]^{-1} (\mu_1 - \mu_3) L_{4i}
 \end{aligned}$$

$$i = 1, 2, 3, 4.$$

(1)

B_1 type

$$\begin{aligned}
 I_i &= \frac{\delta P_x}{\delta Q_i} \\
 &= -\sqrt{2} \epsilon_3 \sin \alpha/2 L_{1i} - 2\sqrt{2} \mu_c \sin \alpha/2 [a\mu_1 + b\mu_3 \cos^2 \alpha/2] L_{i1}^{-1} \\
 &\quad + \frac{4\mu_c}{R} (b \cos^2 \alpha/2 + a) (b \cos^2 \alpha/2 \mu_3 + a\mu_1) \\
 &\quad + \frac{2}{R} (b^2 \cos^2 \alpha/2 \mu_3 \mu_{Cl} + a^2 \mu_H \mu_1) L_{i2}^{-1}
 \end{aligned} \tag{2}$$

 $i = 1, 2.$ B_2 type

$$\begin{aligned}
 I_i &= \frac{\delta P_y}{\delta Q_i} \\
 &= \sqrt{2} \epsilon_1 \sin \alpha/2 L_{1i} + (2\sqrt{2}) \sin \alpha/2 \mu_c [a\mu_1 \cos^2 \alpha/2 + b\mu_3] L_{i1}^{-1} \\
 &\quad - \frac{4\mu_c}{R} (b\mu_3 + a \cos^2 \alpha/2 \mu_1) (a \cos^2 \alpha/2 + b) \\
 &\quad + \frac{2}{R} (a^2 \cos^2 \alpha/2 \mu_H \mu_1 + b \mu_3 \mu_{Cl}) L_{i2}^{-1}
 \end{aligned} \tag{3}$$

where $R = (1 + \cos^2 \alpha/2)^{1/2}$ and $-\cos \phi = \cos^2 \alpha/2$, $a = 1/d$, $b = 1/D$, d and D being the C-H and C-Cl bond length. $\angle \text{HCH} = \angle \text{Cl-C-Cl} = \alpha$, $\angle \text{Cl-C-H} = \angle \text{H-C-Cl} = \phi$

 A_1 type

$$\begin{aligned}
 \Sigma I_z^2 &= 2 \cos^2 \alpha/2 [\epsilon_3^2 G_{11} + \epsilon_1^2 G_{22} - 2\epsilon_1 \epsilon_3 G_{12}] \\
 &\quad + \frac{3}{4} \sin^2 \alpha/2 \cdot \left(\frac{\cos \alpha/2}{R} + 1 \right)^{-2} (\mu_1 - \mu_3)^2 G_{44} \\
 &\quad + \frac{1}{2} \sin^2 \alpha/2 (\mu_1 + \mu_3)^2 G_{33} \\
 &\quad + (\sqrt{6}) \cos \alpha/2 \sin \alpha/2 (\mu_1 - \mu_3) (\epsilon_3 G_{14} - \epsilon_1 G_{24}) \left(\frac{\cos \alpha/2}{R} + 1 \right)^{-1} \\
 &\quad - \frac{\sqrt{3}}{\sqrt{2}} \sin^2 \alpha/2 (\mu_1^2 - \mu_3^2) G_{34} \left(\frac{\cos \alpha/2}{R} + 1 \right)^{-1} \\
 &\quad - 2 \cos \alpha/2 \sin \alpha/2 (\mu_1 + \mu_3) (\epsilon_3 G_{13} - \epsilon_1 G_{23})
 \end{aligned} \tag{4}$$

 B_1 type

$$\begin{aligned}
 \Sigma I_x^2 &= 2 \sin^2 \alpha/2 \epsilon_3^2 G_{11} + 8\mu_c^2 \sin^2 \alpha/2 (a\mu_1 + b\mu_3 \cos^2 \alpha/2)^2 G_{11}^{-1} \\
 &\quad + \frac{4\mu_c}{R} [b \cos^2 \alpha/2 + a] [b \cos^2 \alpha/2 \mu_3 + a\mu_1]
 \end{aligned}$$

$$\begin{aligned}
& + \frac{2}{R} (b^2 \cos^2 \alpha/2 \mu_3 \mu_{Cl} + a^2 \mu_H \mu_1)^2 G_{22}^{-1} \\
& + 8 \sin^2 \alpha/2 \mu_c \epsilon_3 (a \mu_1 + b \mu_3 \cos^2 \alpha/2) \\
& - 4\sqrt{2} \mu_c \sin \alpha/2 (a \mu_1 + b \mu_3 \cos^2 \alpha/2). \\
& \frac{4\mu_c}{R} (b \cos^2 \alpha/2 + a) (b \cos^2 \alpha/2 \mu_3 + a \mu_1) \\
& + \frac{2}{R} (b^2 \cos^2 \alpha/2 \mu_3 \mu_{Cl} + a^2 \mu_H \mu_1) G_{12}^{-1} \tag{5}
\end{aligned}$$

B₂ type

$$\begin{aligned}
\Sigma I_y^2 & = 2 \sin^2 \sqrt{2} \epsilon_1^2 G_{11} + 8\mu_c^2 \sin^2 \alpha/2 (a \mu_1 \cos^2 \alpha/2 + b \mu_3)^2 G_{11}^{-1} \\
& + \frac{4\mu_c}{R} (a \cos^2 \alpha/2 + b) (b \mu_3 + a \mu_1 \cos^2 \alpha/2) \\
& + \frac{2}{R} (a^2 \cos^2 \alpha/2 \mu_1 \mu_H + b \mu_c \mu_3)^2 G_{22}^{-1} \\
& + 8\mu_c \sin^2 \alpha/2 \epsilon_1 (a \mu_1 \cos^2 \alpha/2 + b \mu_3) \\
& - 4\sqrt{2} \mu_c \sin \alpha/2 (a \mu_1 \cos^2 \alpha/2 + b \mu_3). \\
& \frac{4\mu_c}{R} (b \mu_3 + a \cos^2 \alpha/2 \mu_1) (a \cos^2 \alpha/2 + b) \\
& + \frac{2}{R} (a^2 \cos^2 \alpha/2 \mu_H \mu_1 + b \mu_3 \mu_{Cl}) G_{12}^{-1} \tag{6}
\end{aligned}$$

$$\text{and } 2 \cos \alpha/2 (\mu_3 - \mu_1) = 1.62. \tag{7}$$

As explained earlier, since there is an ambiguity regarding the intensity of A_1 and B_2 species, we have added equations (4) and (6) to form (8). Thus we have three equations to solve for μ_1 , μ_3 , ϵ_1 and ϵ_3 —four unknowns. To solve this problem, we have taken similar equations from CD_2Cl_2 —assuming that the μ and ϵ values are the same for C–H and C–D, forming (9) similar to (8). One can have equation (10) similar to (6) where H is replaced by D .

For the sake of uniformity, a similar procedure is adopted for the spectra of the liquid also, though perhaps, the C–D bonds can be separated to some extent.

These values when substituted into (8) and (9) do not give the same value for ϵ_3 , as obtained earlier from (5), (7) and (10). This leads us to suspect that the zero order approximation is not quite valid. Hence, equation (1) to (3) are revised, following Gribov (1960).

In the revised equations, ϵ_3 and ϵ_1 are replaced by a and b respectively in A_1 , ϵ_3 is replaced by c in B_1 and ϵ_1 is replaced by d in B_2 where,

$$a = \left(\frac{\delta \mu_3}{\delta D_1} + \frac{\delta \mu_3}{\delta D_2} - 2 \frac{\delta \mu_1}{\delta D_1} \right),$$

$$b = \left(\frac{\delta\mu_1}{\delta d_1} + \frac{\delta\mu_1}{\delta d_2} - 2 \frac{\delta\mu_3}{\delta d_1} \right),$$

$$c = \left(\frac{\delta\mu_4}{\delta D_1} - \frac{\delta\mu_3}{\delta D_1} \right),$$

$$d = \left(\frac{\delta\mu_1}{\delta d_1} - \frac{\delta\mu_2}{\delta d_1} \right).$$

Now, we have five unknowns

$$\mu_1, \mu_3, \left(\frac{\delta\mu_1}{\delta d_1} + \frac{\delta\mu_1}{\delta d_2} - 2 \frac{\delta\mu_3}{\delta d_1} \right)$$

in place of ϵ_j and two expressions

$$\left(\frac{\delta\mu_3}{\delta D_1} + \frac{\delta\mu_3}{\delta D_2} - 2 \frac{\delta\mu_1}{\delta D_1} \right) \text{ and } \left(\frac{\delta\mu_4}{\delta D_1} - \frac{\delta\mu_3}{\delta D_1} \right)$$

in place of ϵ_3 . Here μ_3 and μ_4 denote the dipolemoments for the two C-Cl bonds. Also $\delta\mu_3/\delta D_2 = \delta\mu_4/\delta D_1$ as they are changes in one C-Cl moment with respect to the other C-Cl bond. Neglecting $\delta\mu_1/\delta D_1$, it is possible to determine $\delta\mu_3/\delta D_1$ and $\delta\mu_3/\delta D_2$. They are -2.9631 and 0.5652 respectively. $\epsilon_1 = \delta\mu_1/\delta d_1$ is by itself small, hence the variation in μ_1 with changes in C-Cl bond length can be ignored. These values may be compared with corresponding figures for liquid state given in table 2.

3. Separation of the symmetric and antisymmetric C-H bond intensities

In the B_2 type, the antisymmetric bending (896 cm^{-1}) is much lower than the antisymmetric stretching. Assuming the validity of Torkington's (1949) principle, L_{12} is neglected and the other three elements are evaluated. Substituting in the intensity equations, we get $I_1 = -0.060175$ and $I_2 = -0.039481$ for the stretching and bending frequencies respectively. The experimental value of $I_2 = 0.130828$, is much higher, though by itself is small. Probably, there is a large experimental error in its deter-

Table 2. Band dipolemoments and their derivatives

Molecule	Phase	μ_1 in D	μ_3 in D	ϵ_1 in $D/\text{\AA}$	ϵ_3 in $D/\text{\AA}$	$\frac{\delta\mu_3}{\delta D_1}$	$\frac{\delta\mu_3}{\delta D_2}$
CH ₂ Cl ₂ and CD ₂ Cl ₂	Vapour	-0.35	1.09	-0.14	-3.53	-2.96	0.57
CH ₂ Cl ₂ and CD ₂ Cl ₂	Liquid	-0.23	1.21	-0.43	-4.14	-3.08	1.06

Table 3. Force constants (10^5 dynes/cm)

Molecule	Symmetry		$F_{\text{vapour+}}$	F_{liquid}
CH ₂ Cl ₂	B_1	F_{11}	2.9791	2.7093
		F_{22}	0.6588	0.6390
		F_{12}	0.5952	0.4195
CD ₂ Cl ₂		F_{11}	2.9406	2.8292
		F_{22}	0.6634	0.6406
		F_{12}	0.5740	0.4792
CH ₂ Cl ₂	B_2	F_{11}	4.9573	5.4038
		F_{22}	0.7877	0.7825
		F_{12}	0.1034	0.1027
CD ₂ Cl ₂		F_{11}	5.4604	5.4553
		F_{22}	0.8005	0.7915
		F_{12}	0.1906	0.1885

†Four figures are shown against each value for the sake of computational consistency

mination. This has, however, not affected the calculation of the bond dipole moments, as they form a very small part of ΣI_i^2 equations. On subtracting I_1 from the composite (experimental) value for C-H stretching, the intensity of the symmetric stretching band is 0.3078917. This separation confirms the assignment of Saeki and Tanabe (1969), that the intensity is mostly due to A_1 . Corresponding values for CH₂Cl₂ in the liquid state and CD₂Cl₂ in the two states are given in table 1.

4. Force constants in the vapour and the liquid states

For the B_1 type, the intensity equations are added on to $LL' = G$ to determine all the L elements and then the force constants. For B_2 type, however, as the intensities are too low, they are not reliable. Hence, the force constants are calculated using Torkington's (1949) principle. The F elements for the two species are given in table 3. Though no immediate inferences can be drawn on the comparison of vapour and liquid values, they may be useful.

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