

## Infrared intensity analysis of $\text{CHCl}_3$ and $\text{CDCl}_3$

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MS received 22 June 1982; revised 19 October 1983

**Abstract.** IR intensity formulae can be derived in the form  $I = L' A$ ;  $I$  being square root of intensity  $I^2$ , has sign ambiguity. Equations like  $I' I = A' LL' A = A' GA$  have been used to solve the sign ambiguity. There is only one equation for each species. This position has now been improved by introducing a new concept about this sign ambiguity and solved for electro-optical parameters taking a pair of molecules  $\text{CHCl}_3$  and  $\text{CDCl}_3$  for demonstration. This incidentally solves the sign ambiguity problem of polar tensors which are calculated for these molecules.

**Keywords.** Infrared intensities; polar tensors.

### 1. Introduction

It is well-known that  $\partial P_\sigma / \partial Q$ , change in the  $\sigma$  component of dipole moment of a molecule during any oscillation  $Q$ , obtained from IR intensities can be related to electro-optical parameters by a formula

$$I = L' A, \quad (1)$$

$I$  is written for  $\partial P / \partial Q$ ,  $L'$  is transpose of  $L$  matrix which connects the symmetry and normal coordinates and  $A$  contains the electro-optical parameters. Since  $I$  is the square root of the intensities  $I^2$ , it has a sign ambiguity. This leads to  $2^n$  sets,  $n$  being the number of frequencies in any species, and correspondingly so many sets of  $A$  elements. The  $L$  matrix elements derived from force constants are not generally reliable. Moreover the intensities cannot be determined with sufficient accuracy. The intensities of the strong lines can be obtained within an accuracy of 5%, and those of medium intensities to about 10%. But there is no limit to the inaccuracy of weak lines.

According to Naik and Rajeswara Rao (1979) equation (1) can be written as

$$I' I = A' LL' A = A' GA \quad (2)$$

thus eliminating all the three defects mentioned above. But this gives only one equation for each species. Therefore, we have taken similar equations from an isotopic molecule to have sufficient number of equations to solve for the eop's (Naik and Rajeswara Rao 1979). We have to admit, however, that the analysis is defective and requires improvement; we now demonstrate how it can be improved and in the

process try to throw light on the sign ambiguity problems. We shall take up a pair of molecules  $\text{CHCl}_3$  and  $\text{CDCl}_3$ .

## 2. Intensity formulae

The derivation of the intensity formulae was discussed at length in our earlier papers (Naik and Rajeswara Rao 1979). We shall only give them in the forms (1) and (2). In deriving these formulae we have used terms involving change in the dipole moment of a bond with the change in the length of the other bonds also. This is called the first order approximation. However, the dipole moment of a bond is assumed to be independent of angle changes.

$$\begin{array}{l} \text{A}_1 \\ \text{---} \end{array} \quad I_i = A_1 L_{1i} + A_2 L_{2i} + A_3 L_{3i}; \quad i = 1, 2, 3. \quad (3)$$

$$\begin{array}{l} \text{E} \\ \text{---} \end{array} \quad I_i = A_4 L_{4i} + A_5 L_{5i} + A_6 L_{6i}; \quad i = 4, 5, 6. \quad (4)$$

Here,

$$A_1 = \partial P_z / \partial D = \epsilon_1; \quad (5a)$$

$$A_2 = \frac{1}{3} \left( \frac{P_z}{d_1} + \frac{P_z}{d_2} + \frac{P_z}{d_3} \right) = \frac{\epsilon_2}{\sqrt{3}} \quad (5b)$$

$$A_3 = \frac{2}{\sqrt{3}} \mu_1; \quad (5c)$$

$$A_4 = \left( \frac{\epsilon_3}{\sqrt{6}} - p \right); \quad (5d)$$

$$A_5 = \left( \frac{2}{\sqrt{6}} \mu_1 + q \right); \quad (5e)$$

$$A_6 = \left( \frac{2}{\sqrt{6}} \mu_1 + r \right); \quad (5f)$$

$$\epsilon_3 = \left( 2 \frac{\partial P_x}{\partial d_1} - \frac{\partial P_x}{\partial d_2} - \frac{\partial P_x}{\partial d_3} \right);$$

$p, q, r$  in (5) are given by

$$p = \frac{P_z}{\Delta} \left( -\frac{3\sqrt{3}}{2} a^3 b (a \mu_{\text{Cl}} - b \mu_{\text{H}}) \mu_{\text{Cl}}, \right.$$

$$q = \frac{P_z}{\Delta} \left[ 15/(2\sqrt{6}) a^2 b^2 \mu_{\text{Cl}}^2 (\mu_{\text{C}} + \mu_{\text{H}}) + \frac{9}{2\sqrt{6}} a^2 b \mu_{\text{C}} \mu_{\text{Cl}} (a \mu_{\text{Cl}} + 4b \mu_{\text{H}}) \right],$$

$$r = \frac{P_z}{\Delta} \left[ -\frac{3}{2\sqrt{6}} a^2 b^2 \mu_{\text{Cl}}^2 (3a \mu_{\text{C}} + b \mu_{\text{C}} + b \mu_{\text{H}}) \right].$$

Here  $\Delta$  is the determinant of the  $G$  matrix and  $P_z$  dipole moment of the molecule.

$$a = 1/d; \quad b = 1/D$$

where  $d$  and  $D$  are the C-Cl and C-H bond lengths respectively. For the two molecules we can write the following equations in the form of (2). The  $I_i$  values =  $\partial P / \partial Q_i$  are taken from table 1.



$$\begin{aligned} \Sigma I_i^2 &= 0.0744 = 0.6525 A_1^2 + 0.03373 A_2^2 + 0.09664 A_3^2 + \\ &2[-0.029 A_1 A_2 + 0.0656 A_1 A_3 - 0.0379 A_2 A_3] \end{aligned} \quad (6)$$

E

$$\begin{aligned} \Sigma I_i^2 &= 1.8362 = 0.01398 \epsilon_3^2 + 0.8165 (0.0547 \mu_1 + 0.053 \mu_4) \epsilon_3 \\ &+ 30.7879 (0.0547 \mu_1 + 0.053 \mu_4)^2 + 45.1754 (0.0526 \mu_1 \\ &+ 0.0424 \mu_4)^2 + 1.2891 (0.066 \mu_1 + 0.6795 \mu_4)^2 \\ &+ 2[-28.3174 (0.0547 \mu_1 + 0.053 \mu_4) (0.0526 \mu_1 + 0.0424 \mu_4) \\ &- 0.8359 (0.0547 \mu_1 + 0.053 \mu_4) (0.0662 \mu_1 + 0.6795 \mu_4) \\ &- 0.5777 (0.0526 \mu_1 + 0.0424 \mu_4) (0.0662 \mu_1 + 0.6795 \mu_4)] \end{aligned} \quad (7)$$



$A_1$

$$\begin{aligned} \Sigma I_i^2 &= 0.0793 = 0.3514 A_1^2 + 0.03373 A_2^2 + 0.0664 A_3^2 \\ &+ 2[-0.029 A_1 A_2 + 0.0656 A_1 A_3 - 0.0379 A_2 A_3] \end{aligned} \quad (8)$$

E

$$\begin{aligned} \Sigma I_i^2 &= 1.7441 = 0.01398 \epsilon_3^2 + 0.8165 (0.0547 \mu_1 + 0.053 \mu_4) \epsilon_3 \\ &+ 31.3072 (0.0547 \mu_1 + 0.053 \mu_4)^2 + 45.4298 (0.0526 \mu_1 \\ &+ 0.0424 \mu_4)^2 + 2.5138 (0.0662 \mu_1 + 0.3709 \mu_4)^2 \\ &+ 2[-27.973 (0.0547 \mu_1 + 0.053 \mu_4) (0.0526 \mu_1 + 0.0424 \mu_4) \\ &- 1.6261 (0.0547 \mu_1 + 0.053 \mu_4) (0.0662 \mu_1 + 0.3709 \mu_4) \\ &- 1.1250 (0.0526 \mu_1 + 0.0424 \mu_4) (0.0662 \mu_1 + 0.3709 \mu_4)] \end{aligned} \quad (9)$$

The above equations contain 5 electro-optical parameters.

$$\epsilon_1 = \partial P_z / \partial D$$

$$\epsilon_2 = \left( \frac{\partial P_z}{\partial d_1} + \frac{\partial P_z}{\partial d_2} + \frac{\partial P_z}{\partial d_3} \right); \quad \epsilon_3 = \left( 2 \frac{\partial P_x}{\partial d_1} - \frac{\partial P_x}{\partial d_2} - \frac{\partial P_x}{\partial d_3} \right)$$

$\mu_1$  (dipole moment of C-Cl) and  $\mu_4$  (dipole moment of CH or CD). We can take the dipole moment of the whole molecule as derived from dielectric constant measurements as the fifth equation.

$$P_z = \mu_1 1z + \mu_2 2z + \mu_3 3z + \mu_4 4z. \quad (10)$$

This makes  $-1.01 = -\mu_1 + \mu_4$ . Here  $P_z$  is the dipole moment of the molecule along  $z$  (CH or CD) direction. Since  $P_x = P_y = 0$ ,  $P_z$  is the value for the whole molecule (Weast 1969). We take  $\mu_1 = \mu_2 = \mu_3$ .  $1z$ ,  $2z$  and  $3z$  are direction cosines of  $d$ 's and  $4z$  of  $D$ . We can write equations similar to (10) for  $P_x$  and  $P_y$  also. Now,

$$\frac{\partial P_z}{\partial D} = 1z \frac{\partial \mu_1}{\partial D} + 2z \frac{\partial \mu_2}{\partial D} + 3z \frac{\partial \mu_3}{\partial D} + 4z \frac{\partial \mu_4}{\partial D}$$

$$= \frac{\partial \mu_1}{\partial D} (1z + 2z + 3z) + 4z \frac{\partial \mu_4}{\partial D} \quad (11)$$

Here,  $\partial \mu_4 / \partial D$  is dipole moment of CH (or CD) with respect to  $D$ . This is called the zero order term and  $\partial \mu_1 / \partial D$  the first order term. The *eop*'s we have to determine are groups like this.

$I_i$  in equations (6)–(9) are taken from Morcillo *et al* (1969) and are given in table 1.

### 3. Intensity analysis

In equations (6) and (8) all terms except  $\epsilon_1^2$  are common. Also,  $\Sigma I_i^2$  is almost the

Table 1. Frequencies and IR intensities.

Species	Frequency (cm <sup>-1</sup> )		$\frac{\partial P}{\partial Q}$	
	CHCl <sub>3</sub>	CDCl <sub>3</sub>	CHCl <sub>3</sub>	CDCl <sub>3</sub>
<u>A<sub>1</sub></u>	3034	2259	0.0676	0.0293
	681	655	0.2505	0.2723
	366	362	0.0844	0.0654
<u>E</u>	1221	914	0.4732	0.7899
	769	744	1.2696	1.0582
	258	258	0.0189	0.0189

same, so that we have  $\epsilon_1 = 0$ . In the  $E$  type equations, substituting for  $\mu_1$  from (10) and subtracting (9) from (7) results in

$$0.2414 \mu_4^2 + 0.3371 \mu_4 + 0.04006 = -0.09207, \quad (12)$$

(four figures are used here for computational consistency).

This makes  $\mu_4$  imaginary and the analysis defective. The left side of (12) is mostly the contribution of the wagging mode to the intensity which is small. While the sum of the intensities is large, in both (7) and (9), the difference is very small and is of the same order of magnitude as error in their determination. Since the intensity of the wagging mode is small, the accuracy of its determination is very low. Hence, the right side of (12) can be very different from the value shown. This defect shows itself whenever difference equations like (12) are to be used for evaluation of  $eop$ 's. Now, we propose to solve the problem by trying to understand the sign ambiguity of  $I$ . One of the equations of (1) can be written as

$$I_1 = A_1 L_{11} + A_2 L_{21} + A_3 L_{31} = A \cdot L_1. \quad (13)$$

The vector  $(L_{11} \ L_{21} \ L_{31})$  which is obtained from force constants, can have a positive or a negative sign. If the sign of  $L_{11}$  changes, the sign of the other elements also have to change. Therefore, since  $A_1, A_2, A_3$  are constants, the sign of  $I_1$  is dependent on the sign of  $L_1$  only. Table 2 gives the  $L$  matrices of  $A_1$  species of  $\text{CHCl}_3$  and  $\text{CDCl}_3$  obtained by us from Raman intensity analysis.

It can be easily seen that the  $G$  elements are independent of the signs of the  $L$  vectors (column triplets referring to frequencies). But we have arranged these vectors so that they have the same sign for the two molecules. Since we are assuming that the  $A$ 's are the same for the two molecules (as they have the same electronic configuration) for any frequency, if we take the  $L$  vectors of the same sign, the  $I$ 's also will be of the same sign, though the exact sign cannot be judged.

Now, in  $A_1$  species,  $I_2$  is large in the two molecules, compared to  $I_1$  or  $I_3$ . Therefore, we shall take it that it is determined with reasonable accuracy. Writing these equations, we have

$$\pm 0.2505 = A_2 L_{22} + A_3 L_{32} \text{ for } \text{CHCl}_3, \quad (14)$$

$$\pm 0.2723 = A_2 L'_{22} + A_3 L'_{32} \text{ for } \text{CDCl}_3. \quad (15)$$

Table 2.  $L$  matrices of  $A_1$  species.

		$L$		
$\text{CHCl}_3$		0.8708	0.0045	0
		-0.0367	0.1553	0.092
		0.0820	-0.2803	0.0983
$\text{CDCl}_3$		0.5928	0.0021	0
		-0.0483	0.1539	0.0891
		0.1087	-0.2693	0.1031

Since  $A_1 = 0$ , it does not occur in these equations. Primes on  $L_{22}$  and  $L_{32}$  indicate that they are for  $\text{CDCl}_3$ . In these equations the signs on the left are both positive or both negative. It is now possible to eliminate the intensities and get an eliminant equation

$$0 = A_2 (0.2723 L_{22} - 0.2505 L'_{22}) + A_3 (0.2723 L_{32} - 0.2505 L'_{32}). \quad (16)$$

This provides the third equation for  $A_1$  species, and  $A_2$  and  $A_3$  can be evaluated. But often when we deal with isotopic molecules that are similar and have nearly equal  $L$  vectors also, so that the coefficients of  $A_2$  and  $A_3$  in (16), are very small, the equation becomes unreliable. This is particularly so because, the  $L$  vectors cannot be determined with great accuracy in spite of one using Coriolis interaction constants and rotation distortion constants.

But (14) or (15) can be individually used with some advantage. Now using (14) and the eliminant of  $A_1$  from (6) and (8), one can calculate

$$\mu_1 = \pm 0.6984; \mu_4 = 0.3116, \quad (17)$$

using (15)

$$\mu_1 = \pm 0.7786; \mu_4 = 0.2314. \quad (18)$$

A negligibly small negative sign under square root in the evaluation of these values is neglected, as it is attributable to small errors in  $I_2$  or  $L$ 's.

Now, in (10) since  $\mu_4$  ( $\mu_{\text{C-H}}$ ) is much smaller than  $\mu_1$  ( $\mu_{\text{C-Cl}}$ ),  $\mu_1$  has to be positive which means it is in the C-Cl direction. Considering that there is some error in the determination of  $I_2$  as well as  $L$ 's the closeness of the  $\mu_1$  values is good. This enables us to determine  $A_2$ .

In the expanded forms,

$$\epsilon_1 = \frac{\partial \mu_4}{\partial D} - \frac{\partial \mu_1}{\partial D} = 0,$$

$$\epsilon_2 = \frac{\partial \mu_1}{\partial d_1} + \frac{2\partial \mu_2}{\partial d_1} - 3 \frac{\partial \mu_4}{\partial d_1} = -5.32 \text{ or } -5.79,$$

$$\epsilon_3 = \frac{\partial \mu_1}{\partial d_1} - \frac{\partial \mu_2}{\partial d_1} = -4.22.$$

In the expressions for  $\epsilon_2$  and  $\epsilon_3$ ,  $\partial \mu_2 / \partial d_1$  is the first order term. Seeing the closeness of  $\epsilon_2$  and  $\epsilon_3$  the first order terms are perhaps small. In  $\epsilon_1$ , this is not to be regarded as an equation between  $\partial \mu_4 / \partial D$  and  $\partial \mu_1 / \partial D$  since both of them are small and negligible.

Another point of interest is that it is not possible to separately evaluate  $\partial \mu_1 / \partial d_1$  and  $\partial \mu_2 / \partial d_1$ , the zero order and first order terms.

## 4. Polar tensors

IR intensity is analysed in another way. In the above method, we have started with a model. We have assumed that the dipole moment of a molecule is the vectorial sum of dipole moments of its bonds. Also, we have taken the dipole moment to be along the bond. It is not obvious that the electronic distribution should be symmetrical with respect to a bond. In fact, Sverdlov (1961, 1963) referred to by Allen Rupprecht (1981) has shown that the dipole moment need not be along the bond and it can have components perpendicular to it. Therefore, bond dipole moment theory may be too much of a simplification.

Biarge *et al* (1961), referred to by Newton and Person (1976), have suggested a method of avoiding a specific model. They defined a tensor

$$P_x(a) = \begin{vmatrix} \frac{\partial P_x}{\partial x_a} & \frac{\partial P_x}{\partial y_a} & \frac{\partial P_x}{\partial z_a} \\ \frac{\partial P_y}{\partial x_a} & \frac{\partial P_y}{\partial y_a} & \frac{\partial P_y}{\partial z_a} \\ \frac{\partial P_z}{\partial x_a} & \frac{\partial P_z}{\partial y_a} & \frac{\partial P_z}{\partial z_a} \end{vmatrix}$$

for each atom  $a$ . The elements show how the dipole moment of the whole molecule changes as the atoms move in various directions. This can be obtained from

$$\begin{aligned} P_X &= (\partial P / \partial X) = (\partial P / \partial Q) (\partial Q / \partial S) (\partial S / \partial R) (\partial R / \partial X) \\ &= I' L^{-1} UB \end{aligned} \quad (19)$$

$$= A' UB \quad (19a)$$

Table 4. Polar tensors.

Molecule	Cl <sub>1</sub>			H			C		
	X	Y	Z	X	Y	Z	X	Y	Z
<u>CHCl<sub>3</sub></u>									
$P_x$	0	0.1670	0	0	-0.6553	0	0	-4.8983	0
$P_y$	3.5354	0	1.5973	-0.6553	0	0	-4.8983	0	0
$P_z$	-1.7955	0	-0.2425	0	0	0	0	0	0.7274
<u>CDCl<sub>3</sub></u>									
$P_x$	0	0.1923	0	0	-0.6594	0	0	-4.9339	0
$P_y$	3.5366	0	1.6084	-0.6594	0	0	-4.9339	0	0
$P_z$	-1.7955	0	-0.2425	0	0	0	0	0	0.7274

Table 3. Expressions for polar tensors.

	Cl <sub>1</sub>			H			C			
	x	y	z	x	y	z	x	y	z	
$\frac{\partial P_x}{\partial \sigma} \frac{\partial P_x}{\partial Q_i}$	—	$-\frac{\sqrt{3}a}{\sqrt{2}} A_6$	—	—	$\frac{\sqrt{3}b}{\sqrt{2}} A_6$	—	—	$\left\{ \frac{2}{\sqrt{3}} A_4 + \frac{2\sqrt{2}a}{\sqrt{3}} A_5 \right.$	—	—
$\frac{\partial P_y}{\partial \sigma} \frac{\partial P_y}{\partial Q_i}$	$\left\{ \frac{-4}{3\sqrt{3}} A_4 + \frac{a}{3\sqrt{6}} A_6 + \frac{2a}{3\sqrt{6}} A_6 \right\}$	—	$\left\{ \frac{-2}{3\sqrt{6}} A_4 - \frac{2a}{3\sqrt{3}} A_5 \right.$	$\frac{\sqrt{3}b}{\sqrt{2}} A_6$	—	—	$\left\{ \frac{2}{\sqrt{3}} A_4 + \frac{2\sqrt{2}a}{\sqrt{3}} A_5 \right.$	—	—	—
$\frac{\partial P_z}{\partial \sigma} \frac{\partial P_z}{\partial Q_i}$	$\left\{ \frac{-2\sqrt{2}}{3\sqrt{3}} A_3 - \frac{2a}{3\sqrt{6}} A_6 \right\}$	—	$\left\{ \frac{-1}{3\sqrt{3}} A_3 + \frac{4a}{3\sqrt{3}} A_6 \right\}$	—	—	A <sub>1</sub>	—	—	$\left\{ -A_1 + \frac{A_2}{\sqrt{3}} \right.$	$\left. - \frac{4a}{\sqrt{3}} A_6 \right\}$

$\sigma$  indicates  $x_\sigma, y_\sigma$  and  $z_\sigma$ .



$I'$  is transpose of  $I$  and using (1),  $L$  and  $L^{-1}$  cancel off. Newton and Person (1976) have however used (19) and obtained  $P_x$  for various atoms. Their procedure suffers from all the defects that the earlier workers experienced in evaluating the  $eop$ 's.

- (i)  $I$ , having sign ambiguity, means that we can have  $2^n$  sets of the row vector  $I'$ .
- (ii) Evaluation of  $L^{-1}$  matrix from force constants which are uncertain and
- (iii) Inaccuracy in the determination of  $I$  elements will affect these results also.

Our suggestion of using (19a) takes away all these defects, but we need a model. Therefore, we look at the polar tensor problem as a check on the model, so that one can improve the theory to make the polar tensors obtained by (19) and (19a) to be equal. In any case, this method dispenses with sign ambiguity trouble once for all. While choosing the signs of  $I$ 's and  $L^{-1}$  vectors, one can look for the values obtained from (19a). Then, the differences in the numerical values can be discussed to improve either the model or the methods of determining  $L^{-1}$  elements.

We now give the polar tensors of  $\text{CHCl}_3$  and  $\text{CDCl}_3$  using (19a) both in the form of expressions and in numbers.

We are now not discussing a rotation correction that is necessary to get  $P_X$ . This comes about because the  $B$  matrix is rectangular and rotation and translation of the molecule have to be added to make it, a square. These corrections have been worked out by Newton and Person (1976). They have to be added to (19) as well as (19a) to get the correct  $P_X$ . But, for the purpose we have suggested, rotation correction need not be considered.

In table 3, we have given expressions only for  $\text{Cl}_1$  as those for  $\text{Cl}_2$  and  $\text{Cl}_3$  can be obtained by symmetry operations. Similarly in table 4, columns under  $\text{Cl}_2$  and  $\text{Cl}_3$  can be obtained by symmetry operation on  $\text{Cl}_1$ .

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