

Raman and infrared intensity analysis of CHCl_3 and CDCl_3

PRATIBHA NAIK, V A PADMA and N RAJESHWARA RAO
Physics Department, College of Science, Osmania University, Hyderabad 500 007

MS received 30 December 1978

Abstract. Raman and infrared intensity analysis of CHCl_3 is attempted to determine the bond polarisability derivatives and bond dipole moments and their derivatives respectively, on lines explained in our earlier papers.

Keywords. Electro-optical constants; Raman intensity; infrared intensity.

1. Introduction

Recently Tanabe and Saeki (1970) have analysed infrared intensities of chlorinated methanes and obtained entirely different sets of intensity parameters (bond dipole moments and their derivatives) for different molecules. For example, in the case of μ_{CH} , the dipole moment of C-H bond varied from 0.01 to 0.95. The analysis of infrared intensities of a variety of molecules attempted in this laboratory by Buddha and Rao (1976) shows that μ_{CH} varies within a narrow limit of 0.35 for CH_2Cl_2 , 0.48 for CH_3Cl and 0.53 for CH_3Br . The method followed by us takes care of a number of uncertainties as explained earlier by Buddha and Rao (1976). We now adopt it for CHCl_3 and CDCl_3 . The Raman intensities of CHCl_3 are also analysed.

2. Infrared intensity analysis

The infrared intensities for these molecules as reported by Tanabe and Saeki (1970) on the one hand and Morcillo *et al* (1969) on the other, are given in table 1. It may be observed that the intensities vary widely. We take the average of these sets in our analysis, as they are two independent sets of observations and there is no reason to prefer one against the other.

2.1. Intensity formulae

The intensity formulae for similar molecules like CX_3Y by Wahegaonkar and Rao (1977) using zero order approximation are now adopted for CHCl_3 and CDCl_3 . They are,

A_1 type:

$$I_{iz} = (\delta P_z / \delta Q_i) = \epsilon_1 L_{1i} - \frac{1}{\sqrt{3}} \epsilon_2 L_{2i} + \frac{2}{\sqrt{3}} \mu_2 L_{3i} \quad i = 1, 2, 3. \quad (1)$$

Table 1. Frequencies, assignments, Raman, and infrared intensities.

Species	Frequency (cm ⁻¹)		($\delta P/\delta Q$) values in e.s.u.				Hess <i>et al</i> (1969) for CHCl ₃		
			Tanabe and Saeki (1970)		Morcillo <i>et al</i> (1969)				
	CHCl ₃	CDCl ₃	CHCl ₃	CDCl ₃	CHCl ₃	CDCl ₃	$\pm a_i$	γ_i^2	γ_i
A ₁	3034	2259	0.0676	0.0293	0.0702	0.0393	1.0067	1.7542	1.3245
	681	655	0.2505	0.2723	0.2699	0.2576	0.5435	0.0449	-0.2119
	366	362	0.0844	0.0654	0.0646	0.0787	0.3174	0.1546	0.3932
E	1221	914	0.4732	0.7899	0.5828	0.7038	—	0.1002	—
	769	744	1.2696	1.0582	1.3815	1.2211	—	0.4263	—
	258	258	0.0189	0.0189	0.0303	0.0332	—	0.2235	—

E Type:

$$I_{i\sigma} = \frac{\delta P_\sigma}{\delta Q_i} = \frac{2}{\sqrt{3}} \epsilon_2 L_{2i} + \frac{1}{2\sqrt{6}} (5\mu_2 - \mu_1) L_{3i} - \frac{\sqrt{2}}{\sqrt{3}} \mu_1 L_{1i} - \frac{3\sqrt{3}}{4\sqrt{2}} \frac{\mu_{Cl}}{d^2} (L_{i3}^{-1} + L_{i3}^{-1}) (\mu_2 - \mu_1) \quad i = 1, 2, 3. \quad \sigma = x \text{ or } y. \quad (2)$$

In the above equations D and d denote the bond lengths C-H and C-Cl respectively, μ_1 and μ_2 , the bond dipole moments of C-H and C-Cl respectively; ϵ_1 and ϵ_2 their derivatives, μ_{Cl} the inverse mass of the chlorine atom. We have similar equations for CDCl₃ assuming $\mu_{CH} = \mu_{CD}$ and $\epsilon_{CH} = \epsilon_{CD}$.

Following the procedure described earlier by Budha and Rao (1976), we have the following equations.

CHCl₃ A₁ type:

$$\sum_i I_{iz}^2 = \epsilon_1^2 G_{11} + \epsilon_2^2 \frac{G_{22}}{3} + \frac{4}{3} \mu_2^2 G_{33} - \frac{2}{\sqrt{3}} \epsilon_1 \epsilon_2 G_{12} + \frac{4}{\sqrt{3}} \epsilon_1 \mu_2 G_{13} - \frac{4}{3} \epsilon_2 \mu_2 G_{23}. \quad (3)$$

E Type:

$$\sum_i I_{i\sigma}^2 = \frac{4}{3} \epsilon_2^2 G_{22} + \frac{G_{33}}{24} (5\mu_2 - \mu_1)^2 + \frac{\sqrt{2}}{3} G_{23} (5\mu_2 - \mu_1) \epsilon_2 + \frac{2}{3} \mu_1^2 G_{11} + \frac{27}{32} \frac{\mu_{Cl}^2}{d^4} (G_{33}^{-1} + G_{11}^{-1} + 2G_{13}^{-1}) (\mu_2 - \mu_1)^2 - \frac{4\sqrt{2}}{3} \epsilon_2 \mu_1 G_{12} - \frac{(5\mu_2 - \mu_1)}{3} \mu_1 G_{13} - \frac{15}{8} \frac{\mu_{Cl}}{d^2} (\mu_2 - \mu_1)^2. \quad (4)$$

Similar equations for CDCl₃ may be numbered (5) and (6); (5) differing from (3) only in G_{11} and (6) differing from (4) in $(G_{33}^{-1} + G_{11}^{-1} + 2G_{13}^{-1})$ and G_{11} .

To these, one can add the expressions for dipole moment obtained from dielectric constant data by Weast 1968-69.

$$P_z = \mu_1 + 3\mu_2 \cos a \quad (7)$$

where a is the Cl- \hat{C} -Cl angle. We thus, have five equations ((3) to (7)) to determine four constants μ_1 , μ_2 , ϵ_1 and ϵ_2 .

2.2. Analysis

Equations (3) and (5) are sufficient to determine ϵ_1 . But it is noticed that their difference gives a very small quantity, quite within the range of experimental error. Hence, these intensities cannot be made use of quantitatively to determine ϵ_1 . ϵ_1 is a satisfactory solution. It is not also an unreasonable solution considering the fact that we have consistently obtained either a negligibly small or a zero value for ϵ_1 in the case of CH_3Cl by Wahegaonkar and Rao (1977) and CH_2D_2 by Buddha and Rao (1976) worked out earlier in our laboratory. Using a similar procedure, from (4), (6) and (7) one can obtain $\mu_1 = -0.83$, $\mu_2 = 0.18$, $\epsilon_2 = -3.52$. Again, upon substituting μ_1 and μ_2 in A_1 type equations $\epsilon_2 = -2.99$. This, though not very small, difference between the two values of ϵ_2 may be due to the fact that only zero order approximation has been considered while deriving the intensity formulae. If the first order approximation following Gribov (1960) is taken into consideration, one gets the following terms.

$$- (\epsilon_2 + \epsilon_2^1) \text{ in place of } - \epsilon_2 \text{ in 'A' type} \quad (8)$$

$$\text{and } (\epsilon_2 - \epsilon_2^1) \text{ in place of } \epsilon_2 \text{ in 'E' type,} \quad (9)$$

where ϵ_2^1 is the first order term, denoting the terms like variation of the dipole moment of bond 2 with the change in the length of bond 1 and ϵ_2 is the zero order term, denoting the variation of the dipole moment of bond 2 with the change in the length of bond 2.

Thus, perhaps, the first order approximation cannot be overlooked, at least when highly electronegative atoms like chlorine, are present in a molecule. One can thus determine ϵ_2 and ϵ_2^1 from equations (3) to (6) and (8) and (9). They are, $\epsilon_2 = -3.26$ and $\epsilon_2^1 = 0.27$.

3. Discussion

The value of $\mu_1 = -0.8373$ seems to be rather high when compared to the earlier values obtained for CH_4 , CH_3Cl and CH_2Cl_2 (referred to earlier). Perhaps, the three chlorine atoms pull the electrons on the carbon atom away from the hydrogen, making the electronic charge of the hydrogen atom move towards the carbon. Also, $\mu_2 = 0.18$ is not comparable with that of CH_2Cl_2 and others. But, the analysis shows

that this value is not sensitive to small variations of intensity and hence is not to be taken as spurious.

3.1. Calculation of L elements

Writing equations (1) and (2) in the form $I=L'A$ and supplementing them with $LL'=G$, it is possible to determine all the L -elements. Now, these elements satisfy not only the infrared intensities but also the Raman intensity equations (10). Thus, there are twelve equations for nine elements for A_1 type. The L -elements thus obtained satisfy all the equations except I_1 of infrared, for which the experimental value is 0.07 while the calculated one is 0.02. It may be seen that this intensity is so small that there can be a large error in its determination. Hence, this difference is not taken seriously.

One obtains different L sets for different signs of I elements. But it is observed by calculating L 's for different sets of I 's, the sign change of any I element produces a corresponding change in the L vector relating to that frequency. For instance, for A_1 type for I_1 positive, the L vector is (0.7842 0.0052 0.0565) but for I_1 negative, it is $-(0.7842 0.0052 0.0565)$. Thus, the different sets of L matrices differ only in the signs of the L vectors relating to different frequencies. They, thus, represent the opposite phases of the same oscillation. The consequent changes in the I 's are related to the corresponding changes in the amplitudes.

It may be recalled that the L vectors relating to any frequency obtained from the force constants also do not have fixed signs, since the normalisation equation $L'FL=\lambda$, used for this purpose contains squares of L elements. The intensity equations $I=L'A$, thus have the sign ambiguity not only for I 's, but also for L vectors. The vector A has a fixed sign. But the relative sign of I and L vectors for any frequency is fixed and is decided by the sign of A . Hence, only if this relative sign is known for all the frequencies can A be determined uniquely. Since, these relative signs cannot normally be guessed one cannot get reliable values for the elements of A i.e., the electro-optical constants. But our method overcomes these difficulties as we use $I \cdot I = A'LL'A = A'GA$ as explained earlier by Buddha and Rao (1976).

Now, once A is correctly determined, L matrices can be calculated, but with sign uncertainty for each L vector. But, the F elements obtained from $L'FL=\lambda$ are unique and do not suffer from any uncertainty. But we do not use the L elements to determine F elements as the individual L elements depend on the accuracy of I values. As the infrared intensities from different authors vary so divergently, one cannot take the individual I 's to be accurate (though this does not come in the way of getting a reliable A vector as explained earlier).

3.2. Raman intensity analysis

The intensity equations for CHCl_3 as given by Long (1954) are:

$$A_1: \quad \alpha'_p = \frac{1}{3} (\sqrt{3} L_{2,p} \alpha'_x + L_{1,p} \alpha'_y) \quad (10)$$

$$\gamma'_p = \pm \left(-\frac{1}{\sqrt{3}} L_{2,p} \gamma'_x + L_{1,p} \gamma'_y - \frac{2}{\sqrt{3}} L_{3,p} \gamma'_z \right) \quad p = 1, 2, 3. \quad (11)$$

$$E: \quad \alpha'_p = 0$$

$$(\gamma'_p)^2 = 3 [(\sqrt{2} D_{x,p} \gamma'_x + E_{x,p} \gamma_x)^2 + (D_{x,p} \gamma'_x + E'_{x,p} \gamma_x + E'_{y,p} \gamma_y)^2] \quad p = 1, 2, 3. \quad (12)$$

In the above equations, α'_x and α'_y denote the polarisation of the C-Cl and C-H bonds respectively. γ'_x and γ'_y denote the derivative of the anisotropy of the C-Cl and C-H bonds respectively. $D_{x,p}$, $E_{x,p}$, $E'_{x,p}$ and $E_{y,p}$ contain various molecular parameters. For a clear understanding of the various other terms in the above equations, Long's (1953) paper may be referred to. The Raman intensities as reported by Hess *et al* (1969) are quoted in table 1. From equation (10)

$$\sum_i \alpha_i'^2 = \frac{1}{9} (3\alpha_x'^2 G_{22} + \alpha_y'^2 G_{11} + 2\sqrt{3}\alpha'_x \alpha'_y G_{12}). \quad (13)$$

This contains $\alpha'_x = \alpha'_{\text{C-Cl}}$ and $\alpha'_y = \alpha'_{\text{C-H}}$. The value for $\alpha'_{\text{C-Cl}} = 8.006$ is taken from CCl_4 (1975) and $\alpha'_{\text{C-H}} = 3.75$ is obtained. This compares with $\alpha'_{\text{C-H}} = 4.001$ for CH_4 obtained by Bernstein and Allen (1955). Now, we have a similar equation for CH_2Cl_2 used by Padma *et al* (1975) and $\alpha'_{\text{C-H}}$ in this equation is similar to the one obtained for CH_4 . A much lower value here shows that either the intensities (α'_i) are not so good or the zero order approximation is not quite valid. Perhaps, the polarisability of C-H bond here cannot be taken to be identical as in CH_4 or CH_2Cl_2 just as the dipole moment of C-H in this molecule is so different from other molecules. The lower value for $\alpha'_{\text{C-H}}$ is not spurious.

In equation (10), the signs of all the α'_i s are taken to be positive and the corresponding set of L vectors obtained. They are substituted in equations (11). The relative signs of γ'_i s and the L -vectors are not known, but are guessed. γ'_1 is mostly contributed by $+0.78 \gamma'_y$ and $\gamma'_y = \gamma'_{\text{C-H}}$ from CH_2Cl_2 is positive. Therefore, here also, γ'_1 is taken to be positive. $\gamma_x = \gamma_{\text{C-Cl}}$ is the difference between the polarisability along the bond and perpendicular to it. Since the value along the bond is generally greater than the perpendicular component, $\gamma_{\text{C-Cl}}$ is positive. The simultaneous equations (11) can give a positive value for $\gamma_{\text{C-Cl}}$ only if γ'_2 is negative and γ'_3 positive. Thus, $\gamma'_y = 1.79$, $\gamma'_x = 0.166$, $\gamma_x = 1.212$. On squaring and adding equations (12), one obtains

$$\begin{aligned} \sum_i \gamma_i^2 = & 3 (0.17301475 \gamma_x'^2 + 0.0417194 \gamma_x^2 - 0.042088 \gamma'_x \gamma_x \\ & - 0.0214293 \gamma_x \gamma_y + 1.763939 \gamma_y^2 - 0.04083 \gamma'_x \gamma_y). \end{aligned}$$

This equation contains the remaining unknown γ_y , which is calculated on substituting the above values. Thus $\gamma_y = 0.34$.

Thus, the infrared and Raman intensities enable one to determine the electro-optical constants of this molecule. In this connection we would like to point out that the Raman intensity analysis done by Sergio *et al* (1978) and Gussoni *et al* (1977) still

depends on the evaluation of L elements from the force constants. The formulae derived by the above authors also can be cast in the form $I=L'A$ and the L elements could be avoided.

Acknowledgement

One of the authors (PN) thanks the University Grants Commission, New Delhi, for a fellowship.

References

- Abbate S, Gussoni M and Massetti G 1978 *Indian J. Pure Appl. Phys.* Raman Memorial Volume 199
Bernstein J H and Allen G 1955 *J. Opt. Soc. Am.* **45** 237
Buddha A V and Rao N R 1976 *Indian J. Pure Appl. Phys.* **14** 117
Gribov L A 1960 *Opt. Spectrosc.* **8** 404
Hess W R, Hacker H, Schrotter H W and Brand Muller J 1969 *Z. Angew Phys.* **27** 233
Long 1954 *Proc. R. Soc. London* **A217** 203
Morcillo J, Biarge J F, Heredia J M V and Medina A 1969 *J. Mol. Struct.* **3** 77
Naik P and Rao N R communicated to *Pramana*
Padma *et al* 1975 *Indian J. Pure Appl. Phys.* **13** 31
Tanabe K and Saeki S 1970 *Spectrochim. Acta* **A26** 1469
Wahegaonkar L D and Rao N R 1977 *Indian J. Pure Appl. Phys.* **15** 372
Weast C R 1968-69 *Hand Book of Chemistry and Physics* (Cleveland, Ohio: Chemical Rubber Co.)
49th Edition