

Infrared intensity analysis of some MX_2 type molecules*

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Abstract. Infrared intensity analysis of MX_2 type molecules has been attempted. The dipole moment μ of C=O is obtained to be different for different molecules viz. for CH_2O , 1.9052; for COCl_2 , 1.1517; for COF_2 , 0.6340; and for COBr_2 , 0.7687. Similarly in the case of CSF_2 and CSCl_2 $\mu_{\text{C=S}}$ it was found to be 0.2473 and 0.2983 respectively. This shows that the effect of the electro-negative halogen atoms is very important.

Keywords. Infrared intensity analysis; dipolemoment.

1. Introduction

The method of derivation of the infrared intensities of some C_{2v} type of molecules like CH_2D_2 , CH_2T_2 and CD_2T_2 , etc. was given by Buddha and Rao (1976). It is quite different from the method given by the earlier authors like Sverdlov (1960) and Hisatsune and Eggers (1955). The later used the relation

$$\frac{\delta P_\beta}{\delta Q_1} = \frac{\delta P_\beta}{\delta S} \cdot \frac{\delta S}{\delta Q_1} = \frac{\delta P_\beta}{\delta S} \cdot L \quad (1)$$

where P_β stands for the dipole moment of the molecules $\beta=x, y, z$; and S the symmetry co-ordinates, of Q the normal co-ordinates. They derived the formulae for $\delta P_\beta/\delta S$ in terms of μ and ϵ , the bond dipolemoment and its derivatives respectively. The notation followed in eq. (1) was explained in the earlier paper by Buddha and Rao (1976). Hisatsune and Eggers (1955) obtained the L elements from the force constants and arrived at sets of values for the bond dipolemoments and their derivatives. But their method has two defects. In the first place, the L elements obtained from the secular equation $(GF-E\lambda) L=0$, could not be determined with certainty, because of the uncertain force constants. Secondly, it is obvious that in the intensity relations $I_\beta = \delta P_\beta/\delta Q = L'A$, I_β can assume either a positive or a negative sign. Therefore, they obtained a large number of sets of $\delta P_\beta/\delta S$ values and with each set, they arrived at a number of sets of μ and ϵ . It is observed that μ and ϵ take any value between 0.004 to 1.10 and 0.57 to 2.44 respectively (Hisatsune and Eggers 1955). It is also different for different species.

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To overcome this difficulty, Buddha and Rao (1976) suggested that the relation $I_\beta = \delta P_\beta / \delta Q = L'A$, can be cast in the form

$$I_\beta' \cdot I_\beta = A'GA. \quad (2)$$

This avoids the use of the L elements and also completely removes the sign ambiguity of $\delta P_\beta / \delta Q$. But this method again has one disadvantage. The relation $\delta P_\beta / \delta Q = L'A$ yields a number of equations and so all the unknowns can be obtained, whereas we have only one equation like (2) for each species. Since in eq. (2) $\sum_i I_i^2 = I_\beta' \cdot I_\beta$, it is insensitive to the large errors involved in the determination of intensities of feeble bands.

2. Intensity equations

We have derived the intensity formulae for the MX_2 type molecules, which belong to C_{2v} point group, exactly on the same lines described by Buddha and Rao (1976). The intensity equations thus derived are,

A_1 type:

$$I_i = \frac{\delta P_z}{\delta Q_i} = \sqrt{2} \epsilon_1 \cos \theta/2 L_{1i} - \epsilon_3 L_{2i} - \frac{\sqrt{2}}{\sqrt{3}} \sin \theta/2 \mu_1 L_{3i}$$

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

B_1 type:

$$I_i = \frac{\delta P_x}{\delta Q_i} = \left[\sqrt{2} \mu_M \sin \theta/2 \left\{ \frac{\mu_1 (1 + \cos \theta)}{d} + \frac{\mu_3}{D} \right\} \right] L_{i4}^{-1} \\ + \left[\sqrt{2} \left\{ \frac{\mu_X}{D^2} + \frac{\mu_M}{D} \left(\frac{\cos \theta/2}{d} + \frac{1}{D} \right) \right\} \mu_3 + \sqrt{2} \mu_1 \left\{ \frac{\mu_Y}{d^2} \cos \theta/2 \right. \right. \\ \left. \left. + \mu_M \frac{(1 + \cos \theta)}{d} \left(\frac{\cos \theta/2}{d} + \frac{1}{D} \right) \right\} \right] L_{i5}^{-1} + \sqrt{2} \epsilon_1 \sin \theta/2 L_{4i}$$

$$i = 4, 5.$$

B_2 type:

$$I = \frac{\delta P_y}{\delta Q} = \left[2\mu_1 \left\{ \frac{\mu_Y}{d^2} \cdot \frac{\sin \theta/2}{\sin \theta} + \frac{\mu_M}{d} \left(\frac{1}{D} + \frac{2 \sin \theta/2}{D \sin \theta} \right) \right\} \right. \\ \left. + \mu_3 \left\{ \frac{\mu_M}{D} \left(\frac{1}{D} + \frac{2 \sin \theta/2}{d \sin \theta} \right) + \frac{\mu_X}{D^2} \right\} \right] L_{66}^{-1}.$$

In the above equations, d and D denote the bond lengths $M-Y$ and $M-X$ respectively, μ_1 and μ_3 the bond dipole moments for $M-Y$ and $M-X$; ϵ_1 and ϵ_3 their derivatives; μ_M , μ_X and μ_Y , the inverse masses for the atoms M , X and Y ; and θ the angle $Y_1 M Y_2$.

We now take the example of CH_2O . It consists of two bonds and hence four unknowns μ_1 , ϵ_1 and μ_3 , ϵ_3 for C-H and C=O bonds respectively. The intensity equations thus derived for the CH_2O molecule are,

A_1 type:

$$I_i = \frac{\delta P_z}{\delta Q_i} = \frac{\epsilon_1}{\sqrt{2}} L_{1i} - \epsilon_3 L_{2i} + \frac{\mu_1}{\sqrt{2}} L_{3i}$$

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

B_1 type:

$$I_i = \frac{\delta P_x}{\delta Q_i} = \left[\frac{\sqrt{3}}{\sqrt{2}} \mu_C \left\{ \frac{\mu_1}{2d} + \frac{\mu_3}{D} \right\} \right] L_{i4}^{-1} \\ + \left[\left\{ \frac{\mu_H}{\sqrt{2}d^2} + \frac{1}{2\sqrt{2}d} \left(\frac{1}{d} + \frac{2}{D} \right) \right\} \mu_1 \right. \\ \left. + \left\{ \frac{1}{\sqrt{2}D} \left(\frac{1}{d} + \frac{2}{D} \right) \mu_C + \frac{\sqrt{2}}{D^2} \mu_0 \right\} \mu_3 \right] L_{i5}^{-1} + \frac{\sqrt{3}}{\sqrt{2}} \epsilon_1 L_{4i}$$

$$i = 4, 5.$$

B_2 type:

$$I = \frac{\delta P_y}{\delta Q} = 2 \left[\left\{ \frac{\mu_H}{d^2} + \frac{\mu_C}{d} \left(\frac{2}{d} + \frac{1}{D} \right) \right\} \mu_1 + \left\{ \frac{\mu_C}{D} \left(\frac{2}{d} + \frac{1}{D} \right) + \frac{\mu_0}{D^2} \right\} \mu_3 \right] L_{66}^{-1}.$$

(The angles about C are taken to be 120°).

The values of the intensities are obtained from the literature Hisatsune and Eggers (1955). In the above equations d and D denote the C-H and C=O bond lengths respectively, μ_C , μ_H and μ_O the inverse masses of C , H and O respectively; μ_1 , μ_3 and ϵ_1 , ϵ_3 the bond dipole moments and the derivatives of C-H and C=O respectively. On squaring and adding the equations for different species, we have,

A_1 type:

$$\sum_i \left(\frac{\delta P}{\delta Q_i} \right)^2 = \frac{\epsilon_1^2}{2} (G_{11}) + \frac{\epsilon_3^2}{2} (G_{22}) + \frac{\mu_1^2}{2} (G_{33}) + \epsilon_1 \mu_1 (G_{13}) \\ - \sqrt{2} \epsilon_1 \epsilon_3 (G_{12}) - \sqrt{2} \mu_1 \epsilon_3 (G_{23}) \quad (3)$$

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

B_1 type:

$$\sum_i \left(\frac{\delta P}{\delta Q_i} \right)^2 = \frac{3}{2} (A)^2 G_{44}^{-1} + B^2 (G_{55}^{-1}) + \frac{3}{2} \epsilon_1^2 (G_{44}) + \sqrt{6} AB (G_{45}^{-1}) + 3A \epsilon_1 \quad (4)$$

$i=4, 5$

Where $A = \mu_c \left(\frac{\mu_1}{2d} + \frac{\mu_3}{D} \right),$

$$B = \left[\left\{ \frac{\mu_H}{\sqrt{2}d^2} + \frac{1}{2\sqrt{2}d} \left(\frac{1}{d} + \frac{2}{D} \right) \mu_c \right\} \mu_1 + \left\{ \frac{\mu_c}{\sqrt{2}D} \left(\frac{1}{d} + \frac{2}{D} \right) + \frac{\sqrt{2}}{D^2} \mu_0 \right\} \mu_3 \right]$$

B_2 type:

$$\left(\frac{\delta P}{\delta Q_8} \right)^2 = 4 \left[C\mu_1 + D\mu_3 \right]^2 G_{66}^{-1} \quad (5)$$

Where

$$C = \left\{ \frac{\mu_H}{d^2} + \frac{\mu_c}{d} \left(\frac{2}{d} + \frac{1}{D} \right) \right\} \text{ and } D = \left\{ \frac{\mu_c}{D} \left(\frac{2}{d} + \frac{1}{D} \right) + \frac{\mu_0}{D^2} \right\}.$$

To these three equations, we add the relation for the molecular dipole moment obtained from dielectric constant measurements, i.e.

$$P = P_z = \mu_3 + 2\mu_1 \cos \alpha \quad (6)$$

$$\text{or, } 2.33 = \mu_3 - \mu_1.$$

The dipole moment P of the molecule is available in the literature (Robert Weast 1968-69).

Using (5) and (6) μ_1 and μ_3 are obtained. Upon substituting these in (4) and then in (3), ϵ_1 and ϵ_3 are obtained. The final values obtained are,

$$\mu_1 = -0.42 \quad \epsilon_1 = -1.17$$

$$\mu_3 = 1.91 \quad \epsilon_3 = -2.93$$

The negative sign obtained for μ_{C-H} only shows that μ_1 is directed not along the vector C—H, but in the opposite direction. Thus, the above electrooptical parameters for the formaldehyde molecule are obtained without any ambiguity.

Table 1. Bond dipole moments and their derivatives.*

Molecule	μ_1 in D	μ_3 in D	ϵ_1 in D/Å	ϵ_3 in D/Å
COCl ₂	-0.0250	1.1517	-7.1311	-2.9454
COF ₂	1.4219	0.6340	-5.4137	-3.3076
COBr ₂	1.9212	0.7687	-6.0940	-3.4921
CSF ₂	0.2669	0.2473	-4.6533	-6.5274
CSCI ₂	0.5111	0.2983	-4.6219	-4.5636

*Four figures are shown against each value for the sake of computational consistency though the values are accurate only up to three significant places.

The above method is now extended to five more molecules of the same type. The μ and ϵ for $M-X$ and $M-Y$ for these MX_2 type molecules are tabulated in table 1. The intensities and the molecular parameters for the above molecules are taken from the literature (Hopper *et al* 1968, 1972).

We generally suppose that the bond dipole moments of $C=O$ or $C=S$ may be nearly equal for different molecules. Buddha and Rao (1976) obtained the value 0.35 for $C-H$ in CH_2D_2 and 0.40 in CH_4 . But the above table shows that the interaction between various bonds is not negligible as the halogen atoms are highly electronegative. The bond dipole moments are thus affected by these interactions. But in any case, the variation of $C=O$ bond moment in various molecules is not as wide as those reported by the earlier authors (Hopper *et al* 1968). For example, for $COCl_2$ it varies from -0.02 to -5.30 and for $COBr_2$ from -0.43 to -5.75. These variations are due to defective analysis.

3. Determination of the L elements and force constants for CH_2O

After obtaining the values of μ and ϵ without making use of L elements, we insert these values in the intensity equations. Supplementing these equations to $LL'=G$, all the L elements could be determined. These in turn can be made use of to determine the force constants using $L'FL=\lambda$. Now that, we have a method of determining F elements correctly it is worthwhile to test the general assumption that the force constants are the same for isotopically substituted molecules. The force constants obtained above are substituted in the equations for CD_2O , to obtain:—

$$\lambda_1 + \lambda_2 + \lambda_3 = 2.9343 \quad (2.9634) \quad (7a)$$

$$\lambda_1 \lambda_2 + \lambda_2 \lambda_3 + \lambda_1 \lambda_3 = 2.7375 \quad (2.6411) \quad (7b)$$

$$\lambda_1 \lambda_2 \lambda_3 = 0.6330 \quad (0.6702). \quad (7c)$$

It is observed that the experimental values given in the brackets do not quite agree with those calculated. This proves that this assumption though very widely used for the determination of the force constants is not quite correct. Force constants calculated from another method, namely Torkington's approximation (Torkington 1949) are also given in table 2 for comparison.

Table 2. Force constants (10^8 dynes/cm)

Symmetry	Present method	Torkington's method
<u>A₁</u>		
F ₁₁	4·3626	4·4700
F ₂₂	13·2220	13·5455
F ₂₃	0·5014	0·5060
F ₁₂	0·2788	0·9757
F ₂₃	0·5342	0·5884
F ₃₁	-0·0233	-0·0225
<u>B₁</u>		
F ₁₁	3·8955	4·3563
F ₂₂	1·0213	0·8262
F ₁₂	0·6306	-0·1360

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