

Calculation of electro-optical parameters, a new approach. Part III. Applications to X_2CZ molecules ($X = H, F, Cl, Br$ and $Z = O, S$)

P. L. PRASAD AND SURJIT SINGH^{1,2}

Structural Chemistry Group, Department of Chemistry, Indian Institute of Technology, Madras 600036, India

Received August 18, 1975

P. L. PRASAD and SURJIT SINGH. Can. J. Chem. **54**, 1550 (1976).

Calculations of electro-optical parameters by the modified first order approximation (MFOA) method have been extended to X_2CZ ($X = H, F, Cl, Br; Z = O, S$) molecules with a view to investigate the transferability of these parameters. The diagonal and cross elements of the bond moment derivative matrix have been evaluated. Unique values of μ_{C-X} are obtained for the A_1 species. The bond moment derivatives are found to be transferable among A_1 and B_1 species. Transferability of the μ_{C-Z} in B_1 and B_2 species is obtained for thiocarbonyl halides. Bond moment derivatives with respect to angle deformations are not found to be very significant whereas other cross elements of the bond moment derivative matrix are found to be of high magnitude.

P. L. PRASAD et SURJIT SINGH. Can. J. Chem. **54**, 1550 (1976).

Faisant appel à une approximation du premier ordre modifié, on a étendu des calculs de paramètres électro-optiques à des molécules X_2CZ ($X = H, F, Cl, Br; Z = O, S$); le but de cette étude était d'évaluer la transférabilité de ces paramètres. On a évalué les éléments diagonaux et croisés de la matrice dérivée du moment des liaisons. On a obtenu des valeurs uniques de μ_{C-X} pour les espèces A_1 . On a trouvé que les dérivés du moment de lien sont transférables entre les espèces A_1 et B_1 . On obtient une transférabilité du μ_{C-Z} dans les espèces B_1 et B_2 pour les halogénures de thiocarbonyles. On trouve que les dérivés du moment de lien par rapport aux angles de déformations ne sont pas importantes; toutefois les autres éléments croisés de la matrice des dérivés du moment des liaisons sont importants.

[Traduit par le journal]

Introduction

In the previous two papers (1, 2) it was shown how the electro-optical parameters in polyatomic molecules can be evaluated using a modified first order approximation (MFOA) method. In this approximation the cross elements of the bond moment derivatives matrix are represented in terms of the ratios of the L matrix elements and the diagonal elements. Applications of the new approach to the calculations of these parameters have been demonstrated for the A_1 species of nitromethane (2).

Infrared band intensities and simple calculations of electro-optical parameters have been reported for X_2CZ molecules (where $X = H, F, Cl, Br$ and $Z = O, S$), by Hopper *et al.* (3) and by Hisatsune and Eggers (4). Recently Bruns *et al.* (5) have performed CNDO molecular orbital calculations on these molecules and, with the correct sign combinations thus determined, carried out the calculations of bond moments

and their derivatives. It was found that the bond moments and their derivatives evaluated were transferable neither in the same molecule among vibrations of different symmetry species nor among the set of molecules considered.

We thought it of interest to carry out the MFOA calculations on these molecules to determine whether or not they lead to transferable electro-optical parameters.

Calculations

Infrared band intensities of the H_2CO molecule have been reported by Hisatsune and Eggers (4). Because of the band overlap in the spectrum of H_2CO , a simulation technique was applied recently by Jalsovszky (6) and improved band intensities were determined. Duncan (7) has reported a refined set of force constants. The L matrix of H_2CO was calculated using Duncan's force field (7) and the optimum geometry (Table 1) calculated using the force method by Kana-kavel *et al.* (8). Employing the improved band intensity data of Jalsovszky (6) and the L matrix of Table 1, $\partial\mu/\partial S_i$ values were calculated for all

¹CIDA/NRCC Research Associate at University of Calgary, Calgary, Alberta, 1974-1975.

²To whom all correspondence should be addressed.

TABLE 1. Geometry and L matrices for H₂CO

| Geometry | <i>A</i> ₁ species | <i>B</i> ₁ species |
|----------------------------|--|--|
| $r_{C=O} = 1.20\text{\AA}$ | $\begin{bmatrix} 0.3653 & 0.0602 & -0.0932 \\ -0.0093 & -1.0229 & -0.0153 \\ 0.7695 & 0.0856 & 1.4325 \end{bmatrix}$ | $\begin{bmatrix} 1.0564 & -0.0095 \\ -0.1622 & 1.0635 \end{bmatrix}$ |
| $r_{C-H} = 1.10\text{\AA}$ | | |
| $\angle HCH = 116^\circ$ | | |

TABLE 2. Comparison of experimental $\partial\mu/\partial S_j$ values with CNDO values

| Sign combination of $\partial\mu_z/\partial Q_i$ | <i>A</i> ₁ species | | | <i>B</i> ₁ species | | |
|--|-------------------------------|------------------------------|------------------------------|--|------------------------------|------------------------------|
| | $\partial\mu_z/\partial S_1$ | $\partial\mu_z/\partial S_2$ | $\partial\mu_z/\partial S_3$ | Sign combination of $\partial\mu_z/\partial Q_i$ | $\partial\mu_z/\partial S_4$ | $\partial\mu_z/\partial S_5$ |
| --+ | -3.29 | 0.96 | 0.13 | -+ | -1.21 | 0.34 |
| +-+ | -2.08 | -1.31 | -0.48 | ++ | 1.31 | 0.36 |
| +++ | 2.07 | -0.99 | 0.46 | | | |
| -++ | -3.29 | -1.33 | 0.11 | | | |
| CNDO | -3.45 | 0.57 | 0.06 | CNDO | -1.20 | 0.57 |

TABLE 3. Bond moments and their derivatives calculated by MFOA^a

| Molecule | <i>A</i> ₁ species | | | <i>B</i> ₁ species ^b | | <i>B</i> ₂ species |
|--------------------|--|-----------------------------|--|--|-----------------------------|-------------------------------|
| | $\frac{\partial\mu_{C-Z}}{\partial r_{C-Z}}$ | $\frac{\mu_{C-X}}{r_{C-X}}$ | $\frac{\partial\mu_{C-X}}{\partial r_{C-X}}$ | $\frac{\partial\mu_{C-X}}{\partial r_{C-X}}$ | $\frac{\mu_{C-Z}}{r_{C-Z}}$ | $\frac{\mu_{C-Z}}{r_{C-Z}}$ |
| H ₂ CO | -3.05 | 0.15 | 0.39 | 0.22 | 1.58 | 0.61 |
| F ₂ CO | -2.11 | -2.21 | -1.44 | 1.12 | 5.58 | 4.99 |
| Cl ₂ CO | -3.82 | -0.98 | -1.10 | 0.81 0.51 | 4.73 4.98 | 2.26 |
| Br ₂ CO | -4.82 | -0.55 | -0.69 | -0.29 | 2.85 | 1.38 |
| F ₂ CS | 0.58 | -1.76 | -3.10 | 1.96 1.64 | 2.56 3.12 | 2.51 |
| Cl ₂ CS | -1.83 | -1.17 | -2.36 | 1.95 1.55 | 2.01 2.71 | 2.15 |

^aThe $\partial\mu/\partial S_j$ values used are of the same sign combination of $\partial\mu/\partial Q_i$ as preferred in ref. 5.

^bTwo sets of values in this species correspond to the two sign combinations of $\partial\mu/\partial Q_i$ which are compatible with the CNDO values (ref. 5). Bending symmetry coordinates are scaled by 1 Å.

possible sign combinations of $\partial\mu/\partial Q_i$ and are given in Table 2. A comparison of these values with the CNDO values obtained by Bruns *et al.* (5) shows that the --+ combination agrees with experimental values (Table 2). The $\partial\mu/\partial S_j$ values from the --+ combination of Table 1 have been used for further calculations on H₂CO. The necessary L matrices and band intensity data for other molecules are taken from ref. 3.

*A*₁ Species

Equations for the evaluation of electro-optical parameters by MFOA for X₂YZ type molecules have been given for the *A*₁ species previously (1, 2). In the present calculations those equations are used by suitably replacing X by H, F, Cl, Br; Y by C; and Z by O or S. The values for μ_{C-X} , $\partial\mu_{C-X}/\partial r_{C-X}$, and $\partial\mu_{C-Z}/\partial r_{C-Z}$ for H₂CO, F₂CO, Cl₂CO, Br₂CO, F₂CS, and Cl₂CS are given in Table 3. To give an example of the use of the L

matrix for cross elements of the bond moment derivatives matrix (for explanation, see refs. 1 and 2) the following relationships may be examined for H₂CO.

$$\frac{\partial r_{C-O}}{\partial r_{C-H}} = \frac{0.0602}{-\left(\frac{1.0229}{\sqrt{2}}\right)} \quad \frac{\partial r_{C-H}}{\partial r_{C-O}} = \frac{\frac{1}{\sqrt{2}}(-0.0093)}{0.3653} \quad \frac{\partial r_{C-O}}{\partial \theta} = \frac{-0.0932}{\frac{2}{\sqrt{6}}(1.4325)}$$

$$\frac{\partial r_{C-H}}{\partial \theta} = \frac{\frac{1}{\sqrt{2}}(-0.0152)}{\left(\frac{2}{\sqrt{6}}\right)(1.4325)} \quad \frac{\partial \theta}{\partial r_{C-O}} = \frac{\frac{2}{\sqrt{6}}(0.7695)}{0.3653} \quad \frac{\partial \theta}{\partial r_{C-H}} = \frac{\frac{2}{\sqrt{6}}(0.0856)}{\frac{1}{\sqrt{2}}(-1.0229)}$$

Similar relationships for other molecules can be given using the **L** matrix elements of ref. 3.

B₁ Species

The equilibrium dipole moment of the molecule X₂YZ along the *x*-axis can be written as follows:

$$\mu_x = \mu_{Y-Z} \cos 90 + \mu_{Y-X_1} \cos (\beta_1 - 90) - \mu_{Y-X_2} \cos (\beta_2 - 90)$$

In a normal vibration of this class the angles are assumed to change as shown in Fig. 1*a*. A small increment in μ_x due to this vibration can be written as follows:

$$\mu_x + \Delta\mu_x = -\mu_{Y-Z} \sin \frac{\Delta\beta}{2} + (\mu_{Y-X_1} + \Delta\mu_{Y-X_1}) \cos \left(\beta_1 - 90 + \frac{\Delta\beta}{2} \right) - (\mu_{Y-X_2} - \Delta\mu_{Y-X_2}) \cos \left(\beta_2 - 90 - \frac{\Delta\beta}{2} \right)$$

With the approximation that $\sin (\Delta\beta/2) = \Delta\beta/2$ and that the product of two small terms like $\Delta\mu \cdot \Delta\beta$ can be neglected, we get the following equation:

$$\Delta\mu_x = -\mu_{Y-Z} \frac{\Delta\beta}{2} - \mu_{Y-X_1} \sin (\beta_1 - 90) \frac{\Delta\beta}{2} + \Delta\mu_{Y-X_1} \cos (\beta_1 - 90) - \mu_{Y-X_2} \sin (\beta_2 - 90) \frac{\Delta\beta}{2} + \Delta\mu_{Y-X_2} \cos (\beta_2 - 90)$$

Since Y—X₁ and Y—X₂ bonds and angles β_1, β_2 are equivalent, this equation can be written as follows:

$$\Delta\mu_x = -\mu_{Y-Z} \frac{\Delta\beta}{2} + \mu_{Y-X} \cos \beta \cdot \Delta\beta + 2\Delta\mu_{Y-X} \sin \beta$$

Hence

$$[1a] \quad \frac{\Delta\mu_x}{\Delta r_{Y-X}} = \frac{\partial \mu_x}{\partial r_{Y-X}} = -\frac{1}{2}\mu_{Y-Z} \frac{\partial \beta}{\partial r_{Y-X}} + \mu_{X-Y} \cos \beta \frac{\partial \beta}{\partial r_{Y-X}} + 2 \frac{\partial \mu_{Y-X}}{\partial r_{Y-X}} \sin \beta$$

and

$$[1b] \quad \frac{\partial \mu_x}{\partial \beta} = -\frac{1}{2}\mu_{Y-Z} + \mu_{X-Y} \cos \beta + 2 \frac{\partial \mu_{Y-X}}{\partial \beta} \sin \beta$$

These expressions are used to evaluate electro-optical parameters in *B₁* species. For example, using MFOA (1, 2), the ratios $\partial\beta/\partial r$ and $\partial\mu_{C-H}/\partial\beta$ for H₂CO can be given as follows:

$$\frac{\partial \beta}{\partial r} = -\frac{0.1622}{1.0564}$$

and

$$\frac{\partial \mu_{C-H}}{\partial \beta} = \frac{\partial \mu_{C-H}}{\partial r_{C-H}} \frac{\partial r_{C-H}}{\partial \beta} = \left(\frac{-0.0095}{1.0635} \right) \frac{\partial \mu_{C-H}}{\partial r_{C-H}}$$

With these approximations, the eqs. 1a and 1b are left with three unknowns, namely, $\partial \mu_{Y-Z} / \partial r_{Y-Z}$, $\partial \mu_{Y-X} / \partial r_{Y-X}$, and μ_{Y-X} . Since μ_{Y-X} has already been evaluated from A_1 species of vibrations, and assuming the transferability of this parameter, the other two parameters $\partial \mu_{Y-X} / \partial r_{Y-X}$ and μ_{Y-Z} can be evaluated. Bond moments μ_{Y-Z} and their derivatives thus evaluated for all the molecules considered are given in Table 3.

B_2 Species

In the literature (3, 5) $\partial \mu_y / \partial S_6$ has been equated either to μ_{Y-X} or μ_{Y-Z} depending on whether the YX_2 frame distorts with respect to a fixed $Y-Z$ bond or vice versa. However, it seems to be more appropriate if it is assumed that both the XYX frame and the $Y-Z$ bonds are distorted by $\Delta \delta$, each, the total distortion being $\Delta \delta$, as shown in Fig. 1b.

The dipole moment of the planar X_2YZ molecule along the y -axis can be given as follows:

$$\mu_y = \mu_{Y-Z} \cos 90 + 2\mu_{Y-X} \cos \theta/2 \cdot \cos 90 \quad (\theta = \angle XYX)$$

For a small increment, $\Delta \mu_y$, along the y -axis, this equation can be written as follows:

$$\begin{aligned} \mu_y + \Delta \mu_y &= (\mu_{Y-Z} + \Delta \mu_{Y-Z}) \cos \left(90 - \frac{\Delta \delta}{2} \right) + 2(\mu_{Y-X} + \Delta \mu_{Y-X}) \cos \theta/2 \cdot \cos \left(90 - \frac{\Delta \delta}{2} \right) \\ \Delta \mu_y &= \mu_{Y-Z} \frac{\Delta \delta}{2} + 2\mu_{Y-X} \cos \theta/2 \cdot \frac{\Delta \delta}{2} \end{aligned}$$

Hence

$$[2] \quad \frac{\Delta \mu_y}{\Delta \delta} = \frac{\partial \mu_y}{\partial \delta} = \frac{1}{2}(\mu_{Y-Z} + 2\mu_{Y-X} \cos \theta/2)$$

Again μ_{Y-X} of the A_1 species is transferred to this equation and the value of μ_{Y-Z} is evaluated. These values for all the molecules considered are given in Table 3.

Discussion

The dipole moments of the $C-X$ bond for all these molecules were evaluated for an A_1 symmetry species. As can be noticed from Table 3, the bond moment decreases in the series $F_2CO > Cl_2CO > Br_2CO > H_2CO$ and $F_2CS > Cl_2CS$. The bond moments can also be calculated roughly by invoking Pauling's (9) relationships on percentage ionic character and electronegativities. The μ/r values

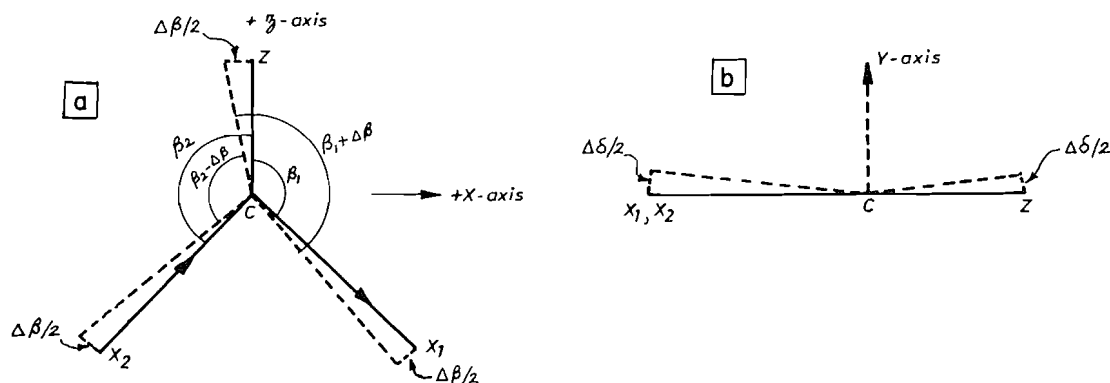


FIG. 1. Distortion of the equilibrium geometry of X_2CZ molecules during (a) B_1 and (b) B_2 vibrations.

TABLE 4. Bond moments and their derivatives after inclusion of rehybridisation moments^a

| Molecule | <i>A</i> ₁ species | | | <i>B</i> ₁ species | | <i>B</i> ₂ species |
|--------------------|---|-----------------------------|---|---|-----------------------------|-------------------------------|
| | $\frac{\partial \mu_{C-Z}}{\partial r_{C-Z}}$ | $\frac{\mu_{C-X}}{r_{C-X}}$ | $\frac{\partial \mu_{C-X}}{\partial r_{C-X}}$ | $\frac{\partial \mu_{C-X}}{\partial r_{C-X}}$ | $\frac{\mu_{C-Z}}{r_{C-Z}}$ | $\frac{\mu_{C-Z}}{r_{C-Z}}$ |
| H ₂ CO | -2.0408 | 0.4563 | 0.2973 | -0.5767 | 0.0969 | 0.6801 |
| F ₂ CO | -1.3508 | -1.5679 | -1.1861 | 1.2822 | 4.0599 | 2.2418 |
| Cl ₂ CO | -2.8696 | -0.5630 | -1.3441 | 1.3892 1.0846 | 3.9573 4.2092 | 1.6530 |
| F ₂ CS | 0.2426 | -1.0558 | -2.1486 | 1.7651 1.4482 | 1.6883 2.2479 | 2.7195 |
| Cl ₂ CS | -1.9455 | -0.6485 | -2.4926 | 2.4961 2.0993 | 0.9095 1.6003 | -0.3040 |

^aRehybridisation moments were obtained from R. E. Bruns by private communication.

for isolated C—X bonds thus calculated are found to be 2.07, 0.34, 0.12, and 0.19 for X = F, Cl, Br, and H respectively. Whereas C—F and C—H bond moments obtained by Pauling's relationships agree well with the values obtained by MFOA, the C—Cl and C—Br bond moments are comparable only as to order of magnitude. The trend in the values of bond moments for C—F, C—Cl, C—Br is, however, similar. The experimental values of bond moments for C—F (10) and C—Cl (11) are fairly close to the values obtained by these calculations.

The bond moment derivatives $\partial \mu_{C-O}/\partial r_{C-O}$ and $\partial \mu_{C-S}/\partial r_{C-S}$ are found only in the *A*₁ species. These values are found to increase in the series F₂CO < Cl₂CO < Br₂CO and F₂CS < Cl₂CS. The value in H₂CO is found to be in between that of Cl₂CO and Br₂CO. Further $\partial \mu_{C-O}/\partial r_{C-O}$ is found to be greater than $\partial \mu_{C-S}/\partial r_{C-S}$ both in fluorinated and chlorinated derivatives. These trends are similar to the trends observed in the bond moment derivatives calculated by Bruns *et al.* (5). Unlike the conclusion drawn by Hopper *et al.* (3), $\partial \mu_{C-O}/\partial r_{C-O}$ is not a characteristic of C=O bond.

The values of $\partial \mu_{C-X}/\partial r_{C-X}$ were found in *A*₁ and *B*₁ species and are found to be transferable within an error of 0.3 except in F₂CS where the difference is 1.1. The values are found to decrease in the series F₂CO > Cl₂CO > Br₂CO > H₂CO and F₂CS > Cl₂CS as observed in the case of μ_{C-X} values. The $\partial \mu_{C-X}/\partial r_{C-X}$ is found to be less in X₂CO molecules than in X₂CS molecules, similar to what is observed in the values of Hopper *et al.* (3) and of Bruns *et al.* (5). A gen-

eral conclusion can be drawn from these values that, whereas $\partial \mu_{C-X}/\partial r_{C-X}$ decreases in the series F₂CO > Cl₂CO > Br₂CO > H₂CO, the $\partial \mu_{C-Z}/\partial r_{C-Z}$ values increase. Further $\partial \mu_{C-X}/\partial r_{C-X}$ in the X₂CO molecule is less than in X₂CS molecules whereas $\partial \mu_{C-O}/\partial r_{C-O}$ in various X₂CZ molecules is greater than the corresponding $\partial \mu_{C-S}/\partial r_{C-S}$ values.

The μ_{C-O} and μ_{C-S} values are found in *B*₁ and *B*₂ symmetry species and are found to decrease in the series F₂CO > Cl₂CO > Br₂CO > H₂CO and F₂CS > Cl₂CS. The values seem to be transferable in *B*₁ and *B*₂ symmetry species for F₂CS and Cl₂CS molecules but are not found to be transferable in all X₂CO molecules. Whereas the bond moments are comparable in *A*₁ species, their derivatives do not seem to be transferable in the set of molecules considered.

Orville-Thomas proposed rehybridisation theory (12) for acquiring transferability of bond moment parameters among different symmetry species of the same molecule. The bond moment parameters are calculated by MFOA including rehybridisation moments obtained by Bruns *et al.* (5) by CNDO calculations. These values are listed in Table 4. As can be noticed the $\partial \mu_{C-X}/\partial r_{C-X}$ values obtained after inclusion of rehybridisation moments are transferable in *A*₁ and *B*₁ species within an error of 0.1. As mentioned previously (2) the difference in parameters obtained before and after including rehybridisation contributions will give the hybridisation contributions of individual bonds. It is interesting to note that the hybridisation contributions to C—X bonds, *i.e.* the differences in values of

TABLE 5. Final values of bond moments and total dipole moments for all molecules^a

| Molecule | $\frac{\mu_{C-Z}}{r_{C-Z}}$ | $\frac{\mu_{C-X}}{r_{C-X}}$ | μ_z | CNDO |
|--------------------|-----------------------------|-----------------------------|---------|-------|
| H ₂ CO | -1.58 | 0.15 | -1.72 | -1.94 |
| F ₂ CO | -3.85 | -2.21 | -1.10 | -0.77 |
| Cl ₂ CO | -2.26 | -0.98 | -0.67 | -0.41 |
| Br ₂ CO | -1.38 | -0.55 | -0.46 | — |
| Cl ₂ CS | -2.14 | -1.18 | -1.31 | -0.57 |
| F ₂ CS | -2.51 | -1.76 | -1.34 | -0.95 |

^aTo calculate total dipole moments μ_{C-X}/r_{C-X} values are taken from A_1 species for all molecules and μ_{C-Z}/r_{C-Z} values are taken from B_2 species except for F₂CO and H₂CO. For F₂CO, μ_{C-O}/r_{C-O} is approximated as 3.85 and for H₂CO μ_{C-O}/r_{C-O} is taken from the B_1 species.

μ_{C-X} of Tables 3 and 4, are found to be -0.84, -0.74, -0.94, and -0.90 in F₂CO, Cl₂CO, F₂CS, and Cl₂CS, respectively. The constancy of this value might indicate that the hybridisation contributions to C—F and C—Cl bonds in both carbonyl and thiocarbonyl halides are the same. However, inclusion of rehybridisation moments did not improve the transferability of μ_{C-O} . The total dipole moments of all these molecules calculated are given in Table 5 where they are compared with CNDO values.

Using $\partial\mu_{C-Z}/\partial r_{C-Z}$ and $\partial\mu_{C-X}/\partial r_{C-X}$ values of A_1 species (Table 3), the cross elements of these bond moment derivatives can be calculated; for example,

$$\frac{\partial\mu_{C-Z}}{\partial r_{C-X}} = \frac{\partial\mu_{C-Z}}{\partial r_{C-Z}} \cdot \frac{\partial r_{C-Z}}{\partial r_{C-X}}$$

and

$$\frac{\partial\mu_{C-Z}}{\partial\theta} = \frac{\partial\mu_{C-Z}}{\partial r_{C-Z}} \cdot \frac{\partial r_{C-Z}}{\partial\theta}$$

The derivatives $\partial r_{C-Z}/\partial r_{C-X}$, $\partial r_{C-Z}/\partial\theta$, etc. are approximated by the ratios of L matrix elements as mentioned earlier in the text. It should be remembered that, since C—X₁ and C—X₂ transform into each other and constitute a symmetry coordinate in the A_1 irreducible representation, $\partial\mu_{C-Z}/\partial r_{C-X_1}$ will be equal to $\partial\mu_{C-Z}/\partial r_{C-X_2}$

and $\partial\mu_{C-X_1}/\partial R_j$ will be equal to $\partial\mu_{C-X_2}/\partial R_j$, where R_j is any other internal coordinate. The values of cross derivatives thus calculated are given in Table 6. The values of cross derivatives of bond moments, especially derivatives with respect to bond angle deformation, are small compared to diagonal derivatives as found earlier (2). The values of $\partial\mu_{C-Z}/\partial r_{C-X}$ and $\partial\mu_{C-X}/\partial r_{C-Z}$ are found to increase in the order F₂CO > Cl₂CO > Br₂CO. In general the cross derivatives of bond moments of H₂CO are not in line with those of other molecules.

The dipole moment of any bond X—Y is written as $\mu_{X-Y} = \epsilon \cdot r_{X-Y}$ where ϵ is the effective charge and r_{X-Y} is the bond length. The bond moment derivative can be written as follows:

$$\begin{aligned} \frac{\partial\mu_{X-Y}}{\partial r_{X-Y}} &= \frac{\partial\epsilon}{\partial r_{X-Y}} \cdot r_{X-Y} + \epsilon \\ &= \frac{\partial\epsilon}{\partial r_{X-Y}} \cdot r_{X-Y} + \frac{\mu_{X-Y}}{r_{X-Y}} \end{aligned}$$

The difference between the bond moment and its derivative will reflect the change in ionic character of the bond during vibration and is known as the delocalisation moment (13).

$$\frac{\partial\epsilon}{\partial r_{X-Y}} \cdot r_{X-Y} = \frac{\partial\mu_{X-Y}}{\partial r_{X-Y}} - \frac{\mu_{X-Y}}{r_{X-Y}}$$

TABLE 6. Cross derivatives of bond moments calculated by MFOA

| Molecule | $\partial\mu_{C-Z}/\partial r_{C-X}$ | $\partial\mu_{C-Z}/\partial\theta$ | $\partial\mu_{C-X}/\partial r_{C-Z}$ | $\partial\mu_{C-X}/\partial\theta$ |
|--------------------|--------------------------------------|------------------------------------|--------------------------------------|------------------------------------|
| H ₂ CO | 0.25 | 0.24 | -0.01 | -0.01 |
| F ₂ CO | -0.45 | 0.07 | 0.52 | -0.17 |
| Cl ₂ CO | -0.31 | 0.04 | 0.37 | -0.18 |
| Br ₂ CO | -0.12 | 0.10 | 0.23 | -0.24 |
| F ₂ CS | 0.47 | -0.09 | 1.82 | -0.08 |
| Cl ₂ CS | 0.61 | 0.00 | 1.03 | -0.39 |

TABLE 7. Comparison of bond moment derivatives calculated by MFOA with literature values

| Molecule | $\partial\mu_{C-Z}/\partial r_{C-Z}$ | | | $\partial\mu_{C-X}/\partial r_{C-X}$ | | |
|--------------------|--------------------------------------|-------------------------|-------|--------------------------------------|-------------------------|-------|
| | Hopper <i>et al.</i> (3) | Bruns <i>et al.</i> (5) | MFOA | Hopper <i>et al.</i> (3) | Bruns <i>et al.</i> (5) | MFOA |
| H ₂ CO | -3.55 | -3.45 | -3.25 | -1.22 | -0.80 | 0.39 |
| F ₂ CO | -4.13 | -5.44 | -2.10 | -4.67 | -5.53 | -1.44 |
| Cl ₂ CO | -4.70 | -7.03 | -3.82 | -3.01 | -1.89 | -1.10 |
| Br ₂ CO | -5.30 | — | -4.83 | -2.07 | — | -0.69 |
| F ₂ CS | -3.07 | -4.64 | 0.58 | -6.15 | -9.71 | -3.10 |
| Cl ₂ CS | -3.70 | -4.93 | -1.83 | -4.63 | -4.11 | -2.36 |

Thus the values of this parameter for all molecules are given below:

| Molecule | $\frac{\partial\epsilon}{\partial r_{C-X}} \cdot r_{C-X}$ |
|--------------------|---|
| F ₂ CO | 0.76 |
| H ₂ CO | 0.24 |
| Cl ₂ CO | -0.12 |
| Br ₂ CO | -0.13 |
| F ₂ CS | -1.34 |
| Cl ₂ CS | -1.19 |

The trend in values of this parameter in X₂CS and X₂CO molecules can be compared with the electronegativity difference of C—X bonds. The difference in electronegativity for C—X bonds is in the order C—F > C—Cl > C—Br > C—H. But in the series of values of $(\partial\epsilon/\partial r_{C-X}) \cdot r_{C-X}$, as can be seen from above, the value for C—H comes next to C—F bond. This might indicate that the percentage of charge migration during vibration is greater for H₂CO than for Cl₂CO and Br₂CO. The change in the sign of these values is due to the fact that the magnitude of $\partial\mu_{C-X}/\partial r_{C-X}$ is greater than μ_{C-X}/r_{C-X} for all molecules except for F₂CO.

Finally it is interesting to compare the various relationships among the bond moment derivatives of these molecules given by Hopper *et al.* (3) and Bruns *et al.* (5). The values of the bond moment derivatives of refs. 3 and 5 and from the present calculation are compared in Table 7. From this table we can notice that semiempirical CNDO calculations predict that $\partial\mu_{C-S}/\partial r_{C-S}$ is smaller than $\partial\mu_{C-O}/\partial r_{C-O}$ by 1.0 and 2.1 in F₂CZ and Cl₂CZ molecules, respectively. Our values predict a difference of 2.6 and 2.0. This difference becomes 1.0 in both the F₂CZ and Cl₂CZ molecules after including rehybridisation

moments (Table 4). The magnitudes of $\partial\mu_{C-F}/\partial r_{C-F}$ and $\partial\mu_{C-Cl}/\partial r_{C-Cl}$ in A₁ species are greater by 1.6 and 1.2 in thiocarbonyl halides than in carbonyl halides, whereas Hopper *et al.* (3) predict them to be greater by 1.5 and 1.6, respectively. The prediction of Hopper *et al.* (3) and Bruns *et al.* (5), that the difference between $\partial\mu_{C-F}/\partial r_{C-F}$ and $\partial\mu_{C-Cl}/\partial r_{C-Cl}$ of carbonyl halides is equal to the corresponding difference in thiocarbonyl halides, is more readily apparent from the values from the present calculation by MFOA in Table 7. From this table it is interesting to note that, even though the magnitudes of the bond moment derivatives calculated by MFOA differ considerably from values of Hopper *et al.* (3) and Bruns *et al.* (5), the values of differences among the derivatives mentioned above, in all calculations, are comparable.

Conclusion

The calculations show that it is possible to evaluate the full set of electro-optical parameters using the MFOA method. Transferability of $\partial\mu_{C-X}/\partial r_{C-X}$ parameters has been achieved in A₁ and B₁ species for all molecules considered, whereas transferability of μ_{C-Z}/r_{C-Z} was achieved only for the thiocarbonyl halides. The magnitudes of the cross derivatives compared to the diagonal derivatives clearly show that the former cannot be ignored and explain why the zero order approximation will not yield transferable values. The main advantage of the MFOA method is that the bond moments and derivatives can easily be calculated even for bigger molecules.

Acknowledgements

We are thankful to Dr. R. E. Bruns, Instituto de Química, Universidade Estadual de Campinas,

Brasil for kindly providing us with his CNDO calculations of rehybridisation moments. Also our thanks are due to members of the Structural Chemistry Group for helpful discussions. The authors acknowledge helpful discussions with Professor P. J. Krueger of the University of Calgary, Calgary, Alberta.

1. P. L. PRASAD and SURJIT SINGH. *Chem. Phys. Lett.* **31**, 535 (1975).
2. P. L. PRASAD and SURJIT SINGH. *Chem. Phys. Lett.* **32**, 265 (1975).
3. M. J. HOPPER, J. W. RUSSELL, and J. OVEREND. *J. Chem. Phys.* **48**, 3765 (1968); *Spectrochim. Acta*, **28**, 1215 (1972).
4. I. C. HISATSUNE and D. F. EGGERS. *J. Chem. Phys.* **23**, 487 (1955).
5. R. E. BRUNS and R. K. NAIR. *J. Chem. Phys.* **58**, 1849 (1973); R. E. BRUNS. *J. Chem. Phys.* **58**, 1855 (1973); R. E. BRUNS and W. B. PERSON. *J. Chem. Phys.* **58**, 2585 (1973).
6. G. JALSOVZSKY. *J. Mol. Struct.* **19**, 783 (1973).
7. J. L. DUNCAN. *Chem. Phys. Lett.* **23**, 597 (1973).
8. M. KANAKAVEL, J. CHANDRASEKHAR, S. SUBRAMANIAN, and SURJIT SINGH. To be published.
9. L. PAULING. *The nature of the chemical bond*. IIIrd ed. Cornell University Press, New York, 1960.
10. J. W. SMITH. *Electric dipole moments*. Butterworth Scientific Publications, London, 1955.
11. J. W. STRALEY. *J. Chem. Phys.* **23**, 2183 (1955).
12. W. J. ORVILLE-THOMAS. *J. Mol. Struct.* **19**, 761 (1973).
13. W. B. PERSON. *Spectrochim. Acta*, **20**, 771 (1964).