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A charge flow model for vibrational rotational strengths

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The valence-optical approach is used to construct a model applicable for the calculation of rotational strengths associated with fundamentals of vibrational transitions. It is shown that the model has the essential property of giving rotational strengths that are independent of the choice of origin.

I. INTRODUCTION

The Born-Oppenheimer approximation is both a boon and a bane as regards the theoretical interpretation of vibrational circular dichroism (VCD) spectra. On the positive side, its application allows one to focus on the vibrational degrees of freedom and the attendant vibrational problem. But the price paid for this convenience can be high. The electronic rearrangements that occur during the course of a molecular vibration in general will contribute to the observed dipole and rotatory intensities; however such contributions may now be lost from the appropriate theoretical expressions for such intensities. The situation for infrared dipole intensities has been discussed by Mead and Moscovitz,¹ and by Cohan and Hameka,² and more recently for VCD intensities by Nafie and Walnut,³ and by Faulkner *et al.*⁴

In the case of infrared intensities, the situation is met by using a dipole length rather than a dipole velocity formulation. However, the analogous problem for VCD intensities has never been solved satisfactorily. Here the difficulty manifests itself through the loss of the contributions of the electrons to the vibrational magnetic dipole transition moment. As a consequence, current workers in the field have devised various models aimed at reintroducing these lost electronic contributions, e.g., the localized molecular orbital model.³

Currently, the most widely used model is the fixed partial charge (fpc)⁵ model. Here the electronic charges are treated as a point charge distribution, in essence as a sum of appropriately scaled Dirac delta functions, with one such delta function situated at each atomic center. The delta functions are assumed to follow the nuclear motions precisely without change in scale factor, and thus a correlation between nuclear and electronic motion is thereby approximated. The model has the virtues of ease of application and interpretive simplicity, but its quantitative successes and its interpretive power are necessarily limited in scope. For example, the fpc model could never provide a satisfactory explanation for the fact that the VCD sign of the carbon-deuterium stretching mode in (+)-(R)-neopentyl chloride is opposite to that in (+)-(R)-neopentyl bromide.⁶

In the present paper, we develop an extension of the fpc model that can, in principle, account for the neopentyl halide data alluded to above. The model derives

from the valence-optical approach⁷ that has proven useful for explaining the observed differences in magnitude between the infrared intensities of stretching and bending modes involving the same groups of atoms. In our model, the charge density distribution is similar in form to that in the fpc model, but our model also allows for changes in the charge density distribution as the molecule vibrates.

II. FORMALISM

A. The electric dipole moment operator

As in the valence-optical approach, we write the total electric dipole moment μ as a sum of individual bond moments:

$$\mu = \sum_{\alpha} \mu_{\alpha} \quad (1)$$

We make the additional assumption that the individual bond moments μ_{α} arise from the existence of effective equal and opposite point charges (hereinafter called bond charges) associated with the bonded atoms. Then for the bond α defined by the atoms A and B:

$$\mu_{\alpha} = e\xi_{\alpha}(\mathbf{r}_A - \mathbf{r}_B) = e\xi_{\alpha}l_{\alpha}\mathbf{e}_{\alpha} \quad (2)$$

Here \mathbf{r}_A and \mathbf{r}_B are the position vectors for the atoms A and B, ξ_{α} is the bond charge in units of electronic charge e , \mathbf{e}_{α} is a unit vector directed from atom B to atom A, and l_{α} is the bond length. Thus each atom has an effective atomic partial charge Z_A (in units of e) which is a sum of its bond charges (see Fig. 1). As in the recent work of Decius,⁸ for example, we allow these

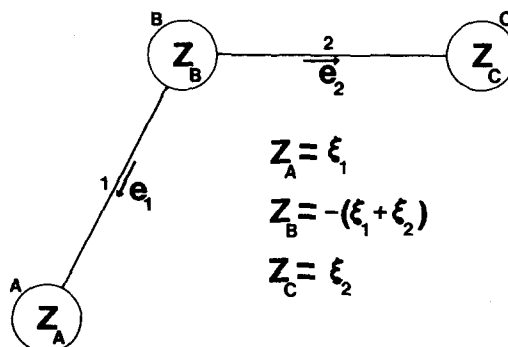


FIG. 1. The positions of the atomic partial charges Z_A , Z_B , and Z_C for a triatomic molecule A-B-C, and their relation to the bond charges ξ_1 and ξ_2 associated with the bonds 1 and 2 are as noted. The directions of the unit vectors \mathbf{e}_1 and \mathbf{e}_2 that specify bond directions are also shown.

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atomic partial charges to vary during the course of a molecular vibration.

We are now in a position to develop an expression for the electric dipole moment operator. Further assumptions will be needed later on to obtain the magnetic dipole moment operator.

We expand the electric dipole moment in terms of the normal coordinates Q_i and retain only terms through the first order in Q_i :

$$\mu = \mu_0 + \sum_i \left(\frac{\partial \mu}{\partial Q_i} \right)_0 Q_i, \quad (3)$$

where the expansion is taken about the equilibrium geometry, as indicated by the subscript zeros. Using Eq. (2), we find that

$$\left(\frac{\partial \mu}{\partial Q_i} \right)_0 = e \sum_{\alpha} \xi_{\alpha}^0 \left[\frac{\partial (l_{\alpha} e_{\alpha})}{\partial Q_i} \right]_0 + e \sum_{\alpha} l_{\alpha}^0 e_{\alpha}^0 \left(\frac{\partial \xi_{\alpha}}{\partial Q_i} \right)_0, \quad (4)$$

where again subscript or superscript zeros refer to equilibrium values. Since the atomic and bond charges are related, the first summation of Eq. (4) can be rewritten in terms of atomic partial charges and displacements

$$e \sum_{\alpha} \xi_{\alpha}^0 \left[\frac{\partial (l_{\alpha} e_{\alpha})}{\partial Q_i} \right]_0 = e \sum_A Z_A^0 \left(\frac{\partial r_A}{\partial Q_i} \right)_0 = e \sum_A Z_A^0 t_{A,i}, \quad (5)$$

where $t_{A,i}$ is the Cartesian displacement coordinate of atom A in normal coordinates Q_i . It is seen that Eq. (5) is the fixed partial charge expression for the electric dipole moment operator.⁵ In order to use valence-optical parameters, which are dependent on bond stretches, interbond angles, etc.,⁷ we expand the second summation of Eq. (4) in a complete set of linearly independent internal coordinates R_k :

$$e \sum_{\alpha} l_{\alpha}^0 e_{\alpha}^0 \left(\frac{\partial \xi_{\alpha}}{\partial Q_i} \right)_0 = e \sum_{\alpha} \sum_k l_{\alpha}^0 e_{\alpha}^0 \left(\frac{\partial \xi_{\alpha}}{\partial R_k} \right)_0 \left(\frac{\partial R_k}{\partial Q_i} \right)_0. \quad (6)$$

The term $(\partial \xi_{\alpha} / \partial R_k)_0$ gives the charge flow in bond α due to the internal deformation R_k . For instance, in the bond A-B of Eq. (2), if $(\partial \xi_{\alpha} / \partial R_k) > 0$, then a deformation $R_k > 0$ would cause an effective transfer of positive charge from atom B to atom A. It should be noted that to first order the charge flows are along the equilibrium directions of the bonds. The terms $(\partial R_k / \partial Q_i)_0$ define the internal eigenvectors which can be expressed in terms of the Cartesian eigenvectors $t_{A,i}$ through the Wilson vectors $s_{k,A}$:

$$\left(\frac{\partial R_k}{\partial Q_i} \right)_0 = \sum_A s_{k,A} \cdot t_{A,i} \quad (7a)$$

and the relation between internal coordinates and normal modes is given by

$$R_k = \sum_i \sum_A s_{k,A} \cdot t_{A,i} Q_i \quad (7b)$$

for small displacements. Putting together Eqs. (4), (5), (6), and (7) we obtain

$$\left(\frac{\partial \mu}{\partial Q_i} \right)_0 = e \sum_A Z_A^0 t_{A,i} + e \sum_{\alpha,k} l_{\alpha}^0 e_{\alpha}^0 \left(\frac{\partial \xi_{\alpha}}{\partial R_k} \right)_0 s_{k,A} \cdot t_{A,i}. \quad (8)$$

Equation (8) is equivalent to the results of various authors who have taken a valence-optical approach.⁷ For

example, the equilibrium parameters ξ_{α}^0 and charge flows $(\partial \xi_{\alpha} / \partial R_k)_0$ are related to the valence-optical parameters of Gribov,^{7(a)} μ_{α}^0 , $(\partial \mu_{\alpha} / \partial l_{\alpha})_0$, and $(\partial \mu_{\alpha} / \partial R_k)_0$ as follows:

$$e \xi_{\alpha}^0 = \frac{\mu_{\alpha}^0}{l_{\alpha}^0}, \quad (9)$$

$$e \left(\frac{\partial \xi_{\alpha}}{\partial l_{\alpha}} \right)_0 = \frac{1}{l_{\alpha}^0} \left[\left(\frac{\partial \mu_{\alpha}}{\partial l_{\alpha}} \right)_0 - \xi_{\alpha}^0 \right], \quad (10)$$

and for an internal coordinate R_k which leaves the bond length unchanged

$$e \left(\frac{\partial \xi_{\alpha}}{\partial R_k} \right)_0 = \frac{1}{l_{\alpha}^0} \left(\frac{\partial \mu_{\alpha}}{\partial R_k} \right)_0. \quad (11)$$

B. The magnetic dipole moment operator

In order to find the magnetic dipole moment operator m we express it in the general form¹⁰

$$m = \frac{1}{2c} \int \mathbf{r}' \times \mathbf{J}(\mathbf{r}') d^3 \mathbf{r}'. \quad (12)$$

The current density $\mathbf{J}(\mathbf{r}')$ is the sum of two parts:

$$\mathbf{J}(\mathbf{r}') = \sum_A \mathbf{J}_A(\mathbf{r}') + \sum_{\alpha,k} \mathbf{J}_{\alpha,k}(\mathbf{r}'). \quad (13)$$

The $\mathbf{J}_A(\mathbf{r}')$ arise from the motions of those charges which rigidly follow the atoms, while the $\mathbf{J}_{\alpha,k}(\mathbf{r}')$ are associated with the changes in the bond charges caused by the internal deformations. The former portion of the current density is just

$$\mathbf{J}_A(\mathbf{r}') = e Z_A \mathbf{v}_A \delta(\mathbf{r}' - \mathbf{r}_A). \quad (14)$$

Here \mathbf{v}_A is the velocity of atom A¹¹:

$$\mathbf{v}_A = \sum_i t_{A,i} \left(\frac{dQ_i}{dt} \right) = \sum_i t_{A,i} P_i, \quad (15)$$

where P_i is the momentum conjugate to normal coordinate Q_i . Using Eqs. (12), (14), and (15), we obtain the contribution of $\mathbf{J}_A(\mathbf{r}')$ to the magnetic moment:

$$\mathbf{m}_A = \frac{e}{2c} \sum_{A,i} Z_A \mathbf{r}_A \times t_{A,i} P_i. \quad (16)$$

Equation (16) leads directly to the usual fpc expression for m .^{5,11}

To build the charge flow contributions to the magnetic dipole moment, we must introduce two further assumptions. First, we assume that the charge flow in a bond arising from the changes in bond charges acts as a localized current along the line between the two pertinent atoms, and that it is zero elsewhere. It follows that

$$\mathbf{J}_{\alpha,k}(\mathbf{r}') = e e_{\alpha} \left(\frac{d\xi_{\alpha}}{dt} \right)_k \delta(\sigma'_{\alpha}). \quad (17)$$

Here

$$\delta(\sigma'_{\alpha}) = \delta(x'_{\alpha}) \delta(y'_{\alpha}), \quad (18)$$

where x'_{α} and y'_{α} define the coordinates perpendicular to the bond α , as shown in Fig. 2. The term $(d\xi_{\alpha}/dt)_k$ represents the rate at which the bond charge ξ_{α} changes because of the deformation R_k . We assume further that this term is constant along the bond α and is related to the time derivative of R_k as follows:

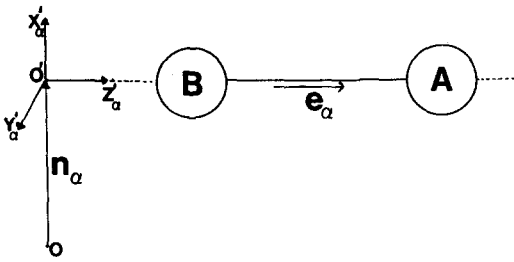


FIG. 2. The bond axis system x'_α , y'_α , and z'_α for bond α . The vector \mathbf{n}_α is directed from the origin 0 to the origin 0' of the bond coordinate system, and is normal to the z'_α axis.

$$\left(\frac{d\xi_\alpha}{dt}\right)_k = \left(\frac{\partial \xi_\alpha}{\partial R_k}\right)_0 \left(\frac{dR_k}{dt}\right). \quad (19)$$

Equation (17) then becomes

$$\mathbf{J}_{\alpha,k}(\mathbf{x}') = e \mathbf{e}_\alpha \left(\frac{\partial \xi_\alpha}{\partial R_k}\right)_0 \left(\frac{dR_k}{dt}\right) \delta(\sigma'_\alpha). \quad (20)$$

Also, differentiating Eq. (7b) with respect to time

$$\left(\frac{dR_k}{dt}\right) = \sum_{i,A} \mathbf{s}_{k,A} \cdot \mathbf{t}_{A,i} P_i \quad (21)$$

and hence Eq. (20) may be written as

$$\mathbf{J}_{\alpha,k}(\mathbf{x}') = e \mathbf{e}_\alpha \left(\frac{\partial \xi_\alpha}{\partial R_k}\right)_0 \left(\sum_{i,A} \mathbf{s}_{k,A} \cdot \mathbf{t}_{A,i} P_i\right) \delta(\sigma'_\alpha). \quad (22)$$

Performing the integration of Eq. (12) we find that

$$\begin{aligned} \mathbf{m}_{\alpha,k} &= \frac{e}{2c} \int \mathbf{x}' \times \mathbf{e}_\alpha \left(\frac{\partial \xi_\alpha}{\partial R_k}\right)_0 \left(\sum_{i,A} \mathbf{s}_{k,A} \cdot \mathbf{t}_{A,i} P_i\right) \delta(\sigma'_\alpha) d^3 x' \\ &= \frac{e}{2c} \left(\frac{\partial \xi_\alpha}{\partial R_k}\right)_0 \left(\sum_{i,A} \mathbf{s}_{k,A} \cdot \mathbf{t}_{A,i} P_i\right) \\ &\quad \times \int \int \delta(\sigma'_\alpha) dx'_\alpha dy'_\alpha \int [\mathbf{n}_\alpha + \mathbf{e}_\alpha z'_\alpha] \times \mathbf{e}_\alpha dz'_\alpha \\ &= \frac{e}{2c} \left(\frac{\partial \xi_\alpha}{\partial R_k}\right)_0 \left(\sum_{i,A} \mathbf{s}_{k,A} \cdot \mathbf{t}_{A,i} P_i\right) \mathbf{n}_\alpha \times \mathbf{e}_\alpha l_\alpha. \end{aligned} \quad (23)$$

For convenience, \mathbf{n}_α was taken to be perpendicular to the bond direction given by the unit vector \mathbf{e}_α (see Fig. 2) and directed from the origin 0 to the origin 0' of the bond coordinate system (x'_α , y'_α , z'_α). However, \mathbf{n}_α may be taken as any vector connecting the origin 0 with any point on the z'_α axis. Summing Eqs. (16) and (23), we obtain the total magnetic dipole moment operator:

$$\mathbf{m} = \sum_A \mathbf{m}_A + \sum_{\alpha,k} \mathbf{m}_{\alpha,k}$$

$$\begin{aligned} &= \frac{e}{2c} \left[\sum_{A,i} Z_A \mathbf{r}_A \times \mathbf{t}_{A,i} P_i \right. \\ &\quad \left. + \sum_{\alpha,k,i} \left(\frac{\partial \xi_\alpha}{\partial R_k}\right)_0 (\mathbf{s}_{k,A} \cdot \mathbf{t}_{A,i} P_i) \mathbf{n}_\alpha \times \mathbf{e}_\alpha l_\alpha \right]. \end{aligned} \quad (24)$$

C. Dipole strength

The dipole strength for a fundamental transition from the ground state $|0\rangle$ to a state $|j\rangle$ excited in normal coordinate Q_j , is given by¹²

$$D_j = |\langle 0 | \mu | j \rangle|^2. \quad (25)$$

Since the wave functions are orthogonal, it follows from Eq. (3) that

$$D_j = \sum_i \left(\frac{\partial \mu}{\partial Q_i}\right)_0^2 |\langle 0 | Q_i | j \rangle|^2. \quad (26)$$

Using the harmonic oscillator matrix elements of Ref. 11 we can write Eq. (26) as

$$D_j = \frac{e^2 \hbar}{4\pi c \omega_j} \left[\sum_A Z_A^0 \mathbf{t}_{A,j} + \sum_{\alpha,k} l_\alpha^0 \mathbf{e}_\alpha \left(\frac{\partial \xi_\alpha}{\partial R_k}\right)_0 \mathbf{s}_{k,A} \cdot \mathbf{t}_{A,j} \right]^2, \quad (27)$$

where ω_j is the harmonic frequency in cm^{-1} .

D. Rotational strength

The rotational strength for the fundamental transition $|0\rangle \rightarrow |j\rangle$ is given by¹²

$$\mathcal{R}_j = \text{Im}\{\langle 0 | \mu | j \rangle \cdot \langle j | \mathbf{m} | 0 \rangle\}. \quad (28)$$

Proceeding as above and using Eqs. (8) and (24), we obtain, in the harmonic approximation:

$$\begin{aligned} \mathcal{R}_j &= \frac{e^2 \hbar}{4c} \left[\sum_A Z_A^0 \mathbf{t}_{A,j} + \sum_{\alpha,k} l_\alpha^0 \mathbf{e}_\alpha \left(\frac{\partial \xi_\alpha}{\partial R_k}\right)_0 \mathbf{s}_{k,A} \cdot \mathbf{t}_{A,j} \right] \\ &\quad \times \left[\sum_A Z_A^0 \mathbf{r}_A^0 \times \mathbf{t}_{A,j} + \sum_{\alpha,k} \mathbf{n}_\alpha^0 \times l_\alpha^0 \mathbf{e}_\alpha \left(\frac{\partial \xi_\alpha}{\partial R_k}\right)_0 \mathbf{s}_{k,A} \cdot \mathbf{t}_{A,j} \right], \end{aligned} \quad (29)$$

where the quantities \mathbf{r}_A , Z_A , \mathbf{n}_α , and $l_\alpha \mathbf{e}_\alpha$ have been expanded in normal coordinates about the equilibrium geometry, and matrix elements containing terms involving third and higher order terms in Q_i and P_j , e.g., $Q_j^2 P_j$, have been neglected.

III. ORIGIN INDEPENDENCE OF THE ROTATIONAL STRENGTH

The magnetic dipole transition moment given by Eq. (24) is origin dependent. Since the rotational strength is an observable, Eq. (29) should be origin independent. To show that Eq. (29) does not depend upon the choice of origin, we allow the coordinate system to be shifted by an arbitrary displacement \mathbf{Y} , giving

$$\begin{aligned} \mathcal{R}'_j &= \frac{e^2 \hbar}{4c} \left[\sum_A Z_A^0 \mathbf{t}_{A,j} + \sum_{\alpha,k} l_\alpha^0 \mathbf{e}_\alpha \left(\frac{\partial \xi_\alpha}{\partial R_k}\right)_0 \mathbf{s}_{k,A} \cdot \mathbf{t}_{A,j} \right] \cdot \left[\sum_A Z_A^0 (\mathbf{r}_A^0 + \mathbf{Y}) \times \mathbf{t}_{A,j} + \sum_{\alpha,k} (\mathbf{n}_\alpha^0 + \mathbf{Y}) \times l_\alpha^0 \mathbf{e}_\alpha \left(\frac{\partial \xi_\alpha}{\partial R_k}\right)_0 \mathbf{s}_{k,A} \cdot \mathbf{t}_{A,j} \right] \\ &= \mathcal{R}_j + \frac{e^2 \hbar}{4c} \left[\sum_A Z_A^0 \mathbf{t}_{A,j} + \sum_{\alpha,k} l_\alpha^0 \mathbf{e}_\alpha \left(\frac{\partial \xi_\alpha}{\partial R_k}\right)_0 \mathbf{s}_{k,A} \cdot \mathbf{t}_{A,j} \right] \cdot \mathbf{Y} \times \left[\sum_A Z_A^0 \mathbf{t}_{A,j} + \sum_{\alpha,k} l_\alpha^0 \left(\frac{\partial \xi_\alpha}{\partial R_k}\right)_0 \mathbf{s}_{k,A} \cdot \mathbf{t}_{A,j} \right]. \end{aligned} \quad (30)$$

The second term of Eq. (30) is of the form $\mathbf{A} \cdot \mathbf{Y} \times \mathbf{A}$, which is zero for any vector \mathbf{Y} .

IV. CONCLUSION

Starting with the Gribov valence-optical approach for the calculation of infrared intensities, we have derived an origin independent expression for the rotational strength associated with a fundamental vibrational transition. The model is less restrictive than the earlier fixed partial charge model by allowing for charge flows along the molecular bonds during the course of a molecular vibration. In this paper we have limited ourselves to charge flows along the molecular bonds. However, once the path of the charge flow is specified, the same approach can be readily extended to account for contributions to R_i from charge flows that do not necessarily follow the molecular bonds. Extensions such as these could prove to be useful in describing the effects of lone pair electrons on dipole and rotational strengths.

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