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Infrared Dichroism of Lattice Vibrations of the B_u Species in a Monoclinic Crystal

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Abstract—Following Hadni *et al.*$^{(1)}$ with the starting point in a theory of the transition moment of a B_u lattice vibration a correct use has been made of symmetry requirements imposed on tensors relating the vectors of molecular displacements with the electric field strength. This leads to a new formula for the orientation of the transition moment in a monoclinic crystal. An expression is also derived for the dichroic ratio of such bands which can be verified experimentally.

In one of the $P2_1/a$ or $P2_1/c$ space groups which are the most frequently met in the monoclinic system, the structure can be realized among others by means of two centro-symmetrical molecules per unit cell. They occupy special positions with a C_i site symmetry. Three optical modes are possible for such a crystal, $2A_u + B_u$, the former having the vector of the transition moment directed along the *b* axis of the crystal, but no predictions based upon symmetry can be made in the lattice case. In 1969, Hadni and coworkers, while interpreting their far infrared spectra of naphthalene, gave a theory of the changes of the electric dipole moment in this crystal for optical translational vibrations.(1) However, the discussion becomes inadequate in the moment when mutual relations are discussed between electric field strengths generated by two sets of molecules at a given lattice point, and consequently, the conclusions concerning the orientation of the transition moment seem to be incorrect. On the other hand, if the experimental results are expected to have physical meaning, they should be carried out with the electric vector **E** of the radiation kept within one of two optical planes of the crystal which are parallel to the incident beam.⁽²⁾ As there is a steady increase of interest in the far infrared spectroscopy of molecular crystals we feel that real progress can be achieved only if both theory and experiment are based on sound physical fundamentals.

In this paper we propose another treatment of the problem of the transition moment of a B_u vibration, consistent with symmetry requirements. As a starting point we will assume that of Hadni

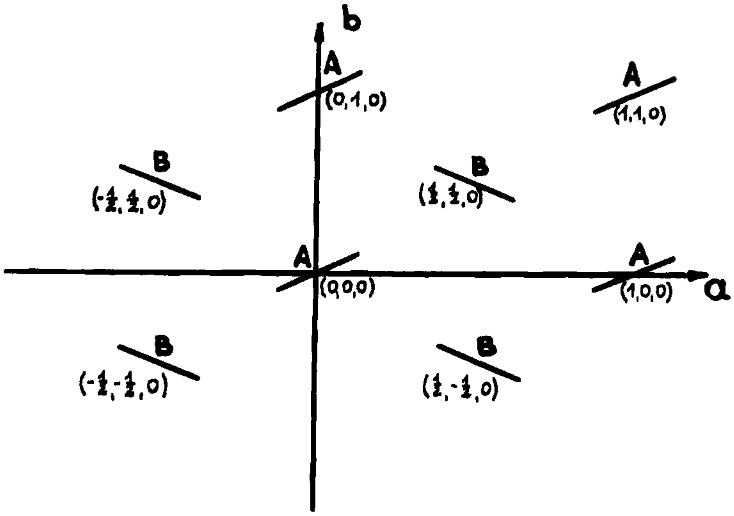

Figure 1. Distribution of molecules on (001) in a crystal of the $P2_1/a$ space group.

et al.⁽¹⁾ The A_u types are of lesser interest because their transition moments are directed along the *b* axis of the crystal. Therefore, the infrared dichroic ratio becomes zero (or infinity).

A distribution of molecules on (001) in a crystal of the $P2_1/a$ space group symmetry is shown schematically in Fig. 1. Two sets of translationally non-equivalent molecules, denoted by A and B, occupy special positions with C_i site symmetry. Following Hadni, we confine our considerations to four nearest neighbours. If the molecule *A* (0,0,0) translates from its equilibrium position by

$\mathbf{dR}_A$ (dx_1, dx_2, dx_3), the electric field at (0,0,0) generated by its four nearest neighbours B is in the a, b, c^* system of axes:

$$\mathbf{dE}_A = \sum_{k=1}^{4} dE_{A,k} = \sum_{k=1}^{4} (K_{A,k} \cdot \mathbf{dR}_A) = \mathbf{dR}_A \sum_{k=1}^{4} K_{A,k}. \tag{1}$$

The second factor of the last term in (1) is a tensor composed of contributions of four molecules B. Now, the important point is that the symmetry requirements should be imposed on each single component and *not* on the resulting tensor. The symmetry elements proper to this space group can be written in the following manner:

inversion centrum—$\{I \mid 0\}$
two-fold screw axis—$\{C_2{}^b \mid (\frac{1}{2}, \frac{1}{2}, 0)\}$
glide plane—$\{\sigma^{ac} \mid (\frac{1}{2}, \frac{1}{2}, 0)\}$.

Making use of the corresponding symmetry operations we get the following relations between $K_{A,k}$ molecular tensors:

$$I \cdot K_{A,1}(A;\ \tfrac{1}{2}, \tfrac{1}{2}, 0) \cdot \tilde{I} = K_{A,3}(A;\ -\tfrac{1}{2}, -\tfrac{1}{2}, 0);$$

$$C_2{}^b \cdot K_{A,1}(A;\ \tfrac{1}{2}, \tfrac{1}{2}, 0) \cdot \tilde{C}_2{}^b = K(\tfrac{1}{2}, \tfrac{1}{2}, 0;\ 0, 1, 0)$$

$$= K(\tfrac{1}{2}, -\tfrac{1}{2}, 0;\ 0, 0, 0) = \tilde{K}_{A,2}(A;\ \tfrac{1}{2}, -\tfrac{1}{2}, 0);$$

$$\sigma^{ac} \cdot K_{A,1}(A, \tfrac{1}{2}, \tfrac{1}{2}, 0) \cdot \tilde{\sigma}^{ac} = K(\tfrac{1}{2}, \tfrac{1}{2}, 0;\ 1, 0, 0)$$

$$= K(-\tfrac{1}{2}, \tfrac{1}{2}, 0;\ 0, 0, 0) = \tilde{K}_{A,4}(A;\ -\tfrac{1}{2}, \tfrac{1}{2}, 0).$$

However, the $K_{A,k}$ tensors are symmetric:

$$K_{A,k} = \tilde{K}_{A,k},$$

so we have:

$$C_2{}^b \cdot K_{4,1} \cdot \tilde{C}_2{}^b = K_{A,2}$$
$$\sigma^{ac} \cdot K_{A1} \cdot \tilde{\sigma}^{ac} = K_{A,4}$$

In view of the above relations, the $K_{A,k}$ tensors have the following symmetry:

$$\begin{array}{cc}
\begin{bmatrix} + & + & + \\ + & + & + \\ + & + & + \end{bmatrix} & \begin{bmatrix} + & - & + \\ - & + & - \\ + & - & + \end{bmatrix} \\
k = 1(\tfrac{1}{2}, \tfrac{1}{2}, 0) & k = 2(\tfrac{1}{2}, -\tfrac{1}{2}, 0) \\
\begin{bmatrix} + & + & + \\ + & + & + \\ + & + & + \end{bmatrix} & \begin{bmatrix} + & - & + \\ - & + & - \\ + & - & + \end{bmatrix} \\
k = 3(-\tfrac{1}{2}, -\tfrac{1}{2}, 0) & k = 4(-\tfrac{1}{2}, \tfrac{1}{2}, 0)
\end{array} \tag{2}$$

Therefore, the overall variation of the field strength at A will be:

$$\mathbf{dE}_A = \left| \begin{array}{l} dE_{A,x_1} = \dfrac{\partial E_{A,x_1}}{\partial x_1} dx_1 + \dfrac{\partial E_{A,x_1}}{\partial x_3} dx_3 \\ dE_{A,x_2} = \dfrac{\partial E_{A,x_2}}{\partial x_2} dx_2 \\ dE_{A,x_3} = \dfrac{\partial E_{A,x_3}}{\partial x_1} dx_1 + \dfrac{\partial E_{A,x_3}}{\partial x_3} dx_3 \end{array} \right| \tag{3}$$

or in a matrix form:

$$dE_{A,x_i} = \sum_{j=1}^{3} K_{ij}{}^{(A)} \cdot dx_j. \tag{3a}$$

Here,

$$K_{ij}^{(A)} = \begin{bmatrix} \dfrac{\partial E_{A,x_1}}{\partial x_1} & 0 & \dfrac{\partial E_{A,x_1}}{\partial x_3} \\ 0 & \dfrac{\partial E_{A,x_2}}{\partial x_2} & 0 \\ \dfrac{\partial E_{A,x_3}}{\partial x_1} & 0 & \dfrac{\partial E_{A,x_3}}{\partial x_3} \end{bmatrix} \tag{3b}$$

Similar considerations apply to a point B placed at the center of mass of a molecule B:

$$dE_{B,x_i} = \sum_{j=1}^{3} K_{ij}{}^{(B)} \cdot dx_{0j} \tag{4}$$

where $\mathbf{dR}_B(dx_{01}, dx_{02}, dx_{03})$ is the displacement vector of a B molecule.

The $K_{ij}^{(A)}$ and $K_{ij}^{(B)}$ are the second derivatives of the electric potential generated at A or B, respectively, by a distribution of charges of chemically identical molecules. Therefore, we should have:

$$K_{ij}^{(A)} = K_{ij}^{(B)},$$

and, since for optical translational vibrations

$$\mathbf{dR}_A = -\mathbf{dR}_B,$$

we obtain

$$\mathbf{dE}_A = -\mathbf{dE}_B. \tag{5}$$

In particular, for a $\mathrm{B_u}$ vibration $\mathbf{dR}_A(0, dx_2, 0)$ and $\mathbf{dR}_B(0, -dx_2, 0)$. The overall change of the electric dipole moment of the unit cell, $\mathbf{dM}$, is equal to:

$$\mathbf{dM} = \mathbf{dM}_A + \mathbf{dM}_B \tag{6}$$

where

$$\mathbf{dM}_A = [\alpha_A]\cdot\mathbf{dE}_A$$

and (7)

$$\mathbf{dM}_B = [\alpha_B]\cdot\mathbf{dE}_B.$$

$[\alpha_A]$ and $[\alpha_B]$ are the polarizability tensors of molecule A and B, respectively, given in the a, b, c^* system of crystal axes, and are also related by symmetry:

$$[\alpha_B] = C_2^b[\alpha_A]\cdot\tilde{C}_2^b.$$

With this condition, the dipole change of the unit cell will be:

$$\mathbf{dM} = \left|\begin{array}{l} dM_{x_1} = 2\alpha_{12}dE_{A,x_2} \\ dM_{x_2} = 0 \\ dM_{x_3} = 2\alpha_{32}dE_{A,x_2} \end{array}\right. \tag{8}$$

The angle Θ made by dM with the $x_1 = a$ axis is:

$$\tan\Theta = \frac{dM_{x_3}}{dM_{x_1}} = \frac{\alpha_{32}}{\alpha_{12}}. \tag{9}$$

This is a simple relation indicating that the orientation of the transition moment for a $\mathrm{B_u}$ vibration depends on certain components of the polarizability tensor of the molecule, expressed in the a, b, c^* system of axes. However, the orientation of dM does not depend on derivatives of the field strength, e.g. $\partial E_{A,xi}/\partial x_i$ etc, as is suggested in the paper of Hadni.(1)

The result[9] can, in principle, be verified experimentally but the absorption must be measured with the electric vector **E** of the incident radiation either parallel to N_1 or to N_3 (Fig. 2). The orientation of the section of indicatrix on (010) of a monoclinic crystal is not related to the unit cell axes directions, and N_1 and N_3, the principal axes of this section, are simultaneously the allowed vibration directions of a radiation beam travelling the crystal.

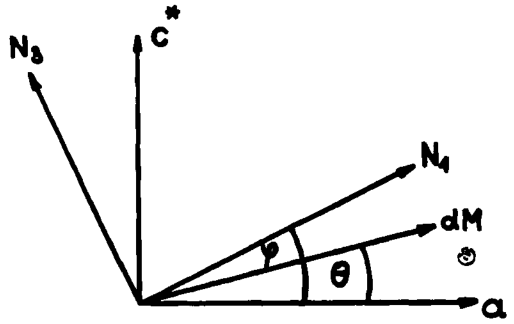

Figure 2. Orientation of principal axes N_1 and N_3 of the indicatrix with respect to crystallographic *a* and *c** axes in a monoclinic crystal.

A more exact measure of conformity between theory and experiment is the dichroic ratio of a band, as defined by the integrated absorption intensity when measured with $\mathbf{E} \parallel N_1$ divided by that measured with $\mathbf{E} \parallel N_3$. In our case[2]:

$$R_{1/3} = \left(\frac{dM_1}{dM_3}\right)^2 \cdot \left(\frac{\epsilon_3}{\epsilon_1}\right)^{1/2}. \tag{10}$$

Since, according to Fig. 2,

$$\frac{dM_1}{dM_3} = \tan(\phi - \Theta),$$

we will have:

$$R_{1/3} = \left[\frac{\tan\phi - (\alpha_{32}/\alpha_{12})}{1 + (\alpha_{32}/\alpha_{12})\tan\phi}\right]^2 \cdot \left(\frac{\epsilon_3}{\epsilon_1}\right)^{1/2}. \tag{11}$$

Therefore, the dichroic ratio depends also on the orientation of indicatrix axes, $\tan\phi$, and on their lengths, $(\epsilon_3/\epsilon_1)^{1/2} = N_3/N_1$, where N_i are the principal refraction indices for a frequency corresponding to a band center. Usually no information is available for the far infrared but with a small error values can be taken for the shorter infrared and even for the visible part of the spectrum. However, the orientation of the N_i axes must correspond to that in the far infrared region. We feel that the best method would involve a careful orientation of the sample in the spectrophotometric assembly.

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