Relation of crystal shape & structure to LO-TO splitting

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In the following sections we present the model of J.C. Decius (1968)[2] which yields a formula for the LO-TO splitting of $k = 0$ optical modes in dipolar crystals, and show how the splitting relates to crystal geometry. The treatment is completely classical and quite simple, so this is really a toy model (although it can reproduce experimental splittings for simple tetragonal crystals). We assume our system is a system of point dipoles on a lattice. Each dipole has a permanent dipole moment $\boldsymbol{m}$ and a polarizability $\boldsymbol{\alpha}$.

0.1 Energy of the dipolar crystal

An expression for the energy of a system of polarizable dipoles in an applied field was derived by Mandel and Mazur in 1958.[5] Although we are interested in the case when the applied field is zero, we perform the derivation with the applied field because the results are interesting. For our case we assume the polarizability tensor $\boldsymbol{\alpha}$ is isotropic. We assume we have an applied field $\boldsymbol{\mathcal{E}}_0$. In what follows we drop the bold notation on all of the vectors and matrices. We introduce the following vectors: $p \equiv (\boldsymbol{p}_1, \boldsymbol{p}_2, \cdots, \boldsymbol{p}_N)$, a vector of length $3N$, and $E_0 \equiv (\boldsymbol{\mathcal{E}}_0, \boldsymbol{\mathcal{E}}_0, \cdots \boldsymbol{\mathcal{E}}_N)$, a vector of the applied electric field, also of length $3N$. When a vector appears to the right of a matrix it is understood to be a column vector, and when on the left, a row vector. We also introduce the following matrices:

$$T \equiv \begin{bmatrix} 0 & \boldsymbol{T}_{12} & \boldsymbol{T}_{13} & \cdots \\ \boldsymbol{T}_{21} & 0 & \boldsymbol{T}_{23} & \cdots \\ \boldsymbol{T}_{31} & \boldsymbol{T}_{32} & 0 & \cdots \\ \vdots & \vdots & \vdots & 0 \end{bmatrix} \quad \alpha \equiv \begin{bmatrix} \boldsymbol{\alpha} & 0 & 0 & \cdots \\ 0 & \boldsymbol{\alpha} & 0 & \cdots \\ 0 & 0 & \boldsymbol{\alpha} & \cdots \\ \vdots & \vdots & \vdots & \boldsymbol{\alpha} \end{bmatrix} \quad I \equiv \begin{bmatrix} 1 & 0 & 0 & \cdots \\ 0 & 1 & 0 & \cdots \\ 0 & 0 & 1 & \cdots \\ \vdots & \vdots & \vdots & 1 \end{bmatrix} \tag{0.1}$$

Then the equation for the dipole moments is:

$$p = m + \alpha(E_0 - Tp) \tag{0.2}$$

This leads to

$$\begin{aligned} p + \alpha T p &= m + \alpha E_0 \\ p &= (I + \alpha T)^{-1}(m + \alpha E_0) \\ p &= (I + \alpha T)^{-1} m + (I + \alpha T)^{-1} \alpha E_0 \\ p &= p_0 + A E_0 \end{aligned} \tag{0.3}$$

Where we define

$$\boxed{p_0 \equiv (I + \alpha T)^{-1} m} \tag{0.4}$$

$$\boxed{A \equiv \alpha (I + \alpha T)^{-1}} \tag{0.5}$$

Since A is a diagonal matrix and T is a symmetric matrix, they commute with each other. Mandel & Mazur employ a non-obvious identity:

$$(I + \alpha T)^{-1} = I - AT = I - AT \tag{0.6}$$

The validity of this equation can be easily checked. We now compute the local field, F:

$$\begin{aligned} F &= E_0 - Tp \\ &= E_0 - T(p_0 + AE_0) \quad \text{using eqn. 0.3} \\ &= (I - TA)E_0 - Tp_0 \quad \text{using eqns. 0.6 \& 0.5} \end{aligned} \tag{0.7}$$

leading to:

$$\boxed{F = \alpha^{-1} A E_0 - T p_0} \tag{0.8}$$

We are now in a position to compute the electrostatic part of the energy of the system. The electrostatic energy is broken into three parts:

$$V_{\text{el}} = V_{\text{in}} + V_{\text{dip}} + V_{\text{E}_0} \tag{0.9}$$

here V_{in} is the "internal" energy of the polarization dipoles, V_{dip} is the the dipole-dipole interaction energy, and V_{E_0} is the interaction energy of the system with the electric field.

The internal energy is:

$$\begin{aligned} V_{\text{int}} &= \sum_j \int_{m_j}^{p_j} F_j \cdot dp_j = \sum_j \alpha \int_0^{F_j} F_j \cdot dF_j \\ &= \frac{1}{2}\alpha (E_0 - Tp)^2 \\ &= \frac{1}{2}\alpha^{-1}(AE_0 - Tp_0)^2 \quad \text{Using 0.8} \\ &= \frac{1}{2}\alpha p_0 T^2 p_0 - E_0 A T p_0 + \frac{1}{2}\alpha^{-1} E_0 A^2 E_0 \end{aligned} \tag{0.10}$$

The dipole-dipole energy, $V_{\text{dip}} = \frac{1}{2} pTp$ is found to be:

$$\boxed{V_{\text{dip}} = \frac{1}{2} p_0 T p_0 + p_0 T A E_0 + \frac{1}{2} A T A E_0} \tag{0.11}$$

When one sums the internal energy and the dipole energy there is a cancellation of terms, leading to:

$$V_{\text{int}} + V_{\text{dip}} = \frac{1}{2} m T p_0 + \frac{1}{2} E_0 A E_0 \tag{0.12}$$

The energy due to interaction with the applied field is

$$V_{\text{E}_0} = -pE_0 \tag{0.13}$$

When we sum up all three energy terms and do some simplification we get:

$$\boxed{V_{\text{el}} = \frac{1}{2} m T p_0 - p_0 E_0 - \frac{1}{2} E_0 A E_0} \tag{0.14}$$

When the applied field E_0 is zero, the energy of the system is:

$$\boxed{V_{\text{el}}^0 = \frac{1}{2} m T p_0 = \frac{1}{2} m T (I + \alpha T)^{-1} m} \tag{0.15}$$

0.2 The frequency shift

We now can compute the *frequency shift* of a dipolar molecule, that is, the shift when the molecule is moved from the gas phase to the solid phase.[2] We are interested in the $k = 0$ case. In this case *all of the dipole moments are equal in magnitude and direction.* As we will see, in general the shift will be different depending whether the dipolar wave travels in the longitudinal or transverse direction.

0.2.1 Single molecule per unit cell

As before, we store all of the dipole moments in a vector of length 3N $\mu = (\boldsymbol{\mu}_1, \boldsymbol{\mu}_2, \cdots \boldsymbol{\mu}_N,)$ We expand the dipole moment vector in terms of the unit cell normal coordinates:

$$\mu = \mu_0 + \sum_k Q_k \frac{\partial \mu}{\partial Q_k} \tag{0.16}$$

We now look for the term in the expansion of the potential energy $\frac{1}{2} m T p_0$ (eqn. 0.15) which is quadratic with respect to the normal coordinates. This term is :

$$V = \frac{1}{2} \sum_k \frac{\partial \mu}{\partial Q_k} T (I + \alpha T)^{-1} \frac{\partial \mu}{\partial Q_k} Q_k^2 \tag{0.17}$$

The entire problem reduces to finding the energy given in eqn. 0.15. We use the index t to label the lattice sites - in otherwords, it labels 3x3 blocks in the matrix T. The problem reduces to calculating the sum:

$$\sum_{t' t''} T_{tt'} (I + \alpha T)^{-1}_{t' t''} \tag{0.18}$$

Since all of the sites are identical, we only need to consider the sum over t'' for fixed t'. Note that we can perform a Taylor expansion:

$$(I + \alpha T)^{-1} = I - \alpha T + \alpha^2 T^2 - \alpha^3 T^3 \cdots \tag{0.19}$$

Thus we can write:

$$\sum_{t''} (I + \alpha T)^{-1}_{t' t''} = I_3 - \alpha S + \alpha^2 S^2 - \alpha^3 S^3 \cdots \tag{0.20}$$

Where we have defined the 3x3 matrix $\boldsymbol{S}$:

$$\boxed{\boldsymbol{S} \equiv \sum_{t''} T_{t' t''}} \tag{0.21}$$

0.2.2 Simple cubic lattice, shape dependence

In the case of a simple cubic lattice, it is well known that the the summation $\sum_{t''}$ vanishes and *only depends on the shape of the boundary.* One possible choice is to consider an infinite slab, with the boundary consisting of two planes parallel to the x and y axes. This geometry allows us to distinguish two types of phonons in the $k = 0$ limit : “longitudinal phonons” travel along x and y and transverse phonons travel along z. Then one finds:[4]

$$\boldsymbol{S} \equiv \frac{4\pi n}{3} \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 2 \end{bmatrix} \tag{0.22}$$

Where n is the ”number density” $n = N/V = 1/v$. For transverse phonons , the shift in the energy is:

$$\frac{1}{2} \boldsymbol{S}_z (1 + \alpha \boldsymbol{S}_z)^{-1} \left(\frac{\partial \boldsymbol{\mu}}{\partial Q_k} \right) Q_k^2 = (4\pi n/3)(1 - 4\pi n \alpha/3)^{-1} \left(\frac{\partial \boldsymbol{\mu}}{\partial Q_k} \right)^2 Q_k^2 \tag{0.23}$$

For longitudinal phonons it is

$$\frac{1}{2}\boldsymbol{S}_x(1+\alpha\boldsymbol{S}_x)^{-1}\left(\frac{\partial\boldsymbol{\mu}}{\partial Q_k}\right)Q_k^2 = (8\pi n/3)(1+8\pi n\alpha/3)^{-1}\left(\frac{\partial\boldsymbol{\mu}}{\partial Q_k}\right)^2 Q_k^2 \tag{0.24}$$

The frequency shifts are:

$$\begin{aligned}\omega_T^2 &= \omega_0^2 - (4\pi n/3)(1-4\pi n\alpha/3)^{-1}\left(\frac{\partial\boldsymbol{\mu}}{\partial Q_k}\right)^2 \\ \omega_L^2 &= \omega_0^2 + (8\pi n/3)(1+8\pi n\alpha/3)^{-1}\left(\frac{\partial\boldsymbol{\mu}}{\partial Q_k}\right)^2\end{aligned} \tag{0.25}$$

The frequency splitting is:

$$\omega_L^2 - \omega_T^2 = \frac{4\pi n}{3}\left(2(1-4\pi n\alpha/3)^{-1} - (1+8\pi n\alpha/3)^{-1}\right)\left(\frac{\partial\boldsymbol{\mu}}{\partial Q_k}\right)^2 \tag{0.26}$$

In the case where the molecules have zero polarizability this formula simplifies to :

$$\boxed{\omega_L^2 - \omega_T^2 = \frac{4\pi n}{3}\left(\frac{\partial\boldsymbol{\mu}}{\partial Q_k}\right)^2} \tag{0.27}$$

This equation assumed the crystal has the shape of a plane (finite in the z direction and infinite in the x and y directions). More generally, one can consider crystals that are ellipsoids. In that case $\boldsymbol{S}$ takes the form:[3][4]

$$\boldsymbol{S} \equiv \frac{4\pi g}{3v}\begin{bmatrix}-1 & 0 & 0\\ 0 & -1 & 0\\ 0 & 0 & 2\end{bmatrix} \tag{0.28}$$

the formula is modified to:

$$\omega_L^2 - \omega_T^2 = \frac{4\pi g}{3v}\left(\frac{\partial\boldsymbol{\mu}}{\partial Q_k}\right)^2 \tag{0.29}$$

Here g is a factor that depends on the ratio c/a. *In the case of a spherical crystal ($c/a = 1$), $g = 0$ and the splitting disappears.*[4][3] Ignoring the effects of polarizability simplifies the analysis by removing the term $(1+\alpha\boldsymbol{S})^{-1} \equiv \boldsymbol{B}$. The equation for the splitting becomes:

$$\boxed{\omega_L^2 - \omega_T^2 = \frac{4\pi n}{3}(S_{zz} - S_{xx})\left(\frac{\partial\boldsymbol{\mu}}{\partial Q_k}\right)^2} \tag{0.30}$$

0.2.3 Non cubic simple lattices

We now consider non-cubic lattices, again with one dipole per unit cell. We assume the crystals have a spherical shape, that is , we perform our sum in a spherical region and let $L \to 0$. In general the sum in this sphere will not be equal to zero as it would be in the case of a simple cubic lattice. However, for certain symmetry groups, the matrix $\boldsymbol{S}$ will be diagonal. According to Decius, these are the groups Cn with $n > 3$, Dn, Cnv, Cnh with $n > 3$ Dnh, Dnd and Sn. For primitive tetragonal or hexagonal lattices, the appropriate sums have been evaluated by Mueller (1935),[6] who reports the “Lorentz factors” L_x, L_y and L_z for simple tetragonal lattices. Lorentz factors are defined by the equation:

$$F_i = E_{0i} + 4\pi L_i P_i \qquad i = x, y, z \tag{0.31}$$

Where $\boldsymbol{F}$ is the local field and $\boldsymbol{E}_0$ is the applied field. This relation assumes that the dipole moments are parallel to the applied field. Decius gives the relations between L_x, L_y and L_z and S_{xx}, S_{yy} and S_{zz}. If k is parallel to z, then

$$\begin{aligned} S_{xx} &= S_{yy} = -4\pi n L_x \\ S_{zz} &= -4\pi n (L_z - 1) \end{aligned} \tag{0.32}$$

If k is perpendicular to z then

$$\begin{aligned} S_{xx} &= -4\pi n (L_x - 1) \\ S_{yy} &= -4\pi n L_y \\ S_{zz} &= -4\pi n L_z \end{aligned} \tag{0.33}$$

A method of efficiently calculating Lorentz factors (internal fields) using rapidly converging sums for lattices of arbitrary symmetry is explained by de Wette and Schacher (1965).[1]

0.2.4 Extension to lattices with a basis

The above theory can be generalized to lattices with a basis - ie. with more than one dipole per unit cell. To accommodate this we use the indices t, t' and t'' to label unit cells. Let us assume m molecules per unit cell. Then A and T become $3mN$x$3mN$, where N is now the number of unit cells. The 3x3 polarizability matrix $\boldsymbol{\alpha}$ becomes a $3m$x$3m$ polarizability matrix for the entire cell. The 3x3 dipole interaction tensors $\boldsymbol{T}$ are replaced with $3m$x$3m$ tensors of the form:

$$\boldsymbol{T}_{t't'} = \begin{bmatrix} \boldsymbol{T}_{11} & \boldsymbol{T}_{12} & \boldsymbol{T}_{13} & \cdots \\ \boldsymbol{T}_{21} & \boldsymbol{T}_{22} & \boldsymbol{T}_{23} & \cdots \\ \boldsymbol{T}_{31} & \boldsymbol{T}_{32} & \boldsymbol{T}_{33} & \cdots \\ \vdots & \vdots & \vdots & \boldsymbol{T}_{mm} \end{bmatrix}_{t,t'} \tag{0.34}$$

where $(\boldsymbol{T}_{ij})_{t't''}$ gives the interaction between a molecule of type i in unit cell t' with a molecule of type j in unit cell t''. The $\boldsymbol{S}$ matrix likewise becomes $3m$x$3m$ and takes the form:

$$\boldsymbol{S}_{t't'} = \begin{bmatrix} \boldsymbol{S}_{11} & \boldsymbol{S}_{12} & \boldsymbol{S}_{13} & \cdots \\ \boldsymbol{S}_{21} & \boldsymbol{S}_{22} & \boldsymbol{S}_{23} & \cdots \\ \boldsymbol{S}_{31} & \boldsymbol{S}_{32} & \boldsymbol{S}_{33} & \cdots \\ \vdots & \vdots & \vdots & \boldsymbol{S}_{mm} \end{bmatrix}_{t,t'} \tag{0.35}$$

If the symmetry class of the crystal falls into one of the classes mentioned in section 0.2.3, then each of the submatrices $\boldsymbol{S}_{ij}$ will be diagonal.

References

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