

APPENDIX A

GROUP-THEORETICAL DERIVATION OF THE NUMBER AND IRREDUCIBLE REPRESENTATIONS OF THE EXTERNAL ZONE-CENTER PHONONS OF CRYSTALLINE CBOOA AND TBBA

As discussed in chapter 1, the number of external zone-center modes of a molecular crystal and their classification according to the irreducible representations of the point group symmetry of the crystal can be determined by treating the individual molecules as rigid units. We associate with each non-linear molecule three translatory and three rotatory degrees of freedom. If there are  $s$  molecules in a primitive cell of the crystal, the number of external zone-center phonons and their representation must be such that

$$\sum_i a_i d_i = 6s \quad (1)$$

where  $a_i$  is the number of phonons belonging to the  $i^{\text{th}}$  irreducible representation and  $d_i$  is the degeneracy of that representation.

A. I Bhagavantam and Venkatarayadu method<sup>1</sup>

The translatory or rotatory motions of the molecules

in a primitive cell transform, in general, according to a reducible representation  $\Gamma$ . Let  $\chi(R)$  denote the character of  $\Gamma$  corresponding to any symmetry operation  $R$  of the point group of the crystal. Only the number of molecules  $U_R$  that are left invariant under the symmetry operation  $R$ , contribute to  $\chi(R)$ . The reducible representation  $\Gamma$  can be decomposed into the irreducible representations of the point group, thus

$$\Gamma = \sum a_i \Gamma_i \quad (2)$$

The number of times the irreducible representation  $\Gamma_i$  occurs in  $\Gamma$  is given by<sup>2</sup>

$$a_i = \frac{1}{h} \sum_R \chi(R) \chi_i^*(R) \quad (3)$$

where  $h$  is the total number of symmetry elements in the point group and  $\chi_i(R)$  is the character of  $\Gamma_i$  corresponding to the operation  $R$ .

For modes which involve only translations of the molecules, it can be shown that<sup>1</sup>

$$(R) = U_R (\pm 1 + 2 \cos \varphi_R) \quad (4)$$

where  $\varphi_R$  is the angle of rotation in the operation  $R$ . The + sign corresponds to 'proper' operations of the type

$C_n$  and the - sign corresponds to 'improper' operations of the type  $S_n$  wherein the rotation is followed by a reflection.

In a similar manner, for modes which involve only rotation of the molecules,<sup>1</sup>

$$\chi(R) = U_R(1 \pm 2\cos \varphi_R) \quad (5)$$

Using equations (3) and (5), the representations of the  $3s$  rotatory external modes can be deduced. Similarly, using equations (3) and (4), the representations of the  $3s$  translatory external modes can also be determined. Among the latter category, three degrees of freedom must correspond to the acoustic modes. Thus, there exist  $6s-3$  external optical modes of which  $3s-3$  are of the translatory type,

(1) Application to CBOOA (Phase II): Phase II of crystalline CBOOA belongs to the space group<sup>3</sup>  $C_{2h}^5$ . The point group symmetry of the crystal is  $C_{2h}$ . The primitive cell is identical to the crystallographic unit cell and there are four molecules per unit cell. The analysis along with the character table for the  $C_{2h}$  group is shown in Table A.1. We see that the representation of the external optical modes is given by

$$6A_g + 5A_u + 6B_g + 4B_u .$$

Table A1

| $C_{2h}$                | E  | $C_2$ | $\sigma_h$ | I     | $a_1$ |                | Raman active | Infrared active |     |
|-------------------------|----|-------|------------|-------|-------|----------------|--------------|-----------------|-----|
|                         |    |       |            |       | total | acoustic optic |              |                 |     |
| $A_g$                   | 1  | 1     | 1          | 1     | 6     | 0              | 6            | yes             | no  |
| $A_u$                   | 1  | 1     | -1         | -1    | 6     | 1              | 5            | no              | yes |
| $B_g$                   | 1  | -1    | -1         | 1     | 6     | 0              | 6            | yes             | no  |
| $B_u$                   | 1  | -1    | 1          | -1    | 6     | 2              | 4            | no              | yes |
| $U_R$                   | 4  | 0     | 0          | 0     |       |                |              |                 |     |
| $\varphi_R$             | 0  | $\pi$ | 0          | $\pi$ |       |                |              |                 |     |
| $1+2\cos \varphi_R$     | 3  | -1    | 1          | -3    |       |                |              |                 |     |
| $1-2\cos \varphi_R$     | 3  | -1    | -1         | 3     |       |                |              |                 |     |
| Translatory type        | 12 | 0     | 0          | 0     |       |                |              |                 |     |
| $\chi(R)$ Rotatory type | 12 | 0     | 0          | 0     |       |                |              |                 |     |
| Total                   | 24 | 0     | 0          | 0     |       |                |              |                 |     |

## A.2 The method of coupling<sup>4,5</sup>

The point group corresponding to the site symmetry of the molecules in the crystal is a subgroup of the point group of the crystal. For equivalent molecules related by symmetry elements of the crystal, the site symmetry determines the irreducible representations to which the translatory and rotatory motions must belong. These irreducible representations of the site point group must, in turn, be compatible with the point group symmetry of the crystal itself. Thus, the representations originating from all the equivalent molecules in a primitive cell are obtained by the group theoretical correlation<sup>5</sup> of the appropriate representations of the site point group with the representations of the point group of the crystal. This procedure, as is to be expected, leads to identical results as the Bhagavantam-Venkatarayadu method. However, the physical origin of the external modes is more explicitly incorporated in the method of coupling.

(1) Application to CBOOA (Phase II): The site symmetry of the molecules in the primitive cell is  $C_1$ . In the point group  $C_1$ , the translatory and rotatory motions of a molecule belong to the representation 6A. A correlation of the species A in the site symmetry group  $C_1$  with the representations of the point group  $C_{2h}$  gives the irreducible representations of all the external modes.

$$C_1 : 6A \longrightarrow C_{2h} : 6(A_g + B_g + A_u + B_u) .$$

This is the same result as obtained in A.1(i). Again, after subtracting the acoustic modes, the reduction of the optical modes is given by

$$6A_g + 5A_u + 6B_g + 4B_u .$$

(ii) Application to TBBA (Phase VIII)<sup>6</sup> : At room temperature, TBBA crystallizes in the monoclinic system  $C_{2h}^3$  with eight molecules per unit cell.<sup>6</sup> In this case, the primitive or Bravais cell is not identical to the crystallographic unit cell, but is half the crystallographic unit cell. Hence the number of molecules in the Bravais cell is 4. The point group symmetry of the Bravais cell is  $C_{2h}$  and the site symmetry of molecules is  $C_1$ . The analysis is now identical to that in the case of CBOOA, so that the reduction of the external optical modes is again given by

$$6A_g + 6B_g + 5A_u + 4B_u .$$

References

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APPENDIX BDERIVATION OF THE RESULTANT LINESHAPE WHEN  
TWO LORENTZIAN SPECTRA ARE CONVOLVED

Let the intrinsic spectral distribution of the vibrational band be represented by a Lorentzian  $A_V(\nu)$ :

$$A_V(\nu) = \frac{a_V}{(\nu - \nu_{OV})^2 + \Gamma_V^2} \quad (1)$$

where,  $\nu_{OV}$  is the frequency of the band center,  $\Gamma_V$  is the half width at half maximum (HWHM) and  $a_V$  is a constant. Similarly, we represent the reorientational spectrum by another Lorentzian,

$$A_R(\nu) = \frac{a_R}{(\nu - \nu_{OR})^2 + \Gamma_R^2} \quad (2)$$

when  $\nu_{OR}$ ,  $\Gamma_R$  and  $a_R$  are the corresponding parameters of the reorientational spectrum.

The observed lineshape  $A'_V(\nu)$  is the convolution of  $A_V(\nu)$  and  $A_R(\nu)$ . Symbolically,

$$A'_V(\nu) = \frac{A_V(\nu) \otimes A_R(\nu)}{\int_{-\infty}^{\infty} A_R(\nu) d\nu} \quad (3)$$



By the convolution theorem we have

$$\mathcal{F}[A_V(\nu) \otimes A_R(\nu)] = \sqrt{2\pi} \mathcal{F}[A_V(\nu)] \mathcal{F}[A_R(\nu)] \quad (4)$$

Conversely

$$A_V(\nu) \otimes A_R(\nu) = \sqrt{2\pi} \mathcal{F}^{-1} \left\{ \mathcal{F}[A_V(\nu)] \mathcal{F}[A_R(\nu)] \right\} \quad (5)$$

In equations (4) and (5),  $\mathcal{F}$  and  $\mathcal{F}^{-1}$  denote, respectively, the direct and inverse Fourier transformations. Now,

$$\begin{aligned} \mathcal{F} \left\{ \frac{a}{(\nu - \nu_0)^2 + \Gamma^2} \right\} &= \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \frac{a}{(\nu - \nu_0)^2 + \Gamma^2} e^{-it\nu} d\nu \\ &= \sqrt{\frac{\pi}{2}} \frac{a}{\Gamma} e^{-it\nu_0 - |\Gamma t|} \end{aligned} \quad (6)$$

Substituting the appropriate expressions in (5), we have

$$\begin{aligned} A_V(\nu) \otimes A_R(\nu) &= \sqrt{2\pi} \mathcal{F}^{-1} \left\{ \frac{\pi}{2} \cdot \frac{a_V a_R}{\Gamma_V \Gamma_R} e^{-i(\nu_{OV} + \nu_{OR})t - |(\Gamma_V + \Gamma_R)t|} \right\} \\ &= \frac{\pi}{2} \frac{a_V a_R}{\Gamma_V \Gamma_R} \int_{-\infty}^{\infty} e^{-i(\nu_{OV} + \nu_{OR})t - |(\Gamma_V + \Gamma_R)t|} e^{i\nu t} dt \\ &= \frac{\pi a_V a_R (\Gamma_V + \Gamma_R) / \Gamma_V \Gamma_R}{(\nu_{OV} + \nu_{OR} - \nu)^2 + (\Gamma_V + \Gamma_R)^2} \end{aligned} \quad (7)$$

Now,

$$\int_{-\infty}^{\infty} \frac{a_R}{(\nu_{OR} - \nu)^2 + \Gamma_R^2} d\nu = \frac{\pi a_R}{\Gamma_R} \quad (8)$$

Combining equations (3), (7) and (8), we have

$$A'_V(\nu) = \frac{a_V(\Gamma_V + \Gamma_R)/\Gamma_V}{(\nu_{OV} + \nu_{OR} - \nu)^2 + (\Gamma_V + \Gamma_R)} \quad (9)$$

It is seen that  $A'_V(\nu)$  is another Lorentzian whose peak is at  $\nu_{OV} + \nu_{OR}$  and its HWHM,  $\Gamma$ , is given by

$$\Gamma = \Gamma_V + \Gamma_R .$$

We note that the observed peak frequency is shifted from that of the true vibrational spectrum. However,  $\nu_{OR}$  generally lies in the microwave region while  $\nu_{OV}$  is in the infrared region. Hence  $\nu_{OR} \ll \nu_{OV}$  and in most practical cases, the shift is negligible.

APPENDIX CRELATIONSHIP BETWEEN THE ORDER PARAMETER AND THE 'DICHROIC'  
RATIO FOR A HOMEOTROPICALLY ALIGNED SAMPLE

Consider a sample aligned in the  $z$  direction of a space fixed coordinate system  $(x, y, z)$ . Let  $\alpha$  be the angle made by the transition moment,  $\mu$ , with the long axis. We choose a coordinate system  $(x', y', z')$  fixed to the molecule such that the long axis is along  $z'$  and the transition moment lies in the  $y'z'$  plane, so that

$$\mu_{x'} = 0, \quad \mu_{y'} = \mu \sin \alpha, \quad \mu_{z'} = \mu \cos \alpha \quad (1)$$

If the radiation is incident along the direction of alignment, i.e., the  $z$  axis, the absorption due to the molecule is given by

$$A' = k'(\mu_x^2 + \mu_y^2) \quad (2)$$

where  $k'$  is a constant, so that the absorption due to an ensemble of  $N$  molecules is given by

$$A = k(\langle \mu_x^2 \rangle + \langle \mu_y^2 \rangle) \quad (3)$$

where  $k = Nk'$  and the brackets denote an ensemble average.

The coordinate system  $(x', y', z')$  may be related to the system  $(x, y, z)$  by means of the Eulerian angles

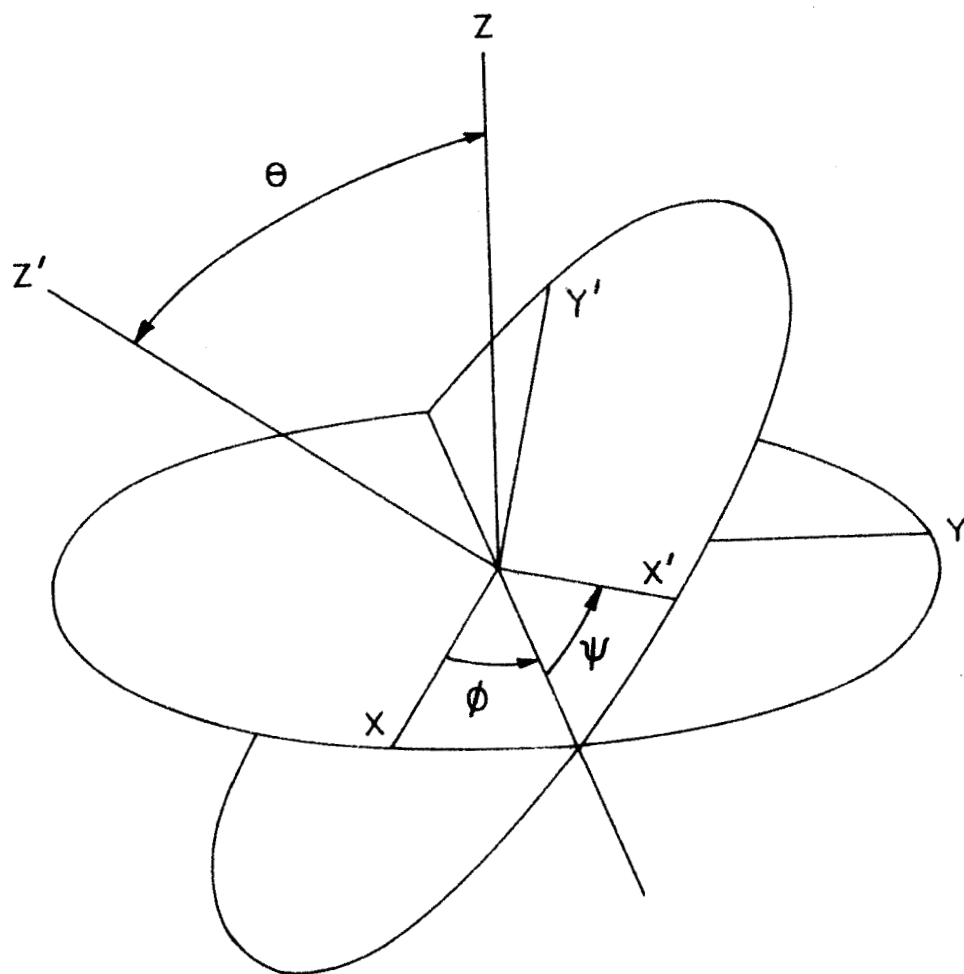


Figure C. 1: The rotations defining the Eulerian angles.

$(\psi, \varphi, \theta)$  shown in Fig. C.1. Transforming the components of  $\mu$  from  $(x', y', z')$  to  $(x, y, z)$ ,<sup>1</sup> we have,

$$\begin{aligned} \mu_x &= -(\sin \psi \cos \varphi + \cos \theta \sin \varphi \cos \psi) \mu_{y'} \\ &\quad + \sin \theta \sin \varphi \mu_{z'}, \end{aligned} \quad (4)$$

$$\begin{aligned} \mu_y &= (\cos \theta \cos \varphi \cos \psi - \sin \psi \sin \varphi) \mu_{y'} \\ &\quad - \sin \theta \cos \varphi \mu_{z'}, \end{aligned} \quad (5)$$

Free rotation about the long axis of the molecule leads to equal probability for all values of  $\psi$  so that

$$\begin{aligned} \langle \sin \psi \rangle &= \langle \cos \psi \rangle = 0 \quad \text{and} \\ \langle \sin^2 \psi \rangle &= \langle \cos^2 \psi \rangle = \frac{1}{2} \end{aligned} \quad (6)$$

Further, in the uniaxial nematic and smectic phases, the structure is symmetrical about the optic axis so that  $\varphi$  can take all values with equal probability. Hence

$$\begin{aligned} \langle \cos \varphi \rangle &= \langle \sin \varphi \rangle = 0, \quad \text{and} \\ \langle \cos^2 \varphi \rangle &= \langle \sin^2 \varphi \rangle = \frac{1}{2} \end{aligned} \quad (7)$$

Squaring (4) and (5) and taking the ensemble average, and using (6) and (7) we have

$$\langle \mu_x^2 \rangle = \langle \mu_y^2 \rangle = \frac{1}{4}(1 + \langle \cos^2 \theta \rangle) \mu_{y'}^2 + \frac{1}{2} \langle \sin^2 \theta \rangle \mu_{z'}^2 \quad (8)$$

The long range orientational order parameter,  $S$ , is defined as

$$S = \frac{1}{2}(3 \langle \cos^2 \theta \rangle - 1) \quad (9)$$

Combining eqns. (1), (3), (8) and (9) we have, for the nematic phase,

$$A_{\text{nem}} = \frac{k\mu^2}{3}[3S \sin^2 \alpha - 2S + 2] \quad (10)$$

In the isotropic phase  $S = 0$ , so that

$$A_{\text{iso}} = \frac{2k\mu^2}{3} \quad (11)$$

The 'dichroic' ratio  $R$  is defined by

$$R = A_{\text{nem}}/A_{\text{iso}} \quad (12)$$

so that, we have, using (10), (11) and (12)

$$R = \frac{1}{2}[3S \sin^2 \alpha - 2S + 2]$$

which yields

$$S = \frac{1 - R}{1 - \frac{3}{2} \sin^2 \alpha} \quad (13)$$

### Reference

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APPENDIX D

AN ESTIMATE OF THE REQUIRED CORRECTION TO THE ORDER  
PARAMETER WHEN A HOMEOTROPICALLY ALIGNED SAMPLE IS  
USED

For a light beam propagating along the optic axis of a uniaxial liquid crystalline sample, the true absorption coefficient  $A_{\odot}$  is related to the experimentally measured absorption coefficient,  $(A_{\text{exp}})_{\odot}$  by<sup>1</sup>

$$A_{\odot} = \frac{n_o}{g_o} (A_{\text{exp}})_{\odot} \quad (1)$$

where  $n_o$  is the refractive index of the ordinary ray in the absence of the absorption and  $g_o$  is the internal field factor:

$$g_o = \frac{n_o^2 + 2 + a(n_o^2 - 1)}{3} \quad (2)$$

Here  $a$  is the anisotropy factor given by

$$\gamma_e = \frac{4\pi}{3}(1 - 2a) \quad (3)$$

where,  $\gamma_e$  is the internal field constant when the electric field is parallel to the optic axis of the medium.

For the isotropic liquid,  $a = 0$  and equations (1) and (2) become,

$$A_{\text{iso}} = \frac{n}{g^2} (A_{\text{iso}})_{\text{exp}} \quad (4)$$

and

$$g = \frac{n^2 + 2}{3} \quad (5)$$

where  $a$  is the refractive index of the isotropic liquid in the absence of the absorption.

The 'dichroic' ratio,  $R$ , is defined as

$$R = \frac{A_{\odot}}{A_{\text{iso}}} \quad (6)$$

Combining equations (1), (2), (4), (5) and (6) we have

$$R = \Lambda R_{\text{exp}} \quad (7)$$

where

$$\Lambda = \frac{n_0(n^2 + 2)^2}{n[n_0^2 + 2 + a(n_0^2 - 1)]^2} \quad (8)$$

We see from equation (7) that the measured dichroic ratios have to be corrected by the factor  $\Lambda$  to obtain the true dichroic ratio.

In the absence of refractive index: data for CBOOA, we have chosen to evaluate  $\Lambda$  for a typical liquid crystal, PAA, at three different temperatures.

The refractive index data for PAA are available in the visible region.<sup>2</sup> We extrapolate these data to 4.45  $\mu$  using the empirical relation,



$$n^2 - 1 = A + \frac{B}{\lambda^2 - \lambda_0^2} \quad (9)$$

where A and B are constants to be determined.  $\lambda_0$  is the resonance wavelength and has been found to be  $0.35 \mu$  for PAA. The temperature dependence of  $a$  was calculated using equation (3) and the values of  $\gamma_e$  taken from Ref. 4.

The results of these calculations and the corresponding values of  $\Lambda$  are shown in Table D1.

We note that at the lowest temperature, i.e.,  $95^\circ \text{C}$  which is  $42^\circ$  below the smectic-isotropic transition, the correction factor  $\Lambda$  is identical to unity whereas on approaching the transition, it increases slightly. Even at  $134^\circ \text{C}$ , which is  $1^\circ$  below the nematic-isotropic transition,  $\Lambda$  differs from unity by only 2%. In contrast, while using a homogeneously aligned sample the estimated correction factors differ from unity by about 8 - 10% over the entire range of measurement.<sup>4</sup>

As the required correction in our geometry is well within the experimental uncertainties, no correction has been made to the S values obtained from our measurements.

References

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TABLE D1

| T   | $n_o$        |              | A     | B     | $n_o$<br>(4.45 $\mu$ ) | s     | $\Delta$ |
|-----|--------------|--------------|-------|-------|------------------------|-------|----------|
|     | 0.6438 $\mu$ | 0.5890 $\mu$ |       |       |                        |       |          |
| 95  | 1.550        | 1.558        | 1.320 | 0.024 | 1.523                  | 0.079 | 1.00     |
| 115 | 1.551        | 1.561        | 1.302 | 0.030 | 1.518                  | 0.062 | 1.01     |
| 134 | 1.568        | 1.581        | 1.323 | 0.040 | 1.525                  | 0.034 | 1.02     |
| 136 | 1.629        | 1.642        | 1.513 | 0.041 | 1.586                  | 0     | ---      |