APPENDIX A

THEORETICAL BACKGROUND CONCERNING THE RAMAN MEASUREMENTS OF $\langle P_2 \rangle$ AND $\langle P_4 \rangle$.[1]

A. Orientational statistics and microscopic order parameters

We assume the molecules to be rigid but of arbitrary shape and consider two coordinate systems: (i) the laboratory frame (x,y,z) fixed with respect to the liquid crystal medium with the z axis parallel to the director $\hat{n}$, and (ii) the molecular frame (1,2,3) fixed to the molecule. The 3 axis is chosen to be parallel to the major molecular axis.

At any instant the orientation of a particular molecule is described by the three Euler angles (α, β, γ) linking the two coordinate systems.[2] The orientational order of the molecules can then be described by a distribution function $f(\alpha, \beta, \gamma)$ which can be expanded in terms of the generalised spherical harmonics, the

Wigner matrices[3] $D^{(L)}_{m'm}(\alpha,\beta,\gamma)$:

$$f(\alpha,\beta,\gamma) = \sum_{L=0}^{\infty} \sum_{m'm=-L}^{L} \frac{2L+1}{8\pi^2} \, a^{(L)}_{m'm} \, D^{(L)}_{m'm}(\alpha,\beta,\gamma) \qquad \text{.. (1)}$$

with

$$a^{(L)}_{m'm} = \int_0^{2\pi} d\alpha \int_0^{\pi} \sin\beta \, d\beta \int_0^{2\pi} d\gamma \, D^{(L)*}_{m'm}(\alpha,\beta,\gamma) f(\alpha,\beta,\gamma)$$

$$= \langle D^{(L)*}_{m'm}(\alpha,\beta,\gamma) \rangle ,$$

where $\langle \ldots \rangle$ represents a statistical average.

The coefficients $a^{(L)}_{m'm}$ with non-zero L depend on the degree of orientational ordering. They are temperature dependent and saturate to constant values if the system becomes completely ______ They therefore be chosen as a set of generalised orientational order parameters characterising the degree of ordering. It can be shown that for each L there are $(2L + 1)^2$

independent real orientational order parameters.

Considering a uniaxial macroscopic system with the unique axis parallel to the 3 axis, the distribution function is independent of α and only terms with m' = 0 contribute to the summation. The physical equivalence of $\hat{n}$ and $-\hat{n}$ leaves only terms with even L. We then have

$$f(\alpha,\beta,\gamma) = \sum_{L\ \mathrm{even}} \sum_{m=-L}^{L} \frac{2L+1}{8\pi^2} a_{om}^{(L)} D_{om}^{(L)}(\alpha,\beta,\gamma) \qquad \ldots (2)$$

where

$$D_{om}^{(L)}(\alpha,\beta,\gamma) = \left(\frac{4\pi}{2L+1}\right)^{1/2} (-1)^m Y_{Lm}^{m}(\beta,\gamma) .$$

Thus we have (2L+1) real, independent order parameters for each (even) L. For the case L = 2 we have five nontrivial order parameters.

Equation (2) can be written explicitly[4] employing the real quantities $A_m^{(L)}$ and $B_m^{(L)}$ given by

$$a_{om}^{(L)} \equiv (-1)^m a_{o,-m}^{(L)*} = A_m^{(L)} + iB_m^{(L)} \ .$$

For molecules having no plane of symmetry, all the (2L+1) parameters for each L are expected to be nonzero, with the $A_o^{(L)}$ characterising the 'axial' ordering with respect to the director and the others the 'azimuthal' ordering around the molecular axis.

If the molecule has a single plane of symmetry the number of nontrivial terms is reduced to (L + 1) for each L. If the molecule has two mutually perpendicular planes of symmetry, the number of nontrivial terms is further reduced to (L/2 + 1).

If the molecule has a threefold or greater axis of symmetry, say the $\underset{\sim}{3}$ axis, only one nontrivial term is left for each L and

$$Y_{LO}(\beta,\gamma) = [(2L + 1)/4\pi]^{1/2} P_L(\cos \beta) \ .$$

Thus, under the commonly adopted assumption that liquid crystals are made up of rigid, cylindrically symmetric rods, one obtains

$$f(\alpha,\beta,\gamma) = \sum_{L\ \text{even}} \frac{2L+1}{8\pi^2} A_0^{(L)} P_L(\cos\beta) \qquad (3)$$

or

$$f_{\hat{u}}(\beta) = \int_0^{2\pi} d\alpha \int_0^{2\pi} d\gamma\, f(\alpha,\beta,\gamma)$$

$$= \sum_{L\ \text{even}} \frac{2L+1}{2} A_0^{(L)} P_L(\cos\beta) \qquad (4)$$

and

$$A_0^{(L)} = \int_0^{\pi} \sin\beta\, d\beta\, P_L(\cos\beta)\, f_{\hat{u}}(\beta)$$

$$= \langle P_L(\cos\beta) \rangle \qquad (5)$$

where $\hat{u}$ is the unit vector along the symmetry axis of the molecule.

The order parameters $A_0^{(L)} = 0$ in the isotropic phase, $=1$ in the completely ordered phase and should take values lying between 0 and 1 in the liquid crystalline phase.

B. Orientational Order by Raman Scattering

The power spectrum of the Raman scattered light can be expressed as a fourth rank tensor which is related to the average orientational correlation function of the molecular Raman polarizability. This suggests that application of Raman scattering to the anisotropic liquid crystalline system will yield not only the order parameters with $L = 2$ but also parameters of the next higher order, i.e., terms with $L = 4$.[5]

Consider a single Raman active vibrational mode with normal coordinate Q and frequency ω. We introduce a Raman polarizability tensor α', whose time dependence in a reference frame fixed with respect to the molecule follows that of Q.

$$\alpha' = \left(\frac{\partial \alpha}{\partial Q}\right)_{Q=0} Q \qquad (6)$$

If α' is interpreted as a microscopic property of the individual molecule one should, in principle, apply local field corrections to connect the macroscopic properties to the microscopic ones. However, several empirical evidences[6,7] suggest that these are not significant here. Thus α' in equation (6) can be treated as a molecular polarisability which is essentially unchanged in the molecular frame when the material changes from the isotropic to any liquid crystalline phase.

Lax and Nelson[8] have developed theoretical expressions relating the observed ratios of integrated intensities (depolarisation ratios) for a particular Raman band to the statistical averages of the Raman polarisability tensors α'_L as expressed in the laboratory frame, taking into account solid angle changes and transmission losses at the sample surfaces. For the geometries employed in our experiments (see figure 6.2, chapter 6) these results are

$$R_1 = C_n \frac{\langle(\alpha_L')^2_{yz}\rangle}{\langle(\alpha_L')^2_{zz}\rangle} ,$$

$$R_2 = \frac{\langle(\alpha_L')^2_{xy}\rangle}{C_n \langle(\alpha_L')^2_{yy}\rangle} , \qquad (7)$$

$$R_3 = \frac{\langle(\alpha_L')^2_{yx}\rangle}{\langle(\alpha_L')^2_{xx}\rangle} ,$$

where the correction factor $C_n = \dfrac{(n_g + n_e)^2}{(n_g + n_o)^2}$.

The Raman tensor for a particular Raman active vibration will have some form α_M' in the molecular frame of reference. However, there is always some other molecular axis, related to this one, in which the Raman tensor has the diagonal form

$$\alpha_d' = \alpha \begin{pmatrix} a & 0 & 0 \\ 0 & b & 0 \\ 0 & 0 & 1 \end{pmatrix} \qquad (8)$$

The components of α_m' in the molecular frame can be expressed in terms of α, a, b and the three Eulerian angles α_c, β_c and γ_c that bring the principal axis of α_m (i.e., the axis for which α has the diagonal form) into coincidence with the special symmetry axis of the molecule.

For a system with macroscopic uniaxial symmetry, there are only four independent orientational averages in terms of which the three ratios (equation 7) can be rewritten as

$$R_1 = Q_m \frac{\langle(\alpha_L')^2_{xz}\rangle}{\langle(\alpha_L')^2_{zz}\rangle} ,$$

$$R_2 = \frac{\langle(\alpha_L')^2_{xz}\rangle}{Q_m \langle(\alpha_L')^2_{xx}\rangle} , \qquad (9)$$

$$R_3 = \frac{\langle(\alpha_L')^2_{xy}\rangle}{\langle(\alpha_L')^2_{xx}\rangle}$$

These ratios can be expressed in terms of the microscopic molecular quantities a and b, the Eulerian angles (α_o, β_o, γ_o), and the orientational order parameters corresponding to L = 2,4.

In the special case of cylindrical symmetry about the 3-axis one obtains[9]

$$A^{-2}\langle(\alpha_L')^2_{xx}\rangle = \frac{1}{9} + \frac{3}{16}B + \frac{1}{4}C + \frac{1}{18}D + \frac{11}{288}D^2$$
$$+ \left(\frac{1}{8}B + \frac{1}{2}C - \frac{1}{6}D - \frac{3}{48}D^2\right)\langle\cos^2\beta\rangle$$
$$+ \left(\frac{3}{16}B - \frac{3}{4}C + \frac{3}{32}D^2\right)\langle\cos^4\beta\rangle\ ,$$

$$A^{-2}\langle(\alpha_L')^2_{xy}\rangle = \frac{1}{16}B + \frac{1}{4}C + \frac{1}{32}D^2 + \left(\frac{3}{8}B - \frac{1}{16}D^2\right)\langle\cos^2\beta\rangle$$
$$+ \left(\frac{1}{16}B - \frac{1}{4}C + \frac{1}{32}D^2\right)\langle\cos^4\beta\rangle\ ,$$

$$A^{-2}\langle(\alpha_L')^2_{xz}\rangle = \frac{1}{4}B + \frac{1}{4}C - \left(\frac{3}{4}C - \frac{1}{8}D^2\right)\langle\cos^2\beta\rangle$$
$$- \left(\frac{1}{4}B - C + \frac{1}{8}D^2\right)\langle\cos^4\beta\rangle\ ,$$

$$A^{-2}\left\langle(\alpha_L')^2_{zz}\right\rangle = \tfrac{1}{9} + \tfrac{1}{2}B - \tfrac{1}{9}D + \tfrac{1}{36}D^2$$
$$- \left(B - 2C - \tfrac{1}{3}D + \tfrac{1}{6}D^2\right)\left\langle\cos^2\beta\right\rangle$$
$$+ \left(\tfrac{1}{2}B - 2C + \tfrac{1}{4}D^2\right)\left\langle\cos^4\beta\right\rangle , \qquad (10)$$

where

$$A = \alpha_{11}' + \alpha_{22}' + \alpha_{33}' ,$$

$$B = (1/A^2)\left[\tfrac{1}{4}(\alpha_{11}' - \alpha_{22}')^2 + \alpha_{12}'^2\right] ,$$

$$C = (1/A^2)\left(\alpha_{13}'^2 + \alpha_{23}'^2\right) ,$$

$$D = (1/A)(2\alpha_{33}' - \alpha_{11}' - \alpha_{22}') .$$

At any particular temperature the three ratios in equation (9) give three equations linear in the two unknowns $\langle\cos^2\beta\rangle$ and $\langle\cos^4\beta\rangle$ with three parameters B, C and D. In addition, the depolarization ratio in the isotropic phase gives another relation between these three parameters.

$$R_{iso} = \frac{3}{4}\left(\frac{12B + 12C + D^2}{5 + 12B + 12C + D^2}\right) \qquad (11)$$

It is then possible to solve from the data for the two order parameters

$$A_o^{(2)} = \frac{1}{2}\left\langle 3\cos^2\beta - 1\right\rangle ,$$

and

$$A_o^{(4)} = \frac{1}{8}\left\langle 35\cos^4\beta - 30\cos^2\beta + 3\right\rangle . \qquad (12)$$

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3 M.E.Rose, Elementary Theory of Angular Momentum (Wiley, New York, 1957).

4 See page 4637 of Ref. 1 above.

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(b) M.Lax and D.F.Nelson, Proc. Third Rochester Conf. on Coherent and Quantum Optics, edited by L.Mandel and E.Wolf (Plenum, New York, 1973).

9 See page 4640 of Ref. 1 above.

APPENDIX B

PROCEDURE AND PROGRAM USED TO CALCULATE $\langle P_2 \rangle$ AND $\langle P_4 \rangle$ FROM RAMAN DEPOLARIZATION RATIOS

A. Procedure

In a frame of reference fixed to the molecule, a particular Raman polarizability tensor can be written in the diagonal form given in equation (8) of Appendix A. From the symmetry of the 7CB and 8 OCB molecules employed in the studies described in chapter 6, it is reasonable to assume that the molecular axis coincides with one of the axes in the Raman tensor. We take this to be the 3 axis.

Assuming that the molecular polarizability is not uniaxial ($a \neq b$), the parameters A, B, C and D in equations (10) of Appendix A reduce to

$$A = 1 + a + b$$

$$B = (a - b)^2/4A^2$$

$$C = 0$$

$$D = (2 - a - b)/A \qquad (1)$$

Also,

$$R_{iso} = \frac{3(a^2 + b^2 + 1 - a - b - ab)}{3(a + b + 1)^2 + 4(a^2 + b^2 + 1 - a - b - ab)} \qquad \ldots (2)$$

Starting with an arbitrary value of $b (0 < b < 1)$ a is determined from equation (2) and hence the parameters A, B and D in equation (1).

Combining equations (10) with equations (9) of Appendix A we obtain,

$$\left[\tfrac{1}{8}D^2 + \frac{R_1}{Q_n}\left(B - \tfrac{1}{3}D + \tfrac{1}{6}D^2\right)\right] \langle \cos^2 \theta \rangle$$

$$- \left[\left(\tfrac{1}{2}B + \tfrac{1}{4}D^2\right)\left(\frac{R_1}{Q_n} + \tfrac{1}{2}\right)\right] \langle \cos^4 \theta \rangle$$

$$= \frac{R_1}{Q_n}\left(\tfrac{1}{9} + \tfrac{1}{2}B - \tfrac{1}{9}D + \tfrac{1}{36}D^2\right) - \tfrac{1}{4}B \qquad (3)$$

and

$$\left[R_2 Q_n\left(\tfrac{1}{8}B - \tfrac{1}{6}D - \tfrac{5}{48}D^2\right) - \tfrac{1}{8}D^2\right] \langle \cos^2 \theta \rangle$$

$$+ \left[\tfrac{3}{16}R_2 Q_n\left(B + \tfrac{1}{2}D^2\right) + \tfrac{1}{4}\left(B + \tfrac{1}{2}D^2\right)\right] \langle \cos^4 \theta \rangle$$

$$= \tfrac{1}{4}B - R_2 Q_n\left[\tfrac{1}{9} + \tfrac{3}{16}B + \tfrac{1}{18}D + \tfrac{11}{288}D^2\right] \qquad (4)$$

Here θ replaces β employed in Appendix A. (3) and (4) give two linear equations in the two unknowns $\langle \cos^2 \theta \rangle$ and $\langle \cos^4 \theta \rangle$. We solve for them and impose the condition $\frac{1}{3} < \langle \cos^2 \theta \rangle < 1$ which is a physical requirement.

We now compute

$$R_3(\text{cal}) = \frac{\frac{1}{8}(3B - \frac{1}{2}D^2)\langle \cos^2 \theta \rangle + \frac{1}{16}(B + \frac{1}{2}D^2)[\langle \cos^4 \theta \rangle + 1]}{[\frac{1}{5} + \frac{3}{16}B + \frac{1}{15}D + \frac{11}{280}D^2 + (\frac{1}{8}B - \frac{1}{6}D - \frac{5}{48}D^2)\langle \cos^2 \theta \rangle + \frac{3}{16}(B + \frac{1}{2}D^2)\langle \cos^4 \theta \rangle]} \quad \ldots (5)$$

and compare the result with the experimental value of R_3.

If $|R_3(\text{cal}) - R_3(\text{expt})| \geq 0.01$ we ignore the results, go back to equation (2) and repeat the series of calculations with an incremented value $b + \Delta b$. The procedure is repeated till $|R_3(\text{cal}) - R_3(\text{expt})| \leq 0.01$. Now the incremental value Δb is reduced to $\Delta b/10$ and the calculations repeated till we obtain $|R_3(\text{cal}) - R_3(\text{expt})| \leq 0.001$. We accept the value of b (and hence the corresponding values of a, A, B and D) which satisfies this requirement and then solve for $\langle \cos^2 \theta \rangle$ and $\langle \cos^4 \theta \rangle$. Finally, we compute the order parameters given by

$$\langle P_2(\cos \theta) \rangle = \frac{1}{2}[3 \langle \cos^2 \theta \rangle - 1] \quad (6)$$

and

$$\langle P_4(\cos\theta)\rangle = \frac{1}{8}[35\langle\cos^4\theta\rangle - 30\langle\cos^2\theta\rangle + 3] \qquad (7)$$

B. Computation Program

$\langle P_2(\cos\theta)\rangle$ and $\langle P_4(\cos\theta)\rangle$ values were calculated from the experimentally determined Raman depolarisation ratios R_1, R_2, R_3 and R_{iso} and the correction factor G_n, employing the above iterative procedure, on a Hewlett-Packard Model 9821A programmable desk-top calculator. The following program was employed.

```
0 :
FMT 2/,30X, "COMPUTATION OF ORDER PARAMETERS P2 A ND P4
FROM" ; TYP ⊢

1 :
FMT /,40X, "RAMAN DEPOLARISATION RATIOS"; TYP ⊢

2 :
FMT 3/,5X, "COMPOUND", 6X, "PHASE" , 6X, "TEMPERATURE" ;
TYP ⊢

3 :
FMT 4/,8X, "θA", 8X, "θB", 8X, "A", 8X, "B", 9X, "D" ,
5X,"COS(B)↑2" , 5X,Z; TYP ⊢
```

```
4 :
FMT  "COS(B)**4" , 5X, "R3(CAL)", 5X, " P(2) ", 5X,
"P(4)",/; TYP ⊢

5 :
ENT  "NO?" , R16, "R(ISO)?" , R5 ⊢

6 :
"READY" ; 0→R19; ENT "NE?" , R17, "NO?" , R18 ⊢

7 :
(R16 + R17)/(R16 + R18) → R3; R5R3 → R3 ⊢

8 :
ENT "R1?" ,R1, "R2?" , R2, "R3(EXPT)?" , R4 ⊢

9 :
ENT "B(MIN) ?" , R10, "B(MAX) ?", R11 ⊢

10 :
ENT "DELTA B?", R 12 ⊢

11 :
" INCREMENT" ; IF (ABS(X-R4)≤ .01)(R19=1); R12/10 → R12 ⊢
```

```
12 :
R10+R12 → R10 ⊢

13 :
IF  R10 > R11;  GTO "END" ⊢

14 :
36(3R5-1)(R5(3R10↑2 + 2R10+3) - (R10↑2 - R10+1)) → Z ⊢

15 :
√((3(R10+1)(2R5+1))↑2 - Z) → R15 ⊢

16 :
(-3(R10 + 1)(2R5 + 1) + R15)/6(3R5 - 1) → R20 ⊢

17 :
(-3(R10+1)(2R5+1) - R15)/6(3R5 - 1) → R30 ⊢

18 :
"START" ; 1 + R20 + R10 → R40; 1 + R30 + R10 → R45 ⊢

19 :
(R20 - R10)↑2/4R40↑2 → R50; (R30 - R10)↑2/4R45↑2 → R55 ⊢
```

```
20 :
(2 - R20 - R10)/R40 -> R60; (2 - R30 - R10)/R45 -> R65 ⊢

21 :
1/8×R60 ↑ 2 + R1/R3×(R50 - 1/3×R60 + 1/6×R60 ↑ 2) -> R70 ⊢

22 :
1/8×R65 ↑ 2 + R1/R3×(R55 - 1/3×R65 + 1/6×R65 ↑ 2) -> R80 ⊢

23 :
-(.5R50 + .25R60 ↑ 2)(R1/R3 + .5) -> R90 ⊢

24 :
-(.5R55 + .25R65 ↑ 2)(R1/R3 + .5) -> R100 ⊢

25 :
R1/R3×(.5R50+1/36×R60 ↑ 2 + 1/9×(1 - R60)) - .25R50 -> R110 ⊢

26 :
R1/R3×(.5R55+1/36×R65 ↑ 2 + 1/9×(1 - R65)) - .25R55 -> R120 ⊢

27 :
R2R3(1/8×R50 - 1/6×R60 - 5/48×R60 ↑ 2) - 1/8×R60 ↑ 2 -> R130 ⊢
```

```
28 :
R2R3(1/8mR55 - 1/6mR65 - 5/48mR65 ↑2) - 1/8mR65 ↑ 2 → R140 ⊢

29 :
.25(R50 + .5R60 ↑ 2)(1 + .75R2R3) → R150 ⊢

30 :
.25(R55 + .5R65 ↑2)(1 + .75R2R3) → R160 ⊢

31 :
.25R50 - R2R3(1/9 + 3R50/16 + R60/18 + 11R60 ↑2/288) → R170 ⊢

32 :
.25R55 - R2R3(1/9 + 3R55/16 + R65/18 + 11R65 ↑2/288) → R180 ⊢

33 :
(R150R110-R90R170)/(R70R150-R130R90) → X → R200 ⊢

34 :
IF (1/3 ≤ X)(X ≤ 1); R20 → R190; R70 → R210; R90 → R220;
R110 → R230; R130 → R240 ⊢

35 :
IF (1/3 ≤ X)(X ≤ 1); R150 → R250; R170 → R260; R40 → A; R50 → B;
R60 → C ⊢
```

```
36 :
(R160R120-R100R180)/(R80R160-R140R100) → Y ⊢

37 :
IF (1/3≤Y)(Y≤1); Y → R200; R30 → R190; R80 → R210;
R100 → R220; R120 → R230 ⊢

38 :
IF (1/3≤Y)(Y≤1); R140 → R240; R160 → R250; R180 → R260;
R45 → A; R55 → B; R65 → C ⊢

39 :
(R210R260-R240R230)/(R210R250-R240R220) → R400 ⊢

40 :
1/9+5B/16+C/18+11CC/288+(B/8-C/6-50C/48)R200 → Z ⊢

41 :
Z+3/16×(B+CC/2)R400 → Y ⊢

42 :
(1/8×(5B-.50C)R200+1/16×(B+.50C)(R400+1))/Y → X ⊢

43 :
IF .01 > ABS (X-R4); R19+1 → R19 ⊢
```

```
44 :
IF ABS (X-R4) > .001; GTO "INCREMENT" ⊢

45 :
"PRINT" ; (3R200-1)/2 → R410; (35R400-30R200+3)/8 → R420 ⊢

46 :
FMT/,2X,5FXD 9.6,2FXD 12.6,3FXD 12.6; TYP R190,R10,A,B,C,
R200,R400,X,R410,R420 ⊢

47 :
FMT /,2X,9FXD 8.4; TYP R1,R2,R4,R5,R18,R17,R3,R1/R3,R2R3 ⊢

48 :
GTO "READY" ⊢

49 :
"END" ; END ⊢
```