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# ORIENTATIONAL DISTRIBUTION COEFFICIENTS OF GUEST-HOST SYSTEMS DETERMINED BY DIFFERENT METHODS

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Abstract Order parameters determined by different spectroscopic methods are not identical because they refer to different "pseudo" orientation axes if an orientational distribution function  $f=f(\beta, \gamma)$  holds. The angles between these axes and those referring to the system of principal axes of the orientational distribution coefficients  $g_{ij33}^0$  are determined by the molecular properties owing to the spectroscopic method used. This is shown by an analysis of the frequency and temperature dependence of a relative order parameter for testosterone propionate in cholesteryl chloride/cholesteryl laurate measured with ultraviolet absorption (UV) and circular dichroism (ACD) as an example.

For the ultraviolet absorption (UV) and the circular dichroism (ACD) of anisotropic samples the measurable quantity  $Y_\beta$  can be described by <sup>1,2</sup>

$$Y_\beta = g_{ij\beta\beta} X_{ij} \quad (\beta = 1, 2 \text{ or } 3; \text{ no summation}) \quad (1)^{+}$$

The molecular properties for UV and ACD are given by

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<sup>+</sup>) We use here the index notation for vectors and tensors.

$X_{ij} = \epsilon_{ij}$  and  $\Delta\epsilon_{ij}$ , respectively.  $g_{ijkl}^0$  are the orientational distribution coefficients, defined for a uniaxial system by

$$g_{ijkl}^0 = \frac{1}{4\pi} \int f(\beta, \gamma) a_{ik} a_{jl} \sin\beta \, d\beta d\gamma. \quad (2)$$

$a_{ij}$  are the elements of the transformation matrix from the space-fixed ( $x_i'$ ) to the molecule-fixed ( $x_i$ ) coordinate system.  $f(\beta, \gamma)$  represents the orientational distribution function, for which the axis  $x_3'$  is chosen parallel to the optical axis (indicated by symbol  $^0$  in  $g_{ijkl}^0$ ).  $\beta$  and  $\gamma$  are the Eulerian angles.  $g_{ijkl}^0$  is a tensor of second rank with respect to the first two indices which refer to a transformation of the molecule-fixed coordinate system.  $g_{ij\beta\beta}^0$  and  $X_{ij}$  can be diagonalized because they are symmetric tensors. But, in general, the principal axes of  $g_{ij\beta\beta}^0$  and  $X_{ij}$  are different, because the behaviour of  $X_{ij}$  is determined by the type of the molecules only, while  $g_{ij\beta\beta}^0$  depends on the molecular properties and on the type of orienting forces or mechanisms. If the tensor  $X_{ij}$  is known the  $g_{ij\beta\beta}^0$  can be determined from independent measurements of  $Y_{\beta}^{(q)}$  corresponding to its number of unknowns. Then the  $g_{ijkl}^0$  can be described with respect to any coordinate system by the transformation

$$g_{ijkl}^0 = a_{ir} a_{js} \bar{g}_{rskl}^0 \quad (3)$$

if the molecule-fixed coordinate system is transformed by  $x_i = a_{ij} \bar{x}_j$ . In most methods for the determination of the  $g_{ij\beta\beta}^0$  the molecular tensor  $X_{ij}$  is unknown. In these cases  $X_{ij}$  has to be determined in one and the same experiment as the order parameters which are defined by

$$\rho = 1/2 (3g_{3333}^0 - 1) = 1 - 3/2 (g_{2233}^0 + g_{1133}^0), \quad (4)$$

$$\eta = 1/2 (2g_{2233}^0 + g_{3333}^0 - 1) = 1/2 (g_{2233}^0 - g_{1133}^0). \quad (5)$$

Then these order parameters refer to the coordinate system of the  $X_{ij}$  and order parameters measured with different methods UV and ACD, e.g., may be different in their magnitude. For a simple case this may be demonstrated easily: There are two properties  $X_{ij}^{(1)}$  and  $\bar{X}_{ij}^{(2)}$  for which only  $X_{33}^{(1)}$  and  $\bar{X}_{33}^{(2)}$  are different from zero in the coordinate systems  $x_i$  and  $\bar{x}_i$ , respectively. The order parameters  $\rho^{(q)}$  are then given by

$$\frac{Y_l^{(q)} - Y_{iso}^{(q)}}{2 Y_{iso}^{(q)}} = \rho^{(q)}. \quad (6)$$

$Y_l^{(q)}$  may be an absorption of linearly polarized light with a direction of polarisation parallel to the optical axis ( $\epsilon_l$ ) or a circular dichroism measurement with a light beam propagating parallel to the optical axis ( $\Delta\epsilon^A$ )<sup>2</sup>. If there is an angle of  $\beta_0$  between  $x_3$  and  $\bar{x}_3$  the evaluated order parameters are connected by

$$\rho^{(1)} = \rho^{(2)} - 3/2 \sin^2 \beta_0 (\rho^{(2)} + \eta^{(2)}). \quad (7)$$

$\rho^{(1)}$  and  $\rho^{(2)}$  are different because they refer to different axes which are determined by the properties of  $X_{ij}^{(q)}$ . The coordinate axes  $x_3$  or  $\bar{x}_3$  may be called "approximate orientation axes". "Approximate" because the behaviour of  $X_{ij}^{(q)}$ , i.e. only  $X_{33}^{(q)} \neq 0$  in this special case omits the existence of  $\eta^{(q)}$  (eq.(11)).

With this simple spectroscopic example it is easily seen that different methods yield different values of  $\rho$ . For testosterone propionate the tensors  $\epsilon_{ij}$  and  $\Delta\epsilon_{ij}$  for the  $n - \pi^*$ -transition are more complicated. Therefore, the explanations given above are only in principle sufficient for the interpretation of the different  $\rho$  values, calculated from UV and ACD measurements, as shown in fig. 1

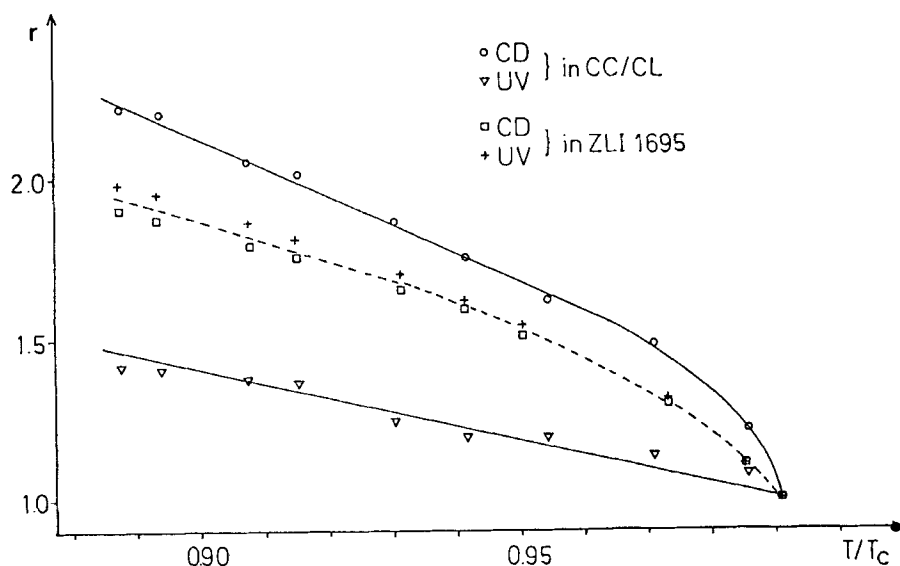


FIGURE 1:  $r_{ACD}$  and  $r_{UV}$  of testosterone propionate as a function of temperature (concentration: 0.06 mol/l).

Fig. 1 presents relative order parameters

$$r_q(T, T_0) = \frac{(Y_l^{(q)} - Y_{iso}^{(q)})_T}{(Y_l^{(q)} - Y_{iso}^{(q)})_{T_0}} \quad (q = UV, ACD) \quad (8)$$

for testosterone propionate dissolved in a compensated nematic phase of cholesteryl chloride/cholesteryl laurate (CC/CL) as a function of temperature<sup>3</sup>.  $T_0$  is the reference temperature.  $r_q$ , a pure experimental quantity, can be given here in a higher accuracy than a derived order parameter  $\rho$ .

In view of the discussion above it seems desirable to have a representation of the order parameters independent of any condition of molecular properties which were used for their measurement. We propose a description of  $g_{ij33}^0 \approx g_{ij33}^*$  in their principal axes ( $x_i^*$ ). I.e.  $g_{ij33}^0$  has to be diagonalized and the eigenvalues should be given in the order

$$g_{3333}^* \geq g_{2233}^* \geq g_{1133}^* \quad (9)$$

$x_3^*$  is then defined as the orientation axis of the molecule and  $\rho = \rho^*$  and  $\eta = \eta^*$ . For the eigenvalues the relation

$$|g_{3333}^*| \geq \max_{i,j=1,2,3} |g_{ij33}^0| \quad (10)$$

holds. Therefore,  $\rho^*$  is the largest value of  $\rho$ , which is possible for different molecule-fixed axes, i.e. if the reference axis  $x_3$  is varied. From eqs. (1) and (8) and the convention of the discussion above the relative order parameter results in

$$r_q(T, T_0) = \frac{(\rho^* + Q^{(q)} \eta^*)_T}{(\rho^* + Q^{(q)} \eta^*)_{T_0}} = \frac{\hat{\rho}_T}{\hat{\rho}_{T_0}} \quad (11)$$

$$Q^{(q)} = \frac{3 (x_{22}^{(q)} - x_{11}^{(q)})}{2 x_{33}^{(q)} - (x_{22}^{(q)} + x_{11}^{(q)})} \quad (12)$$

In general,  $X_{ij} = \varepsilon_{ij}$  or  $\Delta\varepsilon_{ij}$  depends on wavelength and as a consequence  $Q^{(q)}$  and therefore  $r_q$  is a function of wavelength. Furthermore,  $r_q(T, T_0)$  should be different for different spectroscopic methods because  $Q^{(q)}$  is determined by other quantities. If  $\eta^* = 0$ , this dependence disappears and

$$r_q(T, T_0) = \frac{\rho^* T}{\rho^* T_0} \quad (13)$$

is a true relative order parameter independent of the method used for its determination. The orientation axis is then the molecular axis about which the rotational symmetry of the distribution exists, i.e.  $f = f(\beta)$ .

The temperature dependence of  $r_q(T, T_0)$

$$\frac{dr_q(T, T_0)}{dT} = \frac{1}{(\rho^* + Q^{(q)} \eta^*)_{T_0}} \left( \frac{d\rho^*}{dT} + Q^{(q)} \frac{d\eta^*}{dT} \right) \quad (14)$$

also depends on the spectroscopic constants  $Q^{(q)}$  and is different for different methods as shown in fig. 1. For testosterone propionate in CC/CL the order parameters calculated from the UV and ACD are independent of wavelength in a large spectral region. Eq. (13) seems to be fulfilled. Because of the different temperature dependence (eq. (14)) of  $r_{UV}(T, T_0)$  and  $r_{ACD}(T, T_0)$  the orientational distribution function has to be of the type  $f = f(\beta, \gamma)$ . The independency of wavelength, which results experimentally, demands either a wavelength independent  $Q^{(q)}$  or a temperature independent ratio of  $\rho^*(T)/\eta^*(T)$  for testosterone propionate. Because  $dr_q(T, T_0)/dT$  is independent of wavelength, too,  $Q^{(q)}$  should be constant.



Any  $\rho$  and  $\eta$  can be given by eq. (3) as a linear function of  $\rho^*$  and  $\eta^*$ . Therefore the ratio in eq. (11) can be interpreted as a new ratio of order parameters  $\hat{\rho}$  which owes to an "approximate" ("pseudo") orientation axis. This axis depends on the spectroscopic constant  $Q$  and is therefore different for different spectroscopic methods.<sup>4</sup>

First attempts to evaluate  $r_{ACD}(T, T_0)$  and  $r_{UV}(T, T_0)$  of testosterone propionate in the nematic phase ZLI 1695 (Merck) are shown in fig. 1, too. These relative order parameters are equal within the experimental error. This implies  $\eta^* = 0$  and, therefore, a rotational symmetry about one molecular axis, i.e.  $f = f(\beta)$ . The different behaviour in CC/CL and ZLI 1695 seems to be a kind of a solvent effect but the result has to be verified by further UV and ACD measurements.

#### REFERENCES

1. H.-G. Kuball, J. Altschuh, and A. Schönhofer, Chem. Phys., **43**, 67 (1979)
2. H.-G. Kuball and J. Altschuh, Mol. Phys., **11**, 1 (1982)
3. J. Altschuh, R. Weiland, J.V. Kosack and H.-G. Kuball Ber. Bunsenges. Phys. Chem., in press (1984).
4. The same problem arise by comparison of other methods then UV and ACD or measurements in different frequency regions as e.g. given by J.W. Emsley, R. Hashim, G.L. Luckhurst, G.N. Rumbles and F.R. Vilorio, Mol. Phys. **49**, 1321 (1983)  
R. Seeliger, H. Haspeklo and F. Noack, Mol. Phys. **49**, 1039 (1983)  
M.G. Clark and F.C. Saunders, Mol. Cryst. **82** (1982) (Letters) 267.  
Because of the special conditions such a discussion is not given there.