

Interpretation of Optical Spectra of Partially Aligned Samples

Erik W. Thulstrup

Chemistry Department, Royal Danish School of Educational Studies, Emdrupvej
115 B, DK-2400 Copenhagen NV, Denmark

Received November 19, 1984

Spectroscopic studies with linearly or circularly polarized light of partially aligned molecular samples can provide two kinds of important information. One type of information is the molecular alignment; the complete molecular orientation distribution function can not be found, but its essential properties can be determined, and these frequently enable a detailed interpretation of the spectrum. This leads to the other kind of information, which has to do with the anisotropic molecular optical properties: transition moments, MCD B-terms, Raman polarizability tensors, etc.

A survey of the field is given together with a short description of the mathematical treatment of molecular orientation and optical properties. The different spectroscopic methods are illustrated by a number of examples based on absorption, magnetic circular dichroism, and photoluminescence.

INTRODUCTION

Optical spectroscopy of partially aligned samples has recently attracted considerable interest. It provides two major types of information:¹⁻³

1. Information on the anisotropic optical properties of the molecules in the sample, and
2. Information on the molecular alignment in the sample.

In some cases the objective of investigation is the determination of properties of type 1, in other cases its aim is to study properties of type 2. Very often neither kind of information is available before the investigation, but this does not prevent extraction of useful information of both kinds.

The nature of the information which can be obtained depends on the kind of experiment performed. Presently, the processes of interest are:

One-photon processes:

Electric dipole absorption and chemiluminescence.¹⁻³

Circular dichroism (CD).³

Magnetic circular dichroism (MCD).³⁻⁴

Electric quadrupole absorption.³

Two-photon processes:

In important two-photon processes the first photon is always absorbed, the second may be absorbed or emitted, and the two events may take place simultaneously or may be successive. The four different types of processes are:^{3,5}

Events:	Second photon:	
	absorbed	emitted
simultaneous	two-photon absorption	Raman scattering
successive	photoinduced dichroism	luminescence

In the following text it will be shown how such one- and two-photon processes in partially aligned samples can be described, and a few selected examples: absorption, MCD, and photoluminescence, will be discussed in more detail.

ORIENTATION FACTORS

For the description of processes in a partially aligned sample with an unknown orientation distribution, the mathematical treatment of the molecular alignment is extremely important. On the one hand, it should describe all observed orientational phenomena, and, on the other hand, it should contain as few assumptions as possible or even no assumptions at all about the alignment. The construction of inadequate models for the description of one-photon processes in aligned samples has frequently led to incorrect conclusions about molecular properties and alignment because the models used were too restrictive: they assumed certain properties of the molecular orientation distribution; whenever these were not fulfilled, the result was an incorrect interpretation of the observed spectra.^{6,2}

In the following discussion we shall assume that the molecular alignment is uniaxial. This assumption is frequently fulfilled by nematic liquid crystals, stretched polymers, and lipid bilayers, and by solutes in these.

The simplest description of uniaxial molecular alignment, which fulfills the basic requirements, is based on the so-called orientation factors K , L , M . . .^{5,3,2} They relate the sample axes X , Y , and Z (Z being the unique sample axis) to the molecular axes x , y , z in a set of identical molecules. The orientation factors are defined as averages over the sample molecules, and for the description of the simplest possible experiments such as absorption, chemiluminescence, CD, or MCD the following are needed:

$$K_{uv} = \langle \cos(u, Z) \cos(v, Z) \rangle$$

where u , $v = x$, y , or z , and (u, Z) is the angle between u and Z .

For the description of electric quadrupole absorption or any of the two-photon processes, the L orientation factors are needed in addition to the K 's.^{5,3} They are defined as:

$$L_{stuv} = \langle \cos(s, Z) \cos(t, Z) \cos(u, Z) \cos(v, Z) \rangle$$

Both the K 's and L 's are redundant. In a general uniaxial sample there are only $2n + 1$ independent orientation factors with n indices. In the case of the 6 K 's we have, for example, the relation

$$K_{xx} + K_{yy} + K_{zz} = \langle \cos^2(x, Z) + \cos^2(y, Z) + \cos^2(z, Z) \rangle = 1$$

Furthermore, we can use the freedom in the arbitrary selection of molecular axes system x, y, z with respect to the molecular framework to make off-diagonal K -factors vanish:

$$K_{xy} = K_{xz} = K_{yz} = 0$$

This corresponds to diagonalizing the 3×3 matrix \mathbf{K} . The remaining non-zero K 's are usually labelled $K_x, K_y,$ and K_z and are defined so that

$$K_x \leq K_y \leq K_z$$

Since the alignment in many samples is such that the longest molecular dimension tends to line up with the sample axis Z ,^{7,8} molecular axis z is frequently called the molecular »long« axis.

The diagonalization of the K -matrix and simplifications in the higher orientation factors are easy to obtain in molecules with suitable elements of symmetry. One important example is the case in which the molecule has two perpendicular symmetry planes. Then only orientation factors in which each $\cos(u, Z)$ appears an even number of times will be nonzero. In general, only $n/2 + 1$ independent orientation factors with n indices remain; in other words, two K 's and three L 's.

In the following text we shall see how K values for molecules with this kind of symmetry can be determined from absorption spectroscopy, and later it will be demonstrated how two-photon processes, in this case studied by fluorescence spectroscopy, can enable determination of the non-vanishing L 's.

ABSORPTION

Since the electric vectors of a beam of ordinary light are not isotropic (but perpendicular to the direction of the beam) a set of partially aligned molecules will show absorption which depends on the relative alignment of the sample and the beam. This can be explained by the fact that a set of molecules, all with electric dipole transition moments \mathbf{M} along a specific direction \mathbf{W} , absorbs light with an electric vector along direction \mathbf{U} with probability proportional to $\cos^2(\mathbf{W}, \mathbf{U})$.

In many cases, however, the sample properties are such that the use of linearly polarized light is more convenient than natural light. One example is a set of molecules dissolved in a stretched polymer sheet.^{7,9} Such a sample will frequently be uniaxial around the stretching direction⁸ (the unique sample axis Z), and the two other sample axes, Y in the plane of the sheet, and X perpendicular to the sheet, will be equivalent. Using linearly polarized light, progressing along X , two independent spectra can be recorded, $E_Z(\tilde{\nu})$ with the electric vector along the sample axis Z and $E_Y(\tilde{\nu})$ with the electric vector along Y . The observed absorbance due to transition f with transition moment \mathbf{M}_f may be written

$$E_f(\tilde{\nu}) = \langle \cos^2(\mathbf{M}_f, \mathbf{U}) \rangle_{\text{av}} A_f(\tilde{\nu})$$

where the average is taken over all molecules in the sample, U is the direction of the electric vector of the light, and $A_f(\tilde{\nu})$ is the absorbance which would be observed if all molecules were aligned with their transition moment \mathbf{M}_f along \mathbf{U} . If contributions from all transitions f are added, we obtain for the spectrum $E_Z(\tilde{\nu})$:

$$E_Z(\tilde{\nu}) = \sum_f \langle \cos^2(\mathbf{M}_f, \mathbf{Z}) \rangle_{\text{av}} A_f(\tilde{\nu}) = \sum_f K_f \cdot A_f(\tilde{\nu})$$

where

$$K_f = \langle \cos^2(\mathbf{M}_f, \mathbf{Z}) \rangle_{\text{av}}$$

Similarly, we obtain

$$E_Y(\tilde{\nu}) = \sum_f \frac{1}{2} (1 - K_f) A_f(\tilde{\nu})$$

since

$$\begin{aligned} \sum_f A_f(\tilde{\nu}) &= E_Z(\tilde{\nu}) + E_Y(\tilde{\nu}) + E_X(\tilde{\nu}) = \\ &= E_Z(\tilde{\nu}) + 2 E_Y(\tilde{\nu}) \end{aligned}$$

The contribution from f disappears from the linear combination

$$E_Z(\tilde{\nu}) - E_Y(\tilde{\nu}) \cdot 2 K_f / (1 - K_f)$$

This means that if the transitions are non-overlapping, which is usually the case in infrared absorption,¹⁰ we have

$$2 K_f / (1 - K_f) = E_Z(\tilde{\nu}_f) / E_Y(\tilde{\nu}_f) = D(\tilde{\nu}_f)$$

where $D(\tilde{\nu})$ is called the dichroic ratio, and $\tilde{\nu}_f$ is the wavelength of the peak due to transition f . Now K_f can be determined:

$$K_f = D(\tilde{\nu}_f) / [2 + D(\tilde{\nu}_f)]$$

In the case of overlapping transitions, common for visible-UV spectroscopy, K_f can also be determined. For this purpose a set of linear combinations

$$E_Z(\tilde{\nu}) - d E_Y(\tilde{\nu})$$

are constructed. Of these that one is selected in which the spectral features (peaks, shoulders, etc.) due to transition f disappear. The corresponding value of d is called d_f . We have

$$2 K_f / (1 - K_f) = d_f$$

and

$$K_f = d_f / (2 + d_f)$$

(K_y, K_z) values determined in this way for a large number of aromatic hydrocarbons aligned in stretched polyethylene are shown in Figure 1. Clearly, the alignment depends strongly on molecular shape; in stretched polyethylene, as in many other anisotropic solvents, the molecular long axis becomes z , the one corresponding to the highest K -value. The triangle in the figure shows the theoretical limits for (K_y, K_z) values. The left side: $K_x = K_y = (1 - K_z)/2$ corresponds to orientation distributions, like those obtained for rod-shaped mole-

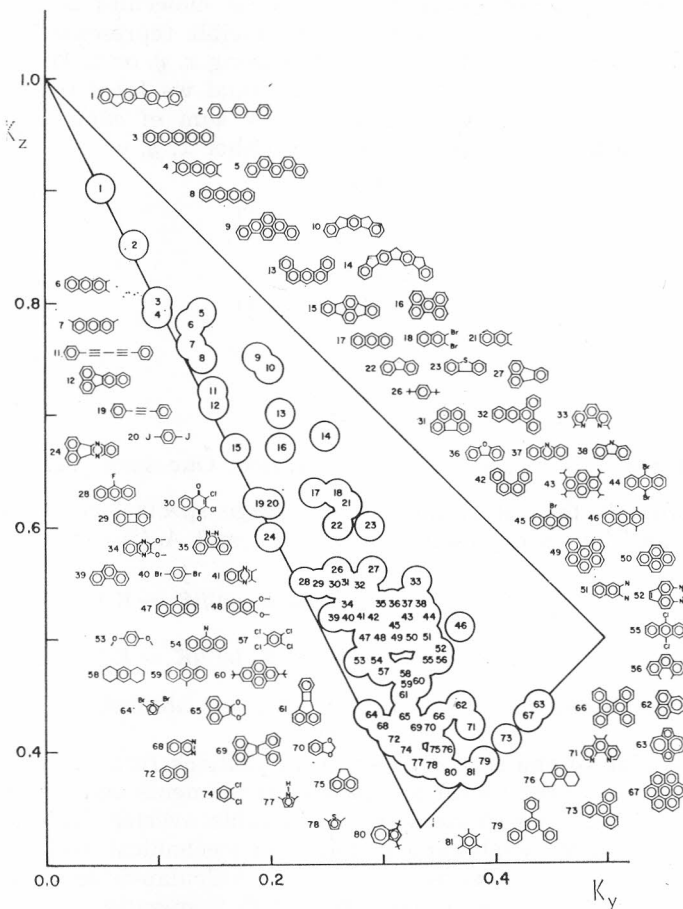


Figure 1. (K_y, K_z) values for aromatic molecules aligned in stretched polyethylene at room temperature.⁹ The orientation of the formulas is such that the best aligned molecular axis, z , is horizontal, the y -axis vertical and x is perpendicular to the plane of the paper. The triangle shows the theoretical limit of (K_y, K_z) . The top corner corresponds to perfect alignment of the molecular z -axis with the stretching direction, the bottom corner represents orientation distributions such as the isotropic distribution. The value of K_z for any point is equal to the vertical distance between the point and the upper side of the triangle.

cules. The bottom: $K_y = K_z = (1 - K_x)/2$ to orientation distributions, like those obtained for disc-shaped molecules, and the upper side: $K_y + K_z = 1$, $K_x = 0$ corresponds to a perfect alignment of the molecular (y, z)-planes with the stretching direction Z . Thus, from the observed molecular alignment information on the molecular shape can be obtained. It is interesting that small molecules, such as chloroform, can also be aligned in the stretched polyethylene. Now, we shall take a closer look at the information on anisotropic molecular properties which can be obtained from the spectra.

The High Symmetry Case

If the symmetry point group for the solute molecules is such that the molecular axes x, y, z belong to different irreducible representations (e. g. C_{2v}, D_{2h}), all transitions moments must be directed along x, y , or z . Then, only three different K_f -values exist: K_x, K_y , and K_z . As usual we label the axes so that $K_x \leq K_y \leq K_z$. Furthermore, we can define the sum of contributions to the absorbance due to transitions polarized along either x, y , or z :

$$A_z(\nu) = \sum_f^{\text{M}_f \text{ along } z} A_f(\nu)$$

$$A_y(\nu) = \sum_f^{\text{M}_f \text{ along } y} A_f(\nu)$$

$$A_x(\nu) = \sum_f^{\text{M}_f \text{ along } x} A_f(\nu)$$

In many important cases these can be separated. One such case, common for many molecules, is that of $A_x(\tilde{\nu}) = 0$ in a large spectral region (e. g. when only $\pi-\pi^*$ transitions are present). Then $A_y(\nu)$ and $A_z(\lambda)$ can be determined:

$$A_y(\tilde{\nu}) = [2K_z E_Y(\tilde{\nu}) - (1 - K_z) E_Z(\tilde{\nu})]/(K_z - K_y)$$

$$A_z(\tilde{\nu}) = [(1 - K_y) E_Z(\tilde{\nu}) - 2K_y E_Y(\tilde{\nu})]/(K_z - K_y)$$

Figure 2 shows an example of separation of $\pi-\pi^*$ absorption into $A_z(\lambda)$ and $A_y(\lambda)$.

The separation of the spectrum into contributions from transitions of different polarization is very useful for spectral assignments and for the detection of hidden transitions in regions with considerable overlap. This has been of great importance in the evaluation of quantum mechanical π -electron models, where transition moment directions are easily calculated, and where transitions, hidden in ordinary absorption spectra, are frequently predicted.

Spectral assignments may be considered as mappings of sets of observed transitions into sets of calculated ones. These mappings are made by means of a number of assignment criteria such as transition energy, transition probability, substituent effects, and transition moment direction. Among these, the latter has the advantage of referring to molecular symmetry. In the high symmetry case, the symmetry properties of the excited states may be considered more fundamental than their energies and the classification of transi-

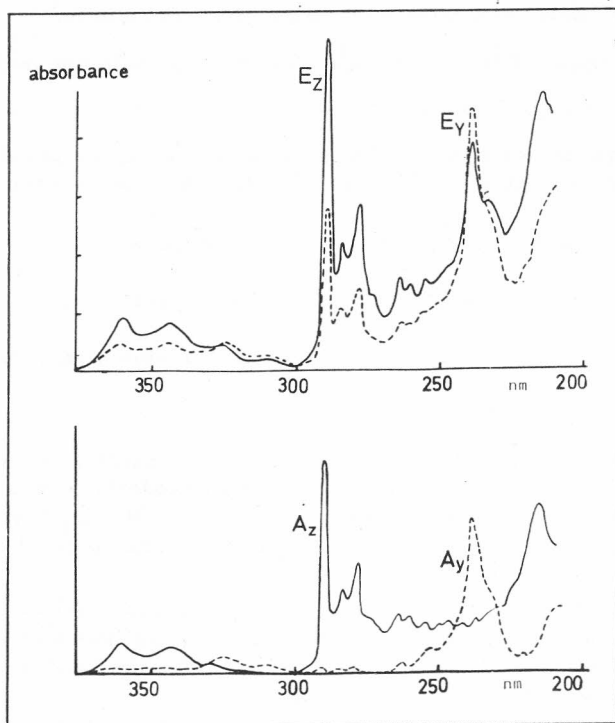


Figure 2. Spectra of fluoranthene in stretched polyethylene at room temperature.¹² Top: observed spectra $E_Z(\tilde{\nu})$ and $E_Y(\tilde{\nu})$. Bottom: linear combinations of the observed spectra corresponding to transitions polarized along the molecular axis z , $A_z(\tilde{\nu})$, and the molecular axis y , $A_y(\tilde{\nu})$. The separation of the spectrum into these components has made it possible to assign 9 electronic transitions in this part of the spectrum instead of the 4 that were recognized earlier. No x -polarized components are present in this region.

tions into groups corresponding to transition moments along x , y , and z provides a very precise assignment criterion.

We have seen how detailed information could be extracted from the observed spectra $E_Y(\tilde{\nu})$ and $E_Z(\tilde{\nu})$ when one of the components, *e.g.* $A_x(\tilde{\nu})$, vanishes. In other cases the orientation distribution is such that the components $A_x(\tilde{\nu})$, $A_y(\tilde{\nu})$, and $A_z(\tilde{\nu})$ can be separated at least partially.

If the orientation distribution corresponds to one of the sides of the triangle in Figure 1, it will be possible to obtain such detailed information:^{6,2}

If $K_x = K_y$ (the left side of the triangle), it is possible to determine $A_z(\tilde{\nu})$ and $A_x(\tilde{\nu}) + A_y(\tilde{\nu})$.

If $K_y = K_z$ (the bottom side of the triangle), it is possible to determine $A_x(\tilde{\nu})$ and $A_y(\tilde{\nu}) + A_z(\tilde{\nu})$.

Expressions for these two cases have been given elsewhere.^{6,2}

If $K_x = 0$ (the upper side of the triangle), it is possible to determine $A_y(\tilde{\nu})$ and $A_z(\tilde{\nu})$ only if *e. g.* $A_x(\tilde{\nu}) = 0$.

In this latter case the expressions for $A_y(\tilde{\nu})$ and $A_z(\tilde{\nu})$ given above for $A_x(\tilde{\nu}) = 0$ apply. Since in this case $K_y + K_z = 1$, they can be written:

$$A_y(\tilde{\nu}) = [2K_z E_y(\tilde{\nu}) - (1 - K_z) E_z(\tilde{\nu})] / (2K_z - 1)$$

$$A_z(\tilde{\nu}) = [K_z E_z(\tilde{\nu}) - 2(1 - K_z) E_y(\tilde{\nu})] / (2K_z - 1)$$

In the following we shall take a closer look at the »low-symmetry case«.

The Low-Symmetry Case

In molecules of lower symmetry, where the transition moment directions are not restricted to the principal molecular orientation axes x , y , and z , useful information on the directions of the vectors \mathbf{M}_f can still be obtained. However, the procedures are less straightforward than in the high symmetry case described above.

First of all, the location of the principal orientation axes must be found. This may be done if transitions with known transition moment directions are available (usually infrared transitions). In other cases the location of x , y , and z may be estimated from the molecular shape.

Secondly, the values of the K 's must be determined. This can often be done by comparison with molecules of similar shape (see Figure 1). The uncertainty in the determination of principal orientation axes and in the K 's will usually be so small that transition moment directions can be determined with an error of less than 10–15°.

The cases for which the most specific information can be obtained are as before:

1. Spectral regions where all transitions are polarized in a plane, *e. g.* the y , z -plane. In this case, the numerical value of the angle between the molecular z -axis and the transition moment \mathbf{M}_f of transition f is determined by:^{6,2}

$$\tan^2(z, \mathbf{M}_f) = \cot^2(y, \mathbf{M}_f) = (K_z - K_f) / (K_f - K_y)$$

2. Orientation distributions which correspond to the sides of the orientation triangle:^{6,2}

If $K_x = K_y$ (the left side of the triangle):

For samples with such orientation distributions the angle between the molecular z -axis and the transition moment \mathbf{M}_f is given by:

$$\tan^2(z, \mathbf{M}_f) = (K_z - K_f) / (K_f - K_y)$$

If $K_y = K_z$ (the bottom side of the triangle):

For orientation distributions of this kind a determination of the angle between \mathbf{M}_f and the molecular x -axis is possible:

$$\tan^2(x, \mathbf{M}_f) = (K_f - K_x)/(K_z - K_f)$$

Even when \mathbf{M}_f is restricted to a plane, the signs of the angles are undetermined. Thus, usually, two directions of the transition moment vector are in accordance with the observed data. In some cases, absolute angles can be determined by means of additional information *e. g.* from fluorescence polarization studies.¹⁴

MAGNETIC CIRCULAR DICHROISM

In the case of absorption of linearly polarized light, two independent spectra could be recorded by varying the angle between the unique sample axis and the electric vector of the light. In the case of absorption of circularly polarized light, the observed circular dichroism will usually be masked by stronger effects such as linear dichroism, unless the experiment is carried out so that the circularly polarized beam coincides with the unique sample axis *Z*. Thus, the possibility of recording two independent spectra on the aligned sample is excluded. As a natural choice for a second independent spectrum the one has been suggested which is obtained for an isotropic solution with the same number of molecules in the light path.^{4,3}

While the information which can be obtained in ordinary circular dichroism measurements on partially aligned samples is quite limited, the magnetic circular dichroism (MCD) spectrum may contain valuable information. We shall here consider only the MCD *B*-terms which describe the MCD effect for molecules without degenerate states.¹⁵⁻¹⁷ We shall assume that the MCD spectra obtained can be separated into contributions from individual transitions. For each transition *f* the observed MCD effect is related to the MCD *B*-term (in units of debye² × Bohr magneton/cm⁻¹) by:

$$B(f) = 33.53^{-1} \int_f \tilde{\nu} d\tilde{\nu} [\theta]_M$$

where $[\theta]_M$ is the molar ellipticity, $\tilde{\nu}$ the wave number and the integration is carried out over the region corresponding to transition *f*.

The assumption of separate transitions is usually fulfilled at best for a few transitions. For most transitions an approximate separation must be performed, *e. g.* based on the assumption of similar lineshapes in the MCD and absorption spectra.

From the two spectra obtained, $B_{XY}(\tilde{\nu})$ from the aligned sample, and $B_{\text{iso}}(\tilde{\nu})$ from an isotropic sample containing the same number of molecules in the light path, quantities $B_{XY}(f)$ and $B_{\text{iso}}(f)$ corresponding to transition *f* can be determined. They fulfill the relations:^{4,3}

$$B_{XY}(f) = 3 \sum_{u,v} K_{uv} B_{uv}(f)$$

$$B_{\text{iso}}(f) = \sum_{u,v} B_{uv}(f)$$

where in case of real wavefunctions:

$$B_{uv}(f) = \sum_{j \neq f} G_u'(fj) H_v'(jf) + \sum_{j \neq 0} G_u''(fj) H_v''(j)$$

Here the summations run over all electronic states except state f and the ground state 0 , respectively. The indices u, v represent molecular axes x, y, z , and G_u, H_v are components of vectors \mathbf{G} and \mathbf{H} , where:

$$\begin{aligned}\mathbf{G}'(fj) &= \mathbf{M}_f \times \mathbf{M}_j \\ \mathbf{G}''(fj) &= \mathbf{M}_f \times \mathbf{M}_{jf} \\ \mathbf{H}'(jf) &= \boldsymbol{\mu}_{jf}/(E_f - E_j) i \\ \mathbf{H}''(j) &= \boldsymbol{\mu}_j/(E_j - E_0) i\end{aligned}$$

Here i is the imaginary unit, \mathbf{M}_{ji} is the electric dipole transition moment between states f and j , $\boldsymbol{\mu}_{jf}$ the magnetic dipole transition moment between the two states, $\boldsymbol{\mu}_j$ the magnetic dipole transition moment between the ground state 0 and state j , and E_f the energy of state f .

For a molecule with two perpendicular symmetry planes (the »high-symmetry case«), only $K_{uu} = K_x, K_y$, or K_z are nonzero and the above expressions for $B_{X,Y}(f)$ and $B_{\text{iso}}(f)$ become^{4,3}

$$\begin{aligned}B_{X,Y}(f) &= 3 [K_x B_{xx}(f) + K_y B_{yy}(f) + K_z B_{zz}(f)] \\ B_{\text{iso}}(f) &= B_{xx}(f) + B_{yy}(f) + B_{zz}(f)\end{aligned}$$

As an example let us consider a z -polarized transition f . From the definition it is clear that the components G_z' and G_z'' vanish; this means that $B_{zz}(f) = 0$. For the remaining two components we have

$$\begin{aligned}B_{xx}(f) &= [B_{X,Y}(f) - 3 K_y B_{\text{iso}}(f)]/3 (K_x - K_y) \\ B_{yy}(f) &= [B_{X,Y}(f) - 3 K_x B_{\text{iso}}(f)]/3 (K_y - K_x)\end{aligned}$$

which shows that $B_{xx}(f)$ and $B_{yy}(f)$ can be determined from experimental observations.

The quantum mechanical description of the term $B_{xx}(f)$ ^{17,4} shows that it can be written as a sum of terms corresponding to magnetic mixing of excited states with electric dipole transition moments \mathbf{M}_j along y into state f , and of excited states with magnetic dipole transition moments $\boldsymbol{\mu}_j$ along x into the ground state 0 . The first kind of terms are usually by far the most important.

Similarly, $B_{yy}(f)$ corresponds to a sum of terms representing magnetic mixing of electric dipole x -polarized excited states into f and magnetic dipole y -polarized excited states into 0 . If the terms corresponding to mixing into the ground state are neglected, the separation of the contributions $B_{xx}(f)$ and $B_{yy}(f)$ corresponds to experimental determination of relative importance of the two major contributions to the MCD of the (z -polarized) transition to state f : The magnetic mixing of states corresponding to electric dipole y -polarization and that of states corresponding to electric dipole x -polarization into state f .

Similar separations can be obtained also for x - and y -polarized transitions. This kind of experimental information may help answer a number of important questions in the theory of MCD spectroscopy. For example, for planar molecules, it will be possible to determine the importance of mixing of out-of-plane (x) polarized $n\pi^*$ transitions into in-plane (y or z) polarized $\pi-\pi^*$ transitions.

For molecules with lower symmetry, where the transition moment directions are not restricted to the directions of the molecular x -, y -, and z -axes,

the interpretation of the MCD of aligned samples will be considerably more complicated, and it will not be discussed here.

TWO-PHOTON PROCESSES

As mentioned in the introduction, four important types of two-photon processes can be studied in uniaxially aligned samples. As for absorption, the observed result depends both on the molecular orientation distribution, on the anisotropic molecular properties, and on the polarization of the electromagnetic radiation used. If both photons are linearly polarized, five different spectra can be recorded:^{5,3}

$$ZZ, ZX (=ZY), XZ (=YZ), XX (=YY), XY (=YX)$$

The two labels indicate the direction in the sample axes system of the electric vectors of the first and second photon, respectively. Thus, the labels UV correspond to an experiment in which the first photon has its electric vector along sample axis U and the second has its electric vector along sample axis V .

If circular polarization is used, two different experiments are relevant. In both cases, the two photons propagate along the sample Z -axis, but in one case they have the same circular polarization, in the other opposite polarizations.^{4,3}

The observed intensity can be written as a sum of contributions due to individual two-photon processes characterized by labels (j, f) , where j refers to the first and f to the second step of the process. Thus, the absorption process in photoluminescence brings the molecule into the excited state j from which the second step takes it to the final state f . In a Raman scattering experiment, j contains information about the wavelength of the incident photon, while f contains information about the final vibrational level. A more detailed description of the information necessary for the characterization of the two-photon process can be found elsewhere, together with a discussion on the relation between the observed intensity and the contributions for individual processes (j, f) .^{5,3}

The general expression for the contribution from the (j, f) process can be written as a scalar product of two tensors of rank four:

$$E_{UV}(j, f) = \sum_{stuv} [{}^{(4)}P_{UV}]_{stuv} [{}^{(4)}O(j, f)]_{stuv}$$

where s, t, u, v are molecular axes x, y, z and tensor ${}^{(4)}P_{UV}$ depends on the choice of polarizations (U, V) and contains only information on the orientation distribution. This is expressed through orientation factors K and L . Tensor ${}^{(4)}O$ depends on the process studied and on the relevant molecular optical properties. The difference between the simultaneous and successive two-photon processes occurs through ${}^{(4)}O$. In the case of Raman scattering ${}^{(4)}O$ corresponds to the direct product of the Raman scattering tensor with itself. For a photoluminescence process it corresponds to a product of transition moments \mathbf{M} :

$${}^{(4)}O(j, f)_{stuv} = M_s(j) M_t(f) M_u(j) M_v(f)$$

where e. g. $M_s(j)$ is the component along molecular axis s of the transition moment of transition j .

General expressions for \mathbf{P}_{UV} have been given elsewhere, both for linear^{18,5} and circular^{3,4} polarization.

In order to illustrate the usefulness of the expression let us consider a very simple example: the photoluminescence using linear polarization of a molecule with two perpendicular planes of symmetry. In this symmetrical case, the tensors $^{(4)}\mathbf{O}_{UV}$ become extremely simple, cf. the general rules given earlier for orientation factors. The nonvanishing elements are:

$$\begin{aligned} (P_{UV})_{stst} &= L_{stst} \\ (P_{XZ})_{stst} &= (K_t - L_{stst})/2 \\ (P_{ZX})_{stst} &= (K_s - L_{stst})/2 \\ (P_{XX})_{stst} &= [(1 + 2\delta_{st})(1 - K_s - K_t) + 3L_{stst}]/8 \\ (P_{XY})_{stst} &= [(3 - 2\delta_{st})(1 - K_s - K_t) + L_{stst}]/8 \end{aligned}$$

Similarly as in absorption, spectral features (peaks, shoulders, etc.), corresponding to the transition moment direction \mathbf{M}_j along molecular axis s in absorption and the direction \mathbf{M}_f along molecular axis t in emission, must be located. Using the above expressions for the elements of tensor \mathbf{P}_{UV} , linear combinations of the spectra can be found in which the s, t -polarized feature disappears, and orientation factors K_s, K_t , and K_{stst} can be determined.¹⁹ The procedure is then repeated for a differently polarized set of transitions j, f . As an example, we show the values obtained in this kind of study for the planar »high-symmetry« molecule 2-fluoropyrene oriented in stretched polyethylene:¹⁹

$K_x = 0.08$	$K_y = 0.29$	$K_z = 0.63$
$L_x = 0.00$	$L_y = 0.12$	$L_z = 0.42$
$L_{yz} = 0.15$	$L_{xz} = 0.06$	$L_{xy} = 0.02$

The knowledge of the orientation factors L in addition to the K 's gives a considerable contribution to the understanding of the orientation distribution.

The second equally important piece of information which can be extracted from the five spectra are the curves corresponding to the absorbing and emitting transitions, separated into x -, y -, and z -polarized contributions. As in absorption, this information may reveal hidden components and make assignments much simpler.¹⁹

CONCLUSIONS

Spectroscopy with polarized light on aligned samples is experimentally becoming more and more simple. If a proper mathematical description of the molecular alignment is used for the interpretation of the spectra, the rewards are considerable. Information is obtained both on molecular alignment and on anisotropic optical properties of molecules. The latter are of interest not only in connection with the spectroscopy of the molecule studied but of importance also for the evaluation of quantum mechanical descriptions of the molecule.

REFERENCES

1. B. Nordén, *Appl. Spectrosc. Rev.* **14** (1978) 157, *Applications of Liquid Crystals*, G. Meier, E. Sackmann, and J. G. Grabmaier, Springer Verlag, Berlin, 1975.
2. *Aspects of the LD and MCD of Planar Organic Molecules*, E. W. Thulstrup, Springer Verlag, Heidelberg, 1980.
3. *Optical Spectroscopy of Partially Aligned Solutes*, J. Michl and E. W. Thulstrup, Academic Press, in press.
4. E. W. Thulstrup and J. Michl, *Int. J. Quantum Chem. Symp.* **17** (1983) 471.
5. J. Michl and E. W. Thulstrup, *J. Chem. Phys.* **72** (1980) 3999.
6. E. W. Thulstrup and J. Michl, *J. Phys. Chem.* **84** (1980) 82.
7. E. W. Thulstrup, J. Michl, and J. H. Eggers, *J. Phys. Chem.* **74** (1970) 3868.
8. J. Michl, E. W. Thulstrup, and J. H. Eggers, *J. Phys. Chem.* **74** (1970) 3878.
9. E. W. Thulstrup and J. Michl, *J. Amer. Chem. Soc.* **104** (1982) 5594.
10. J. G. Radziszewski and J. Michl, *J. Phys. Chem.* **85** (1981) 2934.
11. J. Michl and E. W. Thulstrup, *Spectrosc. Lett.* **10** (1977) 401.
12. E. W. Thulstrup and J. H. Eggers, *Chem. Phys. Lett.* **1** (1968) 690.
13. E. W. Thulstrup, *Int. J. Quantum Chem. Symp.* **3** (1970) 641.
14. J. Kolc, E. W. Thulstrup, and J. Michl, *J. Amer. Chem. Soc.* **96** (1974) 7188.
15. A. D. Buckingham and P. J. Stephens, *Annu. Rev. Phys. Chem.* **17** (1966) 399.
16. P. N. Schatz and A. J. McCaffery, *Q. Rev. Chem. Soc.* **23** (1969) 552.
17. J. Michl, *J. Amer. Chem. Soc.* **100** (1978) 6801; **100** (1978) 6812.
18. E. W. Thulstrup and J. Michl, *J. Mol. Struct.* **61** (1980) 175.
19. F. W. Langkilde, M. Gisin, E. W. Thulstrup, and J. Michl, *J. Phys. Chem.* **87** (1983) 2901.

SAŽETAK

Interpretacija optičkih spektara djelomično uređenih uzoraka

Erik W. Thulstrup

Spektroskopsko istraživanje uzoraka izgrađenih od djelomično orijentiranih molekula s pomoću linearno i kružno polariziranog svjetla daje niz korisnih informacija. Iako razdioba molekulskih orijentacija nije potpuno poznata, njezine glavne značajke omogućuju interpretaciju optičkih spektara. Na taj način dolazimo do podataka o anizotropnim optičkim svojstvima molekula: do prijelaznih momenata, MCD B-terma, Ramanovih tenzora polarizabilnosti itd. U ovom članku dan je pregled najnovijih istraživanja u tom području kao i matematički model za opis molekulskih orijentacija i optičkih svojstava.