Ultraviolet and Infrared Linear Dichroism: Polarized Light as a Probe of Molecular and Electronic Structure

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Introduction

This review marks the 20th anniversary of our collaboration on polarized UV, visible, and IR spectroscopy, primarily on linear dichroism (LD) of organic molecules oriented in stretched polyethylene or by photoselection. This offers a facile way of determining transition moment directions of vibrational and electronic transitions in molecules. A 600-page survey of optical spectroscopy on partially aligned solutes, including also measurements of optical activity, Raman scattering, luminescence, etc., and referring to the work of others, has appeared elsewhere.[2] Here, we focus on UV and IR LD studies by our two research groups and illustrate the application of LD to problems in molecular and electronic structure.

Absorption and emission of light by molecules are mediated primarily by the resonant interaction of the imposed electromagnetic field (or of the spontaneous fluctuations of the zero field of vacuum) with the electric dipole moments of molecular "superposition" states $|\Psi\rangle = \sum_n c_n e^{-iE_n t/\hbar}|n\rangle$ that the field induces by mixing the molecular stationary states $e^{-iE_n t/\hbar}|n\rangle$. There, c_n are the mixing coefficients, E_n is the energy of the nth state, and t is time. The dipole moment of the superposition state is $\langle\Psi|\hat{\mathbf{M}}|\Psi\rangle$, where $\hat{\mathbf{M}}$ is the electric dipole moment operator. Substitution for Ψ shows that the moment oscillates at the beat frequencies dictated by the time-dependent factors $e^{-iE_n t/\hbar}$.

In the superposition state for the excitation from state $|i\rangle$ to state $|j\rangle$, the beat frequency is $\nu_{ij} = (E_j - E_i)/h$ Hz, and the maximum value of the oscillating dipole moment is proportional to $\langle j|\hat{\mathbf{M}}|i\rangle$. The requirement for resonance imposes the familiar condition on the light frequency, $h\nu = E_j - E_i$. The quantity $\langle j|\hat{\mathbf{M}}|i\rangle$ is called the electric dipole transition moment and is denoted $\mathbf{M}_{ij}$. Since it represents an oscillation amplitude, its length and direction are time-independent and meaningful, but its sense is arbitrary and has no effect on observable properties.

While $|\mathbf{M}_{ij}|$ is readily determined from integrated transition intensity in isotropic solution, the determi-

nation of the direction of the vector $\mathbf{M}_{ij}$ in the molecular framework, known as the polarization direction of the transition $i \to j$, requires a directional measurement. In liquids and solids this calls for the use of polarized light and of partially or fully aligned molecular assemblies, since the contribution of a molecule to the absorption or emission of plane-polarized light whose electric vector lies in the laboratory axis U ($U = X,Y,Z$) is proportional to the square of the projection of $\mathbf{M}_{ij}$ into U.

Many absolute polarization measurements have been performed on single crystals. This tedious procedure often suffers from the presence of intermolecular interactions. The use of an inert orienting environment is easier (host single crystal, liquid crystal, membrane, stretched polymer), as is photoselection, in which U-polarized light of a particular frequency is absorbed by interacting with the moments $\mathbf{M}_{ij}$ of a set of randomly oriented but rigidly held molecules. The excited subassembly, as well as the subassembly of molecules that remained unexcited, is partially aligned with respect to U. These methods generally yield only relative polarizations, i.e., relative orientation of the various vectors $\mathbf{M}_{ij}$, unless the nature of molecular alignment is known from an independent source (e.g., for solutes in stretched polyethylene, from the molecular shape). Other tools can be used to orient molecules, e.g., electric field.

In our work, aligned solutions were obtained either (i) by diffusing the substrate into stretched (400–600%) polyethylene from vapor or from a concentrated solution (up to about 400% elongation the degree of solute alignment increases rapidly with the degree of stretching, but then it only grows moderately) or (ii) by photoselection in organic glasses at 77 K (polarized luminescence and UV–vis dichroism) or frozen gas matrices at 5–20 K (also IR dichroism).

In the following survey of our results, we first describe partial alignment quantitatively by introducing "orientation factors". We then show how to extract from the observed linear dichroism of high-symmetry molecules the values of these factors and also the purely polarized spectra. The relations of the orientation factors of molecules contained in stretched polymers to their shape and the relations of those of photoselected molecules to their absorption properties, or to those of their precursors, are discussed next. Two examples are considered in detail. The more difficult analysis of

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linear dichroism of low-symmetry molecules follows and is again illustrated by examples.

The subsequent sections deal with more specialized topics: the use of isotopic substitution, solvent effects, and generalization to two-photon processes. We also mention very briefly possible applications to excitation energy migration dynamics and to optical recording.

Orientation Factors. Polyethylene stretched along Z and samples aligned by photoselection with Z-polarized light are uniaxial, with all directions perpendicular to Z physically equivalent. Only two linearly independent polarized spectra can be measured, and we choose E_Z and E_Y, with the light electric vector along Z and Y, respectively. For a partially aligned molecular assembly, the absorbance E_U ($U = X,Y,Z$) due to the jth transition is proportional to the average of the square of the projection of the jth transition moment $\mathbf{M}_{0j}$ into U

$$E_U \propto \langle (\epsilon_U \cdot \mathbf{M}_{0j})^2 \rangle = |\mathbf{M}_{0j}|^2 \langle \cos^2{(j,U)} \rangle \qquad (1)$$

where ϵ_U is a unit vector along U, (j,U) is the angle between $\mathbf{M}_{0j}$ and U, and the pointed brackets indicate averaging. Since $\langle \cos^2{(j,X)} \rangle$ and $\langle \cos^2{(j,Y)} \rangle$ are equal and since the squares of direction cosines add up to one

$$E_Z(j) \propto |\mathbf{M}_{0j}|^2 \langle \cos^2{(j,Z)} \rangle = |\mathbf{M}_{0j}|^2 \langle \cos^2{\omega_j} \rangle = |\mathbf{M}_{0j}|^2 K_j \qquad (2)$$

$$E_Y(j) \propto |\mathbf{M}_{0j}|^2 \langle \cos^2{(j,Y)} \rangle =$$
$$|\mathbf{M}_{0j}|^2 (1 - \langle \cos^2{\omega_j} \rangle)/2 = |\mathbf{M}_{0j}|^2 (1 - K_j)/2 \qquad (3)$$

$$d_j = E_Z(j)/E_Y(j) = 2K_j/(1 - K_j) \qquad (4)$$

If only the jth transition contributes to absorbance, the polarized absorption intensities E_U and the dichroic ratio d_j are thus dictated by the *orientation factor* of the jth transition moment, $K_j = \langle \cos^2{\omega_j} \rangle$, which can acquire values between zero and one. In a random (isotropic) solution $K_j = {}^1/_3$, $d_j = 1$ for any j. In partially aligned solutions $K_j > {}^1/_3$, $d_j > 1$ for transition moments $\mathbf{M}_{0j}$ that tend to line up parallel to Z and $K_j < {}^1/_3$, $d_j < 1$ for those that prefer to lie perpendicular to Z.

High-Symmetry Molecules[2-4]

In symmetrical molecules, only some transition moment directions are possible. The three components of $\hat{\mathbf{M}}$ transform like the molecular axes x, y, and z. The presence of a symmetry plane σ causes all transition moments either to be perpendicular to σ (antisymmetric) or to lie in σ (symmetric). The presence of a twofold axis C_2 causes all moments either to lie in C_2 (symmetric) or to be perpendicular to C_2 (antisymmetric). The presence of two or more symmetry elements usually leaves only three possible transition moment directions, taken to coincide with the molecular axes, x, y, and z ("high-symmetry" molecules, e.g., point groups C_{2v} and D_{2h}). This allows at most three distinct K_j values and at most three distinct d_j values, permitting the use of linear dichroism to recognize the absence of such molecular symmetry.

In high-symmetry molecules, the orientation factors of the three possible types of transitions immediately provide the orientation factors of the x, y, and z axes, $K_x = \langle \cos^2{\tilde{x}} \rangle$, $K_y = \langle \cos^2{\tilde{y}} \rangle$, and $K_z = \langle \cos^2{\tilde{z}} \rangle$, where $\tilde{x}$, $\tilde{y}$, and $\tilde{z}$ are the angles that the molecular x, y, and z axes form with Z. We use the convention $K_x \leq K_y \leq$

K_z. Since K_x, K_y, and K_z add up to unity, only two of them are independent. For a period of time, claims were made by some authors that already a single such parameter is generally adequate for the analysis of linear dichroism of uniaxial samples and numerous incorrect results appeared in the literature as a result, but this notion now seems to have been abandoned (for a discussion, see ref 2, 4, and 5).

The molecular orientation factors K_x, K_y, K_z are obtained simply from the measured dichroic ratios d_j as long as regions of purely polarized absorption can be found for at least two of them, as is common in IR spectra. In a spectral region purely polarized along u ($u = x,y,z$), (4) yields

$$K_u = d_u/(2 + d_u) \qquad (5)$$

In the general case of overlapping transitions

$$E_Z = K_z A_z + K_y A_y + K_x A_x \qquad (6)$$

$$E_Y =$$
$$[(1 - K_z)/2]A_z + [(1 - K_y)/2]A_y + [(1 - K_x)/2]A_x \qquad (7)$$

where the reduced spectrum A_u is the sum of all contributions to absorption that are due to u-polarized transitions. The dichroic ratio $d = E_Z/E_Y$ now has no simple significance. The orientation factors can be determined as long as spectral features attributable to A_x, A_y, and A_z can be recognized, even if they mutually overlap, by using a trial-and-error method (TEM) in which linear combinations $E_Z - dE_Y$ are constructed until a value $d = d_u$ is found in which u-polarized features just disappear.[2-4,6-8] According to (6) and (7) the weight with which A_u enters is $K_u - d[(1 - K_u)/2]$, so that

$$d_u = 2K_u/(1 - K_u) \qquad (8)$$

In special cases, it is possible to convert the observed polarized spectra E_Z and E_Y into reduced spectra. If $K_x = K_y$, the spectral curves $(A_x + A_y)/2$ and A_z can be obtained, if $K_y = K_z$, $(A_y + A_z)/2$ and A_x can be obtained, and if A_x, A_y, or A_z vanishes in the region of interest, the remaining two can be obtained. In many aromatic molecules the out-of-plane polarized absorption A_x is negligible in the visible and near-UV regions. Then, (6) and (7) yield

$$A_y = [2K_z E_Y - (1 - K_z)E_Z]/(K_z - K_y) \qquad (9)$$

$$A_z = [(1 - K_y)E_Z - 2K_y E_Y]/(K_z - K_y) \qquad (10)$$

and A_z (A_y) is proportional to that linear combination of E_Z and E_Y in which y-polarized (z-polarized) spectral features just disappear.

Figure 1 illustrates the cases of negligible overlap (IR) and of strong overlap (UV) for a high-symmetry molecule. The IR spectra of anthracene[9] led to an immediate symmetry assignment for 36 vibrations and to a correction of prior misassignments. The UV spectra of anthracene[10] identify the short in-plane axis polarized

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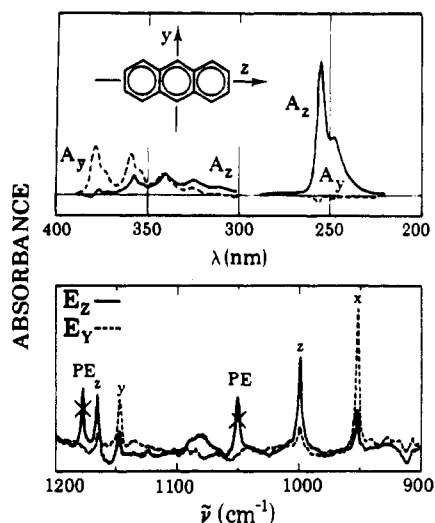
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Figure 1. Anthracene in stretched polyethylene. (top) The reduced UV spectra A_z and A_y. Reproduced with permission from ref 2. Copyright 1986 VCH Publishers. (bottom) The experimental IR spectra E_Z and E_Y. The polarization of the individual vibrations is indicated. PE represents peaks due to polyethylene. Adapted from the material reported in ref 9. Copyright 1985 American Institute of Physics.

L_a transition and the long axis polarized B_b transition. Their assignments were known from prior work and provide an absolute attribution of the three IR dichroic ratios to x-, y-, and z-polarized transitions. The series of long axis polarized peaks in the region of the L_a band (300–400 nm) could be due to vibronic interactions or to the anticipated presence of a "hidden" electronic transition (L_b). Such ambiguity is frequently present in electronic spectra. In this case, subsequent MCD measurements established the L_b assignment.[11]

Similar absolute assignment of one or more transition moment directions was already known for many additional solutes. A comparison revealed that solute alignment in stretched polyethylene is determined primarily, but not solely, by its shape: when viewed in the Z direction, the solute exposes its smallest cross section. In our notation, the "long" axis of the molecule is z and the "short" axis is x. Aromatic molecules tend to orient with their plane (y,z) parallel to Z and their out-of-plane axis x perpendicular to Z; the longer of the two in-plane axes, z, tends to line up preferentially with Z.[12–14]

The Orientation Triangle.[2,4,5,12,13,15–19] A plot of K_z against K_y for a large number of solutes in stretched polyethylene is shown in Figure 2. The condition $K_x \leq K_y \leq K_z$ restricts all possible points to the "orientation triangle". The point $(^1/_3,^1/_3)$ corresponds to samples without useful alignment, such as isotropic solutions. The point $(1,0)$ corresponds to a perfect alignment of all z axes along Z. The line joining the points $(^1/_3,^1/_3)$ and $(1,0)$ corresponds to all alignments

in which $K_x = K_y$ (e.g., rodlike molecules). The point $(^1/_2,^1/_2)$ corresponds to a perfect alignment of the molecular yz plane with Z, with no discrimination between y and z. The line connecting the points $(^1/_3,^1/_3)$ and $(^1/_2,^1/_2)$ corresponds to all orientations in which $K_y = K_z$ (e.g., disklike molecules). The line joining the point $(^1/_2,^1/_2)$ with $(1,0)$ corresponds to a perfect alignment of the yz plane with Z, with y and z inequivalent.

In Figure 2, points for disk-shaped and approximately rod-shaped molecules indeed lie in the expected locations, and an increasing difference between K_y (= K_z) and K_x or between K_z (= K_y) and K_x (= K_y) moves the point away from the lower vertex, $(^1/_3,^1/_3)$. The longest and thinnest molecules approach the limit (1,0) but do not reach it. A gradual deviation from the equality of K_y and K_z or of K_x and K_y moves the point from an edge into the interior of the triangle.

A comparison with molecules with known orientation factors permits a prediction of the orientation factors for a new molecule from its shape alone. Thus, absolute assignments of x, y, and z in the molecular framework are possible using the stretched polyethylene method even without reliance on outside spectroscopic information.

The knowledge of the orientation factors alone does not establish the exact nature of the orientation, and each point in the orientation triangle except for (1,0) corresponds to an infinite number of possible orientation distribution functions. However, knowledge of the distribution function permits a calculation of the K_u values and determines a point in the orientation triangle. For instance, the orientation factors of a very small subset of molecules photoselected from a random sample with Z-polarized light are fully determined by the nature of the absorbing event.[2] If the absorption is purely z-polarized, $K_z = 0.6$, $K_x = K_y = 0.2$. If it has equal y-polarized and z-polarized components, $K_z = K_y = 0.4$, $K_x = 0.2$. In general, $K_u = (1 + 2r_u)/5$, where r_u is that fraction of the photoselecting absorption that is polarized along u. The remaining set of molecules is not oriented ($K_u = {}^1/_3$).

If the degree of depletion of the original ground state is not negligible, both the photoselected and the remaining set of molecules are uniaxially oriented with respect to Z in a predictable fashion.[2] In the limit of nearly complete phototransformation, the remaining infinitesimally small set of untransformed molecules has $K_y = K_z = {}^1/_2$, $K_x = 0$ if the photoselecting absorption was x-polarized and $K_z = 1$, $K_y = K_x = 0$ if it had equally intense components polarized along x and y. In this limit, the transformed set of molecules is not oriented ($K_u = {}^1/_3$).

Examples of Application. We have used the measurement of linear dichroism in stretched polyethylene to obtain UV–vis reduced spectra for many high-symmetry solutes. This permitted the detection of numerous otherwise hidden transitions and symmetry assignment of scores of electronic states, and it thus contributed to the understanding of the relation between molecular structure and electronic structure in numerous alternant[3–5,10,15,20–30] and nonalternant[4,6,16,31–39]

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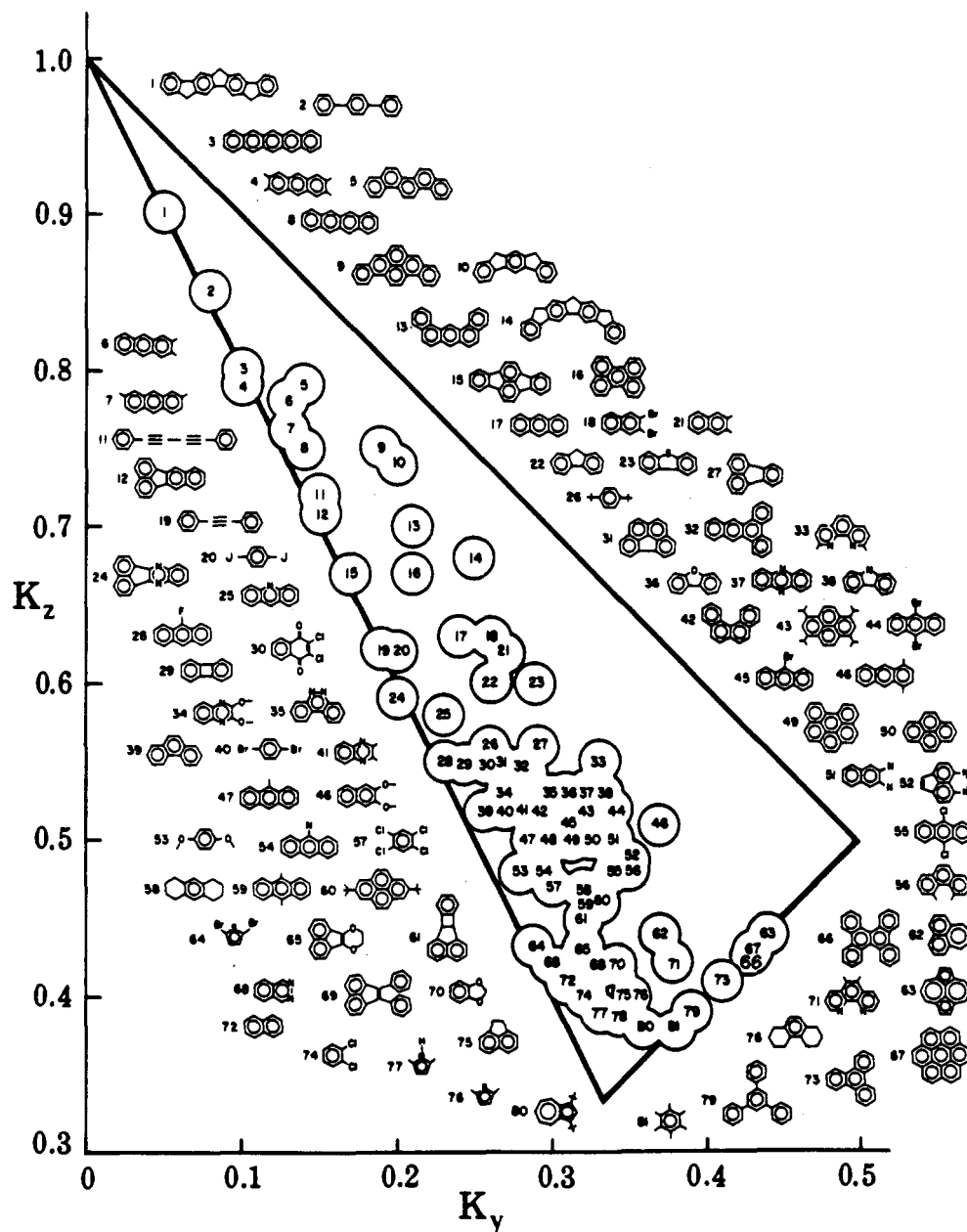(17) Michl, J.; Thulstrup, E. W. *Spectrosc. Lett.* **1977**, *10*, 401.

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Figure 2. Orientation of aromatic molecules in stretched polyethylene at room temperature. The horizontal axis in the formulas is *z*, and the vertical one is *y*. Reproduced by permission from ref 2. The formulas for phenazine (37) and acridine (25) were interchanged by mistake in Figures 5 and 7 of the original paper.[12]

aromatics, their substituted derivatives[10,16,33] and heterocyclic analogues,[17,21,31,40–46] as well as bridged an-

nulenes[47,48] and polyolefinic molecules.[28,49,50] Similar measurements in the IR region permitted symmetry assignments for numerous vibrational states.[9,13,51–53]

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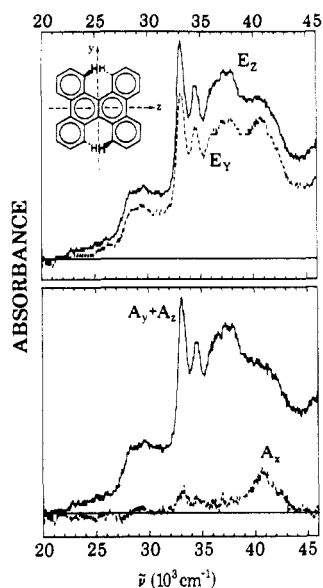
Figure 3. (top) Experimental dichroic spectra of dibenzo[a,j]-chrysene in stretched polyethylene: E_Z (solid) and E_Y (dashed). (bottom) Reduced spectra: $A_y + A_z$ (solid) and A_x (dashed). Reprinted with permission from ref 29. Copyright 1986 North-Holland Physics Publishing.

Measurements of linear dichroism of pleiadene oriented by two-photon photoselection[54] confirmed the first assignment[55] of a predominantly doubly excited state of an organic molecule.

In some cases, structural information resulted as well, and two illustrative examples follow. Stepwise reduction of the polarized spectra of *dibenz[a,j]chrysene* in stretched polyethylene (Figure 3)[29] yields the K value 0.42 for all spectral features except a peak at 40650 cm⁻¹ for which 0.16 is obtained. By difference to unity, K_x = 0.16, $K_y = K_z = 0.42$. By inspection of Figure 2 and of molecular shape, it is clear that the x axis is perpendicular to the "molecular plane". The intense reduced spectrum in Figure 3 represents $A_y + A_z$ and thus the sum of both "in-plane" polarized spectra, while the less intense one is A_x so that the 40650-cm⁻¹ peak is "out-of-plane" polarized. Its intensity is orders of magnitude higher than usual for σ–π^* and π–σ^* transitions in planar π-electron systems. We conclude that the molecule is actually nonplanar (D_2 symmetry) so that transitions that are nominally of the $\pi\pi^*$ type can be polarized along any one of the three axes.

The structure of the *minor conformer of 1,3-buta-diene* has long been a subject of controversy. Some calculations predict a planar equilibrium geometry (1, C_{2v}, s-cis), and others a twisted geometry (2, C_2, gauche). Matrix-isolated samples of 1,3-butadiene enriched in the minor isomer can be obtained by trapping high-temperature vapor.[56] The UV absorption spectrum of the minor conformer suggests that it does not deviate much from planarity.[56,57]

The minor conformer isolated in several matrices was aligned by irradiation into its $\pi\pi^*$ transition, converting about half into the s-trans conformer. IR dichroism of the remaining minor conformer was measured, and in each matrix environment only two distinct orientation factors were observed for the ten observable IR bands.[58] One (K_x) was lower and the other ($K_y = K_z$) was higher than $1/3$, with $\sum_u K_u = 1$. This fits for C_{2v} symmetry: the x axis lies along C_1–C_4; the y and z axes are perpendicular to it. In a C_2 molecule, the x axis would still be parallel to the $\pi\pi^*$ transition moment and therefore would lie nearly along C_1–C_4, but IR transition moments would now lie at a variety of angles to x, virtually all different from the right angle, so that their orientation factors would have a variety of values smaller than K_y = $K_z = (1 - K_x)/2$. The conclusion is that, at least in the condensed phase, the minor isomer has the planar s-cis structure. This is further supported by the absence of IR bands assigned to a₂ symmetry in the C_{2v} symmetry limit.
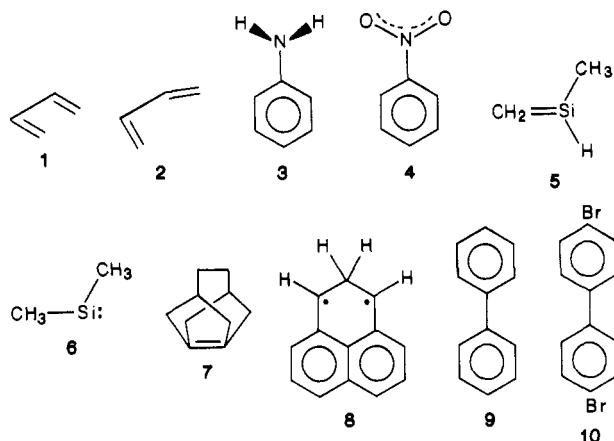
Low-Symmetry Molecules

When molecular symmetry does not define the x, y, and z axes, the natural choice are the principal axes of the orientation tensor: The z axis is that direction firmly connected with the molecular frame that is the best aligned with Z (maximum K_z). The x axis is the direction that is the worst aligned (minimum K_x). The y axis lies at right angles to x and z and aligns the best among all those perpendicular to z and the worst among all those perpendicular to x. These principal axes are determined by choosing an arbitrary orthogonal set of axes x',y',z' and diagonalizing the orientation tensor with elements $K_{u'v'} = \langle \cos u' \cos v' \rangle$ $(u',v' = x',y',z')$. The eigenvalues are K_x, K_y, and K_z, and the eigenvectors define the transformation from the arbitrary system x',y',z' to the principal system x,y,z.

Unless a transition moment $\mathbf{M}_{0j}$ happens to lie in the principal axes x or z, we have $K_x < K_j < K_z$, and K_j may accidentally equal K_y even if $\mathbf{M}_{0j}$ is not directed along y. The orientation of $\mathbf{M}_{0j}$ within the molecular frame of axes x,y,z cannot be determined in such a general case from the mere knowledge of K_j, since it is described by two independent parameters, say two of its direction cosines with respect to x, y, and z, $\cos \phi_j^u$ $(u = x,y,z)$. If additional information is available, the problem can be solved.[2,4,59] For example, if a single element of sym-

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metry restricts $\mathbf{M}_{0j}$ to the yz plane $(\cos \phi_j^x = 0)$

$$\tan^2 \phi_j^z = (K_z - K_j)/(K_j - K_y) \qquad (11)$$

This relation will also hold if the alignment is rodlike with respect to z, $(K_x = K_y)$, as in photoselection using a purely z-polarized absorbing transition.
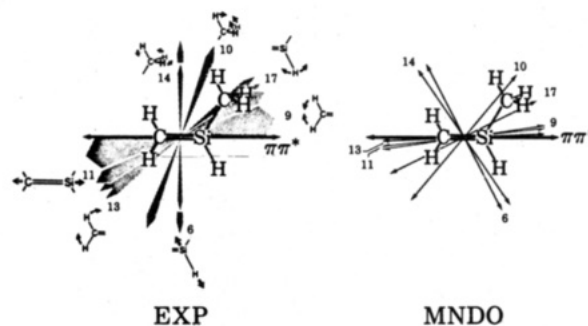
The use of (11) requires the knowledge of the principal orientation factors K_u. These are not accessible from the measurement of the orientation factors K_j even if the latter are determined for a large number of transitions j, except that $K_x \leq K_j \leq K_z$, $K_x \leq K_y \leq K_z$, and $K_x + K_y + K_z = 1$ must be satisfied. These conditions are frequently sufficiently restrictive to define the K_u's within narrow limits. In addition, molecular shape may provide additional information (Figure 2) and an estimate of the K_u's is usually quite easy to obtain. The remaining problem then is to estimate the position of the principal orientation axes in the molecule, and this can again be based on molecular shape.

With additional information, the above uncertainties can be reduced or removed altogether. Already the presence of a single symmetry element defines the direction of one of the principal axes. A priori knowledge of the absolute polarization directions for one or more transitions (e.g., a C=O stretch in the IR is polarized along the C—O axis) will also be extremely helpful.

Examples of Application. We have used the measurement of linear dichroism in stretched polyethylene, often combined with a measurement of polarized fluorescence, to obtain the polarizations of electronic[10,21,22,33,59-62] and vibrational[63-65] transitions in a series of low-symmetry molecules. These quantities provide a stringent test of the quality of computed electronic[66,67] and vibrational[65,68] wave functions. Structural information resulted in several cases, as illustrated below.

Aniline (3) and nitrobenzene (4)[13] have similar structures, but due to the pyramidalization at the amino group, the former is nonplanar (C_s) and the latter planar (C_{2v}). The lower symmetry of **3** is immediately apparent in the IR spectra in stretched polyethylene since its bands exhibit four distinctly different K_j values. Those of **4** display only three, as expected for C_{2v} symmetry.

The K_j's of all aniline vibrations polarized perpendicular to the plane of symmetry, such as the antisymmetric NH_2 stretch at 3485 cm^{-1}, are equal and define $K_y = 0.325 \pm 0.005$. The K_j's of many ring vibrations are equal either to 0.18 ("out-of-plane" bends) or to 0.50 $\pm$ 0.01 (symmetric "in-plane" vibrations). This suggests that their transition moments lie perpendicular to or parallel to the plane of the ring, respectively; the

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EXP   MNDO

Figure 4. Transition moment directions of in-plane polarized transitions of 1-methylsilene in the UV (black arrows) and IR (gray arrows) regions: left, experimental; right, calculated (MNDO for IR and INDO/S for UV transitions). Reproduced by permission from ref 68.
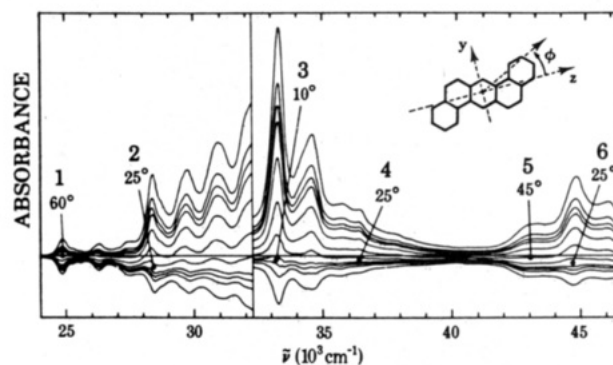
Figure 5. Dibenz[*a*,*h*]anthracene in stretched polyethylene. From top to bottom, linear combinations $aE_Z + bE_Y$ from $a = 0$, $b = -1$ to $a = 1$, $b = 0$, with a and b chosen so as to correspond to 15° increments in the angle ϕ between the molecular z axis and the transition moment (assuming $K_z = 0.75$, $K_y = 0.16$). For instance, spectral features for which $\phi = 75°$ disappear in the linear combination $0.66E_Z - 0.34E_Y$. Reprinted with permission from ref 22. Copyright 1981 Elsevier.

"out-of-plane" axis is assigned to x ($K_x = 0.18$), and the "in-plane" axis to z ($K_z = 0.50$). The polarization directions of the remaining vibrations can be determined from their K_j values and eq 11. If the s NH_2 stretch were polarized along the bisector of the HNH angle, the NH_2 pyramidalization degree would be about 20°. This is only a crude estimate, since any change in the degree of pyramidalization during the vibration may displace the direction of the IR transition moment away from the NH_2 bisector.

1-Methylsilene (5).[68,69] An illustration of the way in which IR transition moment directions map onto molecular structure is provided by 1-methylsilene in argon matrix (Figure 4).[68] Z-polarized irradiation into the $\pi\pi^*$ transition, polarized along Si=C (x), yields dimethylsilylene (6). The remaining molecules are partially oriented, with the Si=C direction possessing the orientation factor K_x. Since $K_y = K_z = (1 - K_x)/2$, eq 11 permits the evaluation of the angles that all IR transition moments make with x. Z-polarized irradiation into the n → p transition of **6**, polarized perpendicular to the CSiC plane, converts it back into **5**. If the conversion is incomplete, the latter is again oriented, but now with the normal to the CSiC plane (z) possessing the orientation factor K_z. Since now $K_x = K_y = (1 - K_z)/2$, eq 11 yields the angles that all IR tran-

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sition moments make with z. These are all either $0°$ or $90°$, and we conclude that 5 possesses a planar double bond. The combined results permit the assignment of IR vibrations as out-of-plane or in-plane polarized and, for each of the latter, yield two possible directions for the IR transition moment in the double-bond plane. The correct one is usually easily recognized by comparison with calculations (Figure 4) or, more simply, since it nearly coincides with a bond direction.

Similar matrix photoselection techniques were used to obtain vibrational polarization directions for the highly strained olefin 7, and it was shown to have lower than C_{2v} symmetry.[70]

Dibenz[a,h]anthracene (Figure 5).[22] The UV–vis transitions of this planar molecule are of $\pi\pi^*$ nature and in-plane polarized. A measurement of the spectra E_Z and E_Y followed by stepwise reduction yielded the K_j values for a series of transitions. These ranged from 0.33 (upper limit for K_x) to 0.74 (lower limit for K_z). From Figure 2, we estimate $K_y \simeq 2K_x$, $K_z \simeq 0.75$. In the following, we adopt the values $K_x = 0.09$, $K_y = 0.16$, $K_z = 0.75$, but slightly different sets such as $(0.10,0.10,0.80)$ yield quite similar results. From the molecular shape, we estimate the orientation axis z to be inclined about $15°$ from the long axis of the anthracene part of the molecule (Figure 5). Using eq 11, one can convert the observed K_j values into the angles $|\phi_j^z|$ of deviation between the jth moment and the z axis. In Figure 5, we have chosen the a and b values in the linear combinations $aE_Z - bE_Y$ such that they directly correspond to $15°$ increments in $|\phi_j^z|$ from $0°$ to $90°$. The sign ambiguity was removed by use of fluorescence polarization.

Use of Isotopic Substitution. This can aid in the identification of molecular vibrations, as illustrated in the first of the following examples. In the second example, we exploit the fact that the different effective sizes of D and H cause detectable isotopic effects on the orientation factors in small molecules, such as the haloforms, but not in large ones. There, it can be used to break molecular symmetry without affecting the position of the orientation axes and the values of orientation factors.

1,3-Perinaphthadiyl (8).[71] The C–H stretching vibrations of the $-\dot{C}H-CH_2-\dot{C}H-$ moiety in this photolabile triplet ground-state biradical produce symmetric and antisymmetric combinations, and specific deuteriation pinpoints these four vibrations in the argon-matrix-isolated molecule. Partially oriented samples resulted from monochromatic irradiation into y-polarized or z-polarized UV–vis absorption bands. These polarizations were known from linear dichroism in stretched polyethylene in which the biradical was produced at low temperature by irradiation of a cyclopropane precursor. The orientation of the latter in the polymer was known from the UV linear dichroism of its naphthalene chromophore. The K_j's for about 20 IR bands of 8 were obtained both for the sample remaining after photoselection on a y-polarized transition $[K_y(y) < K_x(y) = K_z(y)]$ and that remaining after photoselection on a z-polarized transition $[K_z(z) < K_x(z) = K_y(z)]$. (Note that here we abandon our standard

choice $K_x \le K_y \le K_z$ in order to keep the same labels in both aligned samples.) The four stretching vibrations of interest were assigned unambiguously from their dichroism. The results revealed a striking shift of the antisymmetric CH_2 and CD_2 stretches to low frequencies as a result of hyperconjugation with the radical centers and established C_{2v} symmetry for the molecule, anticipated originally but questioned[72] subsequently.

The Twist Angle in Biphenyl (9).[63] Planar in the crystal, 9 is twisted in the gas phase, and its conformation in solutions is unknown. Some derivatives, such as 4,4'-dibromobiphenyl (10), appear to have a twisted equilibrium geometry under all circumstances. The conformations of 9 and 10 dissolved in stretched polyethylene have been determined from measurements of IR linear dichroism of partially deuteriated derivatives.

Compounds 9 and 9-d_{10} have identical orientation factors ($K_x = 0.065$, $K_y = 0.413$, $K_z = 0.525$), as do 10 and 10-d_8 ($K_x = 0.226$, $K_y = 0.285$, $K_z = 0.502$). They were obtained from IR dichroic ratios via (5) since all vibrations have to be polarized along the x, y, or z twofold rotational symmetry axes regardless of the twist angle (D_{2h}, D_2, or D_{2d}). We assume that isotopic effects on the alignment are also absent in 9-$2,3,4,5,6$-d_5 and 10-$2,3,5,6$-d_4, which are of C_2 symmetry. In these, some IR transition moments lie in the symmetry axis z and are observed to share K_z with the corresponding transitions of 9, 9-d_{10} or 10, 10-d_8, respectively. Others are perpendicular to the z axis but need not coincide with the above x or y axes. Rather, if the vibrations of the two rings are weakly coupled, the moment directions will be dictated by local ring symmetry. The C–H (C–D) out-of-plane bends will be polarized perpendicular to the protiated (deuteriated) ring, and the moments of those in-plane vibrations of the two rings that do not lie in z should lie in the plane of the ring in which they are localized. For nonzero twist angles, we then expect two distinct values K_j and $K_{j'}$ for these localized vibrations, with $K_x < K_j$, $K_{j'} < K_y$. This is indeed observed for 10-d_4 ($K_j = 0.250$, $K_{j'} = 0.271$), and (11) yields a twist angle of 30–$40°$. For 9-d_5, however, $K_j = K_x$ and $K_{j'} = K_y$, showing that this molecule is planar. Already the reduced difference between K_x and K_y in 10 compared to 9 suggests that the former is more highly twisted, since at $90°$ twist K_x and K_y must be equal by symmetry, but this argument provides no estimate of the actual values of the twist angles.

Solvent Effects. The principal assumptions made in all of the above are (i) at least some purely polarized, even if possibly mutually overlapping, spectral features can be recognized in the E_Z and E_Y spectra, (ii) the sample is uniaxial, and (iii) solvent effects are isotropic. This level of treatment has become known as the TEM (Thulstrup–Eggers–Michl) model to distinguish it from the Fraser–Beer model,[73] the Popov model,[74] and the Tanizaki model,[75] which contain additional simplifying assumptions and are strictly applicable only to special classes of solutes.[2,4,5]

While the first two assumptions of the TEM model cause no trouble, problems may arise with the as-

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sumption that solvent effects are isotropic. First, the solvent environment affects transition energies and intensities in a fashion related to its refraction index n. In birefringent anisotropic media, corrections for the difference between n_Z and n_Y are necessary. In all of our samples, birefringence is very weak and these effects are hardly detectable. Second, the presence of the solute environment lowers the effective symmetry of a chromophore. This is true even in an isotropic solvent and leads to solvent-induced deviations of transition moments from the directions imposed by molecular symmetry in an isolated molecule. This phenomenon has been detected only for extremely weak electronic transitions,[76-78] but its existence needs to be kept in mind.

Two-Photon Processes. The expressions developed for one-photon absorption and emission by partially oriented samples have been generalized for processes involving two photons:[18,19,79,80] two-photon absorption, Raman scattering, photoluminescence, and photoinduced dichroism. They contain not only the second-rank orientation factors K_x, K_y, and K_z but also the fourth-rank orientation factors of the type $L_{stuv} = \langle \cos \bar{s} \cos \bar{t} \cos \bar{u} \cos \bar{v} \rangle$. All five independent second-rank and fourth-rank orientation factors for 2-fluoropyrene have been determined in stretched polyethylene[77] and revealed that there is very little scatter in the alignment angles $\bar{x}$, $\bar{y}$, and $\bar{z}$ among solute molecules. Results of this kind are important in establishing the microscopic details of the orienting mechanism.

Concluding Remarks

Transition moments of electronic and vibrational transitions are of great intrinsic importance in molecular spectroscopy and enter into expressions for secondary properties (optical activity, intermolecular interactions). They can be exploited in studies of molecular symmetry and conformation.

We believe that the stretched sheet and the photoselection techniques are the two simplest and fastest methods for obtaining transition moment directions in the UV-vis and IR regions. They permit a determination of state symmetries and detection of hidden transitions with remarkable ease, and to a large degree they are mutually complementary. Although we have not concentrated on them, dynamic studies are also possible. An example is a recent investigation of the nature of electronic excitation in a polysilane,[81] which showed that relatively short chain segments serve as nearly independent chromophores between which the excitation can jump.

A potentially practically useful side product has been the development of methods for both permanent[82-84] and erasable[85] optical information storage based on molecular alignment. The former is based on thermal relaxation of the birefringence of a dyed thin stretched polymer sheet in those microscopic areas that are heated as a result of irradiation with focused near IR light. The latter is based on photoinduced generalized pseudorotation of an otherwise rigidly held chromophore molecule capable of existing in two or more forms differing merely in orientation. A memory of the polarization direction of the light used in the most recent irradiation is then preserved in the form of the direction of the birefringence axes.

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