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minimum concentration and on the maximum W_0 values that will yield resolved ^{13}C–^{13}C and ^{13}C–^{15}N satellites. It is clear from Figure 3 that a W_0 of as much as 0.5 Hz still permits the resolution of ^{13}C–^{15}N and even long-range ^{13}C–^{13}C satellites. Here the big advantage of ultrahigh resolution methodology is the elimination of the very large instrumental contributions to the line width at the 0.1–0.5% intensity range (of the major resonance).[5] Even for W_0 = 1 Hz, one should expect to resolve many ^{13}C–^{15}N and long-range ^{13}C–^{13}C satellites. Very many large and complex molecules of chemical and biological interest exhibit ^{13}C line widths of no more than about 1 Hz.[25]

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Nondestructive Photoorientation by Generalized Pseudorotation: A Quantitative Treatment

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Abstract: A quantitative analysis is presented of the photooriented stationary state reached upon irradiation of matrix-isolated molecules capable of undergoing photoinduced pseudorotation or enantiomeric inversion between two forms related by mirroring in a symmetry plane, assuming negligible site memory effects. The photostationary orientation distribution is a simple function of the angle ω between the directions that the absorbing transition moment occupies in two forms. The lowest theoretical dichroic ratio d for the transition that is being pumped results for $\omega = \pi/2$ and equals 0.4. Experiments have been performed on octaethylporphine ($\omega = \pi/2$) in various rigid media; the lowest d value was observed in solid Ne at 3 K and equaled 0.46, revealing the absence of significant site memory effects. The potential of this type of measurement for the determination of UV and IR transition moment directions in matrix-isolated molecules and the potential usefulness of systems of this kind for erasable optical information storage are pointed out.

The anisotropic nature of polarized and/or collimated light can be used to achieve orientation of initially random molecular assemblies (photoorientation[1]). In sufficiently viscous media, such photoinduced orientation can be long-lived and can be exploited in various ways, from spectroscopic studies of the anisotropy of molecular properties to optical recording of information.

The orienting effect of light is due primarily to the interaction of its electric vector with permanent or induced molecular electric dipole moments. Presently, we focus attention on the photoorientation induced by the latter and due to the anisotropic nature of UV, visible, or IR light absorption. For a nondegenerate transition, the electric dipole absorption probability is proportional to $\cos^2 \delta$, where δ is the angle between the electric field direction Z of linearly polarized light and the molecular transition moment, whose position is fixed within the molecular framework. The orientation discriminating action of light is known as photoselection.[1-3]

Destructive photoorientation by photoselection on an originally random sample occurs for photolabile solutes. After partial photodestruction with Z-polarized light, the remaining solute molecules are partially oriented in that δ values close to $\pi/2$ are favored. The orientation is uniaxial with respect to Z and becomes perfect, with $\delta = \pi/2$, as the remaining amount of the original solute goes to zero.[3,4] The photoproduct is partially oriented as well, unless the phototransformation is accompanied by complete positional randomization. Photoproduct orientation is complementary to that of the remaining starting material and decreases with the increasing degree of conversion, finally disappearing when the photoconversion is complete.

Destructive photoorientation has been well-known for a long time and has found frequent use in molecular spectroscopy.[1-3] Cases in which the photoproduct is oriented and cases in which it is not have both been observed.[5]

Nondestructive photoorientation by photoselection on an originally random sample is possible in principle for solutes which are not bleached upon light absorption but has been observed to occur only rarely. This is unfortunate in view of its obvious advantages.

The simplest mechanism for nondestructive photoorientation by anisotropic absorption of Z-polarized light is photoinduced rotational diffusion. This should operate in principle for all solute molecules that convert at least some of the absorbed light energy into heat and a local decrease in viscosity. It should also yield perfect uniaxial orientation ($\delta = \pi/2$) in the limit of infinite irradiation time. However, it has apparently never been observed to produce an observable effect for molecules imbedded in frozen gas matrices, glasses, or polymers.[1] It is conceivable that a suitable choice of viscous solvent and of temperature may yet uncover the operation of this mechanism; evidence for enhanced translational diffusion upon nondestructive photoexcitation in 2-methyltetrahydrofuran glass ("internal melting") was reported some time ago.[6]

Successful nondestructive photoorientation has been reported in several instances in which molecular structural rearrangements are clearly at play, reproducing ultimately the initial solute molecule in a different orientation (orientation by photoinduced pseudorotation) or producing its enantiomer (orientation by photoinduced inversion). We shall refer to these two mechanisms jointly as photoorientation by generalized pseudorotation. Thus, certain metal carbonyls such as $Cr(CO)_5$ have been partially oriented in frozen gas matrices by a photoprocess believed to involve pseudorotation by motion of the CO ligands,[7] and various

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free-base porphyrins and phthalocyanin have been partially oriented in rigid glasses[8] by photoinduced pseudorotation involving the redistribution of the two central hydrogens among the four central nitrogen atoms (cf. ref 9–11). The facile nondestructive photoorientation of the bridgehead imine, azahomoadamantene,[12] is presumably due to the photochemical inversion of its enantiomers. Also, the photoorientation of certain defects in doped ionic single crystals is believed to proceed by a similar mechanism.[13]

Unlike orientation by photoinduced rotational diffusion, orientation by photoinduced generalized pseudorotation is not expected to approach perfect uniaxial alignment in the limit of infinitely long irradiation since the solute molecules now generally do not have the freedom to escape arbitrarily close to an orientation that makes further absorption impossible ($\delta = \pi/2$). The purpose of the present article is to describe the photostationary state of orientation in an initially isotropic system in a quantitative fashion.

We shall treat the simple but common case in which the solute molecule can exist in only two forms, related by mirroring in a plane of symmetry. The theoretical results will be compared with observations of nondestructive photoorientation of octaethylporphine in several rigid media at temperatures low enough to prevent thermal back reactions.

Experimental Section

Materials. Octaethylporphine (OEP) obtained from Sigma Chemical Co. was purified by gradient sublimation. Poly(vinyl chloride) (PVC) and poly(ethylene terephthalate) (PET) samples were prepared by soaking polymer sheets in saturated solution of OEP in benzene for 24–72 h. The poly(methyl methacrylate) (PMMA) sample was prepared by dissolving PMMA powder and OEP in benzene, pouring the solution on a glass plate, evaporating most of the solvent overnight, and removing the rest under reduced pressure.

3-Methylpentane (3-MP) and 2-methyltetrahydrofuran (2-MTHF) matrices were prepared from dried spectral grade solvents (Mallinckrodt) and were degassed immediately before use.

Samples. The doped polymer sheets were mounted on an Air Products Displex DE-202 closed-cycle helium cryostat between two sapphire windows cut for a birefrigence-free orientation. Frozen gas matrices were deposited from the gas phase on a 0.4 mm thick CsI window mounted on the same cryostat (Ar, N_2: 24 K) or on an Air Products LT-3-110 Heli-tran (Ar, 26 K; Ne, 5 K) and were then cooled down further for actual measurement. The OEP deposition cell was heated to 260–270 °C. The 3-MP and 2-MTHF glasses were prepared by immersing solutions in Suprasil quartz cells in liquid nitrogen in a Dewar equipped with flat Suprasil windows.

Measurements. High-pressure Xe arcs (300 W, from ILC Technology, or 1000 W, Oriel) combined with a set of filters (22 cm of water, Corning GG 4, UG 590, RG 610, and UG 3, and Balzers K-5 broadband interference filters) and a Glen-Thompson polarizer as well as a Lambda Physik (Models EMG 102 and FL 2002) XeCl-excimer-pumped dye laser (Rhodamine 101) were used as polarized sources of nearly monochromatic light in the region of the origin of the Q band of OEP (~620 nm). Irradiation was performed within the spectrometer, at sample temperatures ranging from 3 K (Ne matrix) to 77 K (3-MP and 2-MTHF glasses). Matrices were irradiated from the front, so that the light did not pass the CsI window. The dichroic ratio in the region of the origin of the Q band of OEP was recorded, and the irradiation was continued until no further decrease was noted. This took up to several hours.

Spectral measurements were performed on a Cary 17D UV–visible spectrophotometer, using Glan-Thomson polarizers. The matrix samples were oriented so that the light beam passed through the matrix before entering the CsI support window.

Errors in the measured dichroic ratios due to imperfect alignment of the optical components, depolarization by the sample, the windows, and the quartz cells are estimated to be less than 10%. Instrumental uncertainty of about 0.005 absorbance unit translates to less than 10% uncertainty in the dichroic ratio.

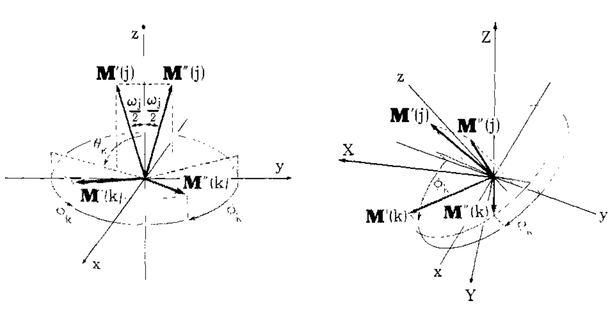

Figure 1. Mirror image relation of the transition moments M' and M'' of the jth and kth transition in the A′ and A″ forms of the solute in the molecular system of axes x, y, z (left) and in the laboratory system of axes X, Y, Z (right) and the definition of the angles ω_j, θ_k, and ϕ_k.

The observed changes in the dichroic ratio were reversible and the values could always be inverted by turning the irradiation polarization by 90 deg.

Results and Discussion

The Model. We assume that the solute molecules A, initially randomly oriented, are imbedded in a high-viscosity medium, which prevents rotational diffusion on the time scale of the experiment. We assume further that they can be interconverted between two forms, A′ and A″, related by mirroring in a plane of symmetry. The interconversion is assumed to involve some internal motion such as a proton shift or internal rotation and to occur upon excitation of a purely polarized transition with light linearly polarized along the laboratory axis Z. The A′ and A″ forms are either chemically identical or enantiomeric, so that they appear identical in all forms of spectroscopy with unpolarized or linearly polarized light. Here, the effect of the environment on the spectra of the forms A′ and A″ is assumed to be identical. This assumption will hold if the solvent effects on the spectra are negligible relative to the absorption bandwidths or if the environment adjusts perfectly to the changes in the solute orientation within the spectroscopic resolution used. If the assumption does not hold, so that A′ and A″ correspond to spectroscopically distinct classes of sites, the model will still apply if the spectral bandwidth of the Z-polarized orienting light is large enough to make all the sites absorb equally and if the resulting dichroism is measured by integration over sites of both classes.

The A′ and A″ forms generally differ in their orientation in space, and this can be detected when linearly polarized light is used. In the following, we neglect site memory effects and assume that in any site the forms A′ and A″ are intrinsically equally likely so that the quantum yields A′ → A″ and A″ → A′ are equal. This is a critical assumption, and it was not clear a priori whether it will be valid for any real system. The most likely way in which the necessary behavior could be realized would be for the environment to adjust rapidly to the shape of a common symmetrical excited intermediate shared by A′ and A″, before a return to the ground state of either A′ or A″ can occur.

Spontaneous interconversion of A′ and A″, either by tunneling or by thermal activation, is assumed to be negligible on the time scale of the experiment, as are both the spontaneous and the photoinduced rotational diffusion of the molecules. The photochemical process is nondestructive; i.e., light absorption causes no photochemical transformation other than the A′ ⇄ A″ interconversion.

Many of the above assumptions could be relaxed with only a moderate increase in the complexity of the treatment, but we believe that already the simple case considered is instructive and useful. The absence of site memory effects is essential to the treatment, however, and must be tested experimentally.

Quantitative Aspects of Nondestructive Photoorientation. We define a site-fixed common orthogonal system of axes for the two forms A′ and A″ in which the molecule can exist, such that the mirror plane that interconverts A′ and A″ contains the x and z axes (Figure 1).

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In form A′, the electric dipole moment responsible for excitation of the jth transition is the vector $\boldsymbol{M}'(j)$. In form A″, it is its mirror image $\boldsymbol{M}''(j)$. The angle between $\boldsymbol{M}'(j)$ and $\boldsymbol{M}''(j)$ is labeled ω_j. The z axis is chosen parallel to the vector $\boldsymbol{M}'(j) + \boldsymbol{M}''(j)$ so that the vectors $\boldsymbol{M}'(j)$ and $\boldsymbol{M}''(j)$ lie in the yz plane. The solution is initially racemic and random, with the site x, y, and z axes pointed equally likely in any direction. Let us consider a subassembly of sites with x, y, and z axes oriented in the infinitesimal vicinity of some particular three directions in the laboratory, described by Euler angles α, β, and γ relative to the laboratory frame X, Y, and Z (the right-hand side of Figure 1; the Euler angles are not shown). Initially, half of the molecules are in the form A′ and half in the form A″. The squares of the projections of $\boldsymbol{M}'(j)$ and $\boldsymbol{M}''(j)$ into Z are

$$\mathrm{A}'_Z{}^2(\alpha,\beta,\gamma;\omega) = |\boldsymbol{M}'(j)|^2[\cos(\omega_j/2)\cos\beta + \sin(\omega_j/2)\sin\beta\cos\gamma]^2 \quad (1)$$

$$\mathrm{A}''_Z{}^2(\alpha,\beta,\gamma;\omega) = |\boldsymbol{M}''(j)|^2[\cos(\omega_j/2)\cos\beta - \sin(\omega_j/2)\sin\beta\cos\gamma]^2 \quad (2)$$

where $|\boldsymbol{M}'(j)|^2 = |\boldsymbol{M}''(j)|^2$ by symmetry.

Photoconversion will cause the population of the two forms within a subassembly to become unequal, the form with the larger projection being depleted, until a photostationary state is reached. In this state, the rate of the photoconversion of A′ to A″, given by $C\Phi f'\mathrm{A}'_Z{}^2(\alpha,\beta,\gamma;\omega_j)$, and the rate of the reverse photoconversion of A″ to A′, given by $C\Phi f''\mathrm{A}''_Z{}^2(\alpha,\beta,\gamma;\omega_j)$, are equal. Here, C is a proportionality constant, and Φ is the quantum yield of the A′ → A″ and A″ → A′ interconversions, assumed to be equal (no site memory effects), while f' and f'' are the fractions of the molecules within the subassembly present in forms A′ and A″, respectively.

The equality of the two rates in the photostationary state requires

$$f'(\alpha,\beta,\gamma;\omega_j) = \frac{1}{2}\,\frac{[\cos(\omega_j/2)\cos\beta - \sin(\omega_j/2)\sin\beta\cos\gamma]^2}{\cos^2(\omega_j/2)\cos^2\beta + \sin^2(\omega_j/2)\sin^2\beta\cos^2\gamma} \quad (3)$$

$$f''(\alpha,\beta,\gamma;\omega_j) = \frac{1}{2}\,\frac{[\cos(\omega_j/2)\cos\beta + \sin(\omega_j/2)\sin\beta\cos\gamma]^2}{\cos^2(\omega_j/2)\cos^2\beta + \sin^2(\omega_j/2)\sin^2\beta\cos^2\gamma} \quad (4)$$

These equations define the orientation distribution functions for the forms A′ and A″ and thus permit the evaluation of all orientation-dependent properties such as linear dichroism.

The ratio of the two forms in the photostationary state will be a function of the orientation angles β and γ characterizing the subassembly. When integrated over all subassemblies, the two forms are still equally abundant, so that the solution still contains equal amounts of form A′ and form A″ and is racemic if they are enantiomers. However, since the differently oriented subassemblies contribute differently to the absorption of linearly polarized light, the optical density due to the jth transition will be different for light whose electric vector lies along Z as opposed to X or Y, and both will be different from the optical density measured on the original random sample. We use the notation $E_Z(j)$ for the base-line-corrected optical density measured with Z-polarized light at the wavelength of the jth transition and $E_Y(j)$ for that measured with Y-polarized light. The measured dichroic ratio of the photooriented assembly in the photostationary state $E_Z(j)/E_Y(j) = d_j$ depends only on the angle ω_j. A quantity with a more direct physical significance is the orientation factor K_j of the jth transition, defined as the average square of the Z projection of a unit vector directed along the jth transition moment (note that the spectroscopic indistinguishability of A′ and A″ requires averaging over both forms). From the properties of direction cosines, for a uniaxial sample the relation between d_j and K_j is[3]

$$d_j = E_Z(j)/E_Y(j) = 2K_j/(1 - K_j) \quad (5)$$

For the polarized bleaching ratio, i.e., the decrease in optical density observed with Z-polarized light in the photostationary state relative to that observed with light of any polarization in the initial random solution,

$$E_Z(j)/E^{\mathrm{iso}}(j) = 3K_j \quad (6)$$

since in a randomly oriented sample the orientation factor of any transition is equal to $^1/_3$. For the unpolarized bleaching ratio, i.e., the decrease in optical density observed with unpolarized light,

$$[E_Z(j) + E_Y(j)]/2E^{\mathrm{iso}}(j) = (3/4)(1 + K_j) \quad (7)$$

Thus, once the orientation factor for a transition is known, its dichroic ratio and its bleaching ratios can be obtained.

The orientation factor K_j for the transition that is being pumped is obtained by integration over all subassemblies:

$$K_j = (1/8\pi^2) \times \int_{\alpha=0}^{2\pi}\int_{\beta=0}^{\pi}\int_{\gamma=0}^{2\pi} \sin\beta\,\mathrm{d}\alpha\,\mathrm{d}\beta\,\mathrm{d}\gamma[f'(\alpha,\beta,\gamma;\omega_j)\mathrm{A}_Z{}^2(\alpha,\beta,\gamma;\omega_j) + f''(\alpha,\beta,\gamma;\omega_j)\mathrm{A}''_Z{}^2(\alpha,\beta,\gamma;\omega_j)]/|\boldsymbol{M}'(j)|^2 \quad (8)$$

$$= (1/4\pi)\int_{\beta=0}^{\pi}\int_{\gamma=0}^{2\pi} \frac{\sin\beta\,\mathrm{d}\beta\,\mathrm{d}\gamma[\cos^2(\omega_j/2)\cos^2\beta - \sin^2(\omega_j/2)\sin^2\beta\cos^2\gamma]^2}{\cos^2(\omega_j/2)\cos^2\beta + \sin^2(\omega_j/2)\sin^2\beta\cos^2\gamma} \quad (9)$$

and the result is

$$K_j = (1/3)[1 - \sin^2\omega_j/(1 + \sin\omega_j)] \quad (10)$$

The fact that the theoretical value of K_j is less than or at most equal to the value which it has in a random solution, $^1/_3$, shows that the molecules avoid orientations in which the transition moment is inclined toward the Z direction. The minimum value of K_j is $^1/_6$, which corresponds to a dichroic ratio $d_j = {}^2/_5$ and is reached at $\omega_j = \pi/2$, when $\boldsymbol{M}'(j)$ and $\boldsymbol{M}''(j)$ are at right angles to each other. This is intuitively acceptable since then the act of photoconversion drives the transition moment as far away from its original direction as is possible. On the other hand, at $\omega_j = 0$ or $\omega_j = \pi$, $K_j = {}^1/_3$, $d_j = 1$, and there is no photoorientation. The former happens when the transition moment lies in the xz plane, the latter happens when it is perpendicular to the xz plane; in either case, the transition moment directions coincide in the forms A′ and A″.

Once ω_j has been determined by measurement of the photoinduced dichroism at the wavelength of the exciting light, the orientation distribution of the molecular assembly is known. It can then be used to predict the orientation factor and thus the dichroism of any other transition moment in the molecule if its orientation in the x, y, z axes system is known. Let such a moment $\boldsymbol{M}'(k)$ in form A′ be located at angle θ_k from the molecular z axis and lie in a plane obtained by rotating the yz plane around the z axis by the angle ϕ_k (Figure 1). If $\boldsymbol{M}'(k)$ and $\boldsymbol{M}'(j)$ lie on the same side of the xz plane, $-\pi/2 \le \phi_k \le \pi/2$ and $\cos\phi_k \ge 0$. If they lie on opposite sides of the xz plane, $\pi/2 \le \phi_k \le 3\pi/2$ and $\cos\phi_k \le 0$. By symmetry, in form A″ the kth transition moment $\boldsymbol{M}''(k)$ will still be located at angle θ_k from z but now will lie in a plane obtained by rotating the yz plane around z by the angle $\pi - \phi_k$.

In order to evaluate the orientation factor K_k for the kth transition, we first note that the square of the projection of $\boldsymbol{M}'(k)$ into the Z direction is given by

$$\mathrm{A}'_Z{}^2(\alpha,\beta,\gamma;\theta,\phi) = |\boldsymbol{M}'(k)|^2[\cos\beta\cos\theta + \sin\theta\sin\beta\cos(\gamma + \phi)]^2 \quad (11)$$

and the square of the projection of $\boldsymbol{M}''(k)$ into the Z direction by

$$\mathrm{A}''_Z{}^2(\alpha,\beta,\gamma;\theta,\phi) = |\boldsymbol{M}''(k)|^2[\cos\beta\cos\theta + \sin\theta\sin\beta\cos(\gamma + \pi - \phi)]^2 \quad (12)$$

so that

$$K_k = (1/8\pi^2) \times \int_{\alpha=0}^{2\pi}\int_{\beta=0}^{\pi}\int_{\gamma=0}^{2\pi} \sin\beta \, \mathrm{d}\alpha \, \mathrm{d}\beta \, \mathrm{d}\gamma [f'(\alpha,\beta,\gamma;\omega_j) \mathrm{A}_Z{}^2(\alpha,\beta,\gamma;\theta,\phi) + f''(\alpha,\beta,\gamma;\omega_j) \mathrm{A}''_Z{}^2(\alpha,\beta,\gamma;\theta,\phi)]/|\boldsymbol{M}'(k)|^2 \quad (13)$$

and

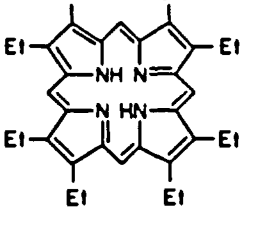
$$K_k = (1/3)[1 - \cos\phi_k \sin 2\theta_k \sin\omega_j/(1 + \sin\omega_j)] \quad (14)$$

This formula also shows the intuitively expected behavior. The *k*th transition moment will not be aligned if $\omega_j = 0$ or $\omega_j = \pi$ since then there is no photoorientation to start with, and it will show a maximum effect if $\omega_j = \pi/2$ since then the photoorientation is most efficient. The dependence on θ_k is similar to that on ω_j: if $\theta_k = 0$ or $\theta_k = \pi/2$, $\boldsymbol{M}'(k)$ lies in the *z* axis or perpendicular to it, respectively. Then, the projection of $\boldsymbol{M}'(k)$ into the *Z* direction will be the same as the projection of $\boldsymbol{M}''(k)$ and there will be no dichroism for such a transition. Finally, the effect is largest when $\boldsymbol{M}'(k)$ lies in the *yz* plane, defined by $\boldsymbol{M}'(k)$, *z*, and $\boldsymbol{M}''(k)$. As long as $\cos\phi_k > 0$, the deviation of K_k from the isotropic value of $^1/_3$ is toward lower values (negative dichroism), in the same direction as for K_j, associated with the transition that is being pumped, and indeed if $\phi_k = 0$ and $2\theta_k = \omega_j$, formulas 10 and 14 are identical. This is sensible, since the photoconversion will drive all those transition moment vectors that are located on the same side of the *xz* plane as $\boldsymbol{M}'(j)$ away from the *Z* direction as it drives from A′ to A″. However, if $\boldsymbol{M}'(k)$ is located on the opposite side of the *yz* plane from $\boldsymbol{M}'(j)$, so that $\cos\phi_k < 0$, the light will flip it toward the *Z* axis as it drives the *j*th transition moment away from this axis and then an increase in K_k above $^1/_3$ (positive dichroism) must be expected. When $\phi_k = \pm\pi/2$, there will be no effect since the *k*th transition moment will then lie in the *xz* plane and have the same orientation in form A′ and in form A″. The largest positive dichroism, $K_k = {}^1/_2$, $d_k = 2$, is expected when $\boldsymbol{M}'(k)$ coincides with $\boldsymbol{M}''(j)$ and is perpendicular to $\boldsymbol{M}'(j)$.

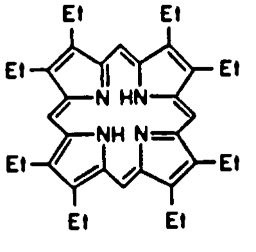
Although a measurement of the dichroic ratio d_k and thus the orientation factor K_k does not in itself permit the determination of the direction of the *k*th transition moment $\boldsymbol{M}'(k)$ in form A′ even if K_j and thus ω_j are known, it fixes a relation between its angles ϕ_k and θ_k. Only one additional piece of information is then needed to determine the transition moment direction.

An Experimental Test: Nondestructive Photoorientation of Octaethylporphine (OEP). The most serious assumption that enters the derivation of eq 10 and 14 is the neglect of the site memory effect. Sites are assumed to differ only in their orientation in the laboratory-fixed *X*, *Y*, *Z* system of axes but to retain no memory of whether they initially contained the solute in form A′ or form A″. Before (10) and (14) can be considered useful for the determination of UV and IR transition moment directions in matrix-isolated molecules, it is important to test this assumption on a case in which ω_j is known and d_j can be readily measured.

We have chosen octaethylporphine, for which $\omega_j = \pi/2$ for any *j* from geometrical considerations alone. The A′ and A″ forms of this solute are shown in formulas **1′** and **1″**.



1′



1″

The 0–0 peak (origin) of the Q band of OEP is located near 620 nm (Table I) and is relatively isolated from other absorption peaks. The 0–0 peak is particularly narrow in the frozen gas matrices, where two separate peaks corresponding to distinct classes of sites can be clearly discerned (Figure 2). We use the expression "class of sites" instead of the simpler "site" in recognition of the fact that both peaks are inhomogeneously broadened so that each is due to a large number of individual distinct sites. In the Ne matrix, the two classes of sites absorb at 613.1 and 618.6 nm. The environments in these two classes of sites almost certainly differ primarily by a 90° rotation[10,11] or, otherwise expressed, by relocation of the internal hydrogens in the solute without relaxation in the surroundings. The inhomogeneous broadening of the two peaks is then due to further fine differences in the solute environment. The photoorienting light used in our experiments was of bandwidth sufficient to ensure excitation of both classes of sites, and the dichroic ratios were measured by integration over both of them as well.

In all matrices except PET, where no effect was observed, irradiation into the Q band origin with *Z*-polarized light induced negative dichroism ($d_j = E_Z/E_y < 1$) at the origin (both sites) and positive dichroism in the 515–525-nm region, where several peaks overlap. The limiting dichroic ratios, d_j, observed at the

Table I. Visible Dichroism of OEP in Various Matrices in the Photostationary State[a]

matrix	λ, nm	*T*, K	d_j[b]	K_j[c]	*F*, %[d]
theory[e]			0.40	0.17	0
Ne	618.6	3	0.46	0.19	14
Ar	618.8	4.5	0.50	0.20	20
N_2	616.8	12	0.50	0.20	20
PMMA[f]	615.9	12	0.52	0.21	26
PVC[f]	614.3	77	0.55	0.22	32
3-MP[f]	622.8	77	0.73	0.27	62
2-MTHF[f]	621.8	77	0.82	0.29	74
PET[f]	616.5	12	1.00	0.33	100

[a] Attained by irradiation with *Z*-polarized 620-nm light. [b] The dichroic ratio $E_Z(\lambda)/E_Y(\lambda)$. [c] The orientation factor $K_j = d_j/(d_j + 2)$. [d] Percentage of solute molecules that can be thought of as unorientable since they occupy sites with perfect memory (see text). [e] See text. [f] See Experimental Section.

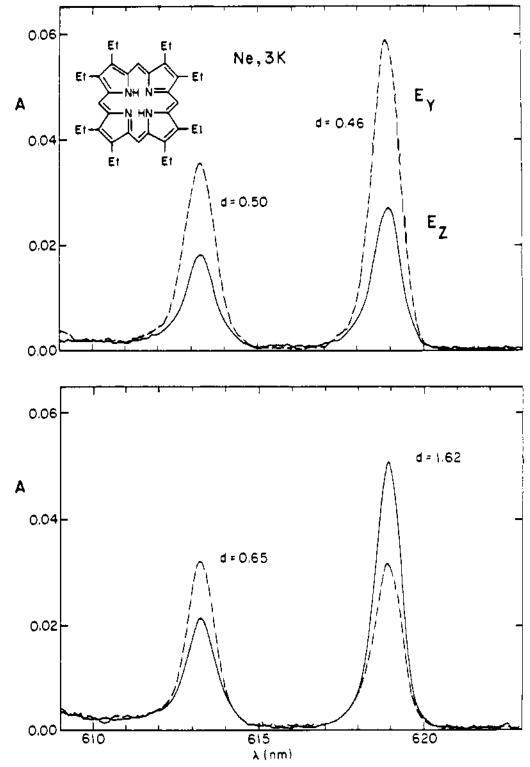


Figure 2. Linear dichroism of octaethylporphine in neon matrix at 3 K. (top) After irradiation with *Z*-polarized light absorbed by both sites. (bottom) After subsequent irradiation with *Y*-polarized light absorbed only by the long-wavelength site. The dichroic ratios are defined by $d = E_Z/E_Y$, where E_Z (E_Y) is the *Z*-(*Y*)-polarized absorbance.

origin after some minutes to hours of Z-polarized irradiation are listed in Table I along with the corresponding orientation factors, K_j, for a series of OEP-containing samples. It seems that the theoretical values of $d_j = 0.40$ and $K_j = 0.17$ are almost reached within the experimental uncertainty of about ±10% in d_j, but only in the least interacting matrix (Ne) at the lowest temperature (3 K). In other environments, the theoretical degree of alignment is not quite reached, and in some of the instances only quite poor alignment is achieved. We believe that this is due primarily to the site memory effects, neglected in our treatment, and possibly to the ability of the OEP molecules to rotate slowly in some matrices, even at the relatively low temperatures used. Even in the Ne matrix, the nearly ideal alignment was observed only at the lowest temperatures used.

The measurement of the polarized bleaching ratio obtained in the Ne matrix combined with the use of eq 6 yielded the same value $K_j = 0.19$, providing an independent check.

The positive dichroism observed on the photooriented samples for the overlapping peaks located in the 515–525-nm region is attributable to their known polarization, predominantly perpendicular to that in the 620-nm region ($\theta_k = \pi/4$, $\phi_k = \pi$).

The site memory effect can be viewed in two extreme ways. It is possible that a certain fraction of the solute molecules F resides in sites with perfect memory, half containing the A′ form and half the A″ form, both incapable of phototransformation into the other, while the remainder of the solute molecules, 1–F, exhibit the ideal interconverting behavior assumed above. Alternatively, the environments of all solute molecules could favor the solute form which they originally contained, half of them A′ and half A″, by a certain margin, so that the quantum yields Φ (A′ → A″) and Φ (A″ → A′) for any one site would differ. In reality, some situation intermediate between the two extremes most probably prevails.

Since our experimental data do not permit us to determine the true state of affairs, we have arbitrarily adopted the first of the extreme descriptions and listed in Table I the fraction of sites F that would have to possess perfect site memory and hence be unorientable, assuming the fraction 1–F to be perfectly orientable, in order to reproduce the observed dichroic ratios ($F = 6K_j - 1$). Regardless of which detailed statistical interpretation is correct, the F value for a particular matrix material characterizes quantitatively its effective site memory capability and thus its suitability for the kind of experiment of interest here.

The dichroic spectra of OEP photooriented with Z-polarized light in a Ne matrix at 3 K were investigated in a little more detail, using narrow-bandwidth laser excitation for selective irradiation of a single site class. The initial spectra obtained after photoorientation with broad-band light are shown in Figure 2, top. The peaks due to the two classes of sites are distinctly separate, and they differ slightly but reproducibly in their degree of alignment, suggesting slightly different memory effects in the two environments. Subsequent selective irradiation of the longer wavelength site class with Y-polarized dye laser light rapidly inverted the sign of its dichroism, while that of the shorter wavelength site class decreased noticeably but remained negative (Figure 2, bottom). This result shows conclusively that the two peaks indeed belong to distinct subassemblies of OEP molecules as expected from previous results in other matrices.[10,11] Each assembly is now oriented totally differently after the second irradiation. The decrease in the degree of alignment of the shorter wavelength site class during the irradiation of the longer wavelength site class is compatible with the notion that the shift of the internal hydrogens upon excitation is accompanied by a relaxation of the environment most of the time (photoorientation without a change of site class occupancy) but proceeds without such relaxation some of the time (photoorientation with site class interconversion).

Similar results were obtained at 4.5 K in the Ar matrix, in which OEP also occupies two distinct classes of sites. The observed d_j values were somewhat higher, perhaps partly because of the somewhat lower optical quality of Ar relative to Ne matrices in general, and partly because of somewhat larger memory effects.

A more quantitative investigation of the competition between photoorientation with and without site class interconversion appears worthwhile, particularly in view of the interest in hole-burning phenomena.[9] It might also contribute to a more detailed understanding of the memory effects.

Conclusions

Using a simple model for photoorientation by generalized pseudorotation, we have derived quantitative relations between the orientation of transition moment directions in a solute molecule and its limiting degree of alignment for the case of negligible site memory effects. The theory has been tested on solutions of octaethylporphine in various rigid media. The theoretical memory-free limiting values were reached within experimental error for samples contained in a neon matrix at 3 K. This result suggests that the procedure may be useful for the determination of unknown transition moment directions in neon matrix isolated molecules. The less complete alignment in other media has been attributed to site memory effects.

Since amorphous rigid samples exhibiting molecular photoorientation by generalized pseudorotation clearly have the capacity to preserve local memory of the state of polarization of light that impinged on them last, they are of interest for erasable optical information storage devices. They can be viewed as a generalization of single-crystal color center[13] and silver-doped silver halide thin film[14] systems with light polarization memory. For this purpose, the presence of partial site memory is not fatal.

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Registry No. OEP, 2683-82-1.

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[14] E.g.: Borrelli, N. F.; Young, P. L. *Proc. SPIE—Int. Soc. Opt. Eng.* **1980**, *222*, 48.