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Polarizability of Molecules in Excited Electronic States

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In an earlier paper we reported the first measurement of the optical anisotropy of a molecule in an excited electronic state by the method of induced birefringence. In the present paper details are presented for the application of this method to the determination of the differences in the components of the polarizability tensors between an excited electronic and ground state. Experimentally we studied naphthalene-d_8 in EPA at 77°K from 4200 to 6300 Å. Our measurement of the dispersion of the polarizability near the triplet–triplet absorption provides evidence for the existence of a previously suspected weak triplet state approximately 18 000 cm^{-1} above the lowest-lying triplet state.

I. INTRODUCTION

The principle means for studying the properties of electronically excited molecules are absorption and emission spectroscopy. In particular, the polarizability of excited molecules has been studied by the solvent shifts of absorption bands and by changes in the absorption spectrum due to an applied electric field.[1–10] In the induced birefringence method, we determine the change in the propagation of a light wave due to the presence of excited state molecules. By varying the frequency of the probe light we can directly measure the dispersion of the polarizability. This is an important feature, not present in the other methods for studying excited state polarizabilities, which permits the determination of the transition moment axis and the identification of very weak transitions. In the absorption methods, the quantity determined is the average change in the polarizability on excitation whereas the induced birefringence method yields the changes between specific components of the polarizability tensors. In particular, the phase change in the probe light which we measure is dependent on the symmetry of the excitation transition and, therefore, different combinations of the elements of the polarizability tensors can be obtained by using different symmetry absorption bands.

In an earlier paper,[11] we reported the first measurement of the optical anisotropy of an excited electronic state using the technique of induced birefringence. These measurements were made on the lowest-lying triplet state of naphthalene-d_8. In this paper we present the theory underlying the technique for the measurement of polarizabilities of excited states and derive the relationship between the actually measured parameters and the physical quantities of interest. We also present details of the experimental arrangement used in our measurements and discuss important experimental problems of relevance to the application of induced birefringence. Finally, we report the results of measurements on naphthalene-d_8.

In each case the quantity measured is an anisotropy parameter Δ defined by

$$\Delta = 2\Delta\alpha_{zz} - \Delta\alpha_{yy} - \Delta\alpha_{xx}, \qquad (1)$$

where x, y, z are the principle axes of the molecular polarizability tensor (α_{ij}) and

$$\Delta\alpha_{ii} = \alpha_{ii}' - \alpha_{ii}^0, \qquad (2)$$

with α_{ii}' and α_{ii}^0 being the molecular polarizability along the i axis in the excited state $|1\rangle$ and the ground state $|0\rangle$, respectively. For our measurement $|1\rangle$ was always the lowest-lying triplet state of the molecules and $|0\rangle$ was the singlet ground state. It is assumed that the symmetry of the molecule does not change on excitation and, therefore, the principle axes directions are identical. It is further assumed that dichroism induced under the same experimental conditions does not contribute significantly to the observed effects provided one operates in a region of the spectrum where absorption is low. This assumption, which is justified in Appendix D, results in a much simpler treatment and analysis than the one reported by Kuball *et al.*[12] Furthermore, we have included saturation effects in our treatment since we found them to be important even for excited state concentrations less than 10% of the total population.

II. THEORETICAL CONSIDERATIONS

A. The Permittivity Tensor

The propagation of an electromagnetic wave, such as light, through a homogeneous material medium is generally described in terms of Maxwell's equations and the phenomenological permittivity tensor of the medium. This tensor reflects the macroscopic symmetry of the medium and is related to the polarizability tensor of the medium. The polarizability tensor of the medium is in turn related directly to the molecular polarizabilities of the constituents of the medium. In the absence of absorption the polarizability and permittivity tensors of the medium will be Hermitian and there will be a set of axes—the principle axes of the medium—for which the real part of the tensors will be diagonal. If the medium does not exhibit optical rotation, as is the case for the systems we consider and as will be assumed in this treatment, the off-diagonal elements of the tensors will have to

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be zero in the principle axes system and the permittivity tensor will have the form

$$(\epsilon_{ij})=\begin{pmatrix}\epsilon_{xx} & 0 & 0\\ 0 & \epsilon_{yy} & 0\\ 0 & 0 & \epsilon_{zz}\end{pmatrix}\tag{3}$$

with the ϵ_{ij} all real.

If the medium is biaxial, no two components will be identical. If the medium is uniaxial, then we can write the permittivity tensor in terms of two parameters ϵ and β, such that with the z axis taken as the axis of symmetry (i.e., the optical axis of the medium) we have

$$(\epsilon_{ij})=\begin{pmatrix}\epsilon+\beta & 0 & 0\\ 0 & \epsilon+\beta & 0\\ 0 & 0 & \epsilon-\beta\end{pmatrix},\tag{4}$$

where

$$\epsilon=(\epsilon_{xx}+\epsilon_{zz})/2\tag{5}$$

and

$$\beta=(\epsilon_{xx}-\epsilon_{zz})/2.\tag{6}$$

Since $\beta/\epsilon\ll 1$ for the frequencies and materials under consideration, we can define

$$n=\epsilon^{1/2}=(n_{||}+n_{\perp})/2\tag{7}$$

as the average refractive index of the medium with

$$n=(\epsilon-\beta)^{1/2}\quad\text{and}\quad n_{\perp}=(\epsilon+\beta)^{1/2},\tag{8}$$

where $n_{\|}$ and $n_{\perp}$, as usual, are the refractive indices of the medium for light polarized parallel or perpendicular to the direction of the optic axis (z axis). If $\beta\equiv 0$, the medium is isotropic and exhibits no birefringence. In other words,

$$\beta=(n_{\perp}^2-n_{||}^2)/2\tag{9}$$

is the parameter determining the birefringence of the medium.

B. Induced Birefringence

Consider an assembly of identical molecules with α_{xx}, α_{yy}, and α_{zz}. Let X, Y, and Z be laboratory axes and let θ, ϕ, and ψ be the Eulerian angles,[13] defining the orientation of a molecule in the laboratory frame. Then the contribution of a molecule with orientation (θ,ϕ,ψ) to the polarizability in the laboratory frame is given by

$$(\alpha_{ij})=(T_{im})(\alpha_{mn})(T_{nj})^{-1},\tag{10}$$

where indices i, j refer to laboratory coordinates and indices m, n refer to molecular coordinates. We also have $\alpha_{ij}=\alpha_{ji}$, $(T_{im})=(T_{mi})^{-1}$, and T_{im} is the direction cosine of the molecular m axis with respect to the laboratory i axis. Let the orientational distribution of the assembly of molecules define a distribution function $n_0(\theta,\phi,\psi)$ so that

$$(1/8\pi^2)n_0(\theta,\phi,\psi)\sin\theta d\theta d\phi d\psi$$

is the number of molecules per unit volume with orientations between θ and $\theta+d\theta$, ϕ and $\phi+d\phi$, and ψ and $\psi+d\psi$. Then for the molecular concentration (in molecules per unit volume) n_0 we have

$$n_0=\frac{1}{8\pi^2}\int_0^{\pi}\int_0^{2\pi}\int_0^{2\pi}n_0(\theta,\phi,\psi)\sin\theta d\theta d\phi d\psi.\tag{11}$$

In the case of low density, i.e., noninteracting molecules, we obtain the polarizability tensor of the medium (A_{ij}) from

$$A_{ij}=\frac{1}{8\pi^2}\int_0^{\pi}\int_0^{2\pi}\int_0^{2\pi}n_0(\theta,\phi,\psi)\alpha_{ij}\sin\theta d\theta d\phi d\psi.\tag{12}$$

For random orientation of the molecules we have

$$n_0(\theta,\phi,\psi)=n_0(\text{a constant}),$$

and thus

$$A_{ij}=(n_0/3)(\alpha_{xx}+\alpha_{yy}+\alpha_{zz})\delta_{ij},\tag{13}$$

where, as customary, δ_{ij} is the Kronecker delta function. Equation (13) implies that the medium is isotropic. Using the Clausius–Mossotti relationship between polarizability and permittivity in the tensorial form[14]

$$(\epsilon_{ij}-\delta_{ij})/(\epsilon+2)=(4\pi/3)A_{ij},\tag{14}$$

we have then in the low-density approximation ($\epsilon\simeq 1$)

$$\epsilon_{ij}=\delta_{ij}+4\pi A_{ij}\tag{15}$$

which reduces to

$$\epsilon_{ij}=\epsilon\delta_{ij}\tag{16}$$

with

$$\epsilon=1+4\pi(n_0/3)(\alpha_{xx}+\alpha_{yy}+\alpha_{zz}).\tag{17}$$

If our assembly of molecules is imbedded in a rigid matrix of host molecules, we can write the total polarizability of the medium $(A_{ij})_T$ as a sum of the polarizability tensor of the host matrix $(A_{ij})_M$ and the polarizability tensor (A_{ij}) of our assembly of molecules, i.e.,

$$(A_{ij})_T=(A_{ij})_M+(A_{ij}).\tag{18}$$

However, we are now not any more in the low-density regime and hence in relating the permittivity tensor of our medium $(\epsilon_{ij})_T$ to the polarizability tensor $(A_{ij})_T$ we have to make full use of the Clausius–Mossotti relationship as given in (14). That this relationship can validly be applied to an organic solid has been shown by Vuks.[14]

Let us assume for the moment that our host matrix is isotropic, i.e.,

$$(A_{ij})_M=A_M\delta_{ij}.\tag{19}$$

This assumption will be dropped later and replaced by a more realistic one which, moreover, from an

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experimental point of view will offer certain advantages when realized in practice. Then for our random assembly of molecules imbedded in the host we shall have a permittivity tensor $(\epsilon_{ij})_T$ given by

$$(\epsilon_{ij})_T=\delta_{ij}+[(\epsilon+2)/3]4\pi[A_M\delta_{ij}+(A_{ij})] \quad (20)$$

with (A_{ij}) given by (13) and, provided the concentration of our molecules of interest is low,

$$\epsilon=n_M^2, \quad (21)$$

where n_M is the refractive index of the host matrix.

Now suppose our molecules of interest can be excited from the ground state directly or indirectly to an excited state by a transition moment parallel to the molecular z axis, such that if we excite our assembly with light polarized parallel to the laboratory Z axis, we will obtain a steady state population n_1 in the excited state given by

$$n_1=\frac{1}{8\pi^2}\int_0^{\pi}\int_0^{2\pi}\int_0^{2\pi}\frac{n_0S\cos^2\theta}{1+S\cos^2\theta}\sin\theta d\theta d\phi d\psi, \quad (22)$$

where S is proportional to the intensity of the exciting light, various rate constants, and the square of the transition matrix element, and θ is, as stated before, the angle between the molecular z axis and the laboratory Z axis. Then we shall in fact have an orientationally selective excitation of our molecules and our assembly will consist under these conditions of two related but nonrandomly distributed populations in the ground and excited states, respectively, with distribution functions

$$n_1(\theta,\phi,\psi)=n_0S\cos^2\theta/(1+S\cos^2\theta) \quad (23)$$

for the molecules in the excited state and

$$n_g(\theta,\phi,\psi)=n_0-n_1(\theta,\phi,\psi) \quad (24)$$

for the molecules still in the ground state.

An alternative case that can be considered is the one where the excitation of the molecules takes place via a transition moment degenerate in the x–y plane of the molecule. In this case, we have to replace (23) by

$$n_1(\theta,\phi,\psi)=n_0S\sin^2\theta/(1+S\sin^2\theta). \quad (25)$$

In general, the polarizability of a molecule is dependent on the electronic charge distribution and hence will not be the same in the excited state as it is in the ground state. If α_{ij}' is the molecular polarizability in the excited state and α_{ij}^0 that in the ground state, the contribution of our molecules of interest to the total polarizability tensor of the medium will be

$$A_{ij}=\frac{1}{8\pi^2}\int_0^{\pi}\int_0^{2\pi}\int_0^{2\pi}[n_1(\theta,\phi,\psi)\alpha_{ij}' + n_g(\theta,\phi,\psi)\alpha_{ij}^0]\sin\theta d\theta d\phi d\psi \quad (26)$$

and, as will be shown, (A_{ij}) will be anisotropic unless $\alpha_{ij}'=\alpha_{ij}^0$ or in Eqs. (23) and (25), respectively, either $S=0$ or $S\rightarrow\infty$.

If (A_{ij}) is anisotropic, then so will be $(A_{ij})_T$ and hence $(\epsilon_{ij})_T$. The resulting anisotropy in $(\epsilon_{ij})_T$ implies the appearance of birefringence induced by the orientationally selective excitation of the molecules of interest imbedded in the passive host medium. This induced birefringence can in principle be measured and, given a knowledge of S and hence of n_1 and n_g, leads to a determination of the parameter Δ defined by (1) and (2).

Writing (26) in the form

$$A_{ij}=\frac{1}{8\pi^2}\int_0^{\pi}\int_0^{2\pi}\int_0^{2\pi}n_0\alpha_{ij}^0\sin\theta d\theta d\phi d\psi+\frac{1}{8\pi^2}\times\int_0^{\pi}\int_0^{2\pi}\int_0^{2\pi}n_1(\theta,\phi,\psi)(\alpha_{ij}'-\alpha_{ij}^0)\sin\theta d\theta d\phi d\psi, \quad (27)$$

we see that

$$A_{ij}=n_0\alpha^0\delta_{ij}+\langle\Delta\alpha_{ij}\rangle, \quad (28)$$

where

$$\alpha^0=\tfrac{1}{3}(\alpha_{xx}^0+\alpha_{yy}^0+\alpha_{zz}^0) \quad (29)$$

and

$$\langle\Delta\alpha_{ij}\rangle=\frac{1}{8\pi^2}\int_0^{\pi}\int_0^{2\pi}\int_0^{2\pi}n_1(\theta,\phi,\psi)\Delta\alpha_{ij}\sin\theta d\theta d\phi d\psi \quad (30)$$

with

$$\Delta\alpha_{ij}=\alpha_{ij}'-\alpha_{ij}^0. \quad (31)$$

The integrals (30) can be evaluated making use of (10) and (23) or (25), respectively, and defining

$$n_1=\frac{1}{8\pi_2}\int_0^{\pi}\int_0^{2\pi}\int_0^{2\pi}n_1(\theta,\phi,\psi)\sin\theta d\theta d\phi d\psi. \quad (32)$$

All the off-diagonal terms involve integrations of the form

$$\int_0^{2\pi}\sin q dq$$

or

$$\int_0^{2\pi}\cos q dq$$

or

$$\int_0^{2\pi}\sin q\cos q dq$$

and hence are identically zero, i.e.,

$$\langle\Delta\alpha_{ij}\rangle=0 \quad \text{for} \quad 1\neq j. \quad (33)$$

For the diagonal terms using (23), we obtain

$$\Delta\alpha_{xx}=(n_0/12)-(n_1/4A)(\Delta\alpha_{xx}+\Delta\alpha_{yy}-2\Delta\alpha_{zz}) +\tfrac{1}{4}n_1(\Delta\alpha_{xx}+\Delta\alpha_{yy}+2\Delta\alpha_{zz}), \quad (34)$$

$$\langle\Delta\alpha_{yy}\rangle=\langle\Delta\alpha_{xx}\rangle, \quad (35)$$

and

$$\langle\Delta\alpha_{zz}\rangle=\tfrac{1}{6}n_0-(n_1/2A)(2\Delta\alpha_{zz}-\Delta\alpha_{xx}-\Delta\alpha_{yy}) +\tfrac{1}{2}n_1(\Delta\alpha_{xx}+\Delta\alpha_{yy}) \quad (36)$$

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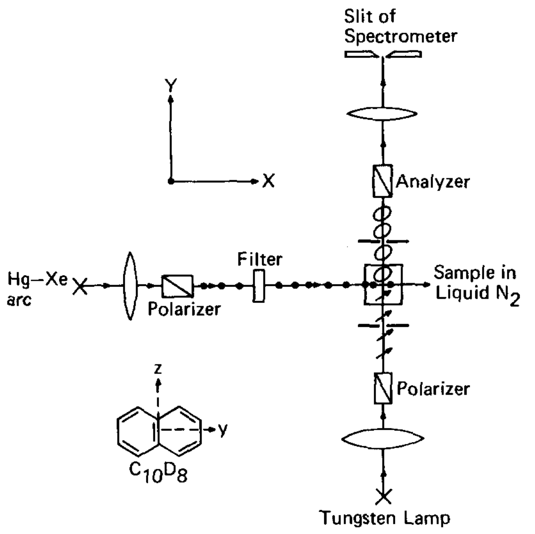

FIG. 1. Experimental arrangement.

so that, finally, we can write

$$(A_{ij})=\begin{pmatrix}\alpha''-\beta' & 0 & 0\\ 0 & \alpha''-\beta' & 0\\ 0 & 0 & \alpha''+\beta'\end{pmatrix} \tag{37}$$

with

$$\alpha''=n_0\alpha^0+(1/24)[n_0+3n_1-(3n_1/S)]$$
$$(2\Delta\alpha_{zz}-\Delta\alpha_{xx}-\Delta\alpha_{yy})+\tfrac{1}{2}n_1(\Delta\alpha_{xx}+\Delta\alpha_{yy}), \tag{38}$$

and the all-important birefringence parameter β' will be given by

$$\beta'=\tfrac{1}{8}[n_0-n_1-(3n_1/S)]\Delta, \tag{39}$$

where Δ is the anisotropy parameter defined by (1) and (2).

A similar result can be obtained with the use of (25) instead of (23), and we find in this case

$$\beta'\tfrac{1}{2}(\langle\Delta\alpha_{xx}\rangle-\langle\Delta\alpha_{zz}\rangle)$$
$$=[(2An_1+3n_1-2An_0)/4S](\Delta\alpha_{xx}-\Delta\alpha_{zz}). \tag{40}$$

The detailed form for α'' is of no interest in this case. It does not contribute to the anisotropy and implies merely a very small change in the average refractive index. Using (37) in (20) we see that

$$(\epsilon_{ij})_T=\begin{pmatrix}\epsilon'-\beta & 0 & 0\\ 0 & \epsilon'-\beta & 0\\ 0 & 0 & \epsilon'+\beta\end{pmatrix} \tag{41}$$

with

$$\beta=[4\pi(n_M{}^2+2)/3]\beta' \tag{42}$$

and

$$\epsilon'\simeq n_M{}^2. \tag{43}$$

If the assumption of an isotropic host medium can be realized, we are now enabled to set up an experiment as follows (see Fig. 1).

Light from the probe source (e.g., tungsten) is polarized 45° with respect to the laboratory Z axis and propagates in the $+Y$ direction through the sample. As long as no excited state population exists in the sample (i.e., the sample is isotropic) the probe beam is extinguished by the analyzer. When the sample is excited by light polarized in the Z direction and propagating in the $+X$ direction a steady state population in the excited state is maintained and an optical anistropy is induced in the sample with an optical axis along the Z direction. The incoming probe beam is decomposed into two equal amplitude components polarized parallel and perpendicular to this optic axis, traveling with different velocities, and recombining with a phase difference δ given by

$$\delta=[l\omega/c(\epsilon')^{1/2}]\beta, \tag{44}$$

where l is the path length in the medium, ω is the frequency of the probe-beam light, c the velocity of light *in vacuo*, and ϵ' and β are as given in (42) and (43). Thus, the probe light leaving the sample will be elliptically polarized and have a component, passed by the analyzer, which is measured by the detector and proportional to the square of the light amplitude along the minor axis of the ellipse (for $\delta<\pi/2$). The relation between the light intensity $I_\perp$ measured along the minor axis of the ellipse and the light intensity measured along the major axis of the ellipse $I_{\parallel}$ (analyzer set parallel to the polarizer) is given by

$$(I_\perp/I_{\parallel})^{1/2}=\tan(\delta/2). \tag{45}$$

In practice we will usually have $\delta\ll\pi/2$, and hence

$$I_{\parallel}\simeq I_0 \quad\text{and}\quad \tan\delta/2\simeq\delta/2. \tag{46}$$

Thus, the measurement of $I_\perp$ yields knowledge of β and hence β'. If by an independent measurement we can determine n_1, the excited state concentration, we are able to deduce S and will then have all the information required to obtain the desired anisotropy parameter Δ.

If an isotropic host medium cannot be physically realized, as will be the case when the host medium is a glass which has a strain-induced birefringence of its own, then the creation of an excited state population will merely induce a change in the birefringence. However, a sensitive measurement of this change is still possible, provided the strain axes are unique along the path of the probe beam. In this case, the following procedure will be used.

The sample will be placed so that its (strain-induced) optic axis will be parallel (or perpendicular) to the

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polarization vector of the incident probe light, i.e., 45° with respect to the laboratory Z axis and in the Z–X plane.

When unexcited, the sample will have in its own principle axis system a permittivity tensor

$$(\epsilon_{ij})_T=\begin{pmatrix} \epsilon-a & 0 & 0 \\ 0 & \epsilon-a & 0 \\ 0 & 0 & \epsilon+a \end{pmatrix}, \tag{47}$$

where a is the parameter describing the strain-induced birefringence. This parameter can be determined in the unexcited sample in a manner identical to the one just described, except that the approximations (46) are not likely to be valid.

In the laboratory frame we will have for the unexcited system

$$(\epsilon_{ij})_T=\begin{pmatrix} \epsilon & 0 & a \\ 0 & \epsilon-a & 0 \\ a & 0 & \epsilon \end{pmatrix} \tag{48}$$

which results from a 45° rotation of (47) about the Y axis.

The incident probe light being polarized parallel to (or perpendicular to) the optic axis will traverse the sample unchanged as it constitutes one of the stable modes (see Appendix A) of propagation for the system, and hence will be fully extinguished by the analyzer. Upon creation of an excited state population by the exciting light (again polarized along the laboratory Z direction), in line with our previous argument (48) will change to

$$(\epsilon_{ij})_T=\begin{pmatrix} \epsilon'-\beta & 0 & a \\ 0 & \epsilon'-a-\beta & \\ a & 0 & \epsilon'+\beta \end{pmatrix}. \tag{49}$$

Under usual conditions we will have $\beta\ll a$ and $a\ll\epsilon'$ as well as $\epsilon'\simeq\epsilon=n_M{}^2$. The physical implication of (49) is that for $\beta\neq0$ we will have a, generally small, shift of the principle axis system in the laboratory frame. More specifically, whereas for $\beta=0$ the stable modes of propagation along the Y axis are linearly polarized along the directions ±45° with respect to the Z axis and thus can be described by a polarization vector (ζ, ξ), where ζ is the X component and ξ the Z component of the polarization, with $\xi=1/\sqrt{2}$, $\zeta=\pm1/\sqrt{2}$, we have for $\beta\neq0$ (see Appendix A)

$$\xi=\left\{1+\left[\frac{\beta}{a}\mp\left(1+\frac{\beta_2}{a^2}\right)^{1/2}\right]^2\right\}^{-1/2}$$

$$\zeta=\left[\frac{\beta}{a}\mp\left(1+\frac{\beta^2}{a^2}\right)^{1/2}\right]\Big/\left\{1+\left[\frac{\beta}{a}\mp\left(1+\frac{\beta^2}{a^2}\right)^{1/2}\right]^2\right\}^{1/2} \tag{50}$$

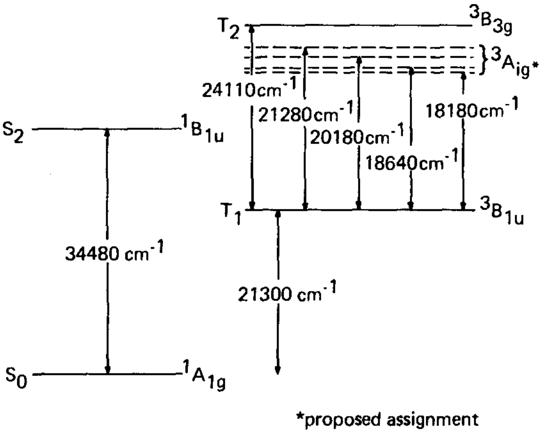

FIG. 2. Principle axes of anisotropic host medium looking along the Y axis (direction of propagation of probe light) 1 and 2 with $\beta=0$, 1′, and 2′ with $\beta\neq0$, $\beta\ll a$.

which reduces under the realistic assumption of $\beta/a\ll1$ and hence $\beta^2/a^2\simeq0$ to the more manageable

$$\xi=\frac{1}{[\sqrt{2}\mp(\beta/a)]},$$

$$\zeta=\frac{\mp[1\pm(\beta/a)]}{[\sqrt{2}\mp(\beta/a)]}, \tag{51}$$

and leads to an actual change in the angle of the stable polarization vectors [and the principle axes of $(\epsilon_{ij})_T$] given by

$$\tan\eta\simeq-\beta/2a \tag{52}$$

or simply

$$\eta\simeq-\beta/2a.$$

This is illustrated in Fig. 2.

Given a, a measurement of η will yield β, hence β', etc., as discussed above. The accurate expression for η would be

$$\tan\eta=\frac{[(\xi/\zeta)-1]}{[(\xi/\zeta)+1]}. \tag{53}$$

While η can in principle be measured directly by rotating both polarizer and analyzer in the probe beam until again extinction is obtained and noting the amount of rotation, this cannot practically be done with great accuracy when the angle is only of the order of 1° or even smaller. A more sensitive way to obtain η is to leave polarizer and analyzer unchanged and measure the intensity of the light passed by the analyzer upon creation of the excited state population. To relate this intensity to η we consider the incident probe light decomposed into components parallel to the new axes of the system. The amplitudes of these components will be different, they will travel through the medium with different velocities and recombine

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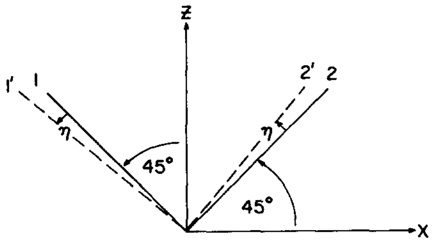

FIG. 3. Level scheme for deuterated naphthalene.

with a phase difference δ' which will now be given by

$$\delta' = [l\omega/c(\epsilon')^{1/2}](a^2+\beta^2)^{1/2}. \tag{54}$$

The light emerging from the sample will then in general be elliptically polarized, with the axes of the ellipse not coincident with either the new or the old axis system. In Appendix B it is shown that for $\beta \ll a$ we have

$$\eta \simeq (I_\perp/I_0)^{1/2}(1+\cos\delta')^{-1}, \tag{55}$$

where in the expression (54) for δ' we may neglect β, i.e., we can use for δ' the same value used for the determination of a.

All remarks made thus far are quite general and their validity is not restricted to any particular system. The analysis remains valid as long as a significant excited state population can be maintained during the time of measurement and as long as the time of measurement is short compared with any rotational relaxation time of the molecules of interest, and it does not matter what the host medium is nor what the particular excited state species is, provided the host is transparent, the concentration of the molecules of interest is low, and the Clausius–Mossotti relationship (14) is applicable. While our measurements were made on excited triplet states of aromatic molecules embedded in an organic glass at 77°K, there is no principle reason why it could not be done equally well on excited singlet states in a liquid host medium by the use of intense pulse excitation with pulse durations short compared with the rotational relaxation times in the liquid. The problems would be purely experimental.

III. EXPERIMENTAL DETAILS AND CONSIDERATIONS

A. The Arrangement

In our experiments we measured the optical anisotropy parameter Δ defined by (1) for the lowest-lying triplet state of deuterated naphthalene (DN) as a function of wavelength from 4200 to 6300 Å. The DN was used in a concentration of 5×10^{-3} molar in a glass matrix of EPA at 77°K. The excitation source was a 1.5-kW mercury–xenon arc lamp. The triplet state was populated by exciting the ${}^1A_{1g}$ to ${}^1B_{1u}$ singlet–singlet transition. The transition moment for this transition lies along the z axis in the plane of the molecule. To insure that excitation took place essentially only through this transition, the source light was suitably filtered. The filtered source light was vertically polarized by a uv Glan-polarizer and focused by a quartz lens into the sample. The extremely rapid intersystem crossing in DN combined with the long lifetime of the triplet state (~21 sec) allowed us to maintain in the focal region approximately 10% of the DN molecules in the triplet state ${}^3B_{1u}$ during excitation. The actual triplet-state concentration was obtained by a triplet–triplet absorption measurement (T_1 to T_2)for each experiment, about which more will be said later. The principle energy levels of concern for DN are given in Fig. 3.

The sample container was a 1×1 cm quartz Opticell, held in an all-quartz Dewar in liquid nitrogen. The probe source was a high-intensity tungsten lamp. Its light was collimated, passed through a Glan–Thompson polarizer, and chopped. A narrow pencil (~1 mm cross section) of light passed, after prefiltering with a suitable Optics-Technology bandpass interference filter, through the Dewar and sample, where it traversed the focal region of the excitation light at right angles; i.e., whereas the excitation light propagated through the sample in the positive X direction of the laboratory coordinates, the probe beam passed in the positive Y direction. After passage through the sample and Dewar the probe beam passed through a Glan–Thompson analyzer and was focused into the entrance slit of a 75-cm Spex scanning grating monochromator equipped with a Bausch & Lomb grating, blazed at 5000 Å. The output from the monochromator was detected by an EMI 6256 photomultiplier, using a load resistor of 10 to 100 $k\Omega$. The signal from the photomultiplier was fed to a PAR HR8 lock-in amplifier and the signal was read out on a digital voltmeter.

B. The Measurement

In making an actual measurement the following procedure was used:

The sample, prepared at room temperature was immersed in a vertical position in liquid nitrogen and allowed to freeze. As strain axes near the walls of the cell usually were parallel (or perpendicular) to the walls, the sample was then placed at an angle of 45° with respect to the laboratory Z axis, as described above, in the quartz Dewar filled with liquid nitrogen. Probe light and excitation light were switched on and it was assured that the two beams overlapped in a region close to the junction of the two walls facing the

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excitation source and the spectrometer, respectively. This was done to minimize the effects of absorption of the excitation light in the sample (such absorption was kept low by using low concentrations of DN, thus keeping excitation uniform over the cross section of the probe beam) and to allow passage of the probe beam directly from the excited region out of the sample without further passage through an unexcited region of the host medium (otherwise the analysis of the results would become extremely complicated). The pathlength of the probe beam through the excited region was approximately 0.3 cm. After sample and light beams were positioned, the excitation was switched off and the phosphorescence allowed to decay. The excitation times were always kept to an absolute minimum, as prolonged excitation lead to a local deterioration of the sample by free radical formation due to successive excitation to higher energy levels, with consequent changes in the optical properties of such a region. When this did occur, the sample was repositioned so that a different region was probed and excited.

The next step was a determination of the strain axes by finding the position of polarizer and analyzer for the absolute minimum of light passed. While this position was not always exactly at 45°, when taking account of the refraction of the exciting beam at the sample walls and defining the laboratory Z axis in terms of the polarization vector of the exciting light inside the sample, any deviation was usually negligible (major deviations can be accounted for in the analysis). The residual light passed by the analyzer in this position had to be of the order of 10^{-4} of full intensity if the sample was to be considered good enough for a measurement. A large ratio was indicative of nonuniform strain axes along the probe beam. In that case, unless a better position for the beam could be found, the sample had to be replaced. Once the strain axes were located, the birefringence parameter a of the host medium was determined at the desired wavelength by changing the polarization of the probe beam to a position of 45° with respect to the strain axes and measuring the $I_{\parallel}$ and $I_{\perp}$ of the elliptically polarized light leaving the sample. This gave the phase shift in the sample. This phase shift ranged usually between 30° and 130°. Since the phase shift depends strongly on λ, whereas a and n_M in these regions vary only slowly with λ, a measurement at a number of different wavelengths insured that no error by a multiple of π was made in this determination. Knowledge of the phase shift, given λ, the pathlength of 1 cm and the refractive index of the glass n_M (as obtained from knowledge of the n of the constituents of the glass, making allowance for a 20% shrinkage in volume upon freezing and cooling to 77°K) yielded the parameter a for the wavelength chosen. In making intensity measurements at any given wavelength, experimentally determined corrections were applied for the polarization dependence (varying with λ) of the grating spectrometer used. Following the determination of a, the excitation was switched on and the probe beam was used to measure the triplet–triplet absorption at 4148 Å. This measurement provided information regarding the triplet concentration and the excitation parameter A (see Appendix C for details).

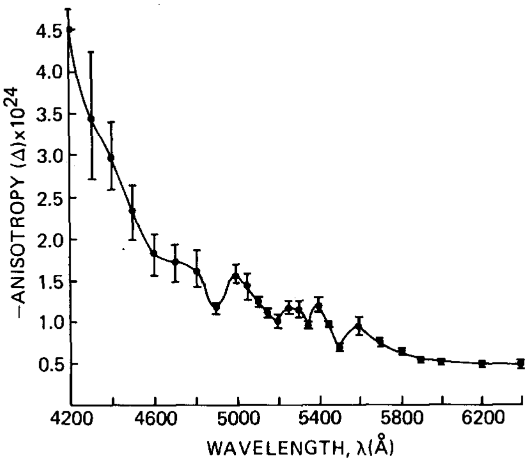

FIG. 4. Optical anisotropy $(-\Delta)\times10^{24}$ cm^3 as a function of the wavelength of the probe light for deuterated naphthalene.

The excitation was then switched off, the phosphorescence allowed to decay, the wavelength of interest was set on the monochromator, and polarizer and analyzer were set to their original position (i.e., maximum extinction). The excitation was switched on again and the resulting increase in light passed by the analyzer (and corrected for the spectrometer transmission) was recorded. From this intensity increase the induced optical axis shift η was obtained [according to (55)]. To obtain the correct sign for η, the direction of the axis shift was also determined by finding the new minimum position for polarizer and analyzer while the sample was excited. The determination of η was frequently followed by another triplet–triplet absorption measurement at 4148 Å to insure that no significant deterioration had occurred in the sample during the measurement. As mentioned before, with a knowledge of η, a, n, and S thus obtained, Δ could be calculated.

C. Further Experimental Considerations

Some of the factors that had to be accounted for such as refraction of the exciting light on the sample wall, the polarization dependence of the transmission of the spectrometer, etc., have already been mentioned in the previous section. Another important factor is the exact composition of the glass. An excess of isopentane will make the glass too soft and allow strain

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relaxation to occur during the measurements, i.e., a and the direction of the strain axes will vary while the measurements are made. Too hard a glass may crack, or have excessive strain inhomogeneities. Bubbles in the nitrogen have to be eliminated, at least from the light path. This was accomplished by keeping the Dewar extremely clean, avoiding condensation of ice in the liquid nitrogen, and by bubbling helium through the liquid nitrogen prior to the measurements.

Even though a lock-in technique was used for the detection, care must be exercised to prevent stray light (including the phosphorescence of the sample) from entering the spectrometer, as any dc signal reaching the photomultiplier will contribute to noise. A high chopping frequency will help in reducing $1/f$ noise.

Care must also be exercised to keep the intensity of the excitation source and of the probe source constant throughout the measurement.

IV. RESULTS OBTAINED ON DEUTERATED NAPHTHALENE

The results obtained on DN with the technique described in this paper have been reported by us[15] in a letter. They are summarized here for completeness.

Figure 4 shows the optical anisotropy Δ as a function of the wavelength of the probe light.

As a resonance is approached from the low-energy side, that component of the polarizability tensor which corresponds to the transition direction increases very rapidly. Thus, the marked decrease in Δ with increasing energy in the neighborhood of 4200 Å can be due to increases in the ground state α_{zz}^G or triplet components α_{yy}^T, α_{xx}^T of the polarizability but not to the α_{zz}^T component. The dispersion of α_{zz}^G in this energy region is too small to explain the change of Δ with energy and is, therefore, neglected.[16] The dispersion of α_{xx}^T can also be neglected since the transitions contributing to α_{xx}^T occur at much greater energies than the energy region studied here. Hence, the increase is in the α_{yy}^T component and, therefore, indicates that a contribution due to a triplet state which has a transition moment with respect to T_1 $(^3B_{1u})$ along the molecular y axis is responsible for the observed changes in Δ as 4200 Å is approached. The y-axis assignment is in accord with the well known $^3B_{3g}^- \leftarrow {}^3B_{1u}^+$ at 4150 Å.[17,18]

Superimposed upon the strong change in Δ near 4200 Å there appears extensive structure in the region between 4500 and 5900 Å. This indicates the presence of weak transitions between T_1 and other electronic states in this region. The transitions are observed at 18 180, 18 640, 20 180, and 21 280 cm^{-1} above T_1. Using the same arguments advanced for the dispersion in the 4200-Å region leads to the conclusion that changes in α_{yy}^T are responsible for the structure at the longer wavelengths. Hence, the transitions in this region are polarized along the molecular y axis.

The existence of excited triplet states in this energy region of symmetries $^3A_{1g}^+$ and $^3B_{1u}^+$ are predicted by theoretical calculations. The positions of these levels above the lowest triplet according to de Groot and Hoytink[19] and Pariser[20] are $^3A_{1g}^+$ (16 370 cm^{-1}, 18 175 cm^{-1}) and $^3B_{1u}^+$ (17 170 cm^{-1}, 16 440 cm^{-1}), respectively. (The B_{1u} and B_{3g} symbols used here correspond to the B_{2u} and B_{1g} notation used in Refs. 19 and 20.) Since T_1 is of B_{1u}^+ symmetry, transitions to these states are forbidden and are made allowed by vibronic mixing with electronic states of suitable symmetry. (The $^3B_u^+ \rightarrow {}^3A_{1g}^+$ forbiddeness arises from the plus→plus prohibition. Even if this transition were weakly allowed, its polarization would be along the z axis which is contrary to our experimental observations.) Since the nearest state of appropriate symmetry is the $^3B_{3g}^-$ (24 100 cm^{-1}), then the resulting transition from the B_{1u}^+ would be y-axis polarized. This prediction is in agreement with our data. Direct experimental evidence of naphthalene transitions in this region prior to the present work were the observations of very weak triplet–triplet transitions in a polymethylmethacrylate host and in an alcohol glass.[21,22]

In line with the arguments based on theoretical predictions[19,20] combined with two-photon measurements on a-chloronaphthalene[16] presented in our letter,[15] it is concluded that the state observed in this study is a $^3A_{1g}^+$.[23] We have also observed the optical anisotropy of the triplet state polarizability using the IBR method for the molecules phenanthrene-d_{10} and triphenylene.

V. CONCLUSIONS

A method for obtaining the optical polarizabilities of excited electronic states by induced birefringence is described. Measurement of the dispersion of the optical anisotropy makes possible a determination of symmetry of the transition as well as the detection of very weak transitions. This method has been successfully applied to identify and assign very weakly absorbing triplet–triplet transitions in deuterated naphthalene. The optical anisotropies of phenanthrene-d_{10} and triphenylene have also been determined by this technique.

ACKNOWLEDGMENTS

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APPENDIX A: STABLE MODES OF PROPAGATION IN AN ANISOTROPIC MEDIUM

Starting with Maxwell's equations for a light wave propagated in an anisotropic dielectric medium, whose properties are described by a permittivity tensor

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(ϵ_{ij}), $(i,j=x,y,z)$

$$(\nabla\times\mathbf{H})_i=(1/c)\sum_j \epsilon_{ij}(\partial E_j/\partial t), \qquad \text{(A1a)}$$

$$(\nabla\times\mathbf{E})_i=-(1/c)(\partial\mathbf{H}_i/\partial t), \qquad \text{(A1b)}$$

$$\nabla\cdot\mathbf{H}=0, \qquad \text{(A1c)}$$

$$\nabla\cdot\mathbf{d}=\sum_i\sum_j \epsilon_{ij}(\partial E_j/\partial X_i)=0, \qquad \text{(A1d)}$$

where the symbols have their usual meaning, i.e., **H** is the magnetic field, **E** the electric field, **d** the electric displacement, and c the velocity of light *in vacuo*, we consider a plane wave propagated in the z direction and put

$$E_x=\xi\exp(i\omega t-\gamma z) \qquad \text{(A2a)}$$

and

$$E_y=\eta\exp(i\omega t-\gamma z). \qquad \text{(A2b)}$$

For such a plane wave, whatever the form of E_z, we have

$$\partial E_z/\partial x=\partial E_z/\partial_y=0. \qquad \text{(A2c)}$$

Substituting (A2) into A1b and solving for the H_i we obtain

$$H_x=-(c\gamma/i\omega)\eta\exp(i\omega t-\gamma z) \qquad \text{(A3a)}$$

$$H_y=(c\gamma/i\omega)\xi\exp(i\omega t-\gamma z) \qquad \text{(A3b)}$$

$$H_z=0. \qquad \text{(A3c)}$$

Equation (A1c) is satisfied identically by (A3). Substituting (A2) and (A3) into (A1a), we obtain

$$(c\gamma^2/i\omega)\xi\exp(i\omega t-\gamma z)=$$
$$(i\omega/c)\exp(i\omega t-\gamma z)(\epsilon_{xx}\xi+\epsilon_{xy}\eta+\epsilon_{xz}\zeta), \qquad \text{(A4a)}$$

$$(c\gamma^2/i\omega)\eta\exp(i\omega t-\gamma z)$$
$$=(i\omega/c)\exp(i\omega t-\gamma z)(\epsilon_{yx}\xi+\epsilon_{yy}\eta+\epsilon_{yz}\zeta), \qquad \text{(A4b)}$$

$$0=(i\omega/c)\exp(i\omega t-\gamma z)(\epsilon_{zx}\xi+\epsilon_{zy}\eta+\epsilon_{zz}\zeta), \qquad \text{(A4c)}$$

where $E_z=\zeta\exp(i\omega t-\gamma z)$.

Equation (A4c) is the same as that obtained when substituting the expressions for **E** and **H** into Eq. (A1d). Hence

$$\zeta=-(\epsilon_{zx}/\epsilon_{zz})\xi-(\epsilon_{zy}/\epsilon_{zz})\eta. \qquad \text{(A5)}$$

Substituting (A5) into (A4a) and (A4b), we finally get

$$\left(\epsilon_{xx}-\frac{\epsilon_{xz}\epsilon_{zx}}{\epsilon_{zz}}\right)\xi+\left(\epsilon_{xy}-\frac{\epsilon_{xz}\epsilon_{zy}}{\epsilon_{zz}}\right)\eta=-\frac{c^2\gamma^2}{\omega^2}\xi \qquad \text{(A6a)}$$

and

$$\left(\epsilon_{yx}-\frac{\epsilon_{yz}\epsilon_{zx}}{\epsilon_{zz}}\right)\xi+\left(\epsilon_{yy}-\frac{\epsilon_{yz}\epsilon_{zy}}{\epsilon_{zz}}\right)\eta=-\frac{c^2\gamma^2}{\omega^2}\eta. \qquad \text{(A6b)}$$

Equations (A6) represent an eigenvalue problem whose eigenvectors give the polarizations (ξ,η) of those waves which are propagated through the medium in the z direction without change of polarization and whose eigenvalues give the propagation constants γ of these waves. These waves are called here the "stable modes of propagation."

If as in the case of pure birefringence the components of the ϵ tensor are all real, then so are the coeffiicents of the eigenvalue equations (A6) and the eigenvectors are linear combinations of ξ and η with real coefficients. Thus, the stable modes are plane-polarized, but travel with different velocities in the medium. An arbitrarily polarized plane wave entering such a medium is decomposed into two such plane-polarized waves with the appropriate amplitude and phase relationship. An additional phase shift is introduced in the medium as the result of the different propagation constants, and upon leaving the medium they are recombined with their original amplitudes and with the new phase relationship, which will now determine the polarization of the emerging wave.

APPENDIX B: DERIVATION OF EQ. (55)

Consider Fig. 2. We have light of intensity $I_0=E_0^2$ polarized along 1 incident on the sample, whose permittivity tensor has principle axes along 1′ and 2′ shifted by a small angle η with respect to 1 and 2. The phase shift in the medium between components parallel to 1′ and 2′ ,respectively, is δ' and the analyzer behind the medium is oriented to pass components parallel to 2. The intensity of light passed by the analyzer is $I_\perp$. $\mathbf{e}_1$, $\mathbf{e}_2$, $\mathbf{e}_1'$, $\mathbf{e}_2'$ are unit vectors along the corresponding directions 1, 2, 1′, and 2′.

The electric-field vector incident on the medium is

$$\mathbf{E}_{\text{in}}=E_0\exp(i\omega t)(\cos\eta\,\mathbf{e}_1'+\sin\eta\,\mathbf{e}_{2'}); \qquad \text{(B1)}$$

that leaving the medium is

$$\mathbf{E}_{\text{out}}=E_0\exp(i\omega t)[\cos\eta\,\mathbf{e}_{1'}+\sin\eta\exp(i\delta')\mathbf{e}_{2'}]. \qquad \text{(B2)}$$

The component $E_\perp$ of E_{out} which is parallel to 2 (and the analyzer) is

$$E_\perp=E_0\exp(i\omega t)[\cos\eta\,\mathbf{e}_2\cdot\mathbf{e}_{1'}+\sin\eta\exp(i\delta')\mathbf{e}_2\cdot\mathbf{e}_{2'}] \qquad \text{(B3)}$$

or

$$E_\perp=E_0\exp(i\omega t)\sin\eta\cos\eta[1+\exp(i\delta')]. \qquad \text{(B4)}$$

Now $I_\perp=\langle E_2^2\rangle$, the time average over one cycle of $E_\perp^2$, i.e.,

$$I_\perp=E_0^2\sin^2\eta\cos^2\eta(2+2\cos\delta')\tfrac{1}{2} \qquad \text{(B5)}$$

for $\eta\ll 1$, $\sin\eta\sim\eta$, and $\cos\eta\sim 1$; and thus with $E_0^2=I_0$ and solving for η, finally

$$\eta=(I_\perp/I_0)^{1/2}, 1/(1+\cos\delta'). \qquad \text{(B6)}$$

APPENDIX C: EVALUATION OF TRIPLET-STATE CONCENTRATION n_1 AND EXCITATION PARAMETER A FROM TRIPLET–TRIPLET ABSORPTION MEASUREMENT

In an absorption experiment on triplet–triplet absorption the ratio of transmitted intensity I to

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incident intensity I_0, together with the triplet state concentration n_1 in moles per liter and the path length l in centimeters, defines the molar extinction coefficient ϵ by the relation

$$I/I_0=10^{-\epsilon n_1 l}. \tag{C1}$$

In our experiment we used an extinction coefficient $\epsilon=3.2\times10^4$ obtained by Brinen[24] under conditions where n_1 is a random distribution, yet used the relation (C1) to obtain n_1. Since in our experiment the molecules in the triplet state are not randomly distributed the triplet concentration we obtain in this matter is an apparent one, called $n_{1\mathrm{app}}$ subsequently, rather than the true one. We, therefore, need the relationship between n_1 and $n_{1\mathrm{app}}$. Also, to evaluate S we need to know n_1 since from an integration of (23), we get

$$n_1/n_0=1-(1/S^{1/2})\arctan S^{1/2}. \tag{C2}$$

Given n_1 we obtain S from a computerized tabulation of (C2).

Now we observe the triplet–triplet absorption with light propagating along the positive laboratory Y axis and plane polarized 45° with respect to the laboratory X and Z axes. For a molecule whose z axis orientation is given by the Eulerian angles (θ,ϕ,ψ) the direction cosines of the molecular y axis (direction of triplet–triplet transition moment) with the laboratory X axis is given by $-\cos\theta\cos\phi\sin\psi-\sin\phi\cos\psi$ and that of the molecular y axis with the laboratory Z axis by $\sin\theta\sin\psi$. We, therefore, find that

$$\frac{n_1}{n_{1\mathrm{app}}}=\frac{n_1}{n_0}\,\frac{\displaystyle\int_0^{\pi}\int_0^{2\pi}\int_0^{2\pi}(\sin^2\theta\sin^2\psi+\cos^2\theta\cos^2\phi\sin^2\psi+\sin^2\phi\cos^2\psi)\sin\theta d\theta d\phi d\psi}{\displaystyle\int_0^{\pi}\int_0^{2\pi}\int_0^{2\pi}\frac{S\cos^2\theta}{1+S\cos^2\theta}(\sin^2\theta\sin^2\psi+\cos^2\theta\cos^2\phi\sin^2\psi+\sin^2\phi\cos^2\psi)\sin\theta d\theta d\phi d\psi}. \tag{C3}$$

[The cross terms of the squares of the direction cosines do not contribute to the integrals and have, therefore, been left out of (C3).]

Evaluating the integrals in (C3) and keeping in mind (22), we obtain

$$\frac{n_1}{n_{1\mathrm{app}}}=\frac{8}{9-(n_0/n_1)+(3/S)} \tag{C4}$$

and

$$\frac{n_1}{n_0}=\frac{8n_{1\mathrm{app}}+1}{9+(3/S)}. \tag{C5}$$

If we define the measured saturation parameter R by

$$R=n_{1\mathrm{app}}/n_0, \tag{C6}$$

we obtain with the use of (C2) the relationship

$$R=\left(1-\frac{1}{S^{1/2}}\arctan S^{1/2}\right)\left(\frac{9+(3/S)}{8}\right)-\frac{1}{8}. \tag{C7}$$

A computer tabulation of (C7) will then yield S for any value of the R obtained from our measurements.

APPENDIX D: INFLUENCE OF DICHROISM ON THE MEASURED PARAMETER η

Just as a birefringent phase shift, an induced dichroic absorption (i.e., differential absorption along the laboratory X and Z axes) will result in an observed signal $I_\perp$ passed by the analyzer and would lead us to deduce a value of η attributable to dichroism given by

$$I_\perp=I_0\eta^2, \tag{D1}$$

where the $I_\perp$ resulting from dichroism is given by

$$I_\perp=(I_X^{1/2}-I_Z^{1/2})^2 \tag{D2}$$

with

$$I_X=\tfrac{1}{2}I_0 10^{-ln\epsilon_X} \tag{D3a}$$

$$I_Z=\tfrac{1}{2}I_0 10^{-ln\epsilon_Z}. \tag{D3b}$$

I_0 is the incident intensity (polarized at 45° with respect to X and Z), l is the pathlength in the region of absorption (in our case 0.3 cm), n the triplet state concentration ($\sim5\times10^{-4}M$), and ϵ_X and ϵ_Z are the molar extinction coefficients for light polarized along the X and Z axes, respectively.

From (D2) and (D3), we obtain

$$I_\perp=\tfrac{1}{2}I_0(10^{-\frac{1}{2}ln\epsilon_X}-10^{-\frac{1}{2}ln\epsilon_Z})^2, \tag{D4}$$

and hence the apparent η due to dichroism alone will be

$$\eta=\tfrac{1}{2}(10^{-\frac{1}{2}ln\epsilon_X}-10^{-\frac{1}{2}ln\epsilon_Z}) \tag{D5}$$

which for the small absorptions in the spectral region of interest reduces to

$$\eta\simeq\tfrac{1}{4}\times0.434\times ln(\epsilon_Z-\epsilon_X). \tag{D6}$$

The ratio ϵ_Z/ϵ_X is determined solely by the anisotropy in the distribution of molecules in the triplet state. Once measured at 4148 Å it can be used also in the wings of the absorption line. We found the typical value under our experimental conditions to be

$$\frac{\epsilon_Z}{\epsilon_X}=\frac{\log(I_Z/I_0)}{\log(I_X/I_0)}\simeq0.975. \tag{D7}$$

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This allows us to obtain an estimate for the apparent η due to dichroism as a function of ϵ_Z under our experimental conditions (i.e., approximately 10% of our molecules of interest being in the triplet state). We find using the experimental values given that

$$|\eta|\simeq 4\times 10^{-7}\epsilon_Z \qquad \text{(D8)}$$

which implies an apparent η of 10 min of arc for $\epsilon_Z \sim 2500$. Such values of ϵ should be easily directly observable under our experimental conditions. Actually, the extinction coefficients estimated for transitions in the region of interest are only of the order of $\epsilon \sim 200$ and hence would account for an apparent η of less than 1 min of arc as the result of dichroism. This is smaller than our observed η by almost two orders of magnitude. We, therefore, conclude that dichroism and its effect on our measurements can be neglected except in the immediate vicinity of the strong absorption at 4148 Å.

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Calculation of the Anharmonicity in the Vibrational Frequencies of Alkane Molecules by the CFF Functions

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The CFF method is extended to include all the first five terms of the Taylor expansion of the molecular potential functions. A scheme for anharmonicity calculations in any molecule, in every equilibrium conformation is suggested. The actual anharmonicity calculation for ethane, *n*-butane, and cyclohexane is described. It is shown that a mixed function of bond stretching and bond angle bending, with Morse type dependence on the bond length is suitable for such calculations. The advantage of using potential functions instead of a force constant field, which is a central idea of the CFF philosophy, is strongly supported by the calculations.

INTRODUCTION

In previous papers[1–3] the vibrational spectra, conformations, molecular excess enthalpies, and crystal properties of alkane molecules were calculated by a "consistent force field" (CFF) method. All these properties were calculated from the same set of empirical energy functions, using the Taylor expansion of the potential field up to the second derivatives. The parameters of the energy functions were fitted by the method of least squares to give the best possible agreement between the calculated properties and the corresponding experimental data. Thus, we evaluated an empirical potential surface which insures the correct representation for the first three terms in the Taylor expansion.

Here we try to extend this study to higher terms in the expansion. The anharmonicity in the molecular vibration is calculated from the CFF functions. It is examined to see if the calculation could account for the experimental results and whether the incorporation of such calculation in the CFF scheme could lead to better understanding of the potential surfaces. For triatomic molecules there are some systematic works[4,5]

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