spectrum was identical for both the $(20\bar{1})$ and (001) [not shown] faces. As will be reported in detail later, the factor group splittings and intensity ratios for a-axis and b-axis polarized spectra obtained from the (001) face are in excellent agreement with published direct absorption measurements. Consequently, we have considerable confidence in the quantitative correctness of the reflection method. It should be noted that reflection monitors the same bulk property that is measured via direct absorption.

The absorption spectrum for radiation polarized parallel to the ac plane on the $(20\bar{1})$ face ($\perp b$ in Fig. 2) is dominated by a very strong absorption band (40 100 cm^{-1}), which is clearly related to the intense band occurring at about the same frequency in the vapor.[7] Neglecting all other components of this band, the oscillator strength of the free molecule is calculated to be 1.1.[8] Theoretical arguments[9–11] predict that the a-axis component of this band (viz., the B_u crystal component of a long-axis molecular transition[12]) will be shifted far to the blue. Lyons and Morris[2] assigned the a-axis component to the absorption occurring in the 2100–1900-Å region. Assuming this assignment to be correct, our result then is in qualitative agreement with the predictions of Fox and Yatsiv[4] to the extent that there is a marked reduction in the magnitude of the blue shift of the B_u component as the propagation direction of the incident radiation becomes more nearly perpendicular to the projection of the molecular transition moment in the ac plane.[13]

The band at 37 300 cm^{-1} of the $\parallel b$ spectrum, which has been assigned as the A_u crystal component of the strong transition, very likely is derived from an entirely different transition which is short-axis polarized in the free molecule. Components of this band are observed in directions on other faces which have zero projection of a long-axis transition moment.[14] The location of the

b-axis component of the strong band is therefore unknown.

Finally, the intensity distribution of the low-energy absorption region of the $\perp b$ spectrum of $(20\bar{1})$ suggests the probable presence of another transition, overlapping the first singlet state, which seems to be derived from a long-axis polarized transition. This observation is supported by additional data (to be reported later) taken from the $(\bar{1}10)$ face. Therefore, agreement between theory, assuming a single transition, and experiment of the $a:b$ intensity ratios of the first excited singlet state must be regarded with skepticism.

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[1] For a review of the literature see: H. W. Wright, Chem. Rev. 67, 581 (1967).

[2] L. E. Lyons and G. C. Morris, J. Mol. Spectry. 4, 480 (1960).

[3] See, however, S. V. Morisova, Opt. Spektrosk. 21, 566 (1967) [Opt. Spectrosc. 22, 310 (1967)].

[4] D. Fox and S. Yatsiv, Phys. Rev. 108, 938 (1967).

[5] For details of the reflection spectrophotometer and the transformation procedure see: H. H. Chen and L. B. Clark, J. Chem. Phys. 51, 1862 (1969).

[6] L. E. Lyons and G. C. Morris, J. Chem. Soc. 1959, 1551.

[7] A frequency of 42 270 cm^{-1}. See Ref. 2.

[8] In order to directly measure the absorption spectrum of the $(20\bar{1})$ face, a crystal thickness of a few hundred angstroms would be required.

[9] R. Silbey, J. Jortner, and S. A. Rice, J. Chem. Phys. 42, 1515 (1965).

[10] M. Tanaka and J. Tanaka, Mol. Phys. 16, 1 (1969).

[11] M. R. Philpott, J. Chem. Phys. 50, 5117 (1969), and other references therein.

[12] Symmetry designations pertain to $|\mathbf{k}| = 0$.

[13] It should also be noted that the 0–0 band of the first singlet transition in the $\perp b$ direction of $(20\bar{1})$ occurs at slightly higher energy ($\sim$80 cm^{-1}) than the a-axis component of (001). Again, this result is in qualitative agreement with the discussion of Ref. 4.

[14] Evidence for this conclusion is clearly seen on the ac face and on a face cut 4° from the c axis and parallel to the b axis.
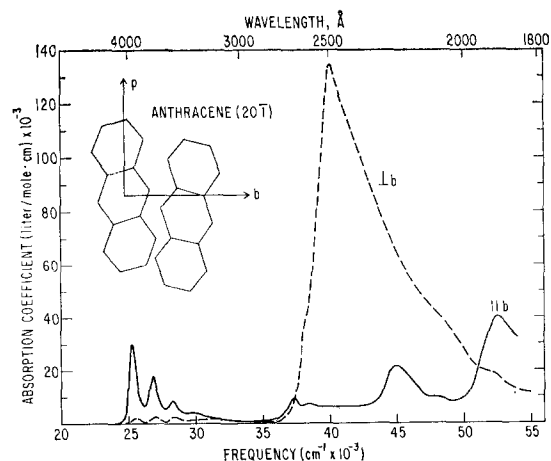

FIG. 2. Absorption spectra of the $(20\bar{1})$ face of anthracene obtained via a Kramers–Kronig transformation of the reflection spectra. The projection of the two molecules of the unit cell onto the $(20\bar{1})$ face is shown.

Measurement of Orientational Relaxation Using Picosecond Light Pulses

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We wish to report the first direct observation of the orientational relaxation of molecules in a liquid environment using picosecond laser pulses. The method consists of exciting a fraction of the molecules dissolved in a liquid to a higher electronic state with a picosecond pulse and then probing at later times with a greatly attenuated picosecond pulse. The first pulse produces an anisotropic distribution by preferentially exciting those molecules whose transition moments have a large component along the polarized light field. The second reflected pulse then measures this anisotropy. If the molecules were in a rigid environment and thus were

unable to rotate, the initial induced anisotropy would decay to the isotropic distribution only via emission or radiationless decay processes. However, in a liquid environment the nonuniform distribution can also be transformed into an isotropic one through rotational Brownian motion. This return to the equilibrium distribution has been monitored by measuring the polarization dependence of absorption (dichroism) of a greatly attenuated picosecond pulse at varying times after the excitation pulse. Before rotational relaxation the absorption was greater for probe light polarized perpendicular to rather than parallel to the polarization of the exciting light. This results from the relative depletion of ground-state molecules oriented in the parallel configuration by the exciting pulse. By probing at successively later times after the excitation pulse, the difference in absorption for the two polarizations was observed to decrease as the isotropic distribution was re-established.

We have used this technique to study the orientational relaxation of rhodamine-6G at a concentration of 5×10^{16} molecule/cm^3 in ethylene glycol. The experiments were performed with a Nd^{+3} glass laser with a cavity 1.2 m long, two plane wedged dielectric mirrors of 85% and 99% reflectivity, and a Brewster cut rod (Kodak ND-11, length $6\frac{5}{8}$ in., diam $\frac{3}{8}$ in.) which was pumped by a linear flash lamp in a cylindrical reflector of elliptical cross section. The laser was mode locked by a solution of Eastman #9860 dye in an Eastman Q-switch cell oriented at the Brewster angle and placed in the center of the cavity. In order to study molecules which absorb in the visible range the 1.06-μ output was frequency doubled to 0.53 μ with a suitably cut and oriented KDP crystal. The time width of the pulses was determined to be 3×10^{-12} sec by a two-photon fluorescence method.[1] The probe was obtained by reflecting a small fraction of the transmitted exciting pulse. The time delay between the probe and the exciting pulse was determined by the separation of the sample from the reflecting element. To minimize problems introduced by the intensity variations in the light pulses, the probe beam was polarized so that it had components parallel and perpendicular to the excitation beam polarization. In this way both components of polarization view the same excitation region and their individual transmitted intensities were simultaneously measured with a fast-rise-time ITT photodiode and displayed on the Tektronix 519 oscilloscope. As expected, the two components of the probe beam had equal intensities in the absence of the absorbing molecules. The relative transmission intensities of the two probe polarizations were then measured at various delay times.

For rhodamine-6G excited by 0.53-μ light, the effects of stimulated emission or excited-state absorption by the probe pulse can be neglected.[2] In addition, the lifetime of the excited molecule is considerably longer than the orientational relaxation time. For these reasons the decay of the measured dichroism depends only on the reorientation time of the ground-state molecules. For those cases where the excited-state lifetime is comparable to the molecular reorientation time, the orientational relaxation time can still be determined by a modification of this method.[2]

To relate our experimental measurements to the orientational relaxation time, we calculated the absorption of the parallel and perpendicular components of the probe light at various times after excitation. The distribution function used to calculate the time dependence of the dichroism was obtained by a solution of the rotational diffusion equation assuming that the diffusion constant is a scalar. In this way we found the orientational relaxation time of rhodamine-6G in ethylene glycol to be $6.5 \pm 0.5 \times 10^{-10}$ sec.

Unlike the light-scattering[3] and dielectric relaxation[4] methods for determining orientational relaxation, the technique we present here is not restricted to pure liquids, concentrated solutions, or polar molecules. Furthermore, the broad band absorption of organic molecules in solution permits the application of this method with available lasers to many molecular systems. By simple variations of the technique presented in this paper, the direct measurement of excited-state orientational relaxation, solvent reorientation, and intermolecular energy transfer are also presently under study.

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[1] J. A. Giordmaine, P. M. Rentzepis, S. L. Shapiro, and K. W. Wecht, Appl. Phys. Letters 11, 216 (1967).

[2] This point will be discussed in a subsequent publication.

[3] I. L. Fabelinskii, *Molecular Scattering of Light* (Plenum Press, Inc., New York, 1968). S. L. Shapiro and H. P. Broida, Phys. Rev. 154, 129 (1967). D. A. Pinnow, S. J. Candau, and T. A. Litovitz, J. Chem. Phys. 49, 347 (1968).

[4] E. J. Hennelly, W. M. Heston, Jr., and C. P. Smyth, J. Am. Chem. Soc. 70, 4120 (1948). V. V. Daniel, *Dielectric Relaxation* (Academic Press Inc., New York, 1967).

Conservation of Spin Direction and Production of Spin Alignment in Triplet–Triplet Energy Transfer

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It is well known[1] that the total spin angular momentum is conserved in triplet–triplet (T–T) energy transfer between aromatic molecules. Furthermore, it can be shown theoretically that the spin direction of the donor is preserved in this process. This is due simply to the fact that the $1/r_{ij}$ operator responsible for the