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OPTICAL ANISOTROPY OF AN EXCITED ELECTRONIC STATE

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We have used an optically induced birefringence to determine the difference in the polarizabilities between the ground state and an excited electronic state. Knowing the polarizability tensor for the ground state we have been able to obtain the optical anisotropy of the excited state, which is to our best knowledge the first direct measurement of this kind. We have measured the quantity $\Delta = 2\Delta\alpha_z - \Delta\alpha_y - \Delta\alpha_x$, where $\Delta\alpha_i$ $(i = x, y, z)$ is the difference in the molecular polarizability along the molecular i axis between the lowest triplet state and the ground state of deuterated naphthalene, $C_{10}D_8$, at optical frequencies. Here z is the short and y the long axis of the molecule. The determination of polarizability tensors has previously been limited to systems in their ground electronic states because of the need to have a sizable population in the electronic state to be studied. We have been able to achieve the requisite density of electronically excited molecules by pumping into a long-lived metastable state, namely the triplet state of $C_{10}D_8$ which has a lifetime of approximately 20 sec.[1]

The measurement we made used the technique of induced birefringence on a sample of 3.0×10^{21} molecules/cm^3 of $C_{10}D_8$, randomly distributed in EPA glass (consisting of an ethanol, ether, isopentane mixture) at 77°K. Figure 1 shows the essentials of the arrangement. Excitation of the triplets is done with the Hg-Xe arc suitably filtered to excite essentially the singlet-singlet transition

$$A_g \xrightarrow{h\nu} B_{1u}$$

(short axis) followed by intersystem crossing to the $^3B_{1u}$ state. This light beam is polarized vertically (Z axis in the laboratory frame) and propagates along the laboratory X axis. As the triplet state is populated in this way, a birefringence is induced in the sample with

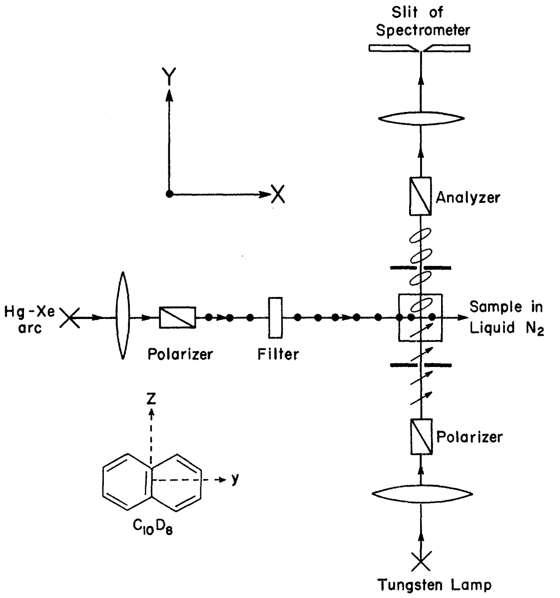

FIG. 1. Experimental arrangement.

the Z axis as axis of symmetry. To measure this induced birefringence a probing beam of plane-polarized tungsten light is propagated along the laboratory Y axis, with a polarization vector inclined approximately 45° with respect to the Z axis. A $\frac{3}{4}$-m Czerny-Turner spectrometer behind the analyzer is used to select the wavelength of interest and also serves to determine the population of the triplet state by a measurement of triplet-triplet

$$^3B_{1u} \xrightarrow{h\nu} {}^3B_{3g}$$

absorption.[2] For the measurement at 6328 Å a He-Ne laser was substituted for the tungsten light. The interaction of the probing light with the sample is determined by the polarizability tensor of the sample. The polarizer and analyzer are crossed when the system is completely in the ground state. Upon the orientationally selective excitation of the triplet state, the polarizability tensor is modified and the change in the polarization of the light leaving the sample is obtained. This measurement, coupled with a knowledge of the triplet-state population, allows a determination of Δ.[3] For the extinction coefficient of the triplet-triplet absorption we used the value of 3.2×10^4 obtained by Brinen.[4]

After appropriate corrections were made for the environment of the deuterated naphthalene, the values for Δ at the wavelengths of 4500, 4600, and 6328 Å were found to be $\Delta_{4500} = -2.60\times 10^{-24}$ cm^3, $\Delta_{4600} = -2.01\times 10^{-24}$ cm^3, and $\Delta_{6328} = -0.604\times 10^{-24}$ cm^3. Using the known ground-state polarizabilities for naphthalene[5] ($\alpha_x{}^0 = 9.6\times 10^{-24}$ cm^3, $\alpha_y{}^0 = 24.4\times 10^{-24}$ cm^3, $\alpha_z{}^0 = 18.2\times 10^{-24}$ cm^3) we find for the excited state that $2\alpha_z - \alpha_y - \alpha_x$ is equal to -0.20×10^{-24} cm^3, 0.39×10^{-24} cm^3, 1.8×10^{-24} cm^3 for 4500, 4600, and 6328 Å, respectively. These values are consistent with the fact that the strongest triplet-triplet transition in the visible and ultraviolet regions is at 4148 Å and has a transition moment along the molecular y axis. Thus, α_y increases more rapidly than α_z and α_x as the wavelength decreases, and the quantity $2\alpha_z - \alpha_y - \alpha_x$ becomes smaller.

The technique used here is of course applicable to other systems and should be able to provide valuable direct information on the polarizabilities of excited electronic states. The authors wish to thank J. Duran for his assistance.

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[2] M. A. El Sayed and T. Pavlopoulos, J. Chem. Phys. 39, 834 (1963); D. P. Craig and I. G. Ross, J. Chem. Soc. 1589 (1954).

[3] A detailed analysis of this technique showing explicitly the dependence of Δ on the measured parameters will be published.

[4] C. S. Brinen, private communication. The data were obtained using ESR to measure the triplet population.

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STIMULATED BRILLOUIN SCATTERING: ORIGINS OF ANTI-STOKES COMPONENTS

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Two independent mechanisms which result in the generation of anti-Stokes Brillouin components in the presence of Stokes scattering have been identified experimentally.

Strong anti-Stokes Brillouin components were recently observed by Wick, Rank, and Wiggins[1] and by Wiggins *et al.*,[2] at 0° to the incident laser beam in a variety of liquids. By focusing light from a 70-MW Q-switched ruby laser into a cell containing CS_2, they recorded 42 Stokes and 20 anti-Stokes lines in the forward direction. They attribute the intense anti-Stokes scattering to optical mixing. Both the Stokes and anti-Stokes lines were of comparable intensity with the transmitted laser line. The high intensities of the lines and their dependence on the laser power suggest very strongly that they were indeed derived from parametric amplification.

In this Letter we suggest a number of other mechanisms for the generation of intense anti-Stokes Brillouin components, and cite experimental evidence which confirms the existance of one of these. We found that under the usu-