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The Stark Effect in the Neat Crystal Triplet State of a Simple Merocyanine Dye

A. P. Marchetti [a]
[a] Research Laboratories, Eastman Kodak Company, Rochester, New York, 14650

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The Stark Effect in the Neat Crystal Triplet State of a Simple Merocyanine Dye

A. P. MARCHETTI
Research Laboratories, Eastman Kodak Company, Rochester, New York 14650

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Recent work on 3-ethyl-5-(1,3-dithiolanylidene)rhodanine (EDR) has located the two allowed (A_u and B_u) triplet factor group states.[1] These two states were found to be only 0.6 cm^{-1} apart. The forbidden factor group states (A_g and B_g) were not located in the direct absorption experiments. The purpose of our investigation was to locate the forbidden factor group states and obtain a value for the dipole moment change of EDR on excitation.

The spectrograph and dewar used in these experiments are described elsewhere.[2] The neat crystals of EDR were placed between quartz discs coated with tin oxide. The voltage (ε) was applied to the crystal immersed in liquid helium by AC and DC power supplies. Spectra were generally recorded in first order, although several spectra were recorded in second order to resolve clearly the two allowed factor group states. The Stark modulation spectra were interpreted in the manner outlined previously.[3] Crystal refractive indices were measured by standard immersion techniques.

The Stark modulation spectra of EDR are shown in Figure 1. The upper spectrum locates the position of the allowed (line derivative) and forbidden (line) factor group levels at zero DC field.[3] In this spectrum, neither the allowed nor the forbidden levels are resolved. The lower spectrum locates the forbidden and allowed factor group levels with a DC field of 5.4 × 10^4 V/cm. In this spectrum, the two allowed factor group levels are resolved but the forbidden levels are not.

No other "lines" were observed in the vicinity (± 20 cm^{-1}) of the 0–0 band. Thus, it is presumed that the two forbidden levels lie close in energy and are not resolved. There is a remote possibility that one of the forbidden

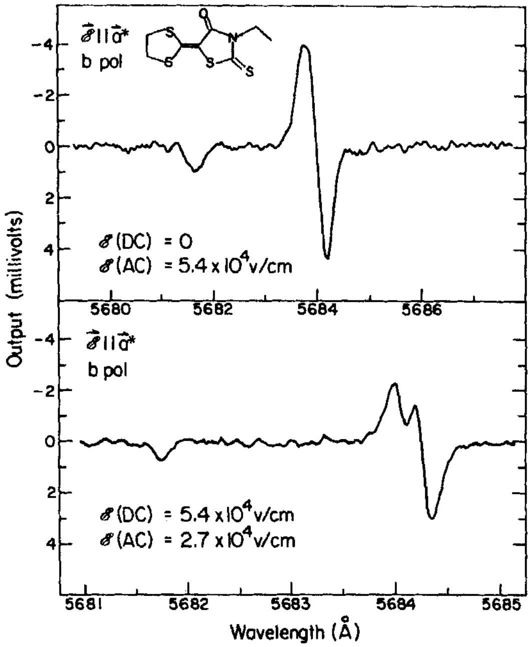

FIGURE 1 Stark modulation spectra of the 0–0 band of EDR. The upper curve was detected at twice the fundamental and locates the factor group states at zero DC voltage. The lower curve was detected at the fundamental and shows the separation of the two allowed (A_u, B_u) factor group states (0.6 cm^{-1}). Note that the two forbidden states are not resolved.

levels is widely separated from the rest and has not been located, but a consideration of the crystal structure and matrix elements involved makes this seem unlikely.

The positions of the factor group levels are used to calculate lower limits to the intermolecular interaction matrix elements.[4,5] These matrix elements are: $V_{12} = 0.4\ \text{cm}^{-1}$, $V_{13} = -0.2\ \text{cm}^{-1}$, and $V_{14} = 3.5\ \text{cm}^{-1}$. The positions of the factor group states as a function of applied DC field are shown in Figure 2 with $\varepsilon \| a$. Using the values of the line position and the applied field, an estimate of the change in dipole moment on excitation can be obtained.†[5,6] The calculated value of $\Delta\mu \cos\theta$ is $0.84 \pm 0.08D$, where θ is the angle between the applied field and the changes in dipole moment. No Stark

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† The local field was approximated by the Lorentz local field expression:

$$\varepsilon_{(\text{loc})} = \frac{\varepsilon + 2}{3}\,\varepsilon_{\text{app}}$$

where $\varepsilon_{ii} = \eta_{ii}^2$. The refractive indices were: $\eta_a = 1.72$, $\eta_b = 1.79$ and $\eta_c = 1.70$, with $b = z$.

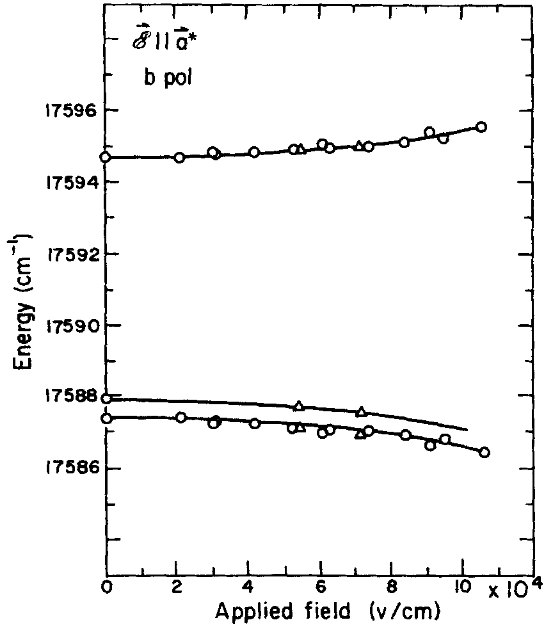

FIGURE 2 Positions of the factor states as a function of applied DC voltage. Triangles represent points taken from higher resolution spectra. Data from three crystals are represented. No signals were observed for $\varepsilon \| c$ or $\varepsilon \| b$.

modulation spectra were observed with $\varepsilon \| c$ or $\varepsilon \| b$. Thus, the dipole moment change is directed mainly along the **a** crystal direction. This corresponds to a short axis moment change and should have major contributions from the changes in electron density on the carbonyl and thiocarbonyl groups.

Stark measurements have been made on the trap phosphorescence. These measurements yield a value for $\Delta\mu \cos\theta$ of $0.73 \pm 0.10D$. Assuming, of course, that the trap molecules are aligned about the same as the other molecule, as is indicated by polarization measurements, then these values are within experimental error of one another.

The relatively small value of the dipole moment change observed in this study is consistent with the modest solvent shift of $\sim 850\ \text{cm}^{-1}$ observed for the triplet state of EDR.[1] This shift was to the blue on going from hydrocarbon solvents to more polar solvents such as 2-methyltetrahydrofuran or alcohol. This solvent shift indicates that the dipole moment change is negative.

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