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A Further Evidence of the Vibronic Coupling through b_{3g} Vibrational Modes in the Fluorescence Spectrum of Anthracene[1)]

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Synopsis. Angular dependence of the fluorescence polarization spectra of anthracene was investigated in polyethylene films using a sample rotation technique. An important role of a nontotally symmetric vibration, the b_{3g} ring vibration at 1655 cm^{-1}, was further confirmed by a combination of this technique and the modulation polarization technique developed previously.

Despite many studies on the fluorescence polarization spectra of anthracene, only a partially successful experiment for the assignment of b_{3g} nontotally symmetric vibrational bands has been reported by Bree and Katagiri.[2)] Very recently Ohta and Ito measured the intensity of Raman lines of crystalline anthracence in the pre-resonance excitation region and found a marked intensity enhancement of the b_{3g} Raman line at 1630 cm^{-1} for such a "resonant" excitation.[3)] The enhancement was then attributed to the vibronic coupling between two $\pi\pi^*$ excited states, *i.e.*, ^1L_a and ^1B_b, of the molecule. Previously we developed a new polarization method, *i.e.*, a modulation polarization (MP) method, and reported its application to studies of emission polarization spectra of some molecules in mixed crystals[4)] and in stretched polyethylene films.[5)] Anthracene was one of these molecules. Several bands of the long molecular axis polarization were clearly confirmed to exist in the fluorescence by the MP method. However, there remained a few ambiguous points about the molecular orientation in the stretched polyethylene films and the degrees of self-polarization of the apparatus. In the present work we examined the angular dependence of the MP spectra and confirmed the validity of the previous conclusion.

Experimental

The MP spectra were observed in a similar way to those described previously.[5)] The axis of an analyzing polarizer was fixed as inclined by 45° from the vertical axis of a Dewar for possible diminution of the systematic error of polarizations coming from the curvature of the Dewar. A sample-rotation device is homemade and it makes the 0°—180° rotation of sample films possible. An angle precision of the device is estimated to be ±3°. An angle θ is defined as that between the stretching film axis and the analyzing polarizer axis.

Results and Discussion

Anthracene is assumed to be embedded in stretched polyethylene films in such a way that its long molecular axis is oriented along the stretching film direction.[6)] Thus this system should roughly approximate a model of the oblate-spheroidal orientation of the molecule, allowing overlapping vibronic bands to be possibly separated by such polarization studies. Since $\pi\pi^*$ transitions of aromatics are of in-plane polarization,[7)] an application of such polarization techniques to oblate or prolate aromatics enables us to discriminate between the short and long molecular axis polarizations. A previous work on the MP spectrum of anthracene has partly demonstrated this possibility.[5)]

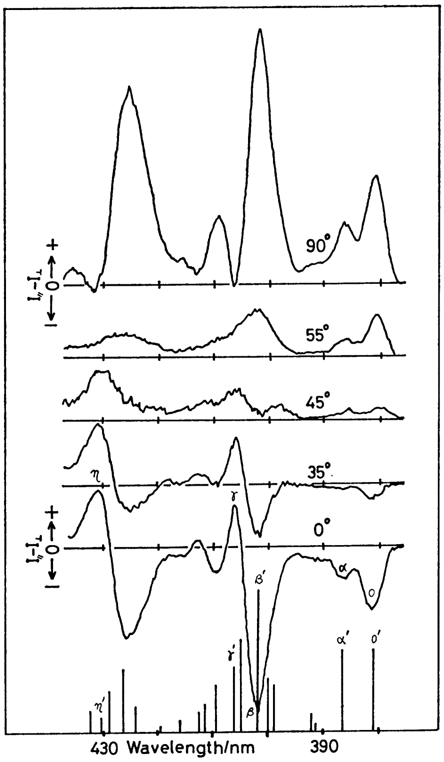

Fig. 1. Angular dependence of the fluorescence polarization spectra of anthracene in stretched polyethylene films at 77 K. For comparison, the fluorescence spectrum in heptane matrix at the same temperature is schematically shown at the bottom of this figure. The spectrum is evenly shifted so that the origin bands of both systems may coincide with one another. See text or the caption of Fig. 2 for band designations.

An angular dependence of the MP polarized fluorescence spectrum of anthracene is shown in Fig. 1. The spectrum at $\theta=0°$ resembles Fig. 3c of Ref. 5 except a better band resolution in the present work and a similar vibrational analysis is made possible by comparing the extrema of the MP spectrum with the vibrational bands of the fluorescence spectrum in heptane. Here let us devote our attention to the following extrema of the MP spectrum: the extrema at 380.6 nm (*o* in Fig. 1), 386.4 nm (α), 402.2 nm (β), 406.2 nm (γ), and 431.3 nm (η). These correspond nicely to five prominent bands in the anthracene/heptane system. They are the bands 0—0 (*o′* in Fig. 1), 0—393 cm^{-1} (α'), 0—1405 cm^{-1} (β'), 0—1637 cm^{-1} (γ'), and 0—1405—1637 cm^{-1} (η'), respectively.

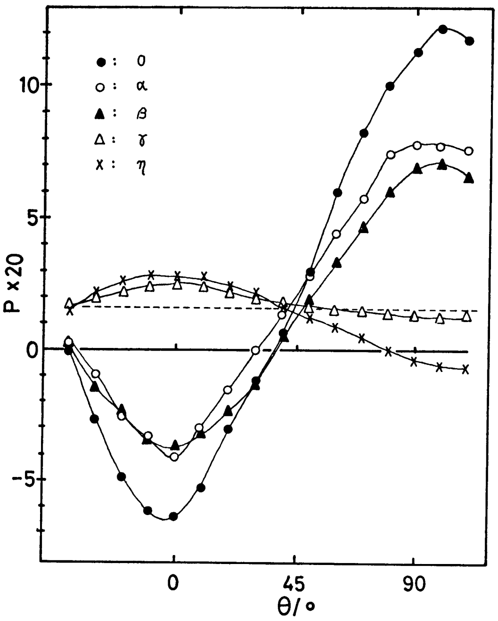

Fig. 2. Angular dependence of the polarizations of five prominent fluorescence bands. Band designations are: *o*, 0—0; α, 0—395 cm^{-1}; β, 0—1410 cm^{-1}; γ, 0—1655 cm^{-1}; η, 0—1655—1410 cm^{-1}.

With respect to the abscissa axis the spectrum at $\theta=0°$ is, as a whole, symmetrical to that at $\theta=90°$, as can be expected. The spectrum at $\theta=35°$, however, is seen far from such a symmetrical relation to that at $\theta=55°$. The spectrum at $\theta=45°$ shows several weak polarization peaks. These peaks were found to come mainly from the instrumental self-polarizations whose correction factor was not equal to unity, but nearly to 1.15 on an average in the present optical arrangement. This correction factor also explains the asymmetric relationship between the MP spectra at $\theta=35°$ and 55°.

Angular dependence of the polarizations of the five prominent fluorescence bands is shown in Fig. 2. Evidently there are four characteristic features to be pointed out. [1] Two types of the polarization angular dependence are found for the bands (*o*, α, β) and the others (γ, η). [2] All the polarization curves of the bands cross at $\theta\approx45°$. [3] The extreme value of the polarization of each band appears at $\theta\approx0°$ or $\theta\approx90°$, depending on the polarization nature of the vibrational band. [4] An even upward shift of the base-line by $P=+0.08$ seems to bring about a nice symmetric situation for the curves. The items [2] and [3] demonstrate that the molecule in the stretched polyethylene film is oriented in such a way that the long molecular axis is nearly parallel to the stretching film axis.[6] An experimental fact described in the item [4] is reasonably explained by the instrumental self-polarizations. The angular dependence of the bands γ and η (the item [1]) clearly proves these bands are certainly of b_{3g} vibrational modes.[5]

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