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POLARIZED TRIPLET-TRIPLET ABSORPTION MEASUREMENTS WITH THE AID OF THE STRETCHED POLYMER FILM TECHNIQUE: PHENANTHRENE

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A procedure to measure a polarized triplet-triplet absorption spectrum using a stretched polymer film was described, and this method was applied to determine the polarizations of the triplet-triplet transitions of phenanthrene.

In 1951, the first systematic experimental work, concerning the light absorption in the lowest triplet states of typical series of aromatic hydrocarbons, was made by McClure.[1] Since then, a considerable number of theoretical and experimental papers on this subject has been published by many investigators.[2-7] The polarizations of the triplet-triplet ($T_n \leftarrow T_1$) transitions have been determined mainly by the method of photoselection.[8-10] In this paper we describe our procedure to measure a polarized $T_n \leftarrow T_1$ absorption spectrum using a stretched polymer (polyvinylalcohol:PVA) film, and apply this method to determine the polarizations of the $T_n \leftarrow T_1$ transitions of phenanthrene, the electronic transitions of which have already been studied in detail.

The commercially available zone refined phenanthrene was used without further purification (Tokyo Kasei Co., Ltd.). The polarized $T_n \leftarrow T_1$ absorption spectrum was measured with a modified Ushio UPF-101 flash spectrophotometer, and the schematic diagram of the optical arrangement has been shown in Fig. 1.

Figure 2 shows the polarized $T_n \leftarrow T_1$ absorption spectrum of phenanthrene, in which the polarized absorption spectrum for $S_n \leftarrow S_0$ transitions is also shown for comparison. In this figure, the notations used are as follows:[11-13] $D_{\parallel}$ and $D_{\perp}$; absorbances measured for incident light polarized respectively parallel to and per-

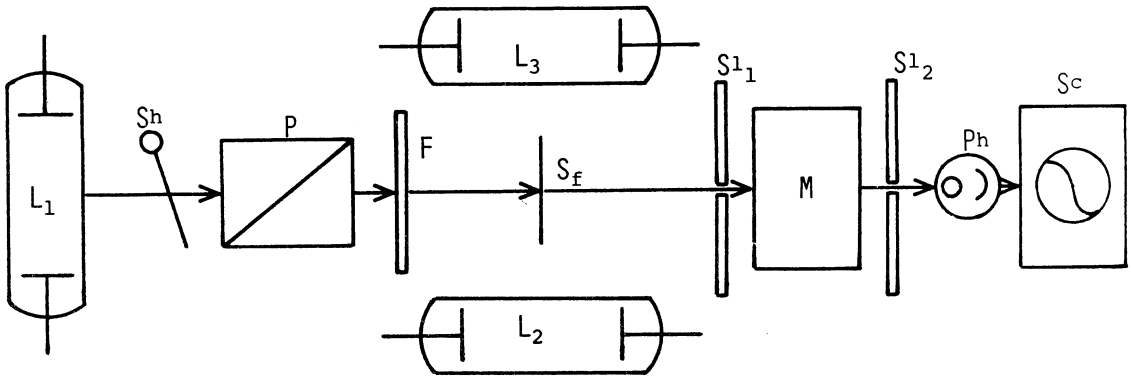

Fig. 1. A schematic diagram of the optical arrangement.
L_1: monitor lamp (150 W Xe-lamp), L_2 and L_3: Xe-flash lamp, Sh: shutter, P: Glan-Thomson type calcite polarizer, F: filter, Sf: sample film, Ph: photomultiplier, Sc: Synchroscope, M: monochrometer, Sl_1 and Sl_2: slit

pendicular to the stretched direction of the polymer film, Rd; ratio between $D_{\parallel}$ and $D_{\perp}$, $D_{\parallel}/D_{\perp}$, Rs; degree of stretching of the polymer film, Θ; orientation angle (an angle between a transition moment and the orientation axis of the molecule).

The $S_n \leftarrow S_0$ spectrum of this compound consists of three apparent electronic transition bands, very intense 39.1 kK, moderately intense 33.7 kK and very weak 28.7 kK bands. The assignment for these electronic transitions has already been established from both experimental and theoretical view points, i. e., the 28.7, 33.7 and 39.1 kK bands are assigned as $^1A_1 \leftarrow {}^1A_1$ (short-axis polarized, y), $^1B_2 \leftarrow {}^1A_1$(x) and $^1B_2 \leftarrow {}^1A_1$ (x) transitions, respectively. The present polarized $S_n \leftarrow S_0$ absorption spectrum is completely consistent with the above-mentioned assignment. That is, the 33.7 and 39.1 kK bands take large Rd values compared with those of the 28.7 kK band, indicating that the former two bands are polarized along the long axis (x) and the latter 28.7 kK band along the short axis (y) of the molecule.

Craig and Ross[2] have reported that the $T_n \leftarrow T_1$ spectrum of phenanthrene shows three peaks at 20.3, 21.7 and 23.2 kK in a rigid glass of EPA. The corresponding peaks are found at 20.2, 21.7 and 23.2 kK in the spectrum of Fig. 2. Besides, in the present spectrum an additional weak band is found at 24.8 kK. The 21.7 and 23.2 kK peaks are regarded as vibrational bands of the 20.2 kK transition from the

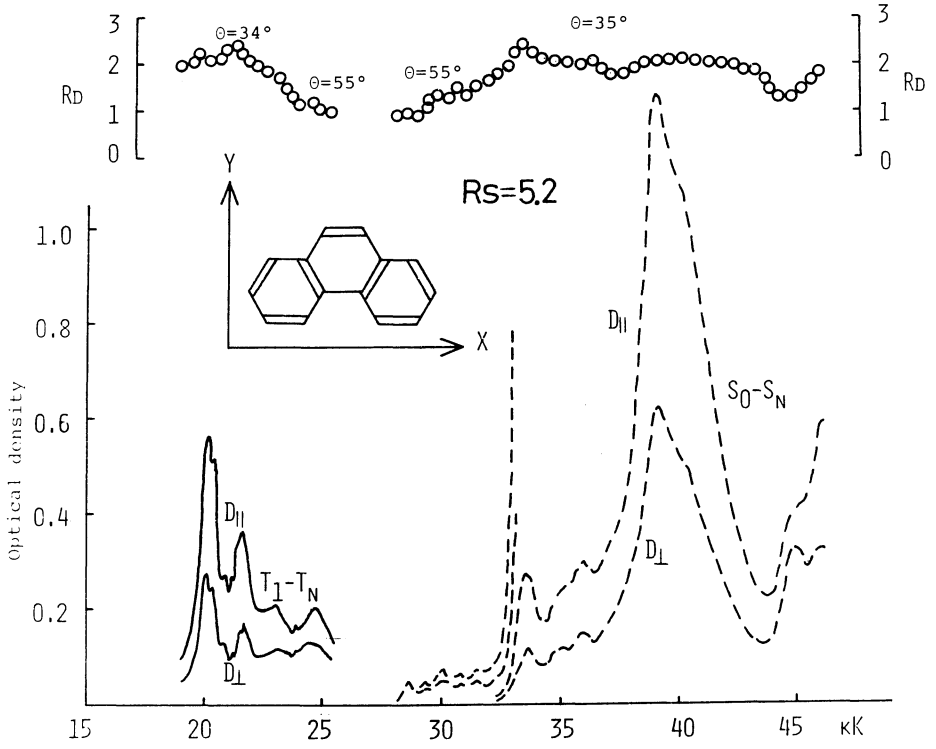

Fig. 2. The polarized $T_n \leftarrow T_1$ and $S_n \leftarrow S_0$ absorption spectra of phenanthrene in the stretched polymer film at room temperature.

following reasons. (1) The progression for each band is 1500 cm^{-1} and this interval well corresponds to the total symmetric vibrational frequency of the benzene skeleton. (2) The Rd values for the 21.7 kK band are almost the same with those for the 20.2 kK transition. As for the 23.2 kK band a mixed polarization is observed, i. e., the Rd values for this band are the intermediate ones, but a shoulder is found in the Rd curve around this band position.

The Rd values for the 20.2 kK band are 2-2.4, and these values are almost the same with those of the 33.7 kK (^1L_a) band of the $S_n \leftarrow S_0$ spectrum. This indicates that the band system, whose 0-0 transition is at 20.2 kK, is polarized parallel to the polarization of the ^1L_a band, that is, the 20.2 kK transition ($T_n \leftarrow T_1$) is polarized along the long axis (x) of this molecule. These results are in good agreement with those obtained by the method of photoselection by Gallivan and Brinen,[8] e. g. in their experiment the 20.2 kK band shows a relatively strong positive polarization with respect to the mixed excitation ($^1L_a + ^1L_b$). The 20.2 kK $T_n \leftarrow T_1$ band is therefore safely assigned as being due to the $^3A_1^- \leftarrow {}^3B_2^-$ transition. The Rd values in

the wavenumber region of 22-25 kK are decreasing with increasing wavenumber, and the values for the 24.8 kK band become the smallest in the observed wavenumber region. From this we may conclude that the structureless weak band at 24.8 kK is due to a different electronic transition from the 20.2 kK band and is polarized perpendicularly to the polarization of the 20.2 kK band. In fact, the orientation angles for the two bands at 24.8 and 20.2 kK are 55° and 34° respectively, and the sum of the two orientation angles is nearly at right angle (55° + 34° = 89°). The 24.8 kK band may be assigned as the $^3B_2^- \leftarrow {}^3B_2^+$ transition.

In conclusion, the advantages of this method may be summarized as follows: (1) The absolute polarization direction for each $T_n \leftarrow T_1$ transition can be obtained easily. (2) This technique can be applicable to wide varieties of substances. (3) The Rd values can be reproducible with very good accuracy.

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