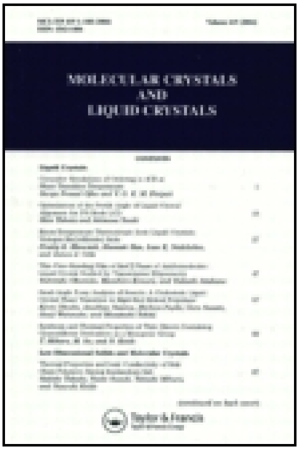

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Impurity Induced Molecular Reorientation in p-Terphenyl

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IMPURITY INDUCED MOLECULAR REORIENTATION IN p-TERPHENYL

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Abstract Molecular reorientation processes of protonated and perdeuterated tetracene guests in *p*-terphenyl crystals are examined using high-resolution fluorescence and fluorescence excitation spectroscopy. Two of the four sites undergo this process and their phonon sidebands observed in the excitation spectra exhibit an exceptionally long and well resolved progression of a low-frequency local phonon mode superimposed on a broad background. The local phonon identified as a guest librational mode is shown to induce the molecular reorientation processes at an angle of ~21° about the *L*-axis of tetracene in the excited singlet state.

INTRODUCTION

The objective of this contribution is to study molecular reorientation processes of tetracene occupying the so-called O_3 and O_4 sites in *p*-terphenyl and to elucidate the nature of the phonon modes involved in these processes. We present high-resolution spectra of tetracene-*h*12 and tetracene-*d*12 guests in *p*-terphenyl[1,2]. The phonon sidebands observed in the excitation spectra of O_3 and O_4 are characterized by an exceptionally long and well resolved progression of a low-frequency local phonon mode superimposed on a broad background. The frequency shift upon perdeuteration of tetracene identifies the progression forming mode as a guest librational mode about the long molecular (*L*) axis. The broad phonon background is tentatively attributed to a convolution of a torsional and librational mode of the host. From the intensity distribution in the progression built on O_3 we have calculated the reorientational angle for the tetracene guest along the librational mode coordinate.

EXPERIMENTAL

Single crystals of tetracene-*h*12 (Aldrich) and tetracene-*d*12 (Medgenix Diagnostics) in extensively zone refined *p*-terphenyl (Merck, scintillation grade) at concentrations of 10^{-6} mol/mol were grown from the melt using standard Bridgman techniques. Fluorescence spectra under broad-band excitation were recorded using a spectrally filtered (Schott, BG3 and GG375) mercury arc (Osram, HBO 200 W) and a 1.5 m monochromator (Jobin Yvon, HR 1500 P) equipped with a cooled PM tube (Hamamatsu, R928). Absorption spectra were obtained by measuring the spectrum of a tungsten lamp before and after the light passes the sample using the 1.5 m monochromator with the cooled PM tube. Fluorescence excitation spectra were recorded at a spectral resolution of 1.2 cm^{-1} by scanning a nitrogen laser (Lambda Physik, M 1000) pumped dye laser (Lambda Physik, FL 2000 with dye Coumarin 102) providing pulses of about 2.5 ns.

FLUORESCENCE AND EXCITATION SPECTRA

Fig.1 displays a section of the fluorescence spectrum containing the electronic origins of tetracene-*h*12 for the sites O_1, O_2, O_3 and O_4 and the first vibronic transitions of O_1 and O_2. The intensities of the O_1 and O_2 origins at 20274 cm^{-1} and 20277 cm^{-1} are diminished by reabsorption, whereas the vibronic transitions appear as pronounced lines with spectral widths of 2.5 cm^{-1}. The electronic O_3 and O_4 origins at 20140 cm^{-1} and 20089 cm^{-1} are comparatively broad bands with widths of *ca.* 25 cm^{-1}. The fluorescence spectrum of tetracene-*d*12 differs from that of tetracene-*h*12 only by an overall shift of *ca.* 35 cm^{-1}. Fig.2 shows the low-energy sections of the absorption spectrum of tetracene-*h*12 (A) and tetracene-*d*12 (B) in *p*-terphenyl (a) and the

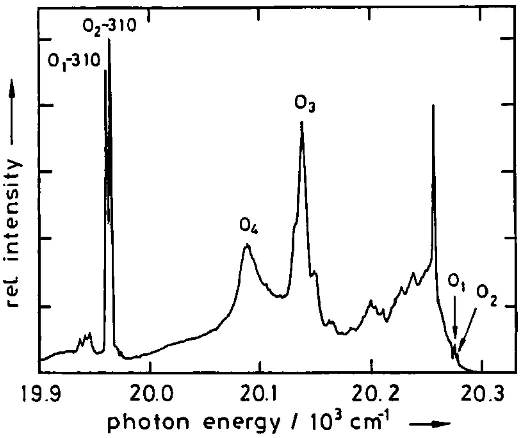

FIGURE 1 Section of the fluorescence spectrum of tetracene-*h*12 in *p*-terphenyl at 4.2 K under broad-band excitation.

excitation spectra of sites O_1 (b), O_3 (c) and O_4 (d). The excitation spectrum of O_2 resembles the spectral features of that recorded for O_1 except for a blue-shift of 3 cm^{-1}. The O_1 and O_2 electronic origins coincide in fluorescence and absorption and the accompanying phonon sidebands in the respective excitation spectrum mirror the structural features of those in the site-selectively excited fluorescence spectrum[1-3]. In contrast, the excitation spectra of O_3 and O_4 differ

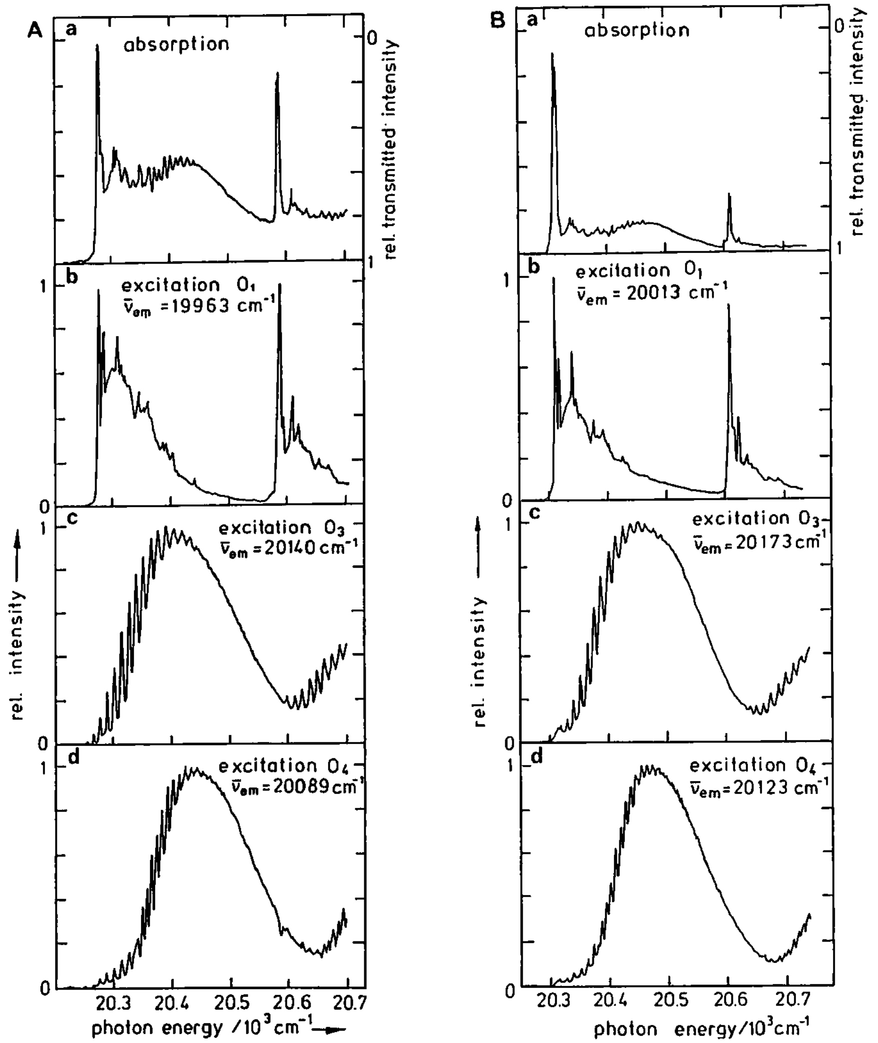

FIGURE 2 Absorption spectrum (a) and fluorescence excitation spectra of tetracene-*h*12 (A) and tetracene-*d*12 (B) in O_1 (b), O_3 (c) and O_4 (d) at 4.2 K.

substantially from the fluorescence spectra. While the electronic origin is the strongest band in fluorescence, it has negligible intensity in the excitation spectra (see figs.2.A/B.c and d). The respective excitation spectra of tetracene-*h*12 and tetracene-*d*12 consist of a long well resolved progression in a low-frequency mode which appears superimposed on a broad phonon band[1,2]. For tetracene-*h*12 the progression built on the O_3 and O_4 origin show a spacing of 12.4±0.1 cm^{-1} and 9.0±0.2 cm^{-1}, respectively. Upon perdeuteration, *i.e.* for tetracene-*d*12, the frequency of the progression forming mode is reduced for O_3 and O_4 by 6% (11.7±0.2 cm^{-1}) and 3.4% (8.7±0.2 cm^{-1}), respectively. The electronic origins in the fluorescence spectrum of O_3 and O_4 are red-shifted by *ca.* 100 cm^{-1} (O_3) and presumably more (O_4) from the respective lowest-energy peak in excitation indicating a significant displacement of the equilibrium site configuration for the guest upon electronic excitation.

DISCUSSION

The observation of a long, nearly equally spaced progression in the phonon sidebands of the O_3 and O_4 in excitation versus a red-shifted strong 0-0 band in fluorescence indicates *first*, that the tetracene guests in these sites undergo a reorientation over a large displacement along the coordinates of the modes involved in the phonon sidebands if excited in the S_1 state, *second*, that the progression forming phonon is largely localized at the tetracene site, *third*, that the S_1 excited tetracene exhibits a quite harmonic site potential along the normal coordinate of the pseudolocal guest mode and *fourth*, that the site potential of the ground-state tetracene guest has to be anharmonic if it is assumed to be one-dimensional[3]. The frequency reduction upon perdeuteration identifies the pseudolocal phonon as a guest librational mode about the *L*-axis[3,4]. This assignment is corroborated by the fact that in particular the coupling between librational guest modes and acoustic host phonons is expected to be rather weak[4]. On the other hand, the broad background of the phonon sidebands points out that at least one host phonon is involved in the reorientation processes. We assume that the *torsional* phonon of *p*-terphenyl which is engaged in the order-disorder phase transition of crystalline *p*-terphenyl[5] participates in the guest reorientation processes. Since this host phonon arises from the torsional motion of the medium phenyl ring with respect to the outer ones around the *L*-axis of non-planar *p*-terphenyl, it is expected to facilitate the librational motion of tetracene about the *L*-axis. The intermolecular potential for tetracene along the host torsional coordinate is tentatively suggested as an asymmetric double-well potential, allowing for the stabilization of the reorientated tetracene in the S_1 state. To obtain a more quantitative understanding of the guest reorientation process, we have analyzed the phonon sideband structure of the excitation spectrum of O_3. Therefore, the intensity distribution in the phonon sideband was calculated by combining linearly the line shape function of the librational progression and that of the broad phonon background[3]. The progression is approximated by a one-dimensional intramolecular distribution[6,7] of the librational guest mode at $\tilde{\nu}_L$= 12.4 cm^{-1}, while the phonon background is simulated by a convolution of a two-dimensional Poisson distribution and the Lorentzian distribution[8] involving the host librational and torsional phonon about the *L*-axis with $\tilde{\nu}_1$= 38.5 cm^{-1} and $\tilde{\nu}_2$= 72 cm^{-1}, respectively. Fig.3 shows the experimental spectrum (thick line) in comparison with the calculated one (thin line). The reorientational angles obtained from the fit amount to ΔQ_L= 21.4°, ΔQ_1= 5.4° and ΔQ_2= 6.8° for the guest librational phonon, the host torsional and the host librational mode, respectively.

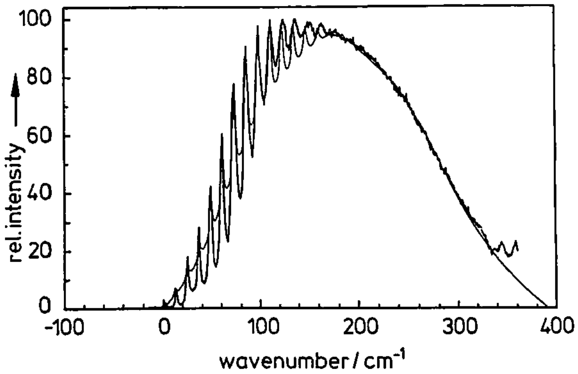

FIGURE 3 Experimental (thick line) and calculated (thin line) fluorescence excitation spectrum of tetracene-*h*12 in O_3.

CONCLUSIONS

Tetracene in the ground state was shown to occupy four sites in triclinic *p*-terphenyl. Two of these sites, O_1 and O_2, exhibit nearly coinciding site configurations for tetracene in the ground state and S_1 state, while tetracene in O_3 and O_4 shows a significant shift in energy upon electronic excitation due to guest reorientation. Analyzing the phonon sideband structure in the O_3 and O_4 excitation spectra we have suggested that the reorientation process arises from the librational guest motion about the *L*-axis with participation of the torsional host phonon. Since rotational reorientation seeks for vacancies at host sites in the surrounding of the guest, we suppose that the host cages of O_3 and O_4 are structurally disordered. It is conceivable that reorientation processes are largely facilitated, if the sites are located in amorphous layers as existing within and between domain walls in order-disorder systems. The formation of domain structures in triclinic *p*-terphenyl crystals could be evidenced by recent optical microscopical measurements[9].

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