STARK ABSORPTION STUDY OF PERYLENE DOPED IN A POLY (METHYL METHACRYLATE) POLYMER FILM AT DIFFERENT CONCENTRATIONS

ANJUE MANE ARA[*] AND MOHAMMAD KAWSAR AHMED

Department of Physics, Jagannath University, Dhaka-1100, Bangladesh

ABSTRACT

In this article, electric field modulated absorption (Stark absorption, SA) study of perylene doped in a poly (methyl methacrylate) (PMMA) polymer film at the concentrations of 1.0 mol%, 2.0 mol% and 3.0 mol% is presented. The field effects on the absorption spectra were found to originate mostly from the Stark shift induced by a change in molecular polarizability between the ground and excited states. The analyses of SA spectra with the aid of Liptay formalism yielded essentially the same magnitude of the average change in molecular polarizability ($\Delta\bar{\alpha}$), evaluated for the $S_0 \rightarrow S_1$ transition, for all the concentrations. This finding implies that $\Delta\bar{\alpha}$ of perylene molecule doped in a PMMA film does not depend on concentration. Moreover, the yielded positive $\Delta\bar{\alpha}$ for both the preparations implies that SA spectroscopy is an essential technique to probe spectroscopically that perylene possesses larger molecular polarizability in the excited states than in the ground state.

Keywords: Polycyclic aromatic hydrocarbons, Stark absorption, Stark shift, PMMA polymer film, molecular polarizability

INTRODUCTION

The perturbation on the molecular energy levels induced by an external electric field is known as Stark effect and is extensively applied in molecular spectroscopy to examine the excited state electronic structures and dynamics of various photoactive chromophores including the polycyclic macromolecules (Ara *et al.* 2006, Ara *et al.* 2006, Ara *et al.* 2007, Iimori *et al.* 2005, Wahadoszamen *et al*. 2012). Stark spectroscopy which monitors field-induced changes in absorption (Stark Absorption, SA) or fluorescence (Stark Fluorescence, SF) can be used to estimate the change in electrostatic parameters such as change in permanent dipole moment and molecular polarizability upon optical excitation and/or relaxation. Actually when a photoactive chromophore possesses nonzero electric dipole moment and molecular polarizability, the state energy is perturbed

(shifted and split) in the presence of external electric field by the interplay of both the quantities. Aside from these two quantities, the magnitude of the perturbation depends on the strength of an applied electric field as well. As a result, the magnitude and direction of the change in these parameters following excitation into the individual electronic states can be determined by measuring the shift and/or broadening of the optical absorption spectra induced by an externally applied electric field. The determination of these parameters is central in characterizing the electronic structures of the molecule under study in the excited state.

Polycyclic aromatic hydrocarbons, those possess high structural symmetry, form a beautiful class of molecules for both experimental and theoretical spectroscopic investigations.

*Corresponding author:<anjueara.phy@gmail.com>.

Perylene is one of such hydrocarbons. Its spectrum has been so far investigated and analyzed by a number of groups (Davidsson *et al.* 1986, Gómez *et al.* 1997, Renge 1992, Suganuma *et al.* 2011, Tanizaki *et al.* 1978, Timbolmas *et al.* 2017) with different points of view. In our previous study (Ara *et al.* 2006) SF spectroscopy was applied to different concentrations of perylene to unravel the electronic structures and dynamics of perylene in the relaxed fluorescence state. It was observed that perylene of concentration above 1 mol% in PMMA film forms excimer in the relaxed fluorescence state. The yield of the resulting excimer was found to be increased with increasing concentration of perylene. The excimer gave very selective response to the external electric field applied during the course of SF experiment, which in turn helped us to obtain the precise estimation of electronic structures and dynamics of perylene in the vibrationally relaxed fluorescence state. To uncover to the excited state dynamic and electronic structures of perylene in the Franck-Condon excited state, in this study, SA spectroscopy was conducted on three perylene preparations doped in a PMMA polymer film at concentrations 1.0 mol%, 2.0 mol% and 3.0 mol%. On the basis of the field effect on the optical absorption of the two samples within the spectral window 325-525 nm, the magnitude of the change in electrostatic parameters following excitation are evaluated by implementing conventional Liptay formalism (Liptay W. 1974).

EXPERIMENTAL

Perylene purified by sublimation (Sigma–Aldrich) was used without further purification.

PMMA (Aldrich, MW 120,000) was purified by precipitation with methanol and benzene. PMMA of 120,000 MW, a long conjugated polymer having sufficient free volume, has routinely been used as inert scaffolds for nestling variety of organic photoactive chromophores for their Stark measurements in film. The concentrations of perylene relative to the monomer unit of PMMA employed in the present study were 1.0 mol%, 2.0 mol% and 3.0 mol%. Spectroscopic grade chloroform (Kanto chemicals) was used as the solvent in which both perylene and PMMA dissolve well. Some selective concentrations such as 1 mol%, 2 mol% and 3 mol% were used for carrying the SA protocol reported in this study. The 1 mol% concentration (estimated in terms of monomeric unit of PMMA) of this specific photoactive chromophore was found to be the minimum concentration that yielded sufficient absorption intensity in PMMA film for carrying Stark measurement with plausible signal to noise ratio. As a matter of fact, 1 mol% is regarded as the minimum concentration in our study. On the other hand, the maximum 3 mol% of perylene could be dissolved along with the PMMA in chloroform solvent (the solvent in which perylene exhibits the maximum solubility), and therefore 3 mol% was considered as the maximum concentration. The 2 mol% is regarded the intermediate concentration. Sample preparation and experimental apparatus used in the present experiments are essentially the same with the ones reported in our previous papers (Ara *et al.* 2006, Ara *et al.* 2006, Ara *et al.* 2007, Iimori *et al.* 2005). A quartz plate which is free from strain and impurity emission was used as a substrate. A certain amount of chloroform solution of perylene and PMMA was cast onto an Indium Tin Oxide (ITO)-coated quartz substrate by a spin coating method. It should be mentioned hear that, because of its superior transparency around the deep UV to far-infrared

optical window couple with its profound stability to high voltage and temperature, transparent ITO-coated quartz substrate has been a unique choice as electrode for Stark spectroscopic measurements for this optical window. The sample was dried slowly in the dark at room temperature and then dried under vacuum condition. Then, a semitransparent aluminum (Al) film was deposited on the dried polymer film by using a vacuum vapor deposition method. The ITO and Al films were used as electrodes for applying electric fields. Hereafter, applied electric field is denoted by F and its strength is represented by rms. The thickness of the polymer film, which was typically 0.5 μm, was determined using a thickness measurement system (Nano Spec/AFT) model 010–0180, Nanometrics). The strength of the external electric fields was calculated from the applied voltage divided by the film thickness. SA spectra were measured using electric field modulation spectroscopy with the same apparatus as described elsewhere (Ara *et al.* 2007, Tayama *et al.* 2009). A sinusoidal ac voltage was applied to a sample with a modulation frequency of 40 Hz. Field-induced change in transmitted excitation light intensity was detected with a lock-in amplifier at the second harmonic of the modulation frequency. The measured change in transmitted signals are converted to equivalent SA signal by using Lambert-Beer formula ($SA = \frac{\Delta I}{\ln} 10I$, (where I is dc transmission intensity and ΔI is modulated change in transmission intensity) and the SA spectra were obtained by plotting SA intensity as a function of wavelength.

RESULTS

The absorption spectra of perylene doped in a PMMA film show strong bsorption with several structured vibrational bands in the region 350 nm to 525 nm in all the concentrations (see Fig. 1 and Fig. 2).
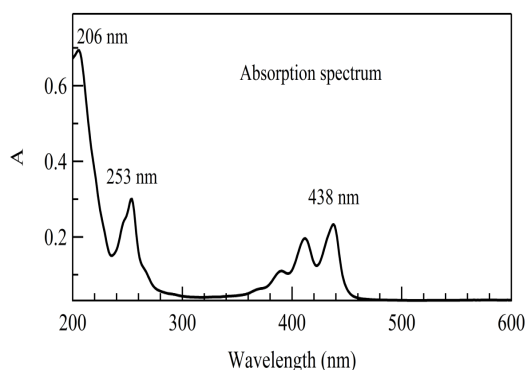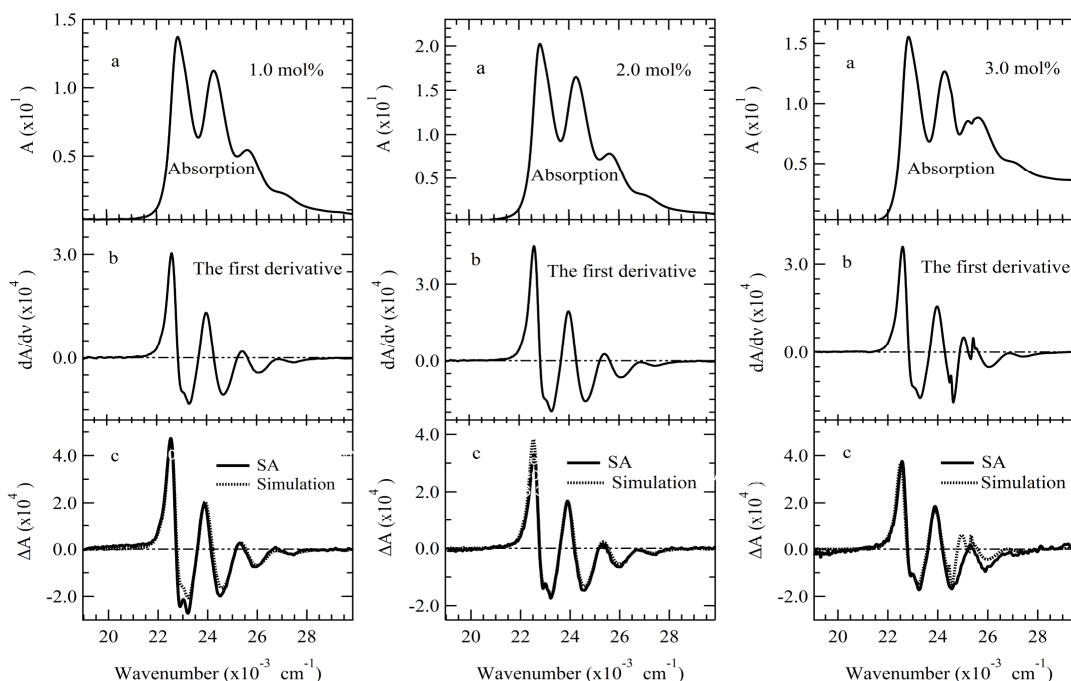

Fig. 1. Absorption spectrum of perylene doped in a PMMA film.

At shorter wavelength region, at 253 nm and at 206 nm, single strong structured vibrational band of absorption is observed. The absorption spectrum of perylene doped in PMMA film is found to be identical to one measured in solution (Tanizaki *et al.* 1978), indicating that the PMMA skeleton does not induce tangible interaction to perylene.

In the present study the field-induced change in absorption intensity (ΔA) at different concentrations were obtained in the region from 350 to 525 nm are considered. The resulting absorption spectra and the SA spectra measured for 1mol%, 2 mol% and 3 mol% concentrations in terms of wavenumber are shown in Fig. 2, together with the first derivatives of their absorption spectra. The shape of the absorption spectrum remains almost unchanged with increasing concentration suggesting that there is no formation of dimer or aggregate with increasing concentration of perylene doped in a

Fig. 2. Absorption spectrum (a), the first derivatives of the absorption spectrum (b) and SA spectrum (c) of perylene doped in a PMMA film with a concentration of 1.0 mol% (left), 2 mol% (middle) and 3.0 mol% (right). The applied field strength was 1.0 MVcm^{-1}.

PMMA film. The molecular symmetry of perylene is D_{2h}. The strong band at 438 nm in the region 350 nm to 525 nm is assigned as the 0-0 band belonging to the $S_0 \rightarrow S_1$ transition with $^1B_{2u}$ symmetry. Other bands associated with $S_0 \rightarrow S_1$ transition are assigned to the vibrational bands belonging to this transition. The direction of the transition moment from the ground state to the $^1B_{2u}$ state is in-plane long axis (y-axis). This state is denoted by ^1L_b in the Platt notation (Platt 1949). The SA spectra was obtained with the field strength of 1.0 MV cm^{-1}. The spectra shown in Fig. 2 were obtained with an incident light whose propagation direction is normal to the surface.

ANALYSIS AND DISCUSSION

For an isotropic, immobilized sample, an applied electric field usually broaden an isolated transition due to the change in electric dipole moment following optical absorption giving rise to a Stark effect lineshape which is essentially similar in shape to the second derivative of the absorption spectrum. If the change in molecular polarizability following optical transition is significant, the Stark effect lineshape resembles the shape of the first derivative of the absorption spectrum. If the transition moment is affected by an applied electric field, the Stark effect lineshape gives the shape identical to the absorption spectrum. Thus, the spectral change in absorbance given in units of wavenumber $\bar{v}$, i.e., $\Delta A (\bar{v})$, in the presence of external electric

field can be expressed by the following equation:

$$\Delta A(\bar{\nu}) = (fF)^2 \left\{ AA(\bar{\nu}) + B\,\bar{\nu}\,\frac{d}{d\bar{\nu}}\left(\frac{A(\bar{\nu})}{\bar{\nu}}\right) + C\,\bar{\nu}\,\frac{d^2}{d\bar{\nu}^2}\left(\frac{A(\bar{\nu})}{\bar{\nu}}\right) \right\} \quad (1)$$

where F is the external electric field, f is the internal field factor, A depends on the transition polarizability and hyperpolarizability, and B and C are given as follows:

$$B = \left[\frac{\Delta\bar{\alpha}}{2} + (\Delta\alpha_m - \Delta\bar{\alpha})(3\cos^2\chi - 1)/10\right]/(hc) \quad (2)$$

$$C = (\Delta\mu)^2[5 + (3\cos^2\xi - 1)(3\cos^2\chi - 1)]/(30h^2c^2) \quad (3)$$

where h is the Planck's constant and c is the light speed. Here, $\Delta\mu$ is the difference in electric dipole moment between the ground state and the excited state, i.e., $\Delta\boldsymbol{\mu} = \boldsymbol{\mu}_g - \boldsymbol{\mu}_e$ and $\Delta\bar{\alpha}$ is related to the difference in polarizability tensor, $\Delta\boldsymbol{\alpha} = \boldsymbol{\alpha}_g - \boldsymbol{\alpha}_e$:

$$\Delta\mu = |\Delta\boldsymbol{\mu}|; \quad (\Delta\bar{\alpha}) = \tfrac{1}{3}\mathrm{Tr}(\Delta\boldsymbol{\alpha}) \quad (4)$$

$\Delta\alpha_m$ denotes the diagonal component of $\Delta\boldsymbol{\alpha}$ with respect to the direction of the transition dipole moment, χ is the angle between the direction of F and the electric vector of the excitation light, and ξ is the angle between the direction of $\Delta\boldsymbol{\mu}$ and the transition dipole moment. This formula was derived for an isolated absorption band due to a single electronic transition with the assumption that the field-induced change is the same for all the vibrational bands.

The observed SA spectra of perylene doped in a PMMA film are essentially the same in shape as the first derivative of the absorption spectra for all the concentrations (see Fig. 2) indicating that the field-induced change in absorption intensity essentially comes from the change in molecular polarizability following absorption, i.e., A and C in Eq. 1 are regarded as zero. Because of the D_{2h} symmetry, isolated molecules of perylene have no permanent electric dipole moment, and so it

is well understood that C is zero at all the used concentrations of perylene in PMMA films.

The result that A is regarded as zero indicates that the transition moment is nearly unaffected by an external electric field for these transitions. If the polarizability is assumed to be isotropic, i.e., $\Delta\alpha_m = \Delta\bar{\alpha}$, $\Delta\bar{\alpha}$ is evaluated to be 30.96, 30.42 and 35.00 in units of $4\pi\varepsilon_0$ Å^3 at 1 mol%, 2 mol% and 3 mol% respectively (see the Table 1) for excitation into the $S_1(^1L_b)$ state. The SA spectra of all the concentrations show that the absorption spectra give a red-shift for the transitions to the S_1 state in the presence of external electric field, indicating that the polarizability of this excited state is larger than that of the ground state at both concentrations. The above-mentioned value of $\Delta\bar{\alpha}$ were evaluated by assuming that the internal field is the same as the externally applied electric field applied to the molecules, i.e., $f = 1$ in Eq. 1. Usually, the internal field is not the same as the applied electric field because of the dielectric properties of the environment, i.e., $f \neq 1$. In a rough approximation, the Lorentz field correction may be used for the internal field; $f = (\varepsilon + 2)/3$ with the dielectric constant ε of the material (Bottcher 1978). ε of PMMA is 3.6 ± 0.3 (Brandrup 1975), and so the internal field may be about twice as large as the applied field. If the Lorentz field correction is employed, the values of $\Delta\bar{\alpha}$ for the transition to the $S_1(^1L_b)$ state of perylene doped in a PMMA film are estimated to be 8.88, 8.73 and 10.07 in units of $4\pi\varepsilon_0$ Å^3 at 1 mol%, 2 mol% and 3 mol% respectively (see Table 1).

SA spectra involve the change in molecular polarizability between the vibrationless level of the ground state and the Franck–Condon excited state. In fact, SA spectra at all the concentrations of interest observed in the present study are essentially the same in shape as the first derivative of the absorption spectra, implying that vibrational state dependence of $\Delta\bar{\alpha}$ is not present in perylene doped in PMMA.

Table 1: Estimated average change in molecular polarizability for perylene upon excitation

Concentration [mol%]	Without Lorentz Field Correction $\Delta\overline{\alpha}$ [$4\pi\varepsilon_0$ Å^3]	With Lorentz Field Correction $\Delta\overline{\alpha}$ [$4\pi\varepsilon_0$ Å^3]
1.0	30.96	8.88
2.0	30.42	8.73
3.0	35.00	10.07

As shown in Table 1, the average change in molecular polarizability upon excitation for all the concentrations is almost the same. The fact is molecular polarizability is the inherent property of the molecule which can be affected only by its surroundings and/or environment. For example if the measurement is done in a solvent there must be a solvent effect since different solvent possess different refractive indices thus different dielectric constant which ultimately shift the absorption band maxima (solvent Stark effect) as a result change its polarizability (Renge 1992). The system like molecule doped in a PMMA film does not hold such possibility. As a result the average change in molecular polarizability upon excitation at all the concentrations is almost the same implying that SA spectroscopy is an essential technique to probe spectroscopically that the $\Delta\overline{\alpha}$ of molecule doped in a PMMA film is not concentration dependent.

Here we calculated the change in electrostatic parameters from ground state to the lowest excited state i.e., $S_1(^1L_b)$ state. The S_1 state is important from many perspective: perylene produces good laser action at room temperature at this state (Meyer *et al.* 1995, Nijegorodov 2001). Induced absorption at this state is of prime importance in dye laser technology for the design of new opto-optic components in photonic technology.

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