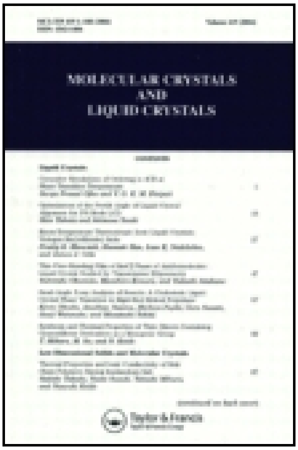


Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl17

A Proposal to obtain Molecular Absorption Spectra of Solid Dye Compounds by Photoacoustic Spectroscopy (PAS)

E. Kanezaki [a]

[a] Department of Applied Chemistry, Faculty of Engineering, Tokushima University, 2-1 Minamijosanjima, Tokushima, 770, Japan

Version of record first published: 22 Sep 2006.

To cite this article: E. Kanezaki (1989): A Proposal to obtain Molecular Absorption Spectra of Solid Dye Compounds by Photoacoustic Spectroscopy (PAS), Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics, 166:1, 245-251

To link to this article: http://dx.doi.org/10.1080/00268948908037153

Mol. Cryst. Liq. Cryst., 1989, Vol. 166, pp. 245–251
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in the United States of America

A Proposal to obtain Molecular Absorption Spectra of Solid Dye Compounds by Photoacoustic Spectroscopy (PAS)

E. KANEZAKI

Department of Applied Chemistry, Faculty of Engineering, Tokushima University, 2–1 Minamijosanjima, Tokushima 770, Japan

(*Received February 16, 1988*)

Solution-like molecular absorption spectra of the typical non- and fluorescent organic solid dye compounds are observed. High dispersion of dye molecules on silica particles results in well band separated photoacoustic spectra. Effectiveness of this method in studying the electronic state of solid dye molecules is described.

INTRODUCTION

Photoacoustic spectroscopy is one of the excellent methods to study the electronic state of solids.[1] Through the non-radiative deactivation process, the relaxation of the excess energy takes place from the photoexcited state followed by the heat flow to the surrounding gas (coupling media). When the incident radiation is modulated, the flow is also modulated in the same frequency. This periodicity produces pressure fluctuations in the sample cell and is detected as an acoustic signal by a microphone. On scanning the wavelength of the incident radiation, a photoacoustic spectrum is obtained.

Among many advantages of this spectroscopy, it is one of the most outstanding features that the electronic spectra can be easily observed without any restrictions in the sample conditions. Nevertheless, clear spectra with good band separation have been rarely obtained so far. According to Rosencwaig and Gersho, photoacoustic spectra correspond to absorption spectra for optically transparent samples (R–G Theory).[2] Unfortunately, the transparency cannot be desired in pure solid organic dye compounds because of the dense nature and the large absorption coefficients in the UV-visible wavelength region.

In connection to the TLC (thin layer chromatography) technique, the method of dye adsorption on the surface of particles has been one of the promising methods in the early pioneering works.[3a,b] In this method, we can control the surface density of dye molecules on the particles resulting in both a good signal to noise ratio and the optical transparency by using the particles with the large specific area. White and inert powders such as SiO_2, $BaSO_4$, Al_2O_3 and MgO have been used in these works because the colorless material produces no disturbing photoacoustic signal in measurements except on some special interests.[4] But in such works, the surface density of dye molecules seems too high to result in disappointing, low resolved and optically saturated spectra. These spectra sometimes mislead to the ambiguity in the elucidation of them. Are they saturated because of the opacity of the sample or low resolved because of the intrinsic nature of the dye itself? It must be emphasized that many organic compounds maintain the molecular properties or, at least, have little perturbed molecular properties even in the solid state as molecular crystals.[5] Therefore, it would be of great value to examine whether or not dye compounds exhibit the molecular absorption spectra when the optical transparency is assured by high dispersion enough to reach below the mono-molecular coverage in average. The using of the high surface density samples in early works needed because the low sensitivity of detectors forced to collect relatively large amounts of samples in measurements. Some other related methods have been attempted such as smearing, physical dilution (co-grinding) and chemical modification[3b,c] with the regard that, in the author's opinion, the dye adsorption method excels others in quantitative aspects, ease of density control and so on.

In this paper, two typical dye compounds are highly dispersed respectively on silica particles to observe the solution-like, molecular photoacoustic spectra successfully by using a sensitive detection system. The purpose of this paper is to exhibit the effectiveness of PAS in revealing the molecular character in highly dispersed solid state.

RESULTS AND DISCUSSION

The pure Rhodamine B(Rh B) powder shows the structureless photoacoustic spectrum in the region of $\lambda \leq 600$ nm (Figure 1a). A shallow concave around 450 nm

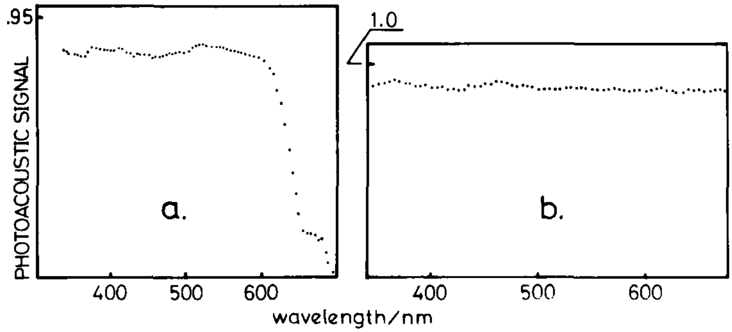


FIGURE 1 Photoacoustic spectra of (a) pure Rh B powder and (b) pure Indigo powder. A figure on the longitudinal axis is the ratio of the photoacoustic signal height of the powder upon that of the reference carbon black.

is always observed, though some false peaks in this region are not reproducible. At 600 nm, the signal height changes largely and decreases in the region of $\lambda \geq$ 600 nm, which accounts for the well known presence of the predominant fluorescent deactivation process.[7] The Rh B/SiO_2 powder exhibits a well band separated spectrum with the prominent maximum at 545 nm with two other maxima and a shoulder at 400, 350 and 510 nm, respectively. Although the location of the most prominent band is blue shifted by 9 nm, the total profile of the photoacoustic spectrum in Figure 2a quite resembles the absorption spectrum in Figure 3a. The band shift implies some interactions between Rh B and silica. The depth profile of Rh B molecules on silica particles has been studied.[6] An equilibrium between two molecular forms has been reported in solutions[8] and the cationic form has been assured on silica particles in the IR spectrum.[9]

The photoacoustic spectrum of the pure Indigo Carmine (Indigo) powder in Figure 1b has no significant structure, too. But the Indigo/SiO_2 powder exhibits the photoacoustic spectrum where a discrete band maximum locates at 590 nm (Figure 2b) which is also blue shifted by 21 nm in comparison with the absorption spectrum in Figure 3b, suggesting the interactions between Indigo and silica as is the case for Rh B. The spectrum in Figure 2b contains the silica originated background signal more prominently than that in Figure 2a. This is ascribed to the relatively weak photoacoustic signal in the former spectrum. Indigo dyes are known to show the *cis-trans* photoisomerization when the UV light irradiates them in solution(s) or as solid.[3d,10] But no spectral changes are observed in this experiment after the several repeated wavelength scan of the incident radiation from 700 to 300 nm. This is presumably because only the stable *trans*-form is observed in Figure 2b and the unstable *cis*-form has so short a lifetime that is unable to be detected for this compound.

Commonly in both cases above, the pure dye powders give poor spectra due to the optical saturation induced by the opacity of samples.[2] Because of the non-zero value of the absorption coefficient in the UV-visible wavelength region, pure dye powders absorb all incident photons and make themselves completely opaque. The saturation always occurs in the photoacoustic spectrum of carbon black which has been known as one of the perfect radiation absorbers and therefore of the complete opaque reference samples in the UV-visible wavelength region.[1] The photoacoustic

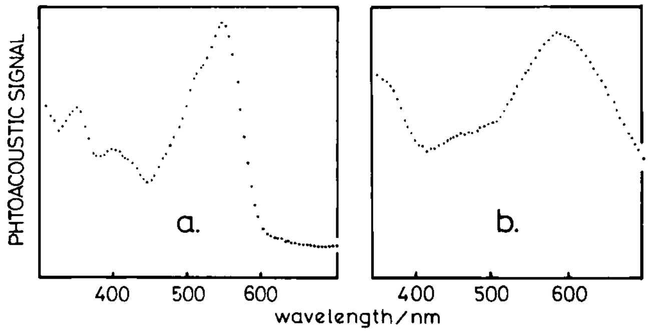


FIGURE 2 Photoacoustic spectra of (a) the Rh B/SiO_2 powder and (b) the Indigo/SiO_2 powder.

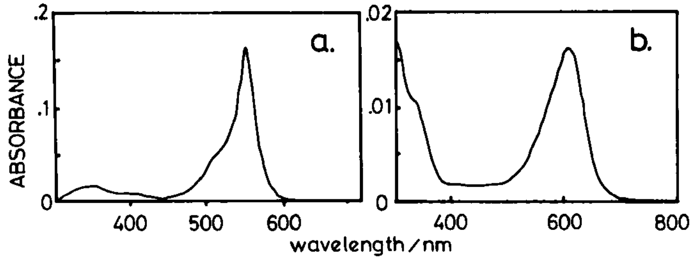


FIGURE 3 Absorption spectra of (a) aqueous Rh B solution ($C = 6.26 \times 10^{-7}$ mol dm^{-3}) and (b) aqueous Indigo solution ($C \sim 10^{-7}$ mol dm^{-3}).

signal height in Figures 1 ($\lambda \leq 600$ nm) and 4 is almost identically as large as that of carbon black, which indicates also the complete opacity of the pure dye powders. The saturation is expected to cease in the wavelength region where the absorption coefficient becomes absolutely zero. For the pure Indigo powder, this region might lie beyond the facility in this experiment.

For the fluorescent Rh B compound, an additional description is necessary. Figure 4 shows the Jablonski diagram of the Rh B molecule. In this molecule, with the fluorescence quantum yield of Q_f, the photoacoustic signal is originated from the excess energy ΔE as,

$$\Delta E = (E_i - E_f) + (1 - Q_f)(E_f - E_0) \qquad (1)$$

where E_i, E_f and E_0 are the energy of the excited state, that of the fluorescent state and that of the ground state, respectively. With strong fluorescent molecules ($Q_f \sim 1$) such as Rh B[7b], the second term in the right hand side of Equation 1 becomes negligible. Therefore, the photoacoustic signal of the pure Rh B powder vanishes when $E_i \leq E_f$. This is the case which takes place in the longer wavelength region than 600 nm in Figure 1a. The location of a weak shoulder band in this region may presumably be due to forbidden transition(s).

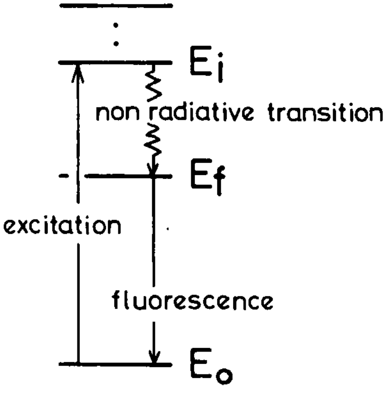


FIGURE 4 Jablonski diagram of fluorescent molecules; E_i, E_f and E_0, see text.

In both cases above, however, the dye molecules on silica particles show the discrete absorption maxima in the photoacoustic spectra because the transparency is realized through the high dispersion of dye molecules as is mentioned below. From the common spectral feature among the photoacoustic spectrum and the absorption spectrum of Rh B, it is safe to calculate the absorption coefficient (α) of solid from the absorbance (A) of the solution as,

$$A = -\log\left(\frac{I}{I_0}\right) = \frac{\alpha \cdot t}{2.303} \tag{2}$$

where I and I_0 are the incident radiation intensity to the solution and the transmitted one through the solution; t is the converted thickness of the solid, respectively. According to the R-G Theory, the optical penetration depth (μ_α) of the incident radiation into the solid dye layer is defined as,[2]

$$\mu_\alpha = \frac{1}{\alpha} \tag{3}$$

In this experiment, the absorption coefficient is calculated with the absorbance of the solution spectrum at 554 nm to be $6.06 \times 10^5\ \mathrm{cm}^{-1}$ from Equation 2, resulting $\mu_\alpha = 1.65 \times 10^{-6}$ cm from Equation 3. As is mentioned in the experimental section, Rh B molecules locate on silica particles below the monomolecular coverage which permits the estimation of the thickness of the Rh B layer on silica(L) as $L \leq 1.0 \times 10^{-7}$ cm. With these values, the relation is obtained as,

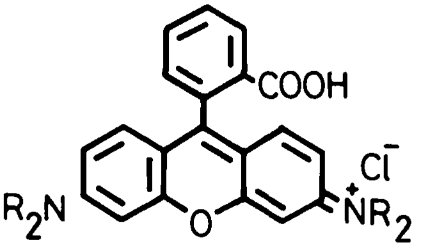
$$\mu_\alpha > L \tag{4}$$

which concludes the optical transparency in the R-G Theory.[2] The absorption at 554 nm is the largest in the solution spectrum. Hence, the absorption coefficient which is calculated with the absorption at the other wavelength than 554 nm is smaller and the penetration depth is larger than those of 554 nm, whereas the thickness is independent of the wavelength. From these reasons, the relation in Equation 4 is hold and the same conclusion is established among all the spectral regions in Figure 2a.

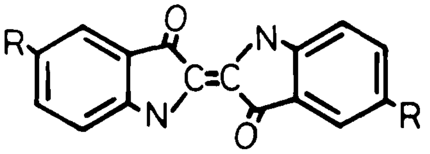
The calculation above ensures that the photoacoustic spectrum of the Rh B/SiO_2 powder reveals the intrinsic absorption spectrum of the Rh B solid. Furthermore, the spectrum is very similar to that of the solution. The same procedure for the Indigo/SiO_2 powder produces the same conclusion. These results strongly indicate that it is not necessary for Rh B and Indigo dyes to take apart from the molecular properties even in the solid state. The electronic state of the adsorbed dye molecules is sensitive to the nature of the surrounding host. Therefore, a wide application of this method is expected to produce the fruitful results not only on the intrinsic nature of dye molecules but also on that of the solid surface of host materials by using dye molecules as a probe.

EXPERIMENTAL

A small amount (~30 mg) of commercial reagent of Rh B(**1**) or Indigo(**2**) was dissolved to the distilled water (50 ml). Silica (SiO_2, powder) had been heated at 600°C in advance. The specific area of the silica was 3.76×10^2 m^2g^{-1} obtained by using the BET method. A small portion (~0.1 g) of silica was added to the dye solution. After centrifuging the mixture, the precipitation was washed with the water once, then dried at 50°C. A dark-blue powder (Indigo/SiO_2) and a red one (Rh B/SiO_2) were prepared. The amount of the adsorbed dye molecules was measured with the absorbance of the dissolved dye molecules from the dye loading silica particles to the water. With this value, the occupied area of a Rh B molecules on a silica particles was calculated to be 5.04×10^2 nm^2 which was much larger than the Rh B molecular area estimated from its molecular structure. From the calculation above, it is reasonable to say that Rh B molecules are adsorbed on silica particles, in average, with less than the monomolecular coverage.



1, R = C_2H_5



2, R = SO_3Na

In PAS experiments, the radiation from a Xe short arc (WACOM KXL-500F) was passed through an optical filter, a remodeled monochromator (Shimadzu-B&L 338626) and a mechanical light chopper and then irradiated the sample in the compact laboratory-made plexiglass (polyacrylonitrile flexible glass) cell (0.8 cm^3) equipped with a sensitive microphone (SONY ECM-150). The output from the microphone was fed into the preamplifier followed by a phase sensitive amplifier (NF 574A) locked on the chopping frequency. In order to determine the appropriate modulation frequency of the exciting radiation, dependence of the signal height upon the frequency was checked in the region of $2 \text{ Hz} \leq f \leq 2 \text{ kHz}$ with the result in Figure 5. The signal height decreased as the frequency increased. The Helmholtz resonance[11] was observed at 1.72 kHz which limited the frequency below 1.5 kHz in order to avoid a sharp sensitivity change during the PAS experiment near the resonance. From the observation above, the modulation frequency of 100 Hz was adopted in this experiment. The photoacoustic signal of the sample was normalized according to the normal procedure[1] by dividing the signal height of a sample with that of the reference carbon black at each wavelength to obtain the photoacoustic spectrum of the sample. Outline of the apparatus has been published before.[6] The

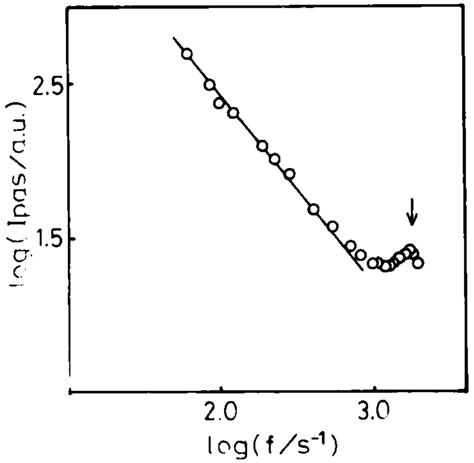


FIGURE 5 Dependence of the PAS signal height (I_{pas}) upon the modulation frequency (f) of the exciting radiation. Arrowed position indicates the Helmholtz resonance frequency of the cell.

specific surface area and absorption spectra were measured by using a CARLO ERBA SORPTOMATIC 1800 and a Shimadzu UV-3000 Spectrophotometer, respectively.

References

1. A. Rosencwaig, *Photoacoustics and Photoacoustic Spectroscopy*, (Wiley, New York, 1980).
2. A. Rosencwaig and A. Gersho, *J. Appl. Phys.*, **47**, 556 (1976).
3. (a) A. Rosencwaig and S. S. Hall, *Anal. Chem.*, **47**, 548 (1975); S. L. Castleden, C. M. Elliot, G. F. Kirkbright and D. E. M. Spillane, *Anal. Chem.*, **51**, 2152 (1979); S. Ikeda, Y. Murakami and K. Akatsuka, *Chem. Lett.*, **1981**, 363; (b) J. W. Lin and L. P. Dudek, *Anal. Chem.*, **51**, 1627 (1979); (c) J. J. Freeman and R. M. Friedman, *J. Phys. Chem.*, **84**, 315 (1980); L. W. Burggraf and D. E. Leden, *Anal. Chem.*, **53**, 759 (1981); (d) H. D. Breuer and H. Jacob, *Chem. Phys. Lett.*, **73**, 172 (1980).
4. R. C. Gray and A. J. Bard, *Anal. Chem.*, **50**, 1262 (1978); T. Iwasaki, S. Oda, T. Sawada and K. Honda, *J. Phys. Chem.*, **84**, 2800 (1980); T. Iwasaki, S. Oda, H. Kamada and K. Honda, ibid., **84**, 1061 (1980).
5. D. P. Craig and S. H. Walmsley, *Excitons in Molecular Crystals*, (Benjamin, New York, 1968).
6. E. Kanezaki, *Chem. Phys. Lett.*, **138**, 352 (1987).
7. (a) K. H. Drexhage, in Dye Lasers, Ed. F. P. Schäfer (Splinger, Berlin, 1973), Chap 4. pp. 144–193; (b) I. L. Arbeloa and K. K. Rohatgi-Mukherjee, *Chem. Phys. Lett.*, **128**, 474 (1986) and references therein.
8. D. A. Hinckley, P. G. Seybold and D. P. Borris, *Spectrochim. Acta*, **42A**, 747 (1986) and references therein.
9. Three molecular forms are reported for Rh B; cationic, zwitterionic and lactonic forms.[7,8] The detailed discussion on the photoacoustic spectrum of the Rh B/SiO$_2$ powder with respect to the Rh B molecular form will appear in future.
10. J. Blanc and D. L. Ross, *J. Phys. Chem.*, **72**, 2817 (1968); G. Hauke and R. Paetzold, *J. Prakt. Chem.*, **321**, 978 (1979); T. Karstens, K. Kobs and R. Memming, *Ber. Bunsenges. Phys. Chem.*, **83**, 504 (1979); S. A. Krysanov and M. V. Alfinov, *Chem. Phys. Lett.*, **82**, 51 (1981); G. R. Seely and E. R. Shaw, *J. Photochem.*, **24**, 383 (1984); H. Görner, J. Pouliquen and J. Kossanyi, *Can. J. Chem.*, **65**, 708 (1987).
11. R. S. Quimby, P. M. Selzer and W. M. Yen, *Appl. Opt.*, **16**, 2630 (1977).