

Photoinduced Dynamics of Azobenzene Dyes in Langmuir Films Investigated by Optical Second Harmonic Generation

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Photoinduced molecular dynamics of a Langmuir film of an azobenzene dye is investigated by means of optical second harmonic generation. The dynamics is induced by turning on and off irradiation with monochromatic light at a wavelength in the dye absorption range. We find different dynamical behaviors depending on the surface pressure of the film. At the lowest pressures, we observe a fully reversible photoinduced dynamics which is most likely related to cis-trans photoisomerization. However, the measured relaxation rate of the dye monolayer on the water surface is somewhat faster than the reported cis-trans rate of the same dye in dilute solutions, probably reflecting the effect of dye-dye or dye-water intermolecular interactions. At the highest pressures, we observe an irreversible or slowly reversible dynamics of still unidentified nature. These results, although still very preliminary, point to a strong influence of the molecular state of aggregation on the photoisomerization processes and possibly also on the related photoinduced reorientation phenomena, in accordance with previous observations on the same dye in Langmuir-Blodgett multilayer films.

Keywords: azodye; Langmuir film; photoisomerization; photosensitivity; second harmonic

INTRODUCTION

In the last fifteen years, azobenzene dyes (azodyes) have been the subject of several studies because of their peculiar photodynamic

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properties [1,2]. Azodyes are known to undergo *cis-trans* photoisomerization, a well understood photochemical single-molecule process [3]. Moreover, many azodyes exhibit strong photoinduced collective molecular reorientation phenomena in polymers [4], liquid crystals [5,6], Langmuir-Blodgett films [7–9], and Langmuir monolayers [10]. Owing to these phenomena, azodyes are a promising class of materials for the development of novel optical media to be employed in nonlinear optical processing, data storage, and phase conjugation.

The physical mechanism of the collective photoinduced reorientation phenomena is still debated. Although most works link it to the photoisomerization [11], in some cases there is evidence favouring different interpretations [7–9]. In particular, detailed experiments performed on an aminoazobenzene dye in Langmuir-Blodgett multilayer films show that while *cis-trans* photoisomerization appears to be fully inhibited owing to the close molecule packing, the photoinduced reorientation still takes place [9].

This result motivated us into starting an investigation of the effect of molecular packing on the two processes of photoinduced *cis-trans* isomerization and collective reorientation. In order to have a well controlled system in which molecular packing can be adjusted more or less continuously, we chose to study Langmuir films, i.e., dye monolayers floating on water. In contrast to the case of Langmuir-Blodgett films, which are deposited on solid substrates and have a fixed degree of molecular packing for a given temperature and pressure, the bidimensional molecular density of Langmuir films can be simply controlled by means of a moving barrier. In other words, one acquires an additional thermodynamic control parameter, namely surface pressure, which allows a greater degree of control on the material state of aggregation.

To probe the photoinduced dynamics of the Langmuir films of azodye molecules, we have used optical second harmonic generation (SHG), a technique which is highly sensitive to interfacial properties and, more specifically, to the average molecular orientation [12]. This technique and its cousin, sum-frequency generation, has been successfully applied to many other studies of Langmuir films [13], including films of azodyes [14,15].

EXPERIMENTAL METHODS

The investigated dye is the hydrophobically-substituted aminoazobenzene 4-[4'-*N*-octadecylamino] phenylazocyanobenzene (**A**), provided by SPECS and BioSPECS, the same dye used in Ref. [8,9] (see Fig. 2 inset). The Langmuir films were prepared by spreading 4 mL of a

solution of **A** in CHCl_3 (0.06 mg/mL) on ultrapure water (Millipore Milli-Q, resistivity $>18 \text{ M}\Omega\text{cm}$) contained in a commercial PTFE trough (311D, NIMA Technology) equipped with a single barrier for film compression and waiting a few minutes for allowing the solvent evaporation. A Wilhelmy balance was used for surface pressure (π) measurements. The trough was inserted into a SHG apparatus, as shown in Figure 1. The laser beam was made to impinge close to the fixed edge of the trough, so that it could probe the compressed film up to the highest pressures. The laser source used for SHG probing is a mode-locked Nd:YAG laser (Ekspla) generating 20-ps pulses at 1064 nm, with a repetition rate of 10 Hz (IR laser beam). We worked with an input pulse energy of about 1 mJ, and a beam waist on the water surface of about 1 mm. At these conditions, as we discuss later, the dye monolayer never showed any photoinduced phenomena triggered by the input IR beam. The second harmonic light generated in reflection at 532 nm is detected by a photomultiplier, with gating-integrator electronics. We worked always in the photon-counting mode, in which an average of less than a SHG photon per pulse is detected. Half-wave plates and polarizing cubes allowed the selection of either the *p* (i.e., electric field in the vertical incidence plane) or *s* (i.e., electric field parallel to the horizontal surface plane) polarization components of both the input and the output light.

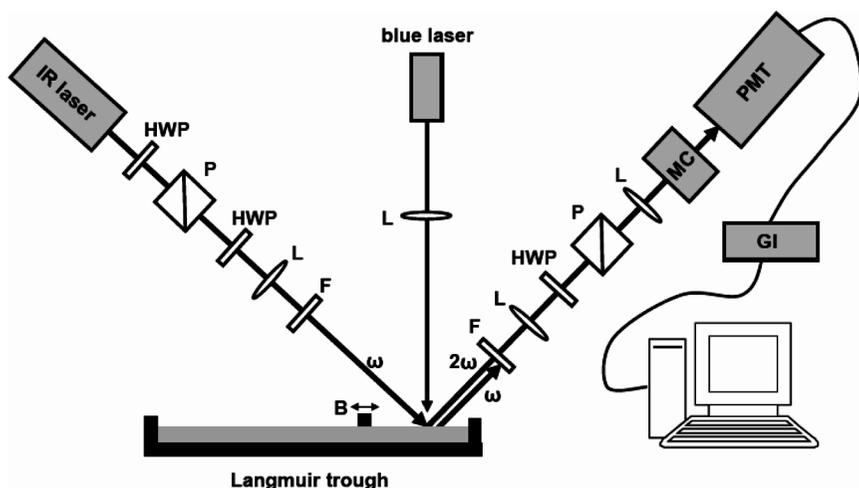


FIGURE 1 Experimental apparatus used for SHG experiment. P: polarizing cube, HWP: half-wave plate, L: lens, F: filter, MC: monochromator, PMT: photomultiplier, GI: gated integrator, B: moving barrier.

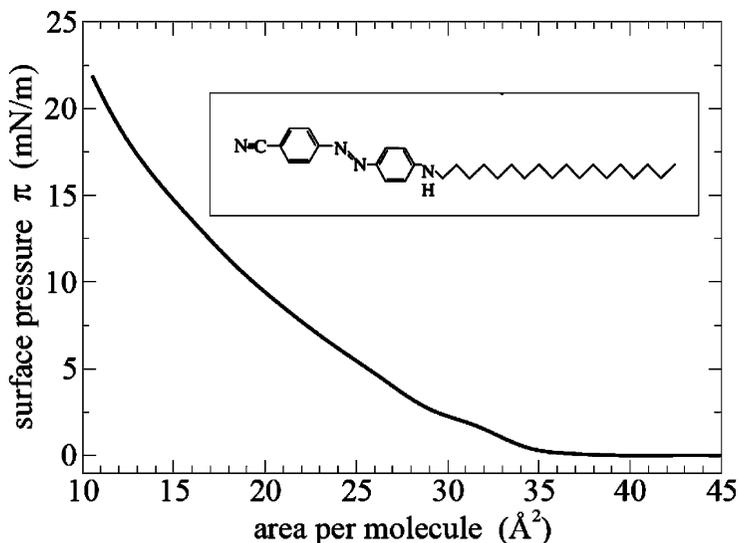


FIGURE 2 Surface pressure-area isotherm at a temperature of about 25°C, for a Langmuir film of azodye **A**. Inset: structure formula of azodye **A**.

In order to induce the photodynamic processes, we irradiated the Langmuir film with light from a continuous-wave diode-pumped solid-state laser at a wavelength of 473 nm (blue laser beam). This blue light beam impinges at normal incidence on the surface and is defocused so as to illuminate a monolayer area of 5 cm² with a power of about 50 mW.

RESULTS AND DISCUSSION

A typical Langmuir isotherm of **A** at about 25°C is shown in Figure 2. For areas larger than about 40 Å² the monolayer is probably in a gas-liquid phases coexistence state. In this region, the surface pressure is too small to be appreciated by our sensor. Compressing gradually the monolayer (barrier speed 2 cm²/min), the surface pressure begins to rise starting at an area per molecule of about 38 Å², showing that the monolayer enters a condensed phase. A small but sudden slope-change in the isotherm appears at about 30 Å² ($\pi = 2.5$ mN/m) and is consistently observed in all experiments. This suggests a change of organization, possibly from a liquid-expanded to a liquid-condensed or solid phase, although we cannot identify the nature of the transition. No film collapse occurs in the observed area range. After the

barrier is stopped, there is initially a relatively rapid decrease of the pressure by few mN/m, which levels off after several minutes, and subsequently the pressure keeps decreasing very slowly (typical decrease rates are below 1 mN/m per hour), showing no sign of reaching a stable value. We believe that the first rapid decrease is due to an equilibration process in the monolayer, while the second slow decrease is probably associated with a continuous depletion of the total number of molecules in the monolayer, possibly due to a micellization process or to formation of multilayers or other three-dimensional structures.

An additional complexity of the investigated system is that the Langmuir films of dye **A** are never fully homogeneous. Indeed, observing with the naked eye the light reflected by the film at about the Brewster angle, domains having different degrees of reflectivity floating on the water surface can be seen. This occurs at all investigated pressures, including regions in which the isotherm is not flat, so that these observations cannot be ascribed to a simple phase coexistence at thermodynamic equilibrium. For lower surface pressures, these domains move slowly and randomly on the surface, while at higher pressures they stop moving. In the latter regime, the film also shows an elastic behavior if mechanically stimulated (for example with a weak air flow).

We measured the SHG as a function of molecular surface density, finding a highly irreproducible signal, most likely due to the film inhomogeneity. When reaching the more condensed states in which the domains are still, the SHG signal stabilizes in time. However, if we repeat the measurements (or move slightly the barrier), we find again large random variations of the SHG signal, still due to the film inhomogeneity.

In order to extract meaningful information from our SHG experiments, we introduced an analysis method to identify data sets in which signal fluctuations can be ascribed mostly to the shot noise, as opposed to the case in which there are substantial additional random fluctuations due to domain diffusion (or other sources of non-Poissonian noise). If there is only shot noise, one can assume that the probability p of observing a SHG photon in each input pulse is constant. Then, the probability distribution $P(n)$ for the pulse-number intervals n between consecutive detected SHG photons is

$$P(n) = p(1 - p)^{n-1} = pe^{(n-1)\ln(1-p)} \quad (1)$$

Therefore, only data sets which were found to be statistically consistent with this prediction (at a confidence level of 68%) were retained for further discussions.

We also verified that the IR laser beam used for SHG probing did not itself induce photoinduced modifications in the Langmuir films (e.g., by two-photon absorption), by measuring the dependence of SHG on the input pulse energy. We found a quadratic rise of the SHG photon number with increasing input energy up to several mJ's per pulse, as expected for unaltered surface properties.

Next, we started investigating the photoinduced dynamics by doing experiments in which the blue laser light is turned suddenly on or off, while the SHG signal is monitored continuously. In order to highlight the effect of the state of molecular packing, we carried out these measurements at two different surface densities (these are preliminary results; work is in progress for extending these studies to the whole range of investigated pressures): (I) 32 \AA^2 per molecule corresponding to a surface pressure of 2 mN/m, in what is probably a liquid-expanded phase; (II) 14 \AA^2 per molecule, with a pressure of 15 mN/m, in what is probably a liquid-condensed or solid phase.

The results obtained at point I (low pressure) are shown in Figure 3. Here, SHG was collected in the *ps* polarization combination, where *ps*

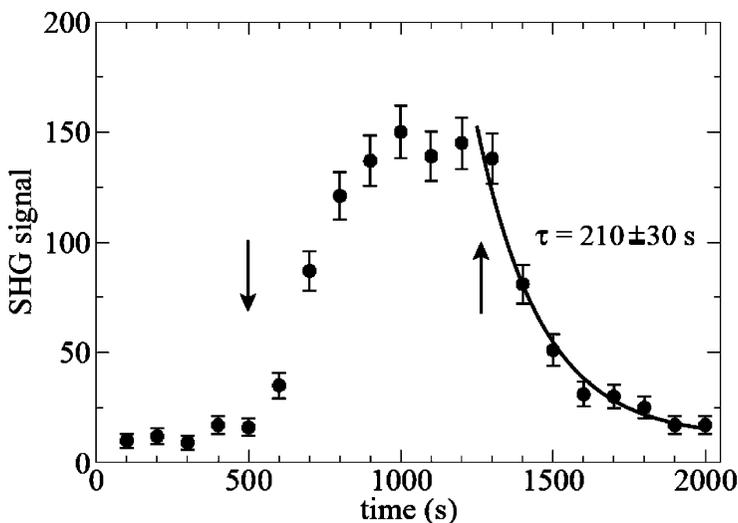


FIGURE 3 Time dependence of SHG from the Langmuir film of dye **A** at a surface pressure of 2 mN/m. SHG signals are photon counts in 1000 laser pulses, corrected for multiple counting. The SHG polarization combination is *p*-in *s*-out (*ps*). The arrows indicate the times at which the illumination with blue light was switched on (↓) and off (↑). The solid line is a single-exponential best-fit (best-fit decay time is given in the figure).

stands for *p*-polarized input and *s*-polarized analysis. It is seen that the SHG signal before irradiation is small (although significantly higher than background level) and constant in time. When switching on blue light irradiation, the SHG signal starts to increase and reaches a new stationary value which is about ten times higher. After switching off the blue light, we observe an exponential decay of the SHG signal, which tends to return to the initial value. We performed a best-fit of the data acquired after the blue-light switching-off with an exponential decay combined with a constant offset. The exponential decay time constant obtained from the fit is $\tau = 210 \pm 30$ s (uncertainties given hereafter are for a confidence level of 68%).

Assuming that the effect of blue irradiation is that of converting a fraction of the dye molecules from *trans* to *cis* state, we can interpret the observed dynamics by the following simple model. The SHG signal is proportional to the squared-modulus of the effective hyperpolarizability constant $\chi^{(2)}$. The latter is in turn given by the following sum of a contribution from each molecular species (local-field effects are neglected):

$$\chi^{(2)} = \alpha_{\text{trans}}^{(2)} N_{\text{trans}}(t) + \alpha_{\text{cis}}^{(2)} N_{\text{cis}}(t) = \alpha_{\text{trans}}^{(2)} N_{\text{tot}} + [\alpha_{\text{cis}}^{(2)} - \alpha_{\text{trans}}^{(2)}] N_{\text{cis}}(t) \quad (2)$$

where N_{trans} and N_{cis} are the molecular surface densities of the respective species, and N_{tot} is the total one. Taking the squared-modulus of the latter, we find

$$\text{SHG} \propto \left| \chi^{(2)} \right|^2 = \left| \alpha_{\text{trans}}^{(2)} N_{\text{tot}} \right|^2 + 2\text{Re} \left[\alpha_{\text{trans}}^{(2)} \Delta\alpha^* \right] N_{\text{tot}} N_{\text{cis}}(t) + \left| \Delta\alpha \right|^2 N_{\text{cis}}^2(t) \quad (3)$$

where $\Delta\alpha = \alpha_{\text{cis}}^{(2)} - \alpha_{\text{trans}}^{(2)}$. Equation (3) in general predicts a double-exponential dependence of the SHG signal, for a single exponential decay of N_{cis} . However, in our case the SHG signal observed before irradiation is very small, so that we can neglect the contribution of *trans* molecules, or $\alpha_{\text{trans}}^{(2)} \approx 0$. In this approximation, Eq. (3) reduces to a single exponential decay proportional to the square of the *cis* molecular density $N_{\text{cis}}(t)$. If our data are interpreted with this simple model, we obtain a *cis-trans* relaxation time of 420 ± 50 s. This value is smaller than the reported relaxation time for dye **A** in CHCl_3 solution (560 ± 20 s) [9] (although the two values are compatible within three standard deviations). This difference is most likely attributable to the different environment, as is well known that *cis-trans* relaxation rates are very sensitive to intermolecular interactions.

We find a similar behaviour also when observing the same process with *pp*, *sp* and *ss* polarization combinations of the SHG apparatus (data not shown here), although we have a lower signal-to-noise ratio.

It is also interesting to note here that a nonvanishing *s*-output SHG is a signature of an azimuthal anisotropy in the film. Therefore, either the film is spontaneously oriented in the surface plane even before irradiation, or the irradiation process itself induces this orientation (photoinduced collective reorientation process).

When compressing the film to the point II, the photoinduced dynamical behaviour drastically changes, as illustrated in Figure 4. In this case, a strong SHG signal is observed before irradiation with blue light (this is for *pp* polarization combination). Irradiation induces a strong decrease of SHG signal. However, when the blue light is switched off, the SHG signal exhibits only a very slow relaxation toward the level it had before irradiation. We were not able to obtain full recovery of the initial SHG signal, as a very long waiting time always led to a depletion of the film, as discussed previously. Therefore, we cannot establish if the photoinduced transformation is irreversible or only very slowly reversible. With other polarization combinations, we observe a similar behavior but at a smaller signal level. Interestingly, in the *sp* case, irradiation leads to an increase of the SHG signal instead of a decrease (see inset of Fig. 4).

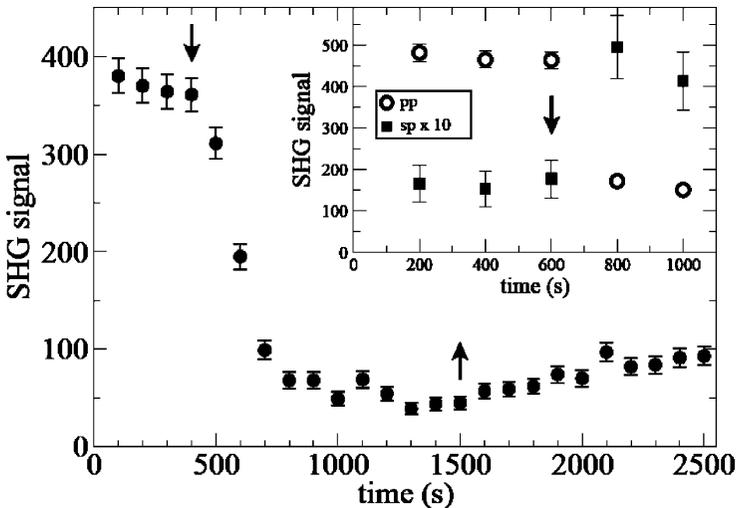


FIGURE 4 Time dependence of SHG from the Langmuir film of dye **A** at a surface pressure of 15 mN/m. SHG signals are photon counts in 1000 laser pulses, corrected for multiple counting. The SHG polarization combination was *p*-in *p*-out (*pp*). The arrows indicate the times at which illumination with blue light was switched on (\downarrow) and off (\uparrow). Inset: Time dependence of *pp* (circles) and *sp* (squares) SHG.

The simplest explanation for these observations would be that *cis* state of the dye is stabilized by the higher surface pressure of the film, so that its relaxation rate to the *trans* state is strongly reduced. The difference in the SHG signal levels observed at the various polarization combinations for small and high pressures can be probably related to the different average orientation of the molecules in the film, e.g., almost lying flat on the water for small pressures and almost vertical at the higher pressures.

However, it is also possible that more complex photoinduced processes take place, associated with some form of coupling between the *trans-cis* isomerization and a collective reorientation or reorganization of the Langmuir film. More experiments will be needed to distinguish among these hypotheses.

CONCLUSIONS

We investigated the photoinduced dynamics of an azobenzene dye in Langmuir monolayers at different states of compression by means of optical second harmonic generation, using a blue laser light for driving the dynamics. At low surface pressures, we observe a reversible dynamics which is most likely associated with simple *trans-cis* photoisomerization of the dye in the film. The *cis-trans* relaxation time has been measured and found to be slightly smaller than the value reported for the same dye in chloroform solution. For higher pressures, we observe a very different behavior, namely an irreversible or very-slowly-reversible photoinduced transformation of a still unidentified nature. These results are only preliminary ones and we plan to extend our investigation to all intermediate pressures and to integrate SHG measurements with other techniques, such as Brewster-angle microscopy and reflection spectroscopy. However, the results reported in this paper already allow us to conclude that the photoinduced dynamics of azodyes in Langmuir films is very sensitive to the degree of molecular packing, as expected. Moreover, Langmuir films have proved to be good model-systems for investigating the dependence of photoinduced phenomena on the molecular state of aggregation.

REFERENCES

- [1] Eich, M., Wendorff, J. H., Beck, J. H., & Ringsdorf, H. (1987). *Macromol. Chem. Rapid Commun.*, 8, 59.
- [2] Natansohn, A., Rochon, P., Gosselin, J., & Xie, S. (1992). *Macromolecules*, 25, 2268.
- [3] Rau, H. (1990). Photoisomerization of Azobenzenes. In: *Photochemistry & Photo-physics*, Rabek, J. F. (Ed.), CRC Press: Boca Raton, Vol. II, Chapter 4, 119–141.

- [4] Gibbons, W. M., Shannon, P. J., Sun, S.-T., & Swetlin, B. J. (1991). *Nature*, *351*, 49.
- [5] Jánossy, I. & Szabados, L. (1998). *Phys. Rev. E*, *58*, 4598.
- [6] Khoo, I. C., Li, H., & Liang, Y. (1993). *IEEE J. Quantum Electron*, *29*, 1444.
- [7] Palto, S. P., Blinov, L. M., Yudin, S. G., Grewer, G., Schonhoff, M., & Losche, M. (1993). *Chem. Phys. Lett.*, *202*, 308.
- [8] Schönoff, M., Chi, L. F., Fuchs, H., & Lösche, M. (1995). *Langmuir*, *11*, 163–168.
- [9] Schönoff, M., Mertesdorf, M., & Lösche, M. (1996). *J. Phys. Chem.*, *100*, 7558.
- [10] Crusats, J., Albalat, R., Claret, J., Ignés-Mullol, J., Reigada, R., & Sagués, F. (2005). *J. Chem. Phys.*, *122*, 244722.
- [11] Dumont, M. & Sekkat, Z. (1992). *SPIE J.*, *188*, 1774.
- [12] Shen, Y. R. (1989). *Nature*, *337*, 519.
- [13] Slyadneva, O., Harata, A., & Hatano, Y. (2002). *Analytical Sciences*, *17*, i1173.
- [14] Zhuang, X., Lackritz, H. S., & Shen, Y. R. (1995). *Chem. Phys. Lett.*, *246*, 279.
- [15] Oh-e, M., Tabe, Y., & Yokoyama, H. (2003). *Phys. Rev. E*, *68*, 061602.