

Effect of pressure on the dynamics of the photostimulated orientational ordering transition in a liquid crystal

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We have investigated the influence of the applied pressure on the shift in the photostimulated phase transition temperature and the dynamics of the system to undergo such a phase transition. The shift is seen to decrease with increasing pressure, a feature that can be countered, to a certain extent, by increase in the intensity of the light used. Whereas the time scales of the system to undergo such a transition increases with pressure, the thermal back relaxation process to recover the original phase occurs faster at elevated pressures. We propose a simple argument to explain these observations.

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The phenomenon of light acting as a stimulus and control parameter to bring about phase transitions has attracted significant interest in recent times [1]. Such photostimulated phase transitions have been reported in a variety of systems including spin-crossover complexes [2], π -conjugated polymers [3], and liquid crystals [4–11]. A beautiful illustration of nature utilizing photoinduced effects is that of the biological photochrome bacteriorhodopsin found in the eye [12]. Molecules containing azo ($-N=N-$) groups are well known to show reversible isomerization transformations upon irradiation with UV and visible light [13]. Upon absorption of UV light (typically 365 nm) the energetically more stable *trans* or *E* configuration with an elongated rodlike molecular form, transforms into a bent bananalike *cis* or *Z* configuration. The reverse transformation of the *Z* isomer into the *E* isomer can be brought about by irradiation of visible light (in the range of 400–500 nm). The latter change also occurs in the “dark” by a process known as “thermal back relaxation” in a period ranging from minutes to tens of hours depending on the system. When such azo entities are incorporated into a liquid crystalline medium, either by physical mixing or by chemical bonding, the photoisomerization can lead to spectacular results. For example, the *E* form, due to its rodlike shape, stabilizes the liquid crystalline phase while the photoinduced *Z* isomer with its bent shape acts like an “impurity” destabilizing the phase. The destabilization can be significant enough to even cause an isothermal photoinduced transition from a liquid crystalline phase, say, the nematic phase to the isotropic phase. This phenomenon has attracted attention, not only from a basic point of view, but also for possible applications in optical switching, image storage and optomechanical devices [14–17]. Photoinduced effects have been well studied in systems exhibiting nematic-isotropic (*N-I*) [4,7,10] and smectic-*C**–smectic-*A* transitions [5,11,18]. Very recently we reported [19], a reentrant nematic–smectic-*A* transition induced by light. (Notice that in this case, contrary to all earlier observations, the photoinduced phase is more

ordered.) Over the years, a variety of probes have been used to investigate photoinduced effects. But only recently, the effect of pressure on the pressure-temperature (*P-T*) phase diagram was reported by us [20]. In this study we observed that as pressure is increased the magnitude of the photoinduced shift in the transition temperature diminishes. To explain this feature we proposed that the applied pressure reduces the volume available and thus makes it difficult for the photoactive molecules to undergo the isomerization transformation. Further, it was argued that this effect can be partially overcome by increasing the level of the UV intensity. Hence acting as a control parameter to vary the degree of isomerization, the applied pressure must have a strong influence on the dynamics associated with both the photochemical (driven by *E-Z* transformation) and the thermal back relaxation (driven by the reverse *Z-E* transformation). Specifically the photochemical change should be slowed down and the reverse process should exhibit faster dynamics. With these expectations we carried out the high pressure study on the dynamics of the photoinduced nematic-isotropic phase transition and the results are reported here.

The liquid crystalline host material is 4-*n*-octyloxy cyano biphenyl (8OCB, for short) from E-Merck and exhibits nematic and smectic-*A* mesophases. The guest, UV-active dopant compound, is *p*-(*p*-ethoxy phenylazo)phenyl hexanoate (EPH) from Eastman Kodak and is also liquid crystalline exhibiting a nematic mesophase. All the results described in this paper have been obtained on a mixture of 5 mol % of EPH in 8OCB, which we refer to as Mixture 1 hereafter. The *N-I* transition temperatures (T_{N-I}), as obtained by DSC 7 (Perkin Elmer) for EPH, 8OCB, and Mixture 1 are 125 °C, 79.8 °C, and 81.9 °C, respectively. The details of the high pressure setup employed have been described elsewhere [20]. The substrate surfaces were treated with a polyimide solution resulting in strong anchoring conditions. Since the crossed polarizer configuration was not employed, the intensity transmitted was usually maximum in the isotropic phase. The actual magnitude of the photoinduced transition obtained at atmospheric pressure using the high pressure setup agreed exactly with that detected using the standard hot stage (Mettler) setup. Further in the latter experiments the possibility of the anchoring transition was ruled out by conoscopic

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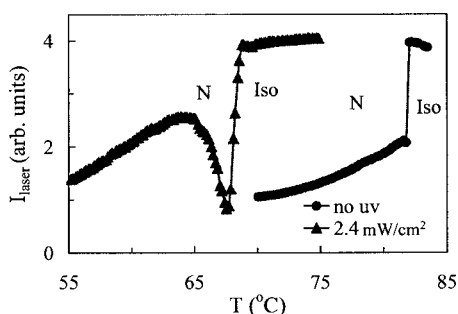


FIG. 1. Raw traces of the laser transmission as a function of temperature obtained at room pressure in the absence of UV irradiation and when the sample is illuminated with UV radiation of 2.4 mW/cm^2 intensity. In the presence of UV, the N - I transition temperature marked by the abrupt change in intensity is shifted by $11.3 \text{ }^\circ\text{C}$.

observations. The UV apparatus used for inducing photoisomerization consisted of an intensity stabilized UV source with a fiber-optic guide (Hamamatsu L7212-01, Japan) in conjunction with a UV-bandpass filter and an IR-block filter. The transitions have been detected by monitoring the intensity of a He—Ne laser beam transmitted by the sample. Photoabsorbance measurements carried out at atmospheric pressure in the nematic phase established the existence of photoinduced E - Z isomerization as well as the thermal back relaxation upon turning the UV radiation off.

Phase diagram: Figure 1 shows traces of the transmitted laser intensity I_{laser} as a function of temperature at room pressure, obtained when there is no UV and when the sample is irradiated with UV illumination of 2.4 mW/cm^2 . In both the cases the transition is signified by an abrupt change in the intensity. The important feature to note is that the transition temperature, T_{N-I} exhibits a significant diminution upon illumination with the UV radiation. Such a downward shift in the transition temperature due to irradiation with UV light and the consequent photoisomerization of the photoactive molecules from their rodlike E form to the bent Z form is now well established at atmospheric pressure [4,7,10]. In fact, we have shown in an earlier presentation [10] that even in guest-host systems (like in the present case) in which the photoactive molecules are present in quite low concentrations, UV light of very low intensities ($\sim 100 \text{ } \mu\text{W/cm}^2$) is sufficient to lower the transition temperature by as much as $15 \text{ }^\circ\text{C}$. To demonstrate the effect of pressure, scans taken as a function of temperature at three representative pressures are shown in Fig. 2. The photoinduced shift in the transition temperature (ΔT) decreases with increasing applied pressure, so much so that the shift which is $11.3 \text{ }^\circ\text{C}$ near atmospheric pressure [Fig. 2(a)], diminishes to $7.5 \text{ }^\circ\text{C}$ at 1.26 kbar pressure [Fig. 2(b)] and finally vanishes at a pressure of 2.54 kbar [Fig. 2(c)]. The P - T phase diagram constructed using such data is shown in Fig. 3(a) and brings out the fact that beyond a certain pressure the irradiation is unable to cause a shift in T_{N-I} . Based on the concept in which the pressure dependence of volume and the energy of the UV radiation counteract each other, we proposed [20] the following argument to explain the existence of a pressure P_0 at which ΔT goes to zero leading to the meeting of the thermal

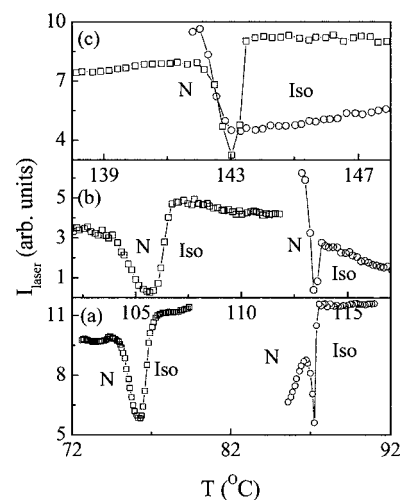


FIG. 2. Raw isobaric traces of I_{laser} obtained without and with UV radiation (10.2 mW/cm^2) at three different pressures, (a) 0.17 kbar, (b) 1.26 kbar, and (c) 2.5 kbar. ΔT , the photoinduced shift in the transition temperature decreases as the pressure is increased. In fact, for the highest pressure scan shown here there is no shift at all.

and photoinduced N - I boundaries. Measurements at constant temperature have established that there is a decrease in the specific as well as transition volumes with higher transition pressures and temperatures [21]. Consequently, the intermolecular space available for the EPH molecule to take a bent conformation decreases with increasing pressure. To accommodate such a feature, the system opposes the formation of the Z isomers. Hence a finite ΔT caused by the Z isomer becomes smaller with increasing pressure and finally vanishes. This opposition resulting from the reduction in the intermolecular space can be countered, at least to a certain extent, by increasing the energy of the UV radiation pumped into the system. This is indeed true as can be seen by measurements done for different UV intensities (I_{UV}). For example, the traces obtained at different I_{UV} show that the pressure up to which the photoinduced I phase is stabilized increases with increasing I_{UV} , indicating that a higher intensity level of the radiation will force the E isomer of EPH to transform to the Z isomer leading to at least a partial restoration of the photoinduced shift in the transition temperature. These features are summarized in the phase diagram shown in Fig. 3(a).

Notice that while for the N - I boundary obtained without the UV radiation, the phase transition temperatures vary linearly with pressure, there is a deviation from linearity for the boundaries obtained in the presence of the UV radiation. In the framework of classical thermodynamics the pressure dependence of the transition temperature of a first order transition can be described by the Clausius-Clapeyron equation,

$$\frac{dT}{dP} = T \frac{\Delta V}{\Delta H}.$$

Although this expression is strictly valid at each point on the transition line, it often fails to describe the whole boundary, unless the pressure dependence of ΔV and ΔH are known.

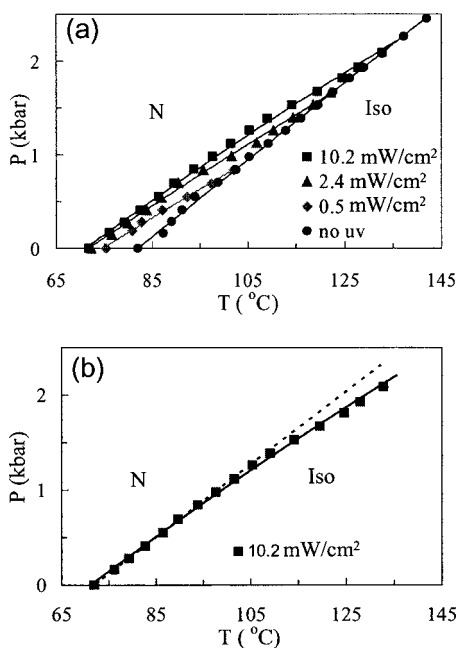


FIG. 3. (a) Pressure-temperature phase diagram showing the nematic-isotropic ($N-I$) boundary obtained when there is no UV radiation as well as in the presence of 0.5 mW/cm², 2.4 mW/cm², and 10.2 mW/cm² UV radiation. For all the three intensities the UV-induced shift in the transition temperature decreases as the pressure is increased. The value of pressure P_0 , above which the UV radiation does not cause any change in the transition temperature, increases with increase in the magnitude of the UV radiation. The lines through the data show the fit to the RD equation discussed in the text. (b) To illustrate the nonlinearity of the phase boundary obtained with UV radiation, the data for 10.2 mW/cm² is shown separately. The dashed line represents fit to a straight line and the solid line to the RD equation.

The usual practice has been to use the values obtained at room temperature, which then can only describe the linear behavior. To address the nonlinear cases different empirical relations are used. The simplest of these is to employ higher degree polynomial equations; but the polynomial equations, by their very nature, do not lend themselves to reliable extrapolations. An equation that has been extensively used to describe, particularly the melting lines, is the Simon-Glatzel (SG) law [22]

$$\frac{P}{a} = \left(\frac{T}{T_0} \right)^m - 1,$$

where a and m are constants and T_0 is the transition temperature at room pressure. Although attractive as it contains only two constants and is amenable to extrapolations, the SG law cannot be used to explain strongly nonlinear curves, especially in cases where there appears to be a maximum in the transition temperature or regions in the vicinity of it. To fit the data on a universal basis, Rein and Demus [23] proposed in 1993 a modified form of the SG rule by including a “damping” part to adjust for the nonlinearity of the phase boundary. The significant feature of this modified SG (mSG)

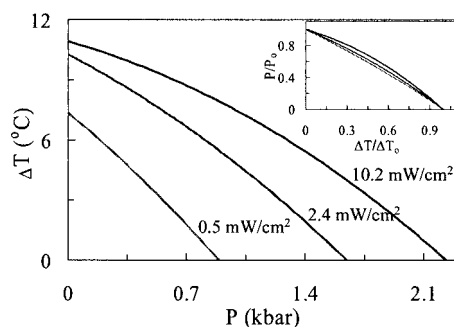


FIG. 4. Pressure dependence of ΔT , the photoinduced shift in the transition temperature for three different I_{UV} values, 0.5 mW/cm², 2.4 mW/cm², and 10.2 mW/cm². Notice that as the UV intensity increases the pressure at which a finite value of ΔT is seen, increases. The inset shows the universal behavior of the normalized data set realized by taking the ratio of P to P_0 (the pressure at which ΔT goes to 0) and ΔT to ΔT_0 (ΔT_0 is the value of ΔT value at room pressure). The I_{UV} value decreases from the top data set to the bottom one.

expression is that it is not empirical but based on thermodynamic arguments. The mSG is given as

$$\frac{T}{T_0} = \left(1 + \frac{P}{B} \right)^A \exp(fP).$$

Notice that with $f=0$ and $A=1/m$, this equation is reduced to the SG form. This equation was also proposed by Kechin [24] and since then has been used to fit the pressure-temperature boundary in various systems, such as melting of H₂ [25]. In fact, this equation has come to be known as Kechin model. However, owing to its first application for liquid crystals, we prefer to call it the Rein-Demus (RD) equation. The RD equation has been successfully employed by us to describe the columnar-isotropic boundary in the P - T plane of many compounds belonging to a homologous series [26]. The solid lines drawn through the data points in Fig. 3(a) are the result of fitting to the RD equation. For the no-UV data the RD equation made hardly any difference as against the fitting to a straight line, but it improved the fitting substantially for the data obtained in the presence of the UV radiation. To illustrate the nonlinearity of the phase boundary in the presence of the UV radiation, the data for $I_{UV} = 10.2$ mW/cm² is plotted separately in Fig. 3(b) showing the fit to a straight line as well as that to the RD equation. The better fit with the RD equation is evident.

The pressure dependence of ΔT , the UV-induced shift in the transition temperature, is shown in Fig. 4. Two salient features to be noted are (i) at all UV intensities, ΔT decreases as pressure is increased and goes to zero at a certain pressure, which we denote as P_0 . (ii) P_0 increases as I_{UV} is increased. These features are in agreement with the argument presented above regarding the influence of pressure on the extent of photoisomerization. To find out whether the dependence of ΔT on pressure has a universal behavior for different I_{UV} values, we replotted the data by normalizing the pressure as P/P_0 and ΔT as $\Delta T/\Delta T_0$ with ΔT_0 being the value at room pressure (see inset of Fig. 4). Given the simplicity of this

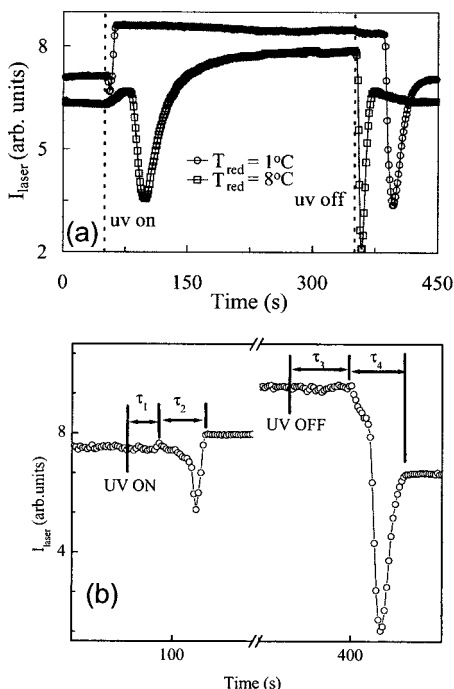


FIG. 5. (a) Temporal variation of I_{laser} upon switching on the UV radiation and subsequently switching it off at two reduced temperatures: $T_{\text{red}} = 1^\circ\text{C}$ and 8°C . The data was collected at a pressure of 0.9 kbar. (b) Schematic diagram to show the notations used to describe the delay and response times in the on and off conditions.

normalization it is interesting to see that data for all the three intensities seem to collapse to a single curve, perhaps suggesting the universal nature of the phenomenon.

Dynamics: The temporal variation of I_{laser} upon turning the UV on and subsequently off, at a constant pressure and constant I_{UV} but at two reduced temperatures $T_{\text{red}} (=T_{\text{iso}} - T)$ is shown in Fig. 5(a). The response upon turning the UV on and the consequent photoinduced N - I transition takes place on a much faster scale compared to the recovery of the system when the UV is turned off. This is to be expected since the former is UV stimulated and the latter is a relaxation of the system whose time scale is decided, amongst other parameters, by viscosity. For both conditions we define the delay time (τ_1 for on and τ_3 for off conditions) as the period between the instant when the UV is turned on (or off) and the instant at which there is a significant change in the I_{laser} value. Also defined is the response time (τ_2 for on and τ_4 for off conditions) which is the period over which the entire change in I_{laser} takes place; these notations are indicated in Fig. 5(b). Notice that the profiles for the off condition become sharper as the value of T_{red} is increased, i.e., as the system moves away from the N - I clearing point. For the on condition the opposite is true, viz., the width of the transition increases as T_{red} is increased. More interestingly the delay time for the off condition (τ_3) shows a drastic decrease with increasing T_{red} . In contrast for the on condition, the delay (τ_1) which is hardly present at $T_{\text{red}} = 1^\circ\text{C}$ becomes measurable at higher values of T_{red} . These features can be understood in terms of the following argument. As already discussed the Z isomer of EPH is less supportive of the liquid

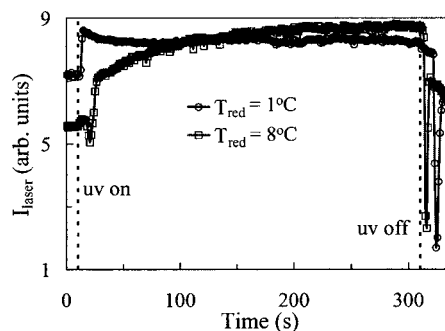


FIG. 6. The effect on the data shown in Fig. 5(a), when the magnitude of I_{UV} is increased from 2.4 mW/cm^2 to 10.2 mW/cm^2

crystalline phase (equivalently stabilizes the isotropic phase) than the E isomer. Thus if the photoisomerization occurs at a temperature closer to the pristine T_{NI} , then the photoinduced isothermal transition takes place very fast. As the system moves away from the equilibrium isotropic phase, the ordering established in the N phase will try to oppose the effect of the UV radiation, thus causing a delay as well as broadening of the transition. The opposite feature would be seen for the thermal back relaxation (UV off process) since at smaller T_{red} values the system would be driven effectively deeper into the isotropic phase causing a longer delay before the N phase is recovered. As T_{red} increases the increasing order parameter of the N phase will help in a faster recovery. Increasing the energy of the UV radiation appears to influence the UV on transformation more significantly than the thermal back relaxation process (see Fig. 6), as is to be indeed expected.

Figures 7 and 8 show the data collected for the UV on transformation and the back relaxation process at various pressures for the same reduced temperature of 5°C (T_{iso} being the transition temperature without UV at the corresponding pressure) and $I_{\text{UV}} = 2.4 \text{ mW}/\text{cm}^2$. The delay times as well as the response times are significantly influenced by the application of pressure, the delay time τ_1 for the UV on

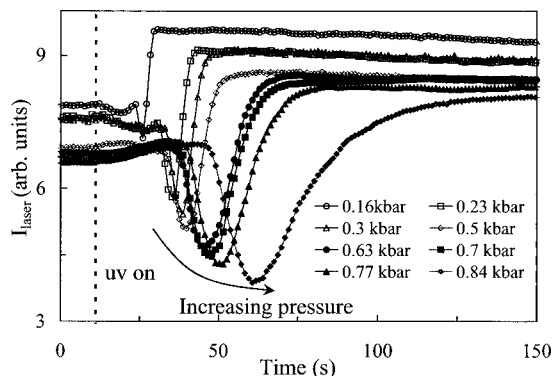


FIG. 7. Influence of pressure on the temporal characteristics upon UV illumination with a fixed $T_{\text{red}} = 5^\circ\text{C}$ and UV intensity of 2.4 mW/cm^2 . Particularly notice that the time delay between the instant at which the UV radiation is switched on and the time at which the sample response commences as well as the duration over which the sample response gets completed, increase with increasing pressure.

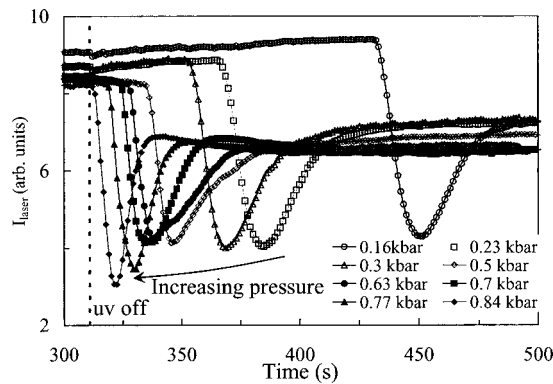


FIG. 8. Temporal characteristics obtained when the UV illumination is turned off, data collected at a constant $T_{\text{red}}=5^\circ\text{C}$ as a function of pressure. In contrast to the switch on condition the delay reduces and the response becomes faster with increasing pressure.

transformation, which is hardly seen at lower pressures, becomes substantial at elevated pressures. The profiles also become broader (increase in τ_2) as the pressure is increased. In contrast, the delay as well as the response time for the thermal back relaxation (τ_3 and τ_4) gets shortened significantly. Increasing the UV intensity has the overall effect of shortening the time scale for both the UV on and UV off processes, although the change is hardly present for τ_3 .

The pressure dependence of the four quantities τ_1 to τ_4 obtained at $T_{\text{red}}=5^\circ\text{C}$ and I_{UV} values 2.4 and 10.2 mW/cm^2 is shown in Figs. 9(a)–9(d), respectively. The main feature to be noted is that the delay and response times for the UV on process *increase linearly* with increasing pressure whereas the corresponding parameters for the back relaxation *decrease nonlinearly* with pressure and can quite well be described by an exponential function. In fact, the pressure dependence of the relaxation time associated with director fluctuations has been explained in terms of an activation volume ΔU , characterizing the rotational degree of freedom of molecules in a substance [27]. Taking a similar stand we see that the pressure dependence of the delay (τ_3) and response time (τ_4) values can be written in terms of an activation volume as $\Delta U \sim \partial \ln \tau / \partial P$. Insets in Figs. 9(c) and 9(d) show the data of $\ln(\tau_3)$ and $\ln(\tau_4)$ versus pressure for $I_{\text{UV}}=2.4$ and 10.2 mW/cm^2 . In all the cases the data can be very well described by a straight line with the slopes being comparable for the two intensities indicating that a parameter similar to activation volume must be controlling the pressure dependence of the thermal back relaxation process. These features can perhaps be understood as follows. The UV on response is a stimulated one, taking place under the influence of the UV radiation, whereas the time durations for the recovery to the original state through the thermal back relaxation process happens in the absence of the UV and is thus controlled by the viscous forces of the medium. As has been argued above, an increase in the applied pressure reduces the ability of the EPH molecules to undergo the conformational change from the *E* to the *Z* form. Therefore for a given I_{UV} value, the stimulation by the UV radiation to control the dynamics of the transformation decreases with increasing pressure. Of course, increasing the magnitude of the I_{UV} will help the

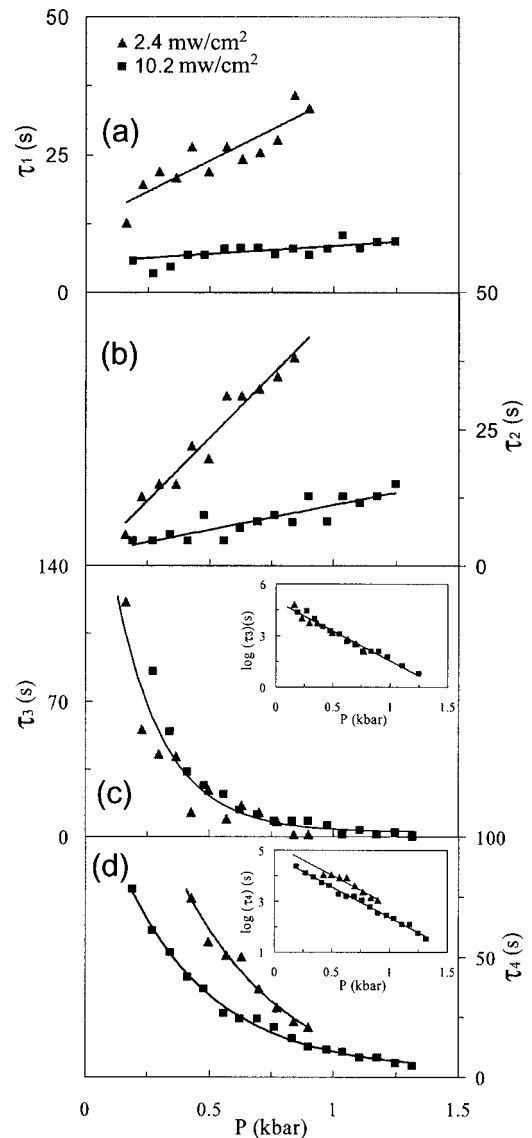


FIG. 9. Pressure dependence of (a) the switch-on delay time τ_1 , (b) the switch-on response time τ_2 (c) the switch-off delay time τ_3 , and (d) the switch-off response time τ_4 for two different values of the UV intensity triangles, 2.4 mW/cm^2 and squares, 10.2 mW/cm^2 (data collected at a constant $T_{\text{red}}=5^\circ\text{C}$). The switch-on delay and response times get reduced upon increasing the UV intensity but increase linearly with pressure. At both I_{UV} values, τ_3 as well as τ_4 decrease nonlinearly with pressure, although the magnitude of τ_4 is slightly lower for the higher I_{UV} measurement. The exponential dependence of both these parameters on pressure is obvious from the data shown in the insets of (c) and (d).

system to retain the stimulation up to a much higher pressure value.

In summary we have carried out detailed investigations of the influence of pressure on the phase boundary and the dynamics of the photoinduced nematic-isotropic transition. It is observed that the shift in the *N-I* transition temperature induced by light, decreases with increasing pressure finally vanishing at a certain pressure. The pressure at which this happens is found to increase with increasing magnitude of the UV intensity. The dynamics studied as a function of pres-

sure shows that the delay and response of the system in inducing the isotropic phase is slowed down as pressure increases. In contrast, the time scales associated with the thermal back relaxation become shorter (system relaxes

faster) as the pressure is increased. A simple argument based on the competition between the pressure dependence of volume and the energy of the UV radiation is proposed to explain these features.

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