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Switching of spin-state complexes induced by the interaction of a laser beam with their host matrix

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Abstract: We demonstrate that the interaction of a CO₂ laser with a host matrix, in which spin-crossover compounds are diluted, makes it possible to induce a low-spin-to-high-spin transition. The phenomenon is demonstrated for two different compounds diluted in a commercial polymer. The photo-induced transition is due to laser-induced heating of the host-matrix, which results in a localized modification of the properties of the sample. This phenomenon is reversible, and its kinetics are well accounted for by a simple model. This process makes it possible to write optical information at a high speed and to erase it in such materials.

Iron(II) spin-crossover (SCO) compounds in which the iron(II) ion exhibits an abrupt spin-state transition (SST) from a diamagnetic low-spin (LS) state ($S = 0$) to a paramagnetic high-spin (HS) state ($S = 2$) [1-3] have attracted much attention in recent years. Indeed, the SST is accompanied by a phase transition that results in a change in many properties of such materials that is often accompanied by a marked thermal hysteresis loop [4]. One of the most interesting aspects of SCO compounds is their ability to switch from LS to HS states by many different means. In addition to temperature, it has been shown that pressure [5] as well as light [6-12] can drive the spin-state transition, making it possible to write, store and erase information optically at a given location. In the literature, the writing and erasing phenomena recorded at very low temperature ($T < 70$ K) are referred to as light-induced excited spin-state trapping (LIESST) [13] and the reverse LIESST effect, respectively [14]. These processes have been performed using lasers operating in the near-infrared (IR), visible and near-ultraviolet spectral ranges. Although the LIESST and reverse LIESST effects have been reported at low temperature, it has also been shown that these processes can be conducted at room temperature within the thermal hysteresis loop of SCO compounds using a single nanosecond pulse [6-13]. The information is then stored in the compound, as long as the temperature of the sample is kept within its thermal hysteresis loop. The information is erased when the temperature of the sample is brought above or below its thermal hysteresis loop. Different studies have been dedicated to the investigation of the mechanisms that give rise to this photo-switching close to or within the hysteresis loop [15-18]. It has been shown that the switching is mainly triggered by the heating of samples resulting from the absorption of laser light by the SCO complexes. The photo-switching is therefore localized in the area where the SCO complexes have been brought above the temperature of the spin-state phase transition. Such a mechanism is well known and has given rise to phase-change memory chips [19]. One of the main problems with this mechanism is that it occurs only in spectral ranges over which

samples exhibit pronounced absorption. SCO compounds usually exhibit broad absorption bands in the UV, green and near-IR spectral ranges. These bands are associated with ligand absorption, metal-to-ligand charge transfer (MLCT) bands and d-d iron(II) absorption bands, respectively. However, the amplitude of these absorption bands strongly varies from one SCO complex to another. Thus, the intensity of an excitation laser beam can vary greatly from sample to sample. It should also be noted that, when SCO complexes are switched from the LS to the HS state, a marked change in sample color is observed. To circumvent this problem and extend the use of SCO compounds to a larger variety of applications, it is important to rely on physical properties of samples that are less sensitive to the chemical composition of SCO compounds. However, for many applications, SCO complexes are dissolved in a host matrix. These host matrices can be liquids or polymers and are often transparent in the visible spectral range. Consequently, the absorption of such doped polymers or liquids is greatly increased. Thus, it may be posited whether instead of triggering the switching from the LS to the HS state through the interaction of laser light with SCO complexes, one can instead trigger the LS-to-HS transition through the interaction of laser light with the host matrix. The switching of the SCO complex should then result from a laser-induced change in the temperature, pressure, structure, etc. of the host matrix. In this respect, it is worth noting that the sensitivity of SCO compounds to the host-guest chemistry has been used to control the state of SCO compounds [20-22].

In this paper, we demonstrate that such a strategy is indeed efficient and that the interaction of a laser beam with a host matrix can indeed induce a LS-to-HS switching in different SCO compounds. We performed our experiments on polymer films doped with SCO particles. To photo-induce the switching of the SCO particles, we used a CO₂ laser operating at $\lambda=10.6\ \mu\text{m}$. Such lasers are of particular interest because they are inexpensive and known to provide powerful laser beams at wavelengths that are strongly absorbed by most polymers.

The absorption of the laser beam by a polymer matrix induces sample heating. Such laser-induced heating is responsible for both the thermal expansion of the matrices and the switching of SCO particles. The kinetics we recorded provide evidence of these two mechanisms and can be described by a simple model. Finally, we demonstrate that this technique makes it possible to write optical information in such doped polymer matrices.

We studied two types of compounds with different counter-ions, $[\text{Fe}(\text{NH}_2 - \text{trz})_3]\text{Br}_2 \bullet 3 \text{H}_2\text{O}$ and $[\text{Fe}(\text{NH}_2 - \text{trz})_3](\text{NO}_3)_2 \bullet \text{H}_2\text{O}$. Among existing SCO compounds, the iron(II) polymeric complexes $[\text{Fe}(\text{NH}_2 - \text{trz})_3]^{2+}$ are of particular interest. These compounds present an octahedral geometry: the metallic iron ion Fe^{2+} lies in the center of an octahedron and is bonded to $\text{NH}_2 - \text{trz}$ (1,2,4-aminotriazole) ligands. Such materials exhibit a well-known spin-state transition from the LS to the HS state. Depending on the nature of the triazole derivative and of the anion, wide hysteresis can be observed near room temperature. The synthesis of these complexes has been described elsewhere [23]. The SCO compounds we used were particles with a mean diameter of $\sim 1 \mu\text{m}$. The color of these particles is pink when a sample is in the LS state and becomes white when the sample is heated and brought to the HS state. The pink color results from a broad absorption band of the sample at approximately 520 nm, which is characteristic of the d-d transition of Fe^{2+} (${}^1\text{A}_{1g} \rightarrow {}^1\text{T}_{1g}$). The band is shifted toward 830 nm when the sample is in the HS state. The SCO particles were dissolved (15% in weight) in a commercial polymer spray. Samples measuring $120 \pm 10 \mu\text{m}$ in thickness were deposited on a $110 \pm 10\text{-}\mu\text{m}$ thick, transparent coated polyester film (3M). The samples were isotropic in the visible and IR spectral ranges. We measured the infrared absorption of the polymer host matrix with and without the SCO particles and observed that in the LS state and in the 1.5 – 14- μm spectral range, the absorption spectra remained nearly unchanged. This result indicates that the absorption of our samples within this spectral range was mainly due to the polymer host matrix. To record the

thermal hysteresis loop of the polymer matrix doped with the SCO particles, we used the experimental set-up mentioned above and depicted in Fig. 1a. The samples were inserted in an oven whose temperature could be tuned from 5°C to 150°C. The temperature stability of the oven was approximately $\pm 0.1^\circ\text{C}$. Samples were supported within a hole with a diameter $d \sim 1$ cm and illuminated with a halogen light source focused by a lens, yielding a spot diameter $\phi_{\text{sample}} \sim 4$ mm. The light transmitted by the sample was collected by a lens with a large aperture ($\phi \sim 2.5$ cm) and small focal length ($f = 2.5$ cm). The light was then focused onto a silicon photodiode through a small iris ($\phi_{\text{iris}} \sim 0.6$ mm) placed in the image focal plane of the lens. The output of the photodiode was connected to a digital oscilloscope ($R_{\text{input}} \sim 1 \text{ M}\Omega$) that recorded the evolution of the output voltage of the photodiode versus time. Figure 1b presents the thermal hysteresis of the polymer matrix doped with the SCO particles. The temperature shift of the ascending and descending branches of the loop ($\sim 10^\circ\text{C}$) indicate that the host matrix weakly affected the temperature of the spin-state phase transition of the SCO particles. To photo-induce the spin-state transition, we used a continuous wave (CW) CO_2 laser delivering up to 30 watts of average power at a wavelength $\lambda = 10.6 \mu\text{m}$. The spatial profile of the laser beam was approximately that of the TEM_{00} mode ($M^2 \sim 1.3$). To adjust the size of the beam waist on the sample to a spot measuring 6 mm in diameter, we used a gold mirror with a 20-cm radius that was placed out of focus. Because in our experiment the laser beam waist is large compared to the spot size of the white light probing the sample, we will consider our experimental set-up to have recorded the evolution of the sample parameters at the center of the pump beam.

Figures 2a-b present the evolution of the transmission of the polymer films set at room temperature, with or without the SCO doping particles, when they were excited by the CO_2 laser. The pump beam only shone on the samples for approximately 0.6 s (Fig. 2a) and 0.9 s (Fig. 2b), respectively. For the bare polymer film, the transmission decreased upon excitation

by the CO₂ laser and then increased and recovered its initial value as soon as the laser beam was switched off. For a given exposure time and above a certain intensity threshold, the transmission of the sample was observed to decrease linearly with the CO₂ pump power (inset, Fig. 2a). The transmission of the polymer films doped with the SCO particles was very different. Upon laser excitation and above a certain power threshold, the transmission first slightly decreased and then increased abruptly. For the highest pump powers and during the pump excitation, the evolution of the transmission of the sample was more complex. First, the transmission decreased slightly, then increased and finally decreased again. Surprisingly, we observed that when the pump beam was off and for high pump beam powers, the transmission continued to increase for a few moments before it decreased. This lag time depended on the pump power: the higher the pump power was, the longer the lag time became. We performed the experiment at different sample temperatures below the hysteresis loop. We observed that the general trends remained similar and that the pump power required to observe similar phenomena decreased as we increased the temperature.

We now turn to our experimental observations. As mentioned previously, our samples strongly absorbed at the laser wavelength. Hence, most of the laser power absorbed by the sample generated heat that diffused into the bulk, which resulted in an increase in the local temperature of the samples. This problem has been studied by various researchers, and the evolution of the temperature within samples across and along a Gaussian beam pattern has been computed [24]. When the laser beam is on, it can be shown that the temperature increase ΔT at the center of the pump beam reads

$$\Delta T(t) \approx \frac{0.06\alpha P}{k} \frac{8Dt}{w_0^2} \quad (1)$$

where t , P , α , k , D and w_0^2 are the time, laser power, absorption coefficient, thermal conductivity and thermal diffusivity of the sample and the beam waist of the laser beam.

According to the above equation, when the pump beam is applied, ΔT should increase linearly with time and the pump power. The resulting laser-induced heating of the sample results in two different effects.

The first one is related to the thermal expansion of the sample. As mentioned previously, our samples were composed of a host polymer deposited on a transparent coated polyester film (3M). With changes in temperature, and due to the different thermal expansion coefficients of the different polymers, the structure bends. This bending induces a displacement Δz of the exit face of the sample that is imaged by the lens. If z_0 is the initial position of the face, after laser-induced heating, it becomes $z_1 = z_0 + \Delta z$, where $\Delta z(t) \sim d^2 \times \Delta T(t)$ and d is the diameter of the hole supporting the sample [25]. However, a slight change in the position of the exit face of the sample results in a displacement of its image created by the lens. This displacement modifies the intensity of the white light transmitted by the diaphragm placed in the focal plane of the imaging lens. In other words, the diaphragm partially blocks the light rays that are not emanating from the plane located at $z = z_0$. Hence, the transmission decreases (respectively increases) as the object moves closer to (respectively farther from) the imaging lens. When $z \approx 0$, the transmission of the sample is proportional to

$$(\phi_{\text{sample}} / \phi_{\text{iris}})^2 = (z_1/f)^2 \approx (z_0/f)^2 \times (1 + 2\Delta z/z_0) \quad (2)$$

Because the latter term is linearly proportional to ΔT , it is possible to monitor the evolution of ΔT . However, the sensitivity of our experimental set-up only made it possible to record changes in the position of the sample greater than a threshold value that we denote $\Delta z_{\text{critical}}$. Hence, we could only record transmission variations for $\Delta z > \Delta z_{\text{critical}}$.

To account for the evolution of the transmission of the doped polymers, another phenomenon must be introduced. This phenomenon is associated with the change in the

complex index of refraction $\Delta n(r, t) = \Delta n_r(r, t) + i \Delta n_{im}(r, t)$ of the sample that, to a first-order approximation, is related to ΔT as follows:

$$\Delta n_{r,im}(t) = \frac{\partial n_{r,im}}{\partial T} \Delta T(t) \quad (3)$$

The change in the real part of the index of refraction Δn_r does not affect the image created by the collecting lens and therefore does not affect the transmission of the sample. However, the change in imaginary part of the index of refraction Δn_{im} strongly modifies the absorption α ($\alpha = 4\pi n_{im}/\lambda$) and therefore the transmission of the sample: the condition $\Delta n_{im} > 0$ (respectively $\Delta n_{im} < 0$) induces a decrease (respectively an increase) in the transmission of the sample. For the bare polymer, the absorption of the film in the visible spectral range is negligible regardless of the temperature of the sample and can therefore be neglected, in contrast with the transmission of the doped polymer films. As shown in Fig. 1 the transmission of these films strongly varied as the temperature of the sample was brought in the vicinity of the spin-state transition temperature.

The thermal expansion of the sample very well accounts for our experimental data regarding the bare polymer films (see Fig. 2a): 1) When the pump beam was applied, we observed a small lag time before the transmission decreased (i.e., nothing could be recorded before $\Delta z > \Delta z_{critical}$), 2) the transmission decreased almost linearly in time and 3) when the CO₂ laser was on, the transmission decreased almost linearly with the pump power. When the CO₂ laser was stopped, the heat induced by the laser beam diffused and the temperature relaxed towards its equilibrium value. The diffusion of heat is governed by heat equation, and it can be shown that, to a first-order approximation, the temperature should have relaxed exponentially in time [15]. This result is also in very good agreement with the data presented in Fig. 2a, where we have plotted the relaxation of the transmission of the sample considering an exponential decay with the same time constant for all of the used CO₂ power.

To describe the evolution of the transmission of the doped polymer films presented in Fig. 2b, we must take into account both the thermal expansion and the modification of the absorption of the samples. These two processes were driven by the laser-induced heating of the samples. Figure 3 describes the evolution of the samples' transmission resulting from each process. It is important to note that for both the doped and bare polymer films, the thermal expansion resulted in a decrease in the samples' transmission (Fig. 3.I), whereas the LS→HS spin-state transition resulted in an increase in the transmission of the doped samples (Fig. 3.II). If the spin-state transition occurs at high temperature, upon excitation by the pump laser, one should first record a slight decrease in the transmission associated with the thermal expansion of the sample (Fig. 3.III point B) followed by an increase in its transmission. This latter process should last as long as the SCO particles within the sample have not completely been switched from the LS to the HS state (Fig. 3.III from point B to C). It should be noted that an increase in the overall transmission is only observable if the increase in the transmission induced by the spin-state transition overcomes the decrease in the transmission induced by thermal expansion. If the temperature of the sample increases above the thermal hysteresis loop, the thermal expansion of the sample will again result in a decrease in transmission (Fig. 3.III from point C to D). When the pump beam is blocked, heat diffuses and the temperature starts to decrease, which will first induce a decrease in thermal expansion and thus an increase in the transmission of the sample (Fig. 3.III from point D to E). Then, as the temperature of the sample reaches the descending branch of the thermal hysteresis loop, the transmission will start to decrease and relax toward its initial value (Fig. 3.III from point E to A). It is important to note that, due to the presence of the thermal hysteresis loop, the time required to reach the temperature at which the transmission starts to decrease can be quite delayed. Such a scenario is depicted in the Fig. 3.IV, where we have assigned the evolution of the transmission of the sample to different positions within the hysteresis loop. It is interesting

to observe that the two mechanisms we used to describe the evolution of the transmission of the sample make it possible to unambiguously evaluate the local temperature within the sample at any given time.

To illustrate the potential application of this laser-induced heating of the host matrix, we doped polymer films with $[\text{Fe}(\text{NH}_2 - \text{trz})_3](\text{NO}_3)_2 \bullet \text{H}_2\text{O}$ particles. The thermal hysteresis loop for such polymer films spans from 10 °C to 45 °C (Fig. 4). Prior to the experiment, we heated the sample from $T=0$ °C to room temperature ($T \sim 20$ °C) and then wrote simple characters on the sample using the CO_2 laser beam. The laser beam, focused onto a beam spot size of approximately 100 μm , was moved along the X-Y directions using a computer-controlled scanner. With such a device, we were able to write the characters “CNRS” in less than one second. These characters remained readable as long as the temperature T of the sample was kept within the thermal hysteresis loop (i.e., $10\text{ °C} < T < 45\text{ °C}$) and are erased below $T=5$ °C or above $T=50$ °C. By adjusting the laser power and the scanning speed, we achieved a spatial resolution of 120 μm , very close to the CO_2 laser beam spot size. This demonstration clearly illustrates the potential application of laser-induced heating using such polymer film samples.

In conclusion, we have proposed a novel laser host matrix interaction to write optical information within polymers doped with SCO particles. The experiment we performed allowed us to record the kinetics of this writing process. The experiment also made it possible to demonstrate the thermal expansion of samples and the dynamics of the spin-state transition. These results once again underline the applicability of SCO compounds for optical data recording.

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Figure captions

Figure 1: a) Experimental set-up. b) Evolution of the transmission of the polymer thin film doped with $[\text{Fe}(\text{NH}_2 - \text{trz})_3]\text{Br}_2 \bullet 3 \text{H}_2\text{O}$ versus temperature in our experimental set-up. The solid lines are shown as a visual guide. The sample is pink at low temperature, in the low-spin state, and it becomes white at high temperature, in the high-spin state.

Figure 2: a) Evolution of the transmission of the bare polymer thin film in our experimental set-up under irradiation by a CO_2 laser beam for 0.6 s at $t=0$. The inset presents the evolution of the transmission of the sample in our experimental set-up at $t=0.6$ s versus the CO_2 beam power. The solid lines are fittings of the data considering a linear decrease and exponential decay of the transmission when the laser is on and off, respectively b) Evolution of the transmission of the polymer thin film doped with SCO particles under irradiation by a CO_2 laser beam for 0.9 s at $t=0$.

Figure 3: Evolution of the transmission ΔT_r of the polymer thin film doped with the SCO compound used in our experiment. I) Only laser-induced thermal expansion is taken into account. The change in the transmission is denoted ΔT_r^{th} . II) Only laser-induced heating is considered. The change in the transmission is denoted ΔT_r^{TS} . III) Both processes are taken into account. IV) Evolution of the transmission of the sample versus time. The letters A, B, C, D and E denote the position of the sample in the thermal hysteresis loop of the SCO compound.

Figure 4: Demonstration of laser writing within the thermal hysteresis loop of a polymer thin film doped with the $[\text{Fe}(\text{NH}_2 - \text{trz})_3](\text{NO}_3)_2 \bullet \text{H}_2\text{O}$ compound. The solid lines underlying the thermal hysteresis loop are shown as a visual guide. The characters “CNRS” shown in the inset, written by the CO_2 laser beam, remain as long as the temperature of the sample is kept inside the thermal hysteresis loop.

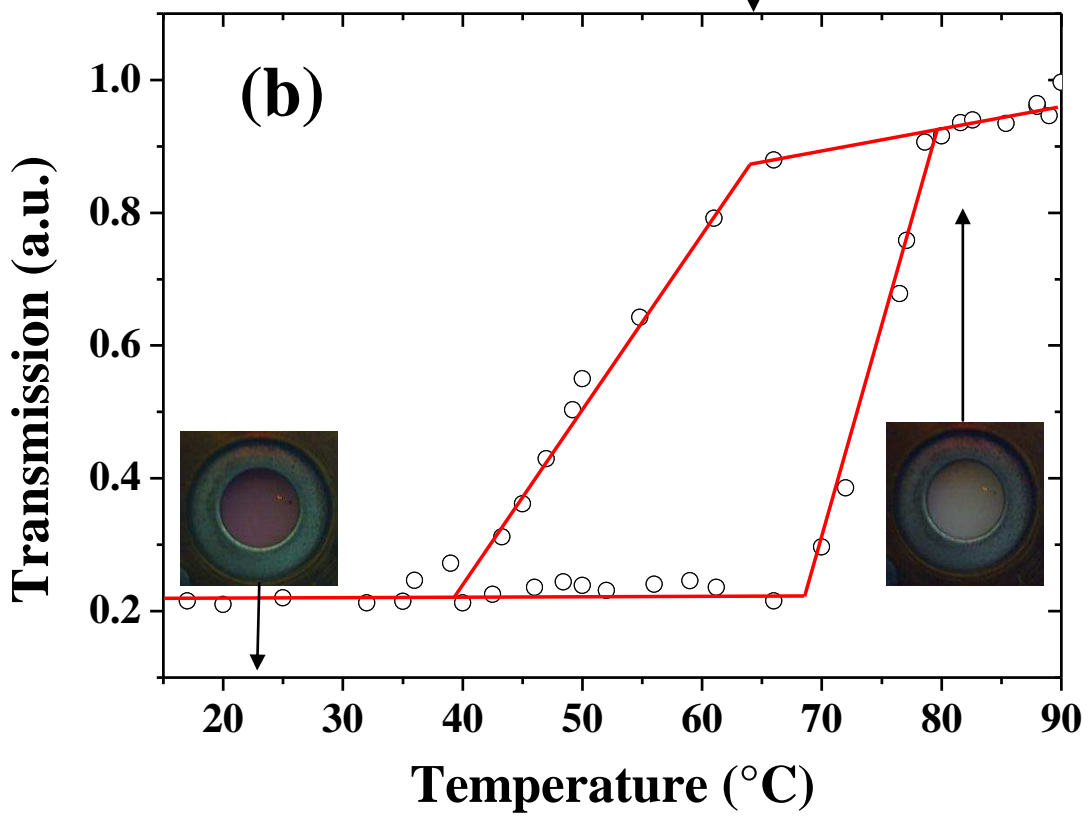
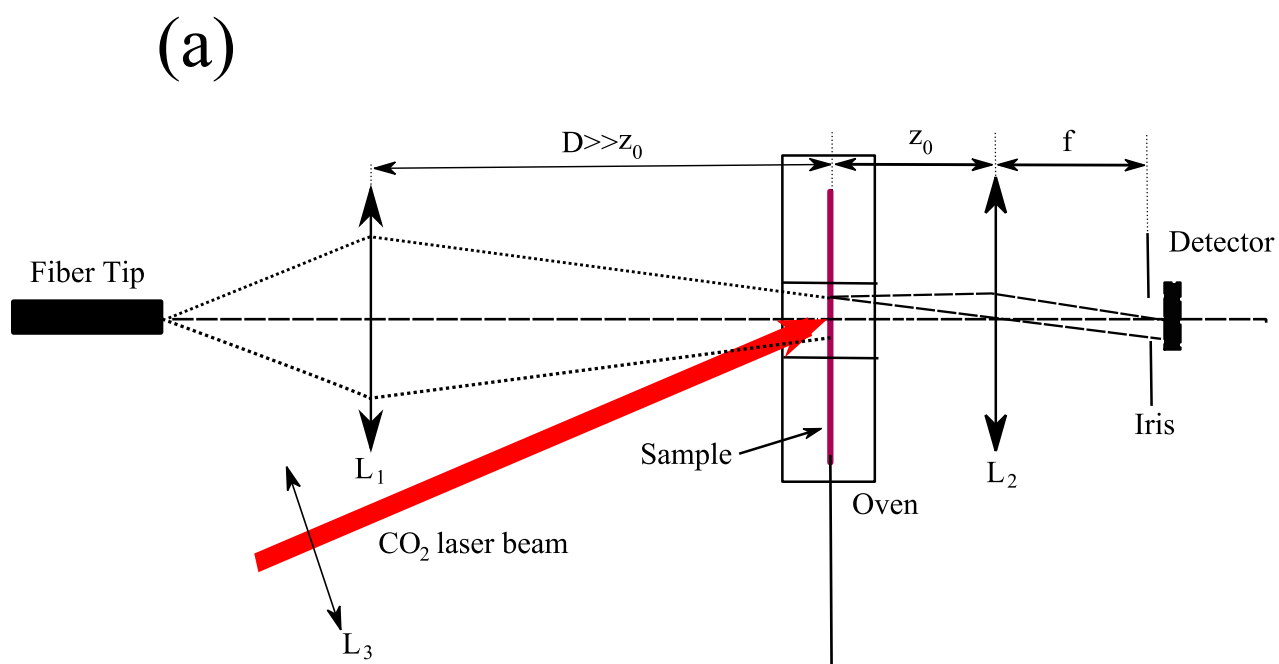


Figure 1

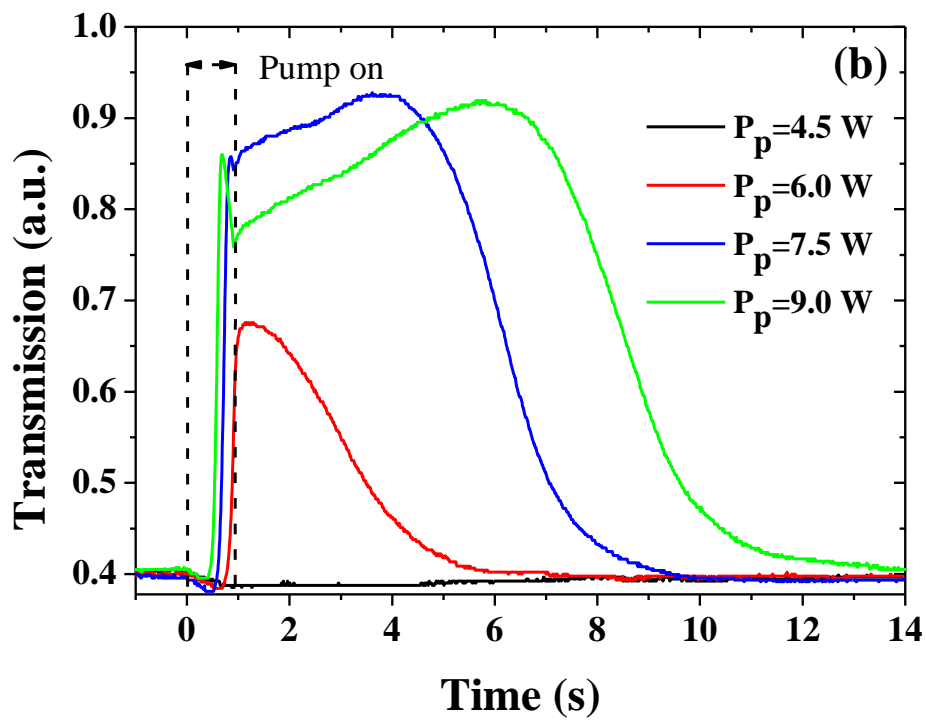
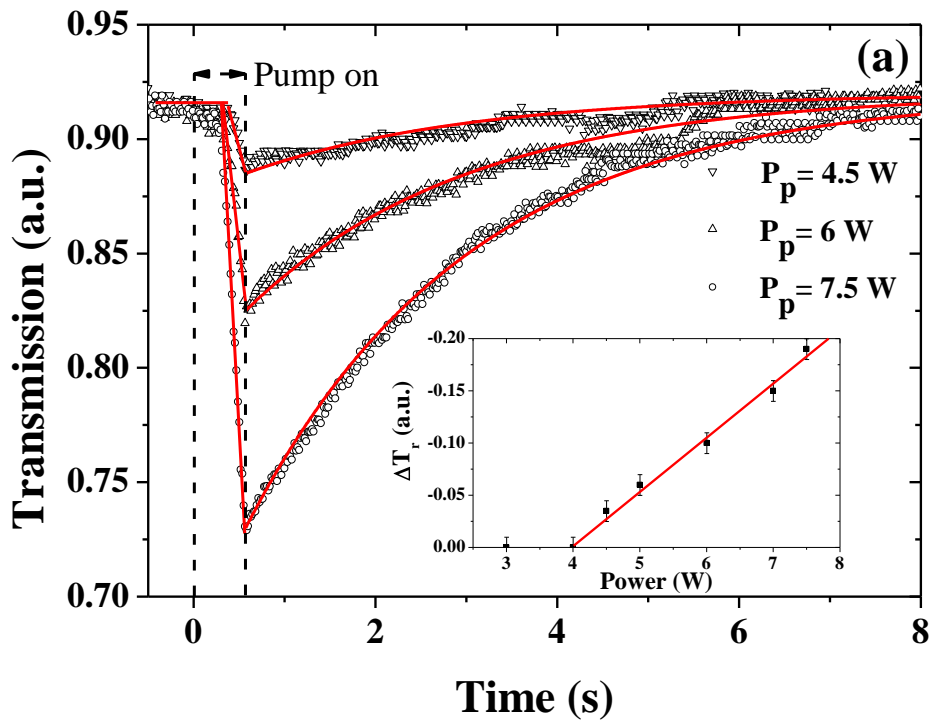


Figure 2

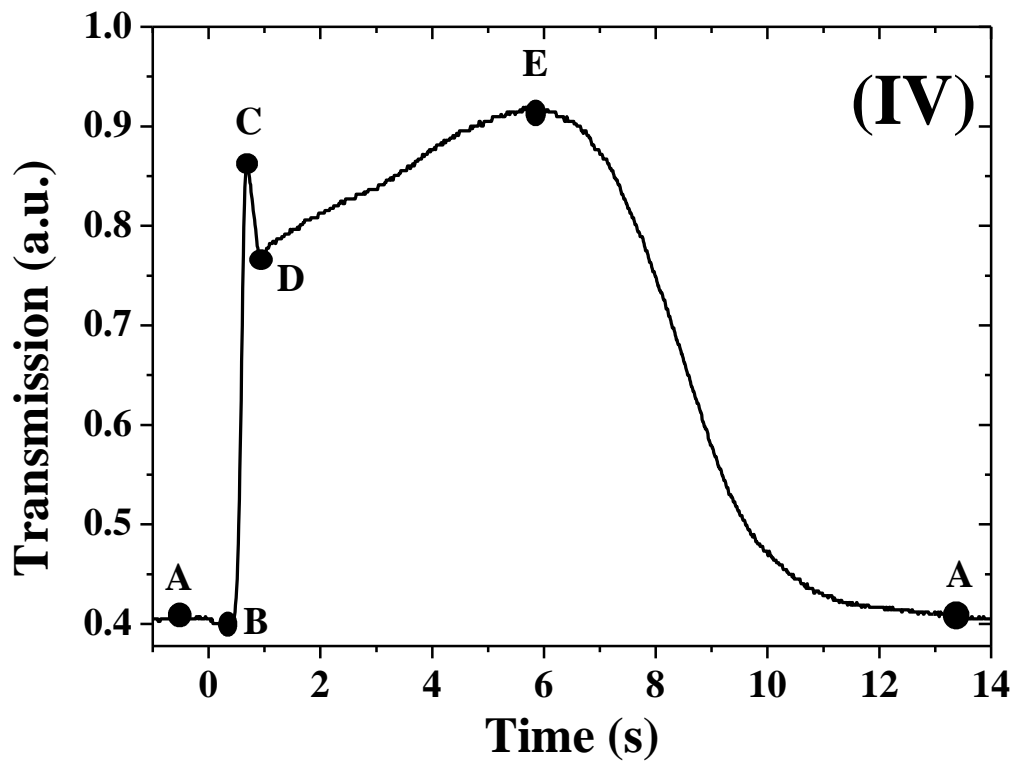
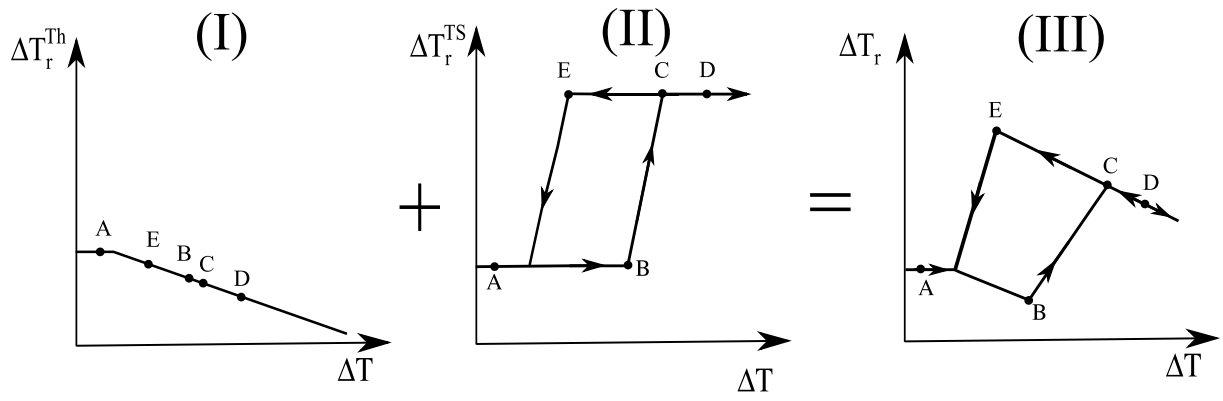


Figure 3

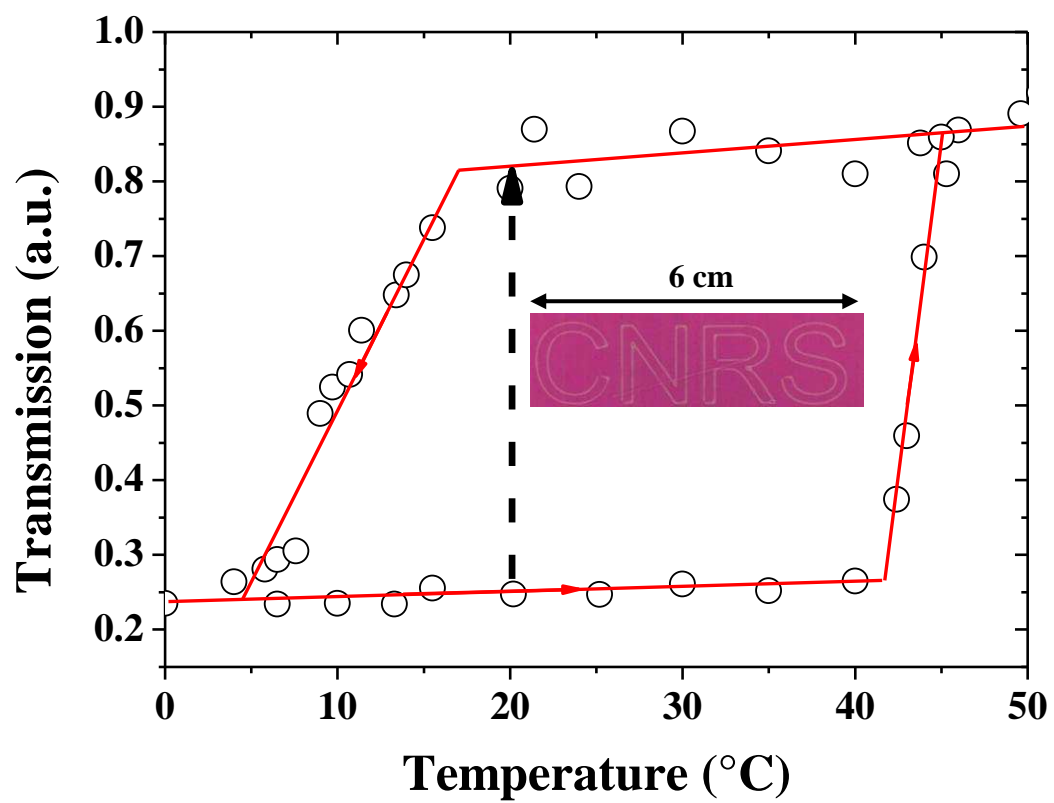


Figure 4