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Photoswitching of the spin crossover polymeric material $[\text{Fe}(\text{Htrz})_2(\text{trz})](\text{BF}_4)$ under continuous laser irradiation in a Raman scattering experiment

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A B S T R A C T

Photoswitching of the $[\text{Fe}(\text{Htrz})_2(\text{trz})](\text{BF}_4)$ spin crossover polymeric material has been investigated by means of confocal Raman spectroscopy upon continuous laser irradiation outside and inside its thermal hysteresis loop. In both cases, the evolution of HS and LS Raman marker bands show that light excitation can trigger the LS to HS transition, but the long-lived HS state can be populated only within the hysteresis loop. Local sample heating can explain this light-induced effect leading to a narrowing of the thermal hysteresis loop for laser intensities higher than $0.02 \text{ mW}/\mu\text{m}^2$, in strong accordance with previous time-resolved pump-probe experiments on similar materials.

1. Introduction

Transition metal complexes in which the spin state of the metal changes under external stimuli such as temperature, light irradiation or pressure have been extensively studied since a few decades due to their high relevance for potential applications in information processing, sensors and/or display devices [1–3], and even more recently in the photovoltaic domain [4]. The spin crossover (SCO) phenomenon is a transition from a low-spin (LS) ground state electron configuration to a high-spin (HS) metastable state of the metal d atomic orbitals. Future applications of SCO materials require such bistability over a broad temperature range centered at $\sim 300 \text{ K}$, as in polymeric SCO compounds [3,5–9] where the highly cooperative spin transition process leads to a large thermal hysteresis loop. Some of the most promising polymeric SCO compounds are formed with the triazole ligands threefold bridging the Fe(II) metal ions (Figure 1). Within this family of SCO compounds, $[\text{Fe}(\text{Htrz})_2(\text{trz})](\text{BF}_4)$ (with Htrz = 1,2,4-*H*-triazole and trz = deprotonated triazolato (–) ligand) has been investigated quite extensively over the last years [4,6,10–14] in particular because it displays a $\sim 40 \text{ K}$ wide thermal hysteresis centered around 370 K .

The present work aims to investigate the effect of the laser intensity of a continuous laser on the hysteresis loops of the $[\text{Fe}(\text{Htrz})_2(\text{trz})](\text{BF}_4)$ compound. It is known that intense nanosecond laser light pulses applied within a thermal hysteresis loop can trigger in SCO materials the LS to HS transition and in some cases the reverse HS to LS transition, [15–20] provided an energy density threshold value is overcome [20,21]. However, the respective contribution of photo-induced and thermally-driven effects in this laser-induced process is still a matter of debate, and might depend on the material. In the case of a purely thermal origin at least, it might be possible to mimic somewhat the observed effects using a continuous laser irradiation.

Hereafter the spin state of the $[\text{Fe}(\text{Htrz})_2(\text{trz})](\text{BF}_4)$ complex will be probed by means of Raman microscopy, where the Raman probe laser will also provide the light excitation allowing thermal effects to be potentially generated. Since several years Raman spectroscopy is a well-recognized technique to characterize the phase transition process in SCO compounds, and especially their thermal hysteresis loops [12,14,22–31]. The spin transition phenomenon in $[\text{Fe}(\text{Htrz})_2(\text{trz})](\text{BF}_4)$ samples has been analyzed recently by Urakawa et al. [12] by means of an experimental approach combining Raman spectroscopy and X-ray powder diffraction measurements (XRPD). In this Letter, hysteresis loops measured with these different techniques were found to differ significantly. According to the Raman data, the spin transition was completed within $320\text{--}340 \text{ K}$ with almost no hysteresis, while the XRPD data showed

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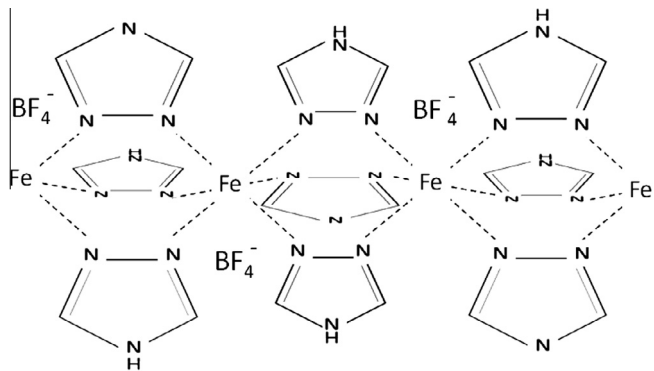


Figure 1. Schematic view of the iron(II) SCO $[\text{Fe}(\text{Htrz})_2(\text{trz})](\text{BF}_4)$ polymer.

a ~ 40 K-wide hysteresis. This result was interpreted by Urakawa et al. [12] as due to the different sensitivities of the techniques towards short- and long-range ordering of the crystal structure or to the distinct penetration depths of the external probes. However, these experimental results may also suggest, as pointed out by Wolny et al. [24] in a recent review, that ‘heating effects due to the Raman laser occurred’. Indeed, we found in a previous study on another material belonging also to this family of SCO compounds [22] that, even at room temperature, outside the hysteresis loop, the laser could induce the LS to HS transition. The impact of the laser intensity in a Raman experiment on the spin state of a SCO material within the hysteresis loop has also been addressed by Craig et al. [32] very recently. Obviously, the laser light interacts with the sample in a conventional Raman experiment and the main objective of this Letter is to get some insight on the impact of the laser excitation on the Raman measurements.

2. Experimental

The powder samples of $[\text{Fe}(\text{Htrz})_2(\text{trz})](\text{BF}_4)$ were synthesized according to the method already published [6]. Raman spectra were collected in backscattering geometry using excitation lines centered at 633 nm and 532 nm and a LabRam HR-Evolution spectrometer (Horiba Jobin-Yvon) with 2 cm^{-1} spectral resolution. A few test measurements with the 785 nm excitation line were also performed in a backscattering configuration using an Xplora Raman spectrometer (Horiba Jobin-Yvon). These spectrometers were coupled to an Olympus microscope with an ultra long working distance $50\times$ MSPlan objective (numerical aperture $\text{NA} = 0.55$). A Linkam THS 600 stage positioned under the microscope objective was used to perform the heating and cooling cycles with a rate of

Table 1
Typical features (T_{up} , T_{down} and hysteresis width) characterizing the thermal transition in the $[\text{Fe}(\text{Htrz})_2(\text{trz})](\text{BF}_4)$ SCO complex obtained using various experimental techniques. In bold are reported the average values of these characteristics to the exclusion of those obtained by Urakawa et al. [12].

Technique	T_{up} K	T_{down} K	Width K
DSC [6]	379	343	39
DTA [6]	383	341	42
Reflectivity [6]	381	347	34
Reflectivity [18]	380	346	34
Magnetic susceptibility [6]	385	345	49
Magnetic susceptibility [11]	384	343	41
Magnetic susceptibility [10]	386	343	43
Mössbauer spectroscopy [6]	380	344	36
Average	382	344	40
X-ray diffraction [12]	370	330	40
Raman spectroscopy [12]	320	320	0

2 K per minute. Once the set temperature was reached, the sample was maintained at this temperature for 5 min for thermal equilibration before exposing it to the laser beam. The sample was initially warmed at 400 K in an atmosphere of dry N_2 to eliminate water. The sample was subsequently held in dry N_2 at atmospheric pressure during all experiments. The laser power at the output of the microscope objective was systematically measured prior to measurements and could be tuned using density filters that attenuate the laser intensity. It should be pointed out that the laser intensity (or power density defined as the ratio power/irradiated sample surface) will obviously depend on the specifications of the microscope objective. In our experiments, the laser spot diameter defined theoretically [33] as $1.22\lambda/\text{NA}$ was approximately $1.4 \mu\text{m}$ at $\lambda = 633 \text{ nm}$ and $1.2 \mu\text{m}$ at $\lambda = 532 \text{ nm}$ using the $50\times$ objective with $\text{NA} = 0.55$.

3. Results and discussion

We have reported in Table 1 the main parameters characterizing the transition temperatures and the width of the hysteresis loop of $[\text{Fe}(\text{Htrz})_2(\text{trz})](\text{BF}_4)$ taken from literature data [6,10,11,18]. The LS to HS transition temperature T_{up} obtained upon sample warming ranges from 379 to 386 K, and the HS to LS transition temperature T_{down} obtained upon sample cooling ranges from 341 to 347 K. The width of the hysteresis loop is about 40 K. Clearly, the values determined by Urakawa et al. [12] by means of Raman scattering ($T_{\text{up}} = T_{\text{down}} = 320 \text{ K}$) are not consistent with the other data listed in Table 1. In the following, we will refer to the averaged transition temperatures indicated in Table 1 as ‘static’ values.

The Raman spectra at 633 nm of the iron(II) SCO $[\text{Fe}(\text{Htrz})_2(\text{trz})](\text{BF}_4)$ polymer at 300 K in the LS state and at 393 K in the HS state are displayed in Figure 2. To minimize the interaction between the laser and the sample, very low laser intensity ($0.8 \mu\text{W}/\mu\text{m}^2$ at the sample) was set. As already mentioned in the paper of Urakawa et al. [12], several Raman bands can be identified as spin state markers (Figure 2). The most spectacular changes when crossing the LS to HS transition are observed below 500 cm^{-1} , i.e. in a spectral region where external vibrations are active, and particularly those involving the metal–ligand stretching or ligand–metal–ligand bending vibrations [22]. The LS marker bands are found at ca. 200, 213, 287 and 300 cm^{-1} and the HS marker bands at ca. 105, 150 and 182 cm^{-1} .

We have carried out preliminary Raman scattering experiments at room temperature to investigate the effect of the laser intensity and the excitation wavelength on the spin state. We found that for

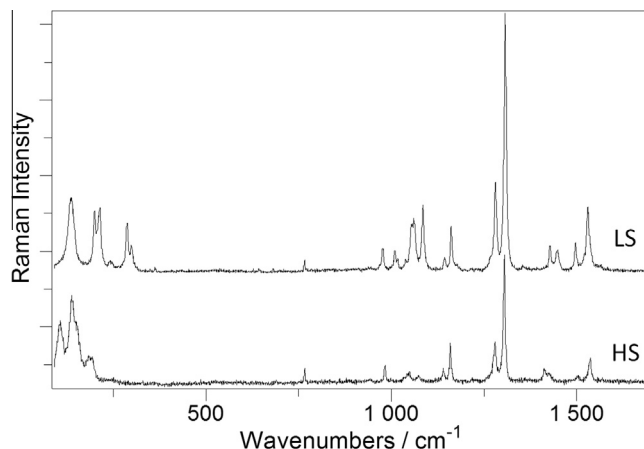


Figure 2. Raman spectra of the iron(II) SCO $[\text{Fe}(\text{Htrz})_2(\text{trz})](\text{BF}_4)$ polymer in the LS state (top) and HS state (bottom).

a 8 s sample irradiation at the $3 \text{ mW}/\mu\text{m}^2$ laser intensity, the complete LS to HS conversion was reached under 532 nm excitation, a partial conversion under 633 nm excitation and no detectable conversion under 785 nm irradiation. This may be understood as a consequence of the sample pink color at room temperature, since the maximum of light absorption due to the $d-d$ ${}^1A_1 \rightarrow {}^1T_1$ transition [18,34] of the iron(II) complex is $\sim 500\text{--}600 \text{ nm}$. The maximum efficiency for the spin conversion LS \rightarrow HS, either photo-induced or thermally induced, is therefore expected for green excitation wavelengths. However, there is still weak absorption at higher wavelengths in the tail of the absorption band, *i.e.* in the near-infrared [35]. The absorption of the focused laser light necessarily heats the sample at the focal point and leads to a rapid increase of its local temperature, which may eventually cause strong sample damages under prolonged light exposition. This latter undesirable effect can be however limited (providing that the laser intensity is not too high) by rotating, swinging [12] the sample, or using galvanometric mirrors [14] to scan it fast.

Figures 3 and 4 show Raman spectra associated with a single region of the $[\text{Fe}(\text{Htrz})_2(\text{trz})](\text{BF}_4)$ sample excited at 633 nm along the ascending branch of its hysteresis loop, at 340 K and 365 K, respectively. The laser exposition time was systematically set to 160 s. Owing to the proportionality of the Raman scattering and incoming laser beam intensities, experimental Raman intensities were divided by the incident laser intensities to allow comparisons between spectra obtained with different laser powers. Note that Raman spectra (2) and (5) related to the highest laser intensities exhibit greater signal to noise ratios than the other spectra resulting from measurements at lower laser powers, because the same integration time was kept for all the spectra.

Outside the hysteresis loop at 340 K, the LS state is preserved under irradiation at the $0.2 \text{ mW}/\mu\text{m}^2$ laser intensity, as revealed by the Raman spectrum (1) in Figure 3 similar to the LS spectrum depicted in Figure 2. The consecutive excitation at the higher $1 \text{ mW}/\mu\text{m}^2$ laser intensity leads however to a mixture of LS and HS species, with a large majority of HS form. This assertion is corroborated by the presence of intense HS marker bands centered at 105 , 150 and 182 cm^{-1} and weak LS marker bands at 200 , 213 , 287 and 300 cm^{-1} (Raman spectrum (2) in Figure 3). This LS/HS mixture relaxes back to the LS state after decreasing the laser intensity down to the $0.2 \text{ mW}/\mu\text{m}^2$ initial value, as evidenced by the sharp resemblance between Raman spectra (1) and (3) in Figure 3. In conclusion, outside the hysteresis loop, the LS to HS transition can be triggered by the continuous Raman-probe laser and it

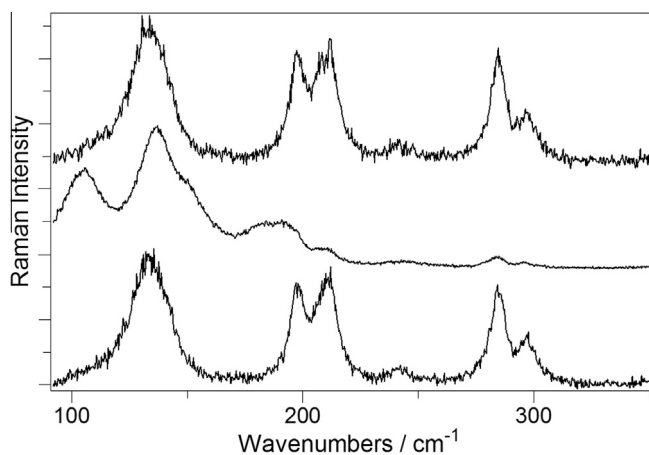


Figure 3. Raman spectra of the iron(II) SCO $[\text{Fe}(\text{Htrz})_2(\text{trz})](\text{BF}_4)$ polymer recorded outside the hysteresis loop at 340 K. The laser intensity is set to $0.2 \text{ mW}/\mu\text{m}^2$ in (1), increased up to $1 \text{ mW}/\mu\text{m}^2$ in (2) and finally reduced to $0.2 \text{ mW}/\mu\text{m}^2$ in (3). The excitation wavelength was 633 nm and the integration time was 160 s.

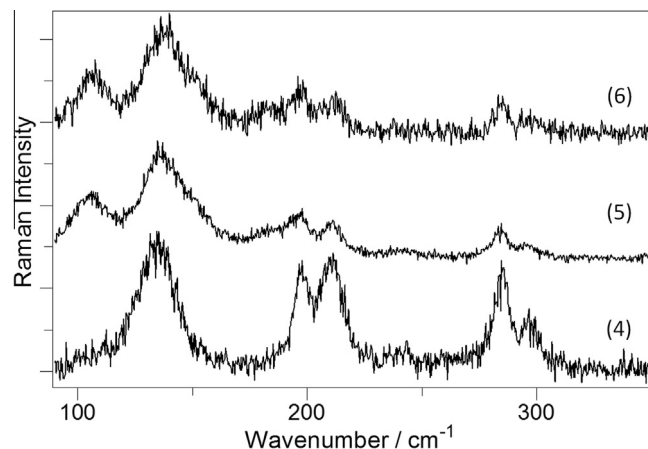


Figure 4. Raman spectra of the iron(II) SCO $[\text{Fe}(\text{Htrz})_2(\text{trz})](\text{BF}_4)$ polymer recorded inside the hysteresis loop at 365 K. The laser intensity is $0.06 \text{ mW}/\mu\text{m}^2$ in (4), increased up to $0.2 \text{ mW}/\mu\text{m}^2$ in (5) and finally reduced down to $0.06 \text{ mW}/\mu\text{m}^2$ in (6). The excitation wavelength was 633 nm and the integration time was 160 s.

produces a stationary HS fraction as long as the irradiation is maintained. As the light-induced HS state is not stable however, the LS state is recovered as soon as the laser power density is sufficiently reduced.

Inside the hysteresis loop at 365 K, the LS state is still preserved under irradiation at the $0.06 \text{ mW}/\mu\text{m}^2$ laser intensity, as revealed by the Raman spectrum (4) in Figure 4 similar to the LS spectra displayed in Figures 2 and 3. This suggests that the $0.06 \text{ mW}/\mu\text{m}^2$ laser intensity is not high enough to induce a spin transition at 365 K. Under $0.2 \text{ mW}/\mu\text{m}^2$ laser irradiation, a HS/LS mixture, as observed under $1 \text{ mW}/\mu\text{m}^2$ irradiation outside the hysteresis loop at 340 K, is seemingly produced as revealed by the striking resemblance between the Raman spectra (5) in Figure 4 and (2) in Figure 3. However, the Raman spectrum (6) obtained under excitation back to the $0.06 \text{ mW}/\mu\text{m}^2$ initial laser intensity matches almost perfectly the Raman spectrum (5). A long-lived metastable laser-induced HS state is populated within the hysteresis loop thereby.

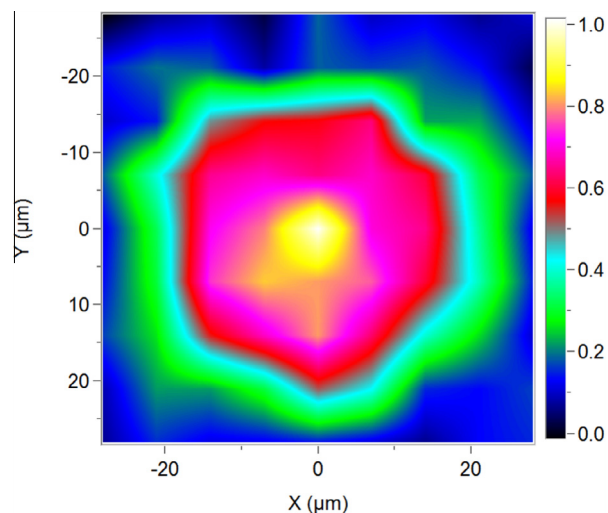


Figure 5. Raman map ($3 \mu\text{m}$ steps) of the powder sample irradiated at 633 nm with a laser intensity $0.4 \text{ mW}/\mu\text{m}^2$ and using a $10\times$ objective. The color scale bar in the inset indicates γ values. The excitation wavelength for recording the map was 633 nm, the laser intensity was $0.06 \text{ mW}/\mu\text{m}^2$ and the integration time was 80 s for each spectrum. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

To further illustrate the effect of continuous light on the $[\text{Fe}(\text{Htrz})_2(\text{trz})](\text{BF}_4)$ SCO material using a conventional Raman spectrometer, the spin transition has been triggered in a planar and uniform region of the powder sample (inside the hysteresis loop at 350 K) with a $10\times$ microscope objective (NA = 0.25) so that the theoretical diameter of the laser spot was estimated to be $\sim 3\ \mu\text{m}$. After 2 s illumination at $0.4\ \text{mW}/\mu\text{m}^2$ power density, this value was reduced down to $0.06\ \text{mW}/\mu\text{m}^2$ in order to image the irradiated region of the sample (with a $50\times$ objective to have a better lateral spatial resolution) without affecting its spin state (Figure 5). For each Raman spectrum of the map the integrated intensity of the HS marker band around $100\ \text{cm}^{-1}$ was measured and normalized to 1 when the sample contains 100% of HS species. The HS fraction is then defined as the parameter γ complying $0 < \gamma < 1$. In Figure 5, the yellow spot in the center (diameter $< 10\ \mu\text{m}$) represents the sample region where more than 85% of the species are in the HS state. It coincides approximately to the laser spot diameter. Interestingly, a $25\ \mu\text{m}$ -broad region between the center in yellow and the border in blue (with more than 90% of LS species) contain both HS and LS species. The population of HS species in a region that was not directly excited by the laser may be explained in terms of heat diffusion and/or cooperative processes. The dissipation of energy following the irradiation that causes the local heating of the sample in neighboring regions of the laser spot would induce the observed partial spin conversion. This phenomenon suggests in particular that the size matching of pump and probe laser spots is crucial to evaluate correctly the light-induced HS fraction under pulsed laser excitation.

A laser-induced thermal effect is expected to perturb the thermal hysteresis loop, and shift in particular transition temperatures T_{up} and T_{down} . Figure 6 shows the change in HS fraction γ (calculated from intensity integration of HS and LS marker bands at $100\ \text{cm}^{-1}$ and $275\ \text{cm}^{-1}$, respectively) upon thermal cycling between 298 K and 420 K. In Figure 6, open symbols are related to γ values obtained upon heating the $[\text{Fe}(\text{Htrz})_2(\text{trz})](\text{BF}_4)$ sample from 298 K to 420 K. Filled symbols correspond to γ values obtained upon cooling the sample from 420 K to 298 K. These data points describe the ascending and descending branches of the hysteresis loop for 3 different laser power densities, namely $\sim 0.02\ \text{mW}/\mu\text{m}^2$ (circles), $\sim 0.06\ \text{mW}/\mu\text{m}^2$ (squares) and $\sim 0.2\ \text{mW}/\mu\text{m}^2$ (diamonds). At low laser power density (below $0.02\ \text{mW}/\mu\text{m}^2$), $T_{\text{up}} = 383\ \text{K}$ and $T_{\text{down}} = 346\ \text{K}$. These temperatures are very

close to their respective static values ($T_{\text{up}} = 382\ \text{K}$ and $T_{\text{down}} = 344\ \text{K}$ in Table 1). Thus, for such low laser intensity, the thermal hysteresis loop deduced from Raman measurements compares very well with those measured using the different techniques listed in Table 1, unlike the assertions of Urakawa et al. [12]. However, upon increasing the laser intensity at the sample up to $\sim 0.2\ \text{mW}/\mu\text{m}^2$, the apparent T_{up} decreases significantly and the LS to HS conversion on the ascending branch becomes more gradual while neither T_{down} nor the shape of descending branch are affected.

Surprisingly, experimental observations reported here reproduce well those published by Gallé et al. who excited the same kind of compounds using a pulsed laser irradiation [16,17]. In their case, a single laser pulse was also able to trigger the formation of stable HS species upon exciting LS species inside the SCO hysteresis loop while these HS entities relaxed back to the LS state within $\sim 1\ \text{ms}$ upon irradiation outside the hysteresis loop [16,17], which agrees well with our own observations. Furthermore, the down-shifted ascending branch upon continuous irradiation at $0.2\ \text{mW}/\mu\text{m}^2$ (open diamonds in Figure 6) show a strong resemblance with the distribution, as function of the temperature, of the LS/HS ratio generated by the one-shot laser pulse experiment in another SCO compound [15] ($[\text{Fe}(\text{PM-BiA})_2(\text{NCS})_2]$ (PM-BiA = N-2'-pyridylmethylene-4-aminobiphenyl). In order to interpret their data, Freysz et al. [15] proposed a model where the partial conversion of LS iron(II) centers to the HS state is due to a laser-induced local heating, which mainly derives from the strong absorption of light by molecular entities in the LS state. According to this model we may suggest, in first approximation, that the weak absorption of HS species at 633 nm can be neglected indeed. As a consequence, the residual LS fraction gradually decreases as the number of HS particles increases owing to the reduced absorption of the 633 nm line in the HS state. Below a critical value of LS fraction there are not enough absorbing centers that would promote further the LS to HS transitions. On the contrary, the local heating is almost negligible above 360 K on the descending branch because all species are in the HS state. When the temperature of the system approaches T_{down} , the LS fraction starts increasing (it is 20% at 345 K for example) but, it is still too small to allow the continuous laser excitation to trigger a thermal LS to HS conversion. This behavior yields the insensitivity to the laser power of the descending branch of the hysteresis loop. A more detailed model will be provided in a near future. Finally, this light-induced spin conversion mechanism should explain the reason why a photo-induced phase transition from the HS to the LS state cannot occur in the triazole-based polymeric samples, using a continuous laser at wavelength 633 nm as well as a single laser pulse.

4. Conclusion

We have shown, in agreement with Craig et al. [32], that a simple continuous laser with relatively small power (a class 2 laser with power 1 mW would be largely sufficient) may be exploited for inducing the photoswitching of a spin crossover material. Furthermore we found that, outside the hysteresis loop, the LS to HS transition can be triggered by the continuous Raman-probe laser and produce a stationary HS fraction as long as the irradiation is maintained. As the light-induced HS state is not stable however, the LS state is recovered as soon as the laser power density is sufficiently reduced. In contrast a long-lived HS state can be populated within the hysteresis loop even at low laser power. Thanks to the microscale spatial resolution of our Raman microscope, we have also shown that the dissipation of energy following the irradiation causes the local heating of the sample in neighboring regions of the laser spot, inducing partial LS to HS conversion. These results indicate that Raman microscopy performed on these

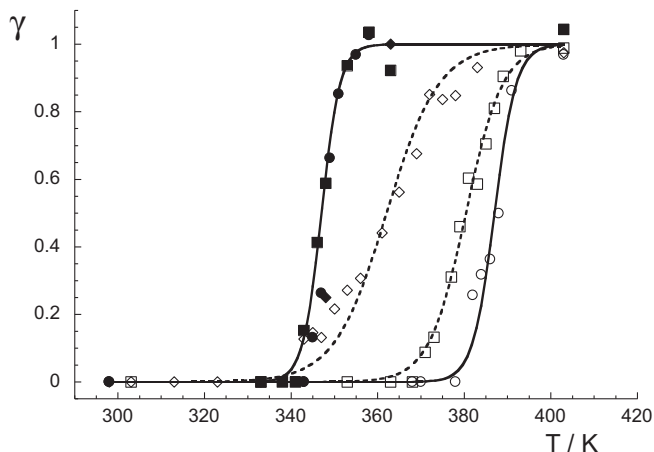


Figure 6. Evolution of the HS fraction γ versus temperature as deduced from the Raman spectra for 3 different laser intensities at 633 nm, namely $\sim 0.02\ \text{mW}/\mu\text{m}^2$ (circles), $\sim 0.06\ \text{mW}/\mu\text{m}^2$ (squares) and $\sim 0.2\ \text{mW}/\mu\text{m}^2$ (diamonds). The temperature is either increased from 298 to 420 K (open symbols) or decreased from 420 to 298 K (filled symbols). The sigmoid functions (solid and dotted lines) were drawn to guide the eyes.

SCO compounds offer many interesting advantages for promoting and characterizing optical data recording.

In addition, providing that very low laser intensities are used ($<0.02 \text{ mW}/\mu\text{m}^2$), the thermal hysteresis loop deduced from Raman measurements compares very well with those measured using different techniques described in the literature. The thermal hysteresis loops are modified for laser intensities larger than $0.02 \text{ mW}/\mu\text{m}^2$ and the observed changes can be interpreted in terms of local heating of the sample. Finally, this light-induced spin conversion mechanism should explain the reason why a photo-induced phase transition from the HS to the LS state cannot occur in the triazole-based polymeric samples, using a continuous laser at wavelength 633 nm as well as a single laser pulse.

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