Spin Crossover

One Shot Laser Pulse Induced Reversible Spin Transition in the Spin-Crossover Complex $[Fe(C_4H_4N_2)\{Pt(CN)_4\}]$ at Room Temperature**

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The use of light is one of the most promising ways to reversibly control various physical properties of organic and metal-organic compounds and opens up the possibility for the generation of new information storage devices.[1,2] Among these materials, iron(II) spin-crossover complexes are particularly interesting as they are known to exhibit a light-induced low-spin (LS) to high-spin (HS) transition.[3] However, this light-induced excited spin state trapping (LIESST) phenomenon is only efficient at cryogenic temperatures (typically below 50 K) because at higher temperatures the photoinduced HS state relaxes rapidly to the ground state. This is a serious limitation for the development of optical switches based on spin-crossover materials.

A possible approach to overcome this problem consists of working within the thermal hysteresis loop, in which the metastable HS or LS states have "infinite" lifetimes.[4] Such hysteresis phenomena have been found in many spin-crossover solids and can be related to long-range elastic interactions between the spin-state-changing molecules.[5] It should be emphasized that the hysteresis loop can be fine-tuned by chemical methods to situate it around room temperature.[6] The first light-induced LS→HS transition in the hysteresis region was recently observed by means of optical reflectivity when an 8-ns laser pulse was applied at 170 K to $[Fe(pm\text{-}bia)_2(NCS)_2]$ (pm-bia = *N*-2′-pyridylmethylene-4-aminobiphenyl), but the reverse phenomenon could not be detected.[2a] Herein, we report spectroscopic evidence for a bi-directional, light-induced spin transition at room temperature in $[Fe(pyrazine)\{Pt(CN)_4\}]$ (Figure 1) by applying a one-shot laser pulse of irradiation.

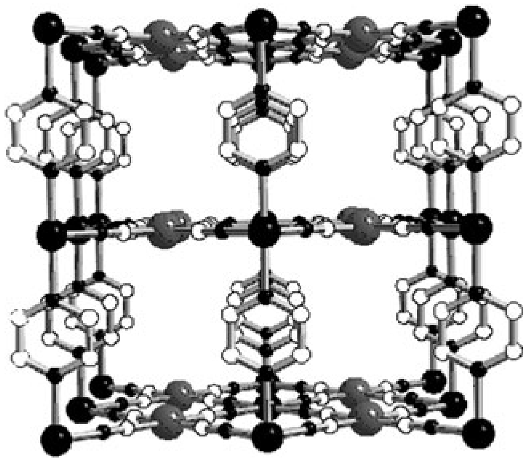

Figure 1. Schematic structure of $[Fe(pyrazine)\{Pt(CN)_4\}]$.

The synthesis of a hydrated form of the above-mentioned compound has been reported elsewhere.[7] Subsequent research has demonstrated that the spin-crossover behavior of this hydrated form ($[Fe(pyrazine)\{Pt(CN)_4\}]\cdot n H_2O$; $n \approx 2$–3) depends dramatically on the water content. Thermogravimetric analysis revealed that heating the sample at 420 K for 30 minutes is necessary to remove the water of crystallization. The dehydrated form $[Fe(pyrazine)\{Pt(CN)_4\}]$ exhibits "improved" spin-crossover behavior in that the transition becomes complete and is centered at room temperature. Moreover, the hysteresis loop becomes wider, square-shaped, and reproducible over several cycles. This compound preserves its spin state (HS or LS) for several months if it is kept in a dry atmosphere at room temperature (295 K).

Figure 2 shows the temperature dependence of the $\chi_M T$ value (χ_M is the molar magnetic susceptibility) for

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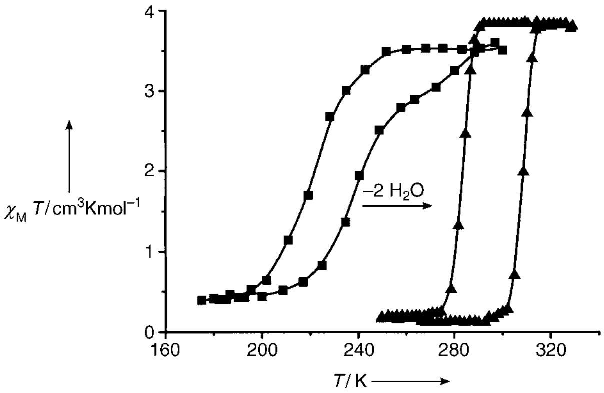

Figure 2. Graph of $\chi_M T$ versus T for [Fe(pyrazine){Pt(CN)$_4$}] in the cooling and heating modes before and after thermal treatment at 430 K.

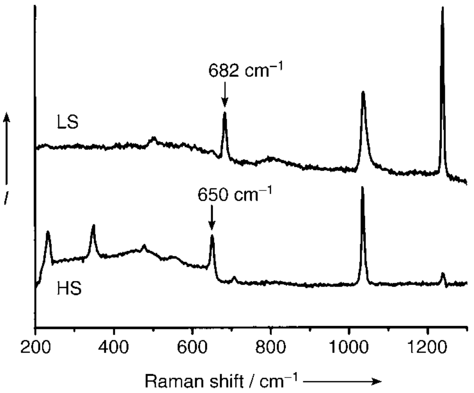

Figure 3. Raman spectra of [Fe(pyrazine){Pt(CN)$_4$}] in the HS and the LS states recorded in the 200–1300 cm^{-1} frequency range at 295 K and 265 K, respectively. Selected Raman marker bands are shown at 650 cm^{-1} (HS) and 682 cm^{-1} (LS). The intensity I on the y axis is given in arbitrary units.

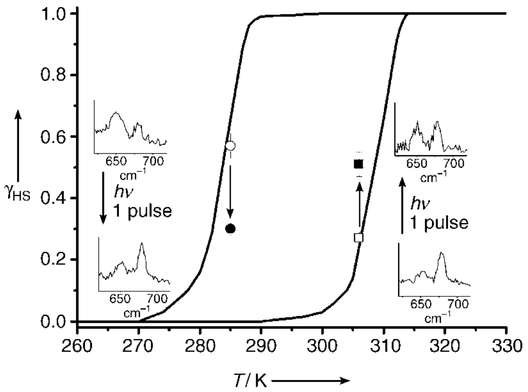

Figure 4. Proportion of HS iron(II) ions before and after a one-shot laser pulse of irradiation on the ascending and descending branches of the hysteresis loop of [Fe(pyrazine){Pt(CN)$_4$}]. The insets show the Raman spectra recorded before and after irradiation.

[Fe(pyrazine){Pt(CN)$_4$}] before and after heating to 430 K. This figure demonstrates the dramatic improvement in the spin-crossover characteristics following the thermal dehydration treatment described earlier. The value of $\chi_M T$ for the dehydrated form at 330 K is 3.81 cm^{3}K mol^{-1}; this value is consistent with the iron(II) ion being in the HS state ($S = 2$). Upon cooling the sample, the value of $\chi_M T$ remains constant down to about 292 K but then undergoes a sharp decrease that is characteristic of a first-order spin transition. The $\chi_M T$ value drops to 0.16 cm^{3}K mol^{-1} at around 270 K, thus indicating that the spin transition is virtually complete. The heating mode reveals the occurrence of a thermal hysteresis with a hysteresis loop that is 24 K wide. The change in the spin state was also confirmed by Mössbauer spectroscopy. The Mössbauer spectrum recorded at 300 K (in the cooling mode) consists of a single doublet with quadrupole splitting (1.159(5) mm s^{-1}) and isomer shift (1.047(3) mm s^{-1}) values typical of Fe^{II} ions in the HS state. A new doublet appears at 80 K with smaller quadrupole splitting (0.306(4) mm s^{-1}) and lower isomer shift (0.439(2) mm s^{-1}) values, as expected for the LS state ($S = 0$) of Fe^{II} ions. The change in the spin state is also accompanied by a marked color change: pale orange for the HS state and deep red for the LS state.

Raman spectra of [Fe(pyrazine){Pt(CN)$_4$}] in the pure HS and LS states were recorded between 200 and 1300 cm^{-1} (Figure 3). In agreement with our previous observations on this family of complexes,[8] the Raman spectra are markedly different, which is in line with the change in the spin state, and several "marker bands" can be chosen to follow the spin transition. For example, peaks around 349 and 233 cm^{-1} (assigned to Pt-CN bending and Fe-N stretching modes, respectively) are associated with the HS state and the feature at 1238 cm^{-1} exhibits a significant increase in intensity in going from the HS to the LS state. However, the most relevant "marker band" near 650 cm^{-1}, previously assigned to an in-plane bending mode of the pyrazine ring,[8] is fairly intense in both spin states and exhibits a well-resolved frequency shift from 650 cm^{-1} (HS) to 682 cm^{-1} (LS).

A pulsed Nd:YAG laser enables the application of 8 ns pulses ($\lambda = 532$ nm) with pulse energies of about 1 mJ at the sample (spot size = 0.4 mm^2) in the ascending and descending branches of the hysteresis loop. Figure 4 exhibits the proportion of HS iron(II) ions before and after the one-shot laser pulse irradiation, as evaluated from the intensities of the Raman peaks. Raman spectra recorded in the 620–720 cm^{-1} frequency range before and after the application of the pulses are also presented in the insets of Figure 4. These spectra, as well as the color change observed just after excitation with light, prove clearly that a single laser pulse ensures both a LS→HS and a HS→LS transition, depending on the position in the hysteresis loop. Thermal effects arising from laser irradiation (either pump or probe beams) must be carefully checked for these light-induced changes to be fully interpreted. In any case, however, laser heating can induce only the LS→HS transition. Therefore, the observed light-induced HS→LS transition proves irrefutably that a simple heating effect cannot play any role here.

The observed change in the spin state appears to be incomplete: only around 20% of the iron ions are apparently converted from one state to the other in the single-pulse experiment. However, the absorption spectra of the compound indicate that the penetration depths of the pump laser (532 nm) and the probe laser (785 nm) are rather different.[9]

In fact, the latter probes a volume that is larger than that irradiated by the green pulse. In other words, the ratio of the Raman peak intensities underestimates the real photoconversion efficiency and can therefore be used only to confirm the change in the spin state and to compare the relative efficiency of the laser pulses as a function of the number of pulses, pulse energy, etc. It should be noted that we could not obtain any useful Raman spectra using a green (514.5 nm) continuous wave laser because of laser heating effects.

A one-shot excitation triggers at least a partial spin conversion. We have therefore studied the effect of applying additional laser pulses and found that while the second pulse increases the spin conversion (to ca. 40% HS), subsequent pulses do not have any measurable additional effect on the HS/LS ratio. The conversion efficiency was also studied at different points around the wide hysteresis loop of [Fe(pyrazine){Pt(CN)$_4$}] which correspond to distinct stability regions for the LS and the HS states (Figure 5). The HS state is the ground state at high temperatures (point B) while the LS state becomes the stable form at low temperatures (points A and C). At points E and D (F, G, and H) the system is in the metastable LS (HS) state. Raman spectra were collected at each point before and after the application of 10 successive laser pulses. The Raman signals at points C, D, and E (Figure 6, points C, D, and E) for the irradiated region clearly demonstrate the appearance of the HS state following the pulsed irradiation, while at points F and G (Figure 6, points F and G) the fraction of the LS state increases. In contrast, we could not observe any irradiation effects at points A, B, and H (Figure 6, point H). As far as points A and B are concerned, this observation is clearly related to the fact that they are situated outside the hysteresis region. On the other hand, the absence of any effect at point H is probably related to the lower optical density of the HS state (relative to the LS form)[10] and the different energy barriers (compared to points F and G).

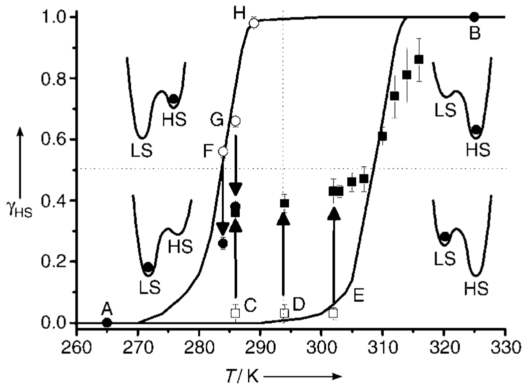

Figure 5. Proportion of HS iron(II) ions before and after irradiation with 10 laser pulses on points A–H of the hysteresis loop of [Fe(pyrazine){Pt(CN)$_4$}]. Points obtained by heating following irradiation at point E are also presented. Schematic diagrams of the free energy with minima corresponding to the LS and HS states at the respective temperatures are drawn in each part of the graph delimited by the two dotted lines. The intensity I on the y axis is given in arbitrary units.

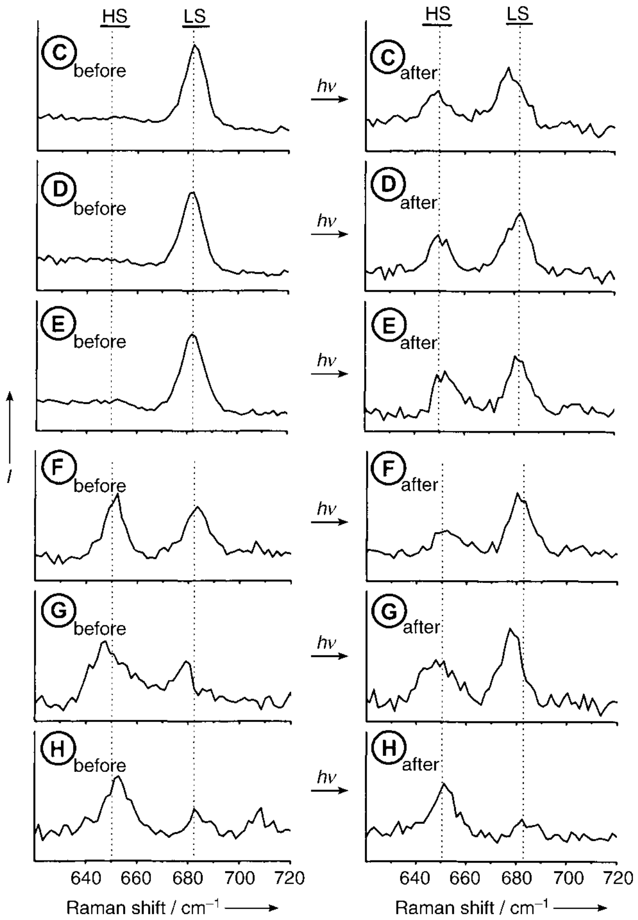

Figure 6. Selected Raman spectra of [Fe(pyrazine){Pt(CN)$_4$}] at points C–H on the hysteresis loop. These Raman spectra were recorded before and after 10 successive laser pulses.

The HS fractions, evaluated before and after an irradiation sequence of 10 pulses, are shown in Figure 5. First of all it should be noted that—within the experimental limits of accuracy—the same final state (ca. 40% HS) was reached from points C, D, and E, thus also confirming the absence of significant heating effects in the LS→HS transition. It appears also that the HS→LS transition can be obtained only in the descending branch (from an initial HS fraction of 0.7) of the hysteresis, which is in contrast with the findings for the LS→HS transition which was observed even in the stability domain for the LS state (point C). Figure 5 also shows data obtained by heating the sample following irradiation at point E. The photoinduced fraction of the HS state does not change within the hysteresis loop. With further heating it follows a similar evolution to that determined by magnetic measurements. This result reveals also that the intensities of the Raman peaks give a fairly reasonable approximation for the HS fraction in the zone irradiated by the laser pulses.

In considering the mechanism of the observed pulsed-laser-induced change in the spin state, we refer to the general concept of photoinduced phase transitions.[1a,b] The phase transition between the two spin states cannot occur thermally in the hysteresis region, because of the existence of a free energy barrier. However, photoexcitation may induce local transformation of the microscopic state of the system. The photoexcited species relaxes rapidly to the initial state when there is a weak excitation density. On the other hand, if the photoexcitation density exceeds a threshold it can lead to the formation of a nucleus of the second phase, which is stabilized by the lattice distortions accompanying the change in the spin state. Such photoinduced phase transitions are always cooperative and highly nonlinear phenomena, because the efficiency is not simply proportional to the total absorbed energy, and a threshold effect on the light intensity exists.

An interesting feature of the photoswitching phenomena observed in [Fe(pyrazine){Pt(CN)$_4$}] is that both the LS→HS and the HS→LS transitions can be triggered by the same irradiation wavelength. Such an unusual effect has also been reported by Liu et al.[2c] for a Prussian blue analogue. These authors took the observation as evidence for the so-called "domino effect": namely that the generation of a small amount of HS (LS) excited species in the LS (HS) lattice initiates the complete transformation of this latter into the second phase. We believe, however, that the effect can be explained more readily by the simple fact that the optical absorption bands of the HS and LS forms overlap at 532 nm. Since the color of the sample is very different in the two spin states, one can anticipate that there exists an excitation photon energy, which induces the LS→HS or the HS→LS transition selectively in this compound.

In conclusion, we have demonstrated by a spectroscopic method that a bi-directional, photoinduced spin transition can be brought about when applying a nanosecond laser pulse to [Fe(pyrazine){Pt(CN)$_4$}]. This phenomenon can be interpreted as a photoinduced structural-phase transformation. Since this transition occurs around room temperature over a wide range of bistability and involves magnetization and color changes as well, it opens up interesting perspectives for applications in memory devices and optical switches. A more detailed study of the dependence of the photoconversion efficiency on the excitation wavelength and pulse energy, as well as a dynamic study, are, however, necessary to find the optimal working conditions as well as to probe more thoroughly the physical mechanisms involved.

Experimental Section

Variable-temperature magnetic susceptibility measurements were carried out between 300 and 1.8 K on the polycrystalline sample (20 mg) using a Quantum Design MPMS2 SQUID magnetometer operated at 0.5 T. The magnetometer was calibrated with $(NH_4)_2Mn(SO_4)_2\cdot 12H_2O$. Experimental susceptibilities were corrected for diamagnetism of the constituent atoms by the use of Pascal's constants.

A Spectra Physics Nd/YAG, model GCR3, pulsed laser operating at 532 nm was used to irradiate the polycrystalline sample with pulses of 8 ns duration. CW Raman spectra were collected from the irradiated region in a backscattering geometry before and after applying the laser pulse. Raman scattering was excited at 785 nm by means of a Ti-sapphire laser (Spectra Physics, model 3900S) pumped by an Ar$^+$ laser (Spectra Physics, model 2060A). The Rayleigh scattering was removed by a holographic notch filter and Raman spectra were recorded with a thermoelectrically cooled CCD detector (Andor Technology, Model DV430-FI) coupled to a Jobin–Yvon spectrograph (model HR640) equipped with a grating containing 300 grooves per mm. The spectral resolution at a slit width of 100 μm was around 7 cm^{-1}. Raman spectra were recorded between 200 and 1300 cm^{-1} with acquisition times of about 3 min. A cylindrical lens was inserted in the beam pathway to reduce the incident power density of the pump and probe beams, which traversed the same optical path close to the sample. CW beam power at the sample was then fixed at 5 mW on a spot size of about 0.4 mm^2, while the energy of each laser pulse on the sample was 1 mJ at the same spot. Under these conditions the experiments could be repeated many times on the same sample without degrading it. The sample temperature was controlled using a Linkam THMS600 liquid-nitrogen cryostage.

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[9] Unfortunately, we were unable to grow crystals to carry out optical density measurements and therefore the penetration depths could not be determined precisely. In practice, the "Raman sampling depth" and the "photoexcitation depth" should be compared. The latter depends not only on the absorption coefficient of the sample, but also on many other parameters such as the threshold photoexcitation density for the phase transition, while the former is determined by the collection optics, in addition to the sample's own optical properties (for example, diffuse scattering). Any quantitative analysis would be feasible only for a very thin film of the sample. To obtain an approximate idea at least of the beam penetration at different wavelengths we have carried out diffuse reflectance measurements on the HS and LS states at 295 K using an integration sphere and a teflon reference sample. These show that the optical density of the LS state at 532 nm is about twice

that in the HS state, while at 785 nm it is 2 times (6 times) smaller than at 532 nm for the HS (LS) state.

[10] The key quantity here is the excitation photon density but its calculation requires the assumption that the total photon flux of the 532 nm pulse is absorbed uniformly within the sample. For our relatively thick and diffuse scattering samples this assumption would be invalid.