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Transient absorption spectroscopy of the $[\text{Fe}(\text{2-CH}_3\text{-phen})_3]^{2+}$ complex: Study of the high spin \leftrightarrow low spin relaxation of an isolated iron(II) complex

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ABSTRACT

We report on the light induced spin crossover dynamics of $[\text{Fe}(\text{2-CH}_3\text{-phen})_3]^{2+}$ complex in solution. The excitation of the complex by pulses centered at $\lambda = 500$ nm along the metal to ligand charge transfer absorption band indicates a selective excitation of the LS state. The excitation of the complex by pulses centered at $\lambda = 330$ nm or $\lambda = 335$ nm reveals an increase of the LS state population and a photo bleaching of the HS state population that is associated to a transient photo dissociation. A method that makes it possible to deduce the kinetics of both the HS \rightarrow LS state and LS \rightarrow HS state is proposed.

1. Introduction

Molecular based materials with photo switchable properties, such as spin crossover (SCO) materials which are based on molecular complexes of transition metal ions, have attracted a lot of attention in the last years [1]. Researches on these materials are motivated by the huge possibilities offered by modern supra molecular chemistry that makes it possible to control the optical, electrical, and magnetic properties of these complexes [1–3]. For ultrafast switching devices [3], one looks for spin crossover (SCO) compounds whose properties can be photo switched on ultra short time scales. Among SCO compounds, it has been shown that iron(II) complexes in solution can be photo switched from the low spin (LS) singlet ground state (1A_1 , $S = 0$) to the low lying excited high spin (HS) quintet state (5T_2 , $S = 2$) in less than 300 fs [4–18]. Since the HS excited state is forbidden by absorption of light from the LS ground state by the spin selection rules, the doorway to the HS state is usually achieved via the singlet Metal to Ligand Charge Transfer ($^1\text{MLCT}$) that exhibits strong absorption bands in the visible spectrum. This latter process has been shown to be very efficient and $\sim 100\%$ of the complexes excited in the $^1\text{MLCT}$ state populate the HS (5T_2) state. Recent experiments resolved a long standing issue about the population mechanism of quintet states in iron(II) based complexes, which were identified as a simple $^1\text{MLCT} \rightarrow ^3\text{MLCT} \rightarrow ^5T_2$ cascade from the initially excited state [13,15,18]. However, while McGarvey et al. were the first to discover that, in a solution of iron(II) complexes, the HS state could be populated efficiently at the expense of the LS state by pulsed laser excitation [4], nobody has, to the best of our knowledge, dem-

onstrated the reverse phenomenon: i.e., the HS to LS photo excitation of a solution of isolated iron(II) complexes. This is in contrast with the work performed in the solid state (crystal), notably by Hauser and coworkers in $[\text{Fe}(\text{ptz})_6](\text{BF}_4)_2$ (ptz = 1-propyltetrazole) crystal [19–22]. At low temperature ($T < 70$ K), when the iron(II) were optically excited along the d-d transition, these authors recorded a long lasting LS to HS photo switching. It was proposed that during this phenomenon, referred as the Light Induced Excited Spin State Trapping (LIESST), the system is driven from the 1A_1 singlet ground state towards the 1T_1 singlet excited state that subsequently relaxes non radiatively towards the high spin quintet state 5T_2 cascading through two inter system crossings (ISC): $^1T_1(S = 0) \rightarrow ^3T_1(S = 1) \rightarrow ^5T_2(S = 2)$. Hauser was also able to demonstrate the reverse LIESST effect [22]. In the latter case, the excitation of the crystal along the d-d optical transition drives the system from the 5T_2 state to the 5E , that relaxes back to its initial ground state through two inter systems crossing phenomena ($^5E(S = 2) \rightarrow ^3T_1(S = 1) \rightarrow ^1A_1(S = 0)$). Therefore, for isolated molecules in solution, one can question if the lack of molecular interactions does not forbid reverse LIESST photo switching.

In this Letter, we study the relaxation of the photo excited $[\text{Fe}(\text{2-CH}_3\text{-phen})_3](\text{BF}_4)_2$ (phen = 1,10-phenanthroline) complex dissolved in acetonitrile (CH_3CN) by means of ultrafast pump-probe time resolved optical absorption spectroscopy. This complex is of particular interest since, at room temperature, both HS ($\sim 80\%$) and LS ($\sim 20\%$) states are populated [23–26]. We first excited the solution with picosecond pulses centered at $\lambda_p = 500$ nm. In good agreement with our previous study of $[\text{Fe}(\text{phen})_3](\text{BF}_4)_2$ complex [18], we recorded a transient bleaching of the $^1A_1 \rightarrow ^1\text{MLCT}$ absorption band that reveals the population of the HS state. The system was found to recover its equilibrium state with a constant time $\tau = 3.6 \pm 0.2$ ns. To understand the ultra short kinetics of this process, we performed similar experiments using two colors

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femtosecond time resolved absorption. This latter kinetics is very close to the one reported for similar iron(II) complexes. Then we excited the solution with picosecond pulses centered at $\lambda = 355$ nm. The transient absorption spectrum reveals an absorption at $\lambda = 500$ nm and weak bleaching bands centered at $\lambda = 450$ and 550 nm. All these bands were found to relax in 3.6 ± 0.2 ns. We could well reproduce this transient absorption spectrum considering that it was partly due to a photo bleaching of the HS state and partial population of the LS state. This subnanosecond experiment reveals therefore the possibility to study HS to LS state kinetics. To analyze in more details the ultra short kinetics of this process, we have also performed two colors femtosecond time resolved absorption. The analysis of these data is complicated by the photo bleaching of the HS state. However, we propose a method that makes it possible to determine some specific relaxation times as well as the relaxation paths that account for our transient absorption measurements.

2. Absorption spectrum of the studied samples

The absorption spectra of $[\text{Fe}(\text{phen})_3](\text{BF}_4)_2$ and $[\text{Fe}(2\text{CH}_3\text{phen})_3](\text{BF}_4)_2$ complexes dissolved in acetonitrile were previously studied at room temperature [18]. As shown on Figure 1a, the steady state optical absorption spectrum of $[\text{Fe}(\text{phen})_3]^{2+}$ solution presents a large and broad ${}^1A_1 \rightarrow {}^1MLCT$ absorption band centered at $\lambda \sim 500$ nm. This latter absorption is drastically reduced for the $[\text{Fe}(2\text{CH}_3\text{phen})_3]$ complex. In fact, this results from the fact that for $[\text{Fe}(2\text{CH}_3\text{phen})_3]^{2+}$ solution, both the HS ($\sim 80\%$) and LS ($\sim 20\%$) states are populated [24–27]. This behavior is the consequence of the steric hindrance to the coordination of iron(II) induced by the presence of the methyl group in the ligand. This lowers the effective strength of the ligand field and reduces the population of the LS state. One should also notice the larger absorption of the $[\text{Fe}(2\text{CH}_3\text{phen})_3]^{2+}$ complexes below 400 nm.

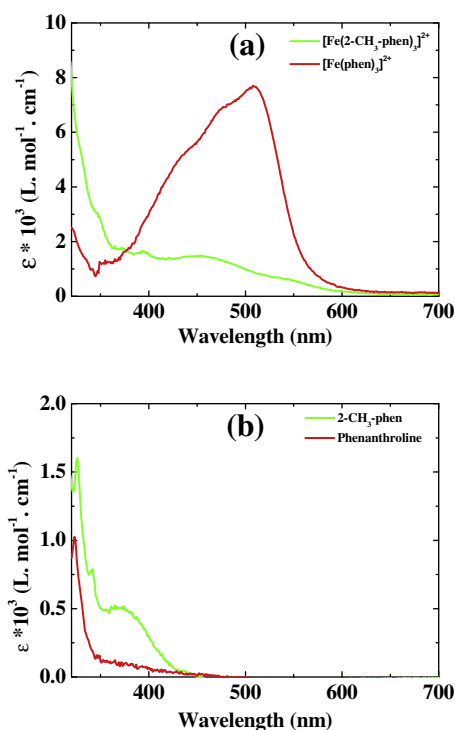


Figure 1. Optical absorption spectrum at 300 K of: (a) our $[\text{Fe}(\text{phen})_3]^{2+}$ and $[\text{Fe}(2\text{CH}_3\text{phen})_3]^{2+}$ complexes in a CH_3CN solution and (b) of the phenanthroline and phenanthroline-methyl in the same solvent.

Two phenomena account for this behavior. Firstly, as shown in Figure 1b and compared to the phenanthroline ligand, the $(2\text{CH}_3\text{phen})$ units absorb more strongly in this spectral range. Secondly, as previously shown in $[\text{Fe}(\text{phen})_3]^{2+}$, the population of the HS state results in an increase of the absorption at wavelengths below 380 nm that is associated to the ${}^5T_2 \rightarrow {}^5MLCT$ transition [18].

3. Experimental set-ups

All the pump-probe experiments presented hereafter were performed exciting the complex with either picosecond or femtosecond pulses centered at $\lambda_p \sim 500$ nm or at $\lambda_p \sim 330$ nm. We noticed that in both complexes such an excitation does not give rise to a noticeable luminescence. To investigate the ultrafast relaxation dynamic of $[\text{Fe}(2\text{CH}_3\text{phen})_3]^{2+}$ and $[\text{Fe}(\text{phen})_3]^{2+}$ complexes, we used two different ultrafast time-resolved pump-probe experiments that we previously described [18]. Hereafter, we will recall the important information.

The first experiment we performed is a nanosecond broadband transient absorption experiment. The experimental set-up was built as follows. The output of a frequency-tripled Nd:YAG amplified laser system (30 ps, 30 mJ @1064 nm, 20 Hz, Ekspla model PL 2143) was used to pump an optical parametric generator (Ekspla model PG 401). This latter produces excitation pulses tunable in the 410–2300 nm spectral range. In this experiment, the wavelength and energy of the pump pulse were either $\lambda_p = 500$ nm and $E \sim 1$ mJ or $\lambda_p = 355$ nm and $E \sim 0.3$ mJ, respectively. The residual of the fundamental laser radiation was focused in a high-pressure breakdown cell filled with Xenon that generated a white light pulse. This latter was used to probe the transient absorption of the sample. It was measured using a spectrograph (Acton) coupled with a high-dynamic range streak camera (Hamamatsu C7700). The focused pump and probe beams were overlapped within a 1 cm optical path cell containing the solution. Sequences of pulses, transmitted by the sample with and without the pump excitation, were digitized and processed by HPDTA (Hamamatsu) software. This software produces a two-dimensional map that provides the evolution of differential transient absorption of the photo-excited complex for pump-probe time delay spanning from 100 ps up to several tens of nanoseconds and over the spectral domain ranging from 300 to 800 nm.

In the second experiment, we performed a femtosecond two-colors pump-probe transient absorption measurement. This makes it possible to measure at given wavelengths and with a femtosecond resolution, the transient absorption evolution of the photo-excited solution over the temporal range of ~ 1 ns. This experiment is based on a 1 kHz Ti:Sapphire regenerative amplifier system producing 50 fs laser pulses having an energy of ~ 4.5 mJ centered at 800 nm (Coherent Legend USP). The output of the laser system was split into two 1 mJ laser pulses which pumped two Optical Parametric Amplifiers (OPA, Model TOPAS from Light Conversion). These OPAs generate the pump and probe pulses. These latter's were tunable between 300 and 2000 nm. The pump pulse, ~ 1 μJ in energy, was centered at 330 nm. The used probe pulse had, at least, a hundred times lower energy. The focused pump and probe beams were overlapped within a 1 mm optical path cell containing the solution. In the optical cell, the duration of the probe and pump pulses was measured to be 100 ± 10 fs. To minimize the thermal lensing and photo-quenching effects, the solution was gently flowing in the cell. The time delay τ between the probe and pump pulses was controlled using a motorized translation stage that has a spatial resolution of 1.5 μm . To measure the transient absorption signal at a given time delay τ , we used two silicon photodiodes, placed before and after the sample, that measure the initial (I_r) and the transmitted ($I_t(\tau)$) intensity of the probe beam

respectively. By computing the logarithm of $I_t(\tau)/I_r$, we determined the absorption signal $s(\tau)$ of the solution. The differential transient absorption signal $\Delta O.D.(\tau)$, at a given delay τ , was then computed by subtracting the absorption signal measured with and without the pump pulse. For that purpose the pump beam was chopped at 40 Hz. For our measurements, the typical measurement error was better than 10^{-3} optical density (O.D.).

4. Study of the LS \rightarrow HS state photo-switching

4.1. Exciting the $[\text{Fe}(\text{2 CH}_3 \text{ phen})_3]^{2+}$ complex at $\lambda_p = 500 \text{ nm}$

The first experiment we performed were aiming at demonstrating we could record LS \rightarrow HS spin state photo switching and evidence the relaxation channels exciting the $[\text{Fe}(\text{2 CH}_3 \text{ phen})_3]^{2+}$ complex at $\lambda_p = 500 \text{ nm}$.

Figure 2 presents the spectro temporal evolution of the differential absorption spectrum measured for $[\text{Fe}(\text{2 CH}_3 \text{ phen})_3]^{2+}$ with a sub nanosecond time resolution upon excitation by picosecond laser pulses centered at $\lambda_p = 500 \text{ nm}$.

On Figure 2a, upon excitation of solution by laser pulses centered at $\lambda_p = 500 \text{ nm}$, one can observe a bleaching of the ${}^1A_1 \rightarrow {}^1MLCT$ absorption band. Figure 2b shows the transient bleaching recorded 1 ns after photo excitation for both $[\text{Fe}(\text{phen})_3]^{2+}$ (Figure 2b solid curve) and $[\text{Fe}(\text{2 CH}_3 \text{ phen})_3]^{2+}$ (Figure 2b dots) complexes. The photo bleaching of the $[\text{Fe}(\text{2 CH}_3 \text{ phen})_3]^{2+}$ is centered at $\lambda \sim 520 \text{ nm}$ and resembles the one we recorded by exciting the $[\text{Fe}(\text{phen})_3]^{2+}$ complexes at 540 nm [18]. This latter observation indicates that, upon excitation, both $[\text{Fe}(\text{2 CH}_3 \text{ phen})_3]^{2+}$ and $[\text{Fe}(\text{phen})_3]^{2+}$ complexes behave similarly: the iron(II) ions initially in the LS ground state are rapidly brought in

the HS excited state. Figure 2b also indicates a slight red shift of the bleaching for $[\text{Fe}(\text{2 CH}_3 \text{ phen})_3]^{2+}$ versus $[\text{Fe}(\text{phen})_3]^{2+}$ complex. We attribute this phenomenon to the lowering of the effective strength of the ligand field for the $[\text{Fe}(\text{2 CH}_3 \text{ phen})_3]^{2+}$ complex that results in a red shifting of the ${}^1A_1 \rightarrow {}^1MLCT$ absorption band. The lowering of the effective strength of the ligand field should also impacts the HS to LS relaxation time. This conclusion is validated by Figure 2c, where the bleaching at $\lambda = 500 \text{ nm}$ is well reproduced considering an exponential decay with a constant time $\tau = 3.6 \pm 0.2 \text{ ns}$. This constant time is about three times longer than the one recorded for the $[\text{Fe}(\text{phen})_3]^{2+}$ ($\tau = 1.1 \pm 0.1 \text{ ns}$) [18].

The previous experiments indicates that an excitation at $\lambda_p = 500 \text{ nm}$ for the $[\text{Fe}(\text{2 CH}_3 \text{ phen})_3]^{2+}$ complex can induce a LS \rightarrow HS photo switching. As we previously mentioned, it is very likely that the mechanism responsible for the LS \rightarrow HS state photo switching for this complex results from the following cascade on the excited state hyper surface: ${}^1MLCT \rightarrow {}^3MLCT \rightarrow {}^5T_2$ [13,15,17,18]. These latter cascading processes are summarized in Figure 6a.

To confirm this relaxation process and to determine the relaxation constants, we performed two color femtosecond time resolved absorption experiments, exciting the $[\text{Fe}(\text{2 CH}_3 \text{ phen})_3]^{2+}$ complex at $\lambda_p = 480 \text{ nm}$. Figure 3a and b presents the data we recorded for the $[\text{Fe}(\text{2 CH}_3 \text{ phen})_3]^{2+}$ complex. As expected, the data recorded at $\lambda = 540 \text{ nm}$ $[\text{Fe}(\text{2 CH}_3 \text{ phen})_3]^{2+}$ (Figure 3a) complex and previously for the $[\text{Fe}(\text{phen})_3]^{2+}$ [18] have the same trends: a rapid decrease of the absorption that is basically limited by the pump probe time overlap followed by a long time recovery. Moreover, for both the $[\text{Fe}(\text{2 CH}_3 \text{ phen})_3]^{2+}$ and $[\text{Fe}(\text{phen})_3]^{2+}$ complexes, the kinetics recorded at $\lambda = 580 \text{ nm}$ (see Figure 3b and [18]) and $\lambda = 450 \text{ nm}$ (not presented here) have similar trends. This indicates that relaxation cascade of the $[\text{Fe}(\text{phen})_3]^{2+}$ and $[\text{Fe}(\text{2 CH}_3 \text{ phen})_3]^{2+}$

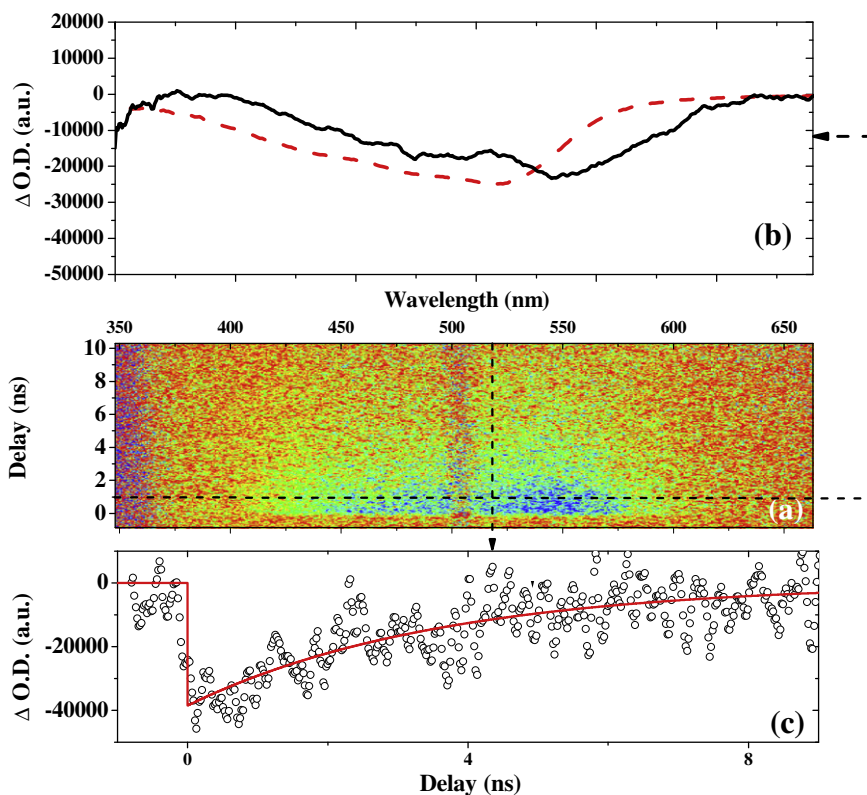


Figure 2. (a): Time resolved differential absorption spectrum of the $[\text{Fe}(\text{2 CH}_3\text{-phen})_3]^{2+}$ complexes after its excitation at $\lambda_p \sim 500 \text{ nm}$. (b): Solid line: Differential absorption spectrum of the $[\text{Fe}(\text{2 CH}_3\text{-phen})_3]^{2+}$ complexes recorded one nanosecond after excitation. Dashed line: Absorption spectrum of the $[\text{Fe}(\text{phen})_3]^{2+}$ complexes. (c): Relaxation kinetic of the differential absorption spectrum at $\lambda \sim 530 \text{ nm}$. In figures b and c the vertical scale are in arbitrary units.

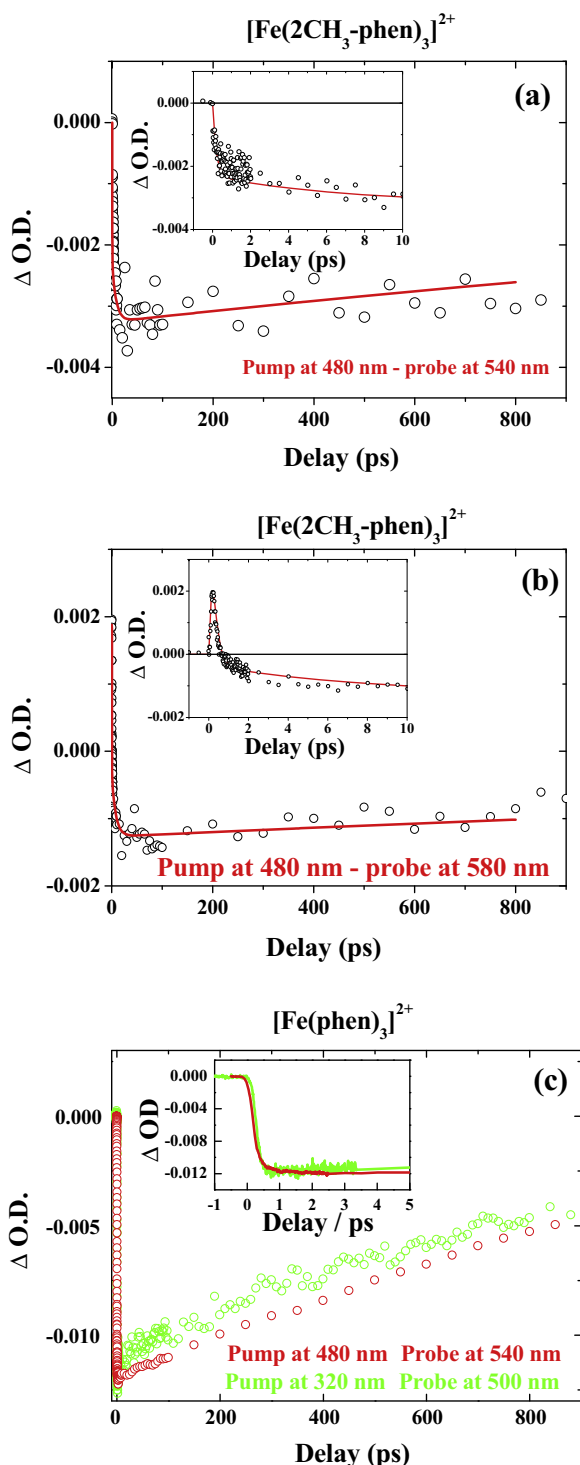


Figure 3. (a) Evolution of the differential absorption of $[\text{Fe}(\text{2 CH}_3\text{-phen})_3]^{2+}$ dissolved in CH_3CN recorded at $\lambda \sim 540$ nm after the excitation by a 100 fs laser pulse centered at $\lambda_p \sim 480$ nm. The solid lines are a fit of the dotted experimental data. (b) Evolution of the differential absorption of $[\text{Fe}(\text{2 CH}_3\text{-phen})_3]^{2+}$ dissolved in CH_3CN recorded at $\lambda \sim 580$ nm after the excitation by a 100 fs laser pulse centered at $\lambda_p \sim 480$ nm. The solid lines are a fit of the dotted experimental data. (c) Evolution of the differential absorption of $[\text{Fe}(\text{phen})_3]^{2+}$ dissolved in CH_3CN recorded at $\lambda \sim 540$ nm (in red) and $\lambda \sim 500$ nm (in green) after the excitation by a 100 fs laser pulse centered at $\lambda_p \sim 480$ nm (in red) and $\lambda_p \sim 320$ nm (in green) respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

$\text{CH}_3\text{ phen})_3]^{2+}$ complexes are similar and evolves according to the following relaxation cascade: ${}^1\text{MLCT}_a \rightarrow {}^3\text{MLCT} \rightarrow {}^5\text{T}_2^* \rightarrow {}^5\text{T}_2 \rightarrow$

${}^1\text{A}_1$. As shown in Figure 3a and b and indicated in Figure 6a, we could well reproduce our experimental data considering the relaxation of the excited $[\text{Fe}(\text{2 CH}_3\text{ phen})_3]^{2+}$ complex occur with the following time constant, $\tau_1 < 100$ fs for the relaxation step ${}^1\text{MLCT}_a \rightarrow {}^3\text{MLCT}_a$, $\tau_2 = 240 \pm 60$ fs for the relaxation step ${}^3\text{MLCT}_a \rightarrow {}^5\text{T}_2^*$, $\tau_3 = 7.8 \pm 0.4$ ps for the relaxation step ${}^5\text{T}_2^* \rightarrow {}^5\text{T}_2$ and $\tau_4 = 3.6 \pm 0.2$ ns for the relaxation step ${}^5\text{T}_2 \rightarrow {}^1\text{A}_1$. As shown in solid lines in Figure 3a and b, these time constants were able to fit very well our experimental data.

4.2. Exciting the $[\text{Fe}(\text{phen})_3]^{2+}$ complex along the blue edge of the MLCT absorption band at $\lambda_p = 355$ nm or $\lambda_p = 320$ nm

While previous experiments was clearly indicating that LS \rightarrow HS spin state photo switching could be recorded exciting a spin state complex at $\lambda_p = 500$ nm around the central wavelength of the MLCT absorption band, one may wonder if the process is also efficient exciting the complex at the very edge of the MLCT absorption band.

With this goal in mind, we performed a similar experiments by exciting a solution of the $[\text{Fe}(\text{phen})_3]^{2+}$ complex by picoseconds laser pulses centered at $\lambda_p = 335$ nm. For $[\text{Fe}(\text{phen})_3]^{2+}$, the transient absorption spectrum (not presented here) is very close, to not say, similar to the one we reported in our previous work [18], and resemble to the one presented in Figure 2. In short, we recorded a broad absorption bleaching at $\lambda = 500$ nm that decays exponential with a constant time $\tau = 1.2 \pm 0.1$ ns. This indicates that, upon an excitation at $\lambda_p = 355$ nm of the $[\text{Fe}(\text{phen})_3]^{2+}$ complex, we induced a LS \rightarrow HS photo switching.

To confirm that the relaxation process and to determine the relaxation constants, we performed two color femtosecond time resolved absorption experiments, exciting the $[\text{Fe}(\text{phen})_3]^{2+}$ complex at $\lambda = 320$ nm. Figure 3c presents the data we recorded for the $[\text{Fe}(\text{phen})_3]^{2+}$ complex. It is presented against the data we previously presented elsewhere [18], where we excited these sample at $\lambda_p = 480$ nm and probed its transient absorption at $\lambda = 500$ nm. The two recorded kinetics are almost similar. Therefore in agreement with previous works [13,15,17,18], we concluded that upon excitation at either 480 nm or 320 nm, the kinetics of the $[\text{Fe}(\text{phen})_3]^{2+}$ complex associated to the LS \rightarrow HS photo switching is the following: ${}^1\text{MLCT} \rightarrow {}^3\text{MLCT} \rightarrow {}^5\text{T}_2$ (Figure 6a).

In conclusion, for both $[\text{Fe}(\text{2 CH}_3\text{ phen})_3]^{2+}$ and $[\text{Fe}(\text{phen})_3]^{2+}$ complexes, the excitation at $\lambda_p = 480$ nm selectively induces the LS \rightarrow HS photo switching. We have also shown that such a LS \rightarrow HS photo switching can be recorded by an excitation of the $[\text{Fe}(\text{phen})_3]^{2+}$ complex at both $\lambda_p = 355$ nm or $\lambda_p = 320$ nm. In agreement with previous work [13,15,17,18], we propose that the mechanism responsible for the LS \rightarrow HS state photo switching for the $[\text{Fe}(\text{2 CH}_3\text{ phen})_3]^{2+}$ complex upon an excitation results from the following cascade on the excited state hyper surface: ${}^1\text{MLCT} \rightarrow {}^3\text{MLCT} \rightarrow {}^5\text{T}_2$.

5. Is it possible to record HS \rightarrow LS photo-switching?

According to the previous experiment, one may expect that an excitation of the $[\text{Fe}(\text{2 CH}_3\text{ phen})_3]^{2+}$ complex at $\lambda_p \sim 355$ nm induces a LS \rightarrow HS photo switching. Hence, upon excitation of the $[\text{Fe}(\text{2 CH}_3\text{ phen})_3]^{2+}$ complex at $\lambda_p = 355$ nm, one naively expected to record a transient absorption spectrum similar to the one presented in Figure 2. Our experimental result presented in Figure 4a reveals that this is not the case. While this signal is weak and is more than an order of magnitude smaller than the signal we recorded for the $[\text{Fe}(\text{phen})_3]^{2+}$, we have been able to extract the most important trends. Upon excitation of $[\text{Fe}(\text{2 CH}_3\text{ phen})_3]^{2+}$ complex at $\lambda_p = 355$ nm, an absorption band centered at about $\lambda = 500$ nm as well as a weak bleaching at $\lambda \sim 550$ nm and $\lambda \sim 560$ nm appear.

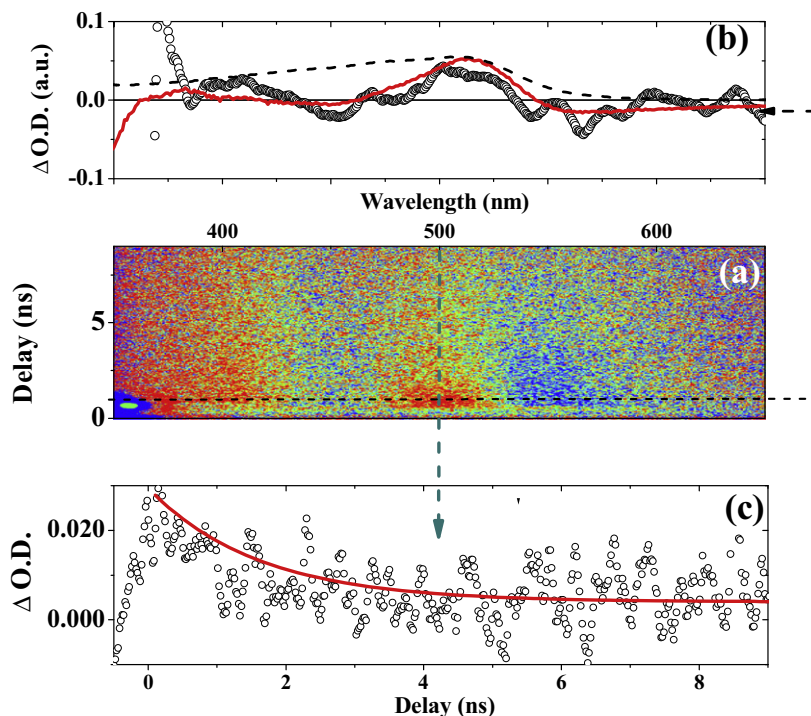


Figure 4. (a): Time resolved differential absorption spectrum of the $[\text{Fe}(\text{2 CH}_3\text{-phen})_3]^{2+}$ complexes after its excitation at $\lambda_p \sim 355$ nm. (b): (o) Differential absorption spectrum recorded one nanosecond after excitation. Dashed line: computed absorption spectra of the $[\text{Fe}(\text{2 CH}_3\text{-phen})_3]^{2+}$ complex in the LS state. Solid line: computed absorption spectra considering bleaching of the HS state and population of the LS state upon excitation of the of the $[\text{Fe}(\text{2 CH}_3\text{-phen})_3]^{2+}$ complex (c): Relaxation kinetic of the differential absorption spectrum at $\lambda \sim 500$ nm. The solid line is a fitting of the relaxation considering a mono-exponential decay with a constant time of 3.6 ns. In figures b and c the vertical scale is in arbitrary units.

Moreover, a long lasting absorption centered at 400 nm also appears and remains up to 10 ns after the photo excitation. This is clearly at variance with the results presented in Figure 2 and stresses that besides the expected LS \rightarrow HS photo switching other processes largely dominate.

This result is however not completely surprising. Indeed, as we previously mentioned, only 20% (resp. 80%) of the $[\text{Fe}(\text{2 CH}_3\text{ phen})_3]^{2+}$ complexes are in the LS (resp. HS) state. Moreover the used excitation wavelength ($\lambda = 355$ nm) is close to the $^5\text{T}_2 \rightarrow ^5\text{MLCT}$ absorption band [18,28]. Hence one should not completely discard a HS \rightarrow LS photo switching induced upon excitation. To put into the light the phenomenon that could take place, we have simulated the atypical absorption shown in Figure 4b (dotted line). The latter was recorded one nanosecond after the photo excitation. We first considered the increase of the LS population of the $[\text{Fe}(\text{2 CH}_3\text{ phen})_3]^{2+}$ complex. This should result in an increase of the $^1\text{A}_1 \rightarrow ^1\text{MLCT}$ absorption band. As the shape and amplitude of this latter was unknown, a first estimation of it was deduced from the stationary spectra of the $[\text{Fe}(\text{phen})_3]^{2+}$ complex (Figure 1a). However, such estimation neglects the larger absorption of the 2 CH_3 phen group in the near UV spectral range (Figure 1b). To account for this effect, the static absorption of the 2 CH_3 phen group was multiplied by three (i.e. the number of ligands attached to each $[\text{Fe}(\text{2 CH}_3\text{ phen})_3]^{2+}$ complex) and added to the estimated spectrum. The result of this latter computation is presented in dashed line in Figure 4b (dashed line). We basically put into evidence a large absorption band that is similar to the $^1\text{A}_1 \rightarrow ^1\text{MLCT}$ absorption band slightly broadened in the UV spectral range. Now it is important to stress that this analysis indicates that the HS \rightarrow LS photo switching cannot account, on its own, for the transient absorption spectrum. As mentioned above in Figure 4a, upon excitation we recorded a long lasting absorption centered along an absorption band of the 2 CH_3 phen group at $\lambda = 400$ nm. Consequently, we also considered that, besides HS \rightarrow LS photo switch

ing, a photo bleaching of the HS state associated to a photo dissociation of the complex could take place [27]. Indeed, we were able to well reproduce the transient absorption spectrum using the following procedure: the computed absorption spectrum of the $[\text{Fe}(\text{2 CH}_3\text{ phen})_3]^{2+}$ in the LS state (solid line Figure 4b) was multiplied by 0.2 and we subtracted to it the experimental absorption of the $[\text{Fe}(\text{2 CH}_3\text{ phen})_3]^{2+}$ (Figure 1a). The latter was previously multiplied by 0.8. In other words, we considered that upon excitation 4/5 of the photo excited HS complexes are photo dissociated while 1/5 are brought in the LS state. It is interesting to notice that this procedure makes it possible to well reproduce our experimental result. Accordingly, this transient absorption measurement should convey some spectral fingerprints of both the photo dissociation and the HS \rightarrow LS photo switching. For instance, as a first order approximation, one could consider that the increase of the absorption at $\lambda = 500$ nm can be regarded as the direct signature of the HS \rightarrow LS photo switching whereas the decrease of the absorption below $\lambda = 560$ and 450 nm can be related to the photo dissociation. It is also important to stress that our transient absorption experiment also put into light the last relaxation steps of these processes. Indeed as shown in Figure 4c, the relaxation of the photo induced absorption at $\lambda = 500$ nm is well reproduced assuming a single exponential decay with a constant time $t = 3.6 \pm 0.1$ ns. According to our first order approximation, it indicates that the $[\text{Fe}(\text{2 CH}_3\text{ phen})_3]^{2+}$ complex photo excited in the LS state relaxes back to the HS state within 3.6 ns.

To analyze in more details the kinetics giving rise to the transient absorption presented in Figure 4, we performed two color femtosecond time resolved absorption experiments, exciting the $[\text{Fe}(\text{2 CH}_3\text{ phen})_3]^{2+}$ complexes at $\lambda_p = 330$ nm. Figure 5 presents the data we recorded probing the sample at $\lambda = 500$ nm (Figure 5a) and $\lambda = 550$ nm (Figure 5b). One can notice that upon excitation, we recorded a large absorption at both probe wavelengths. The photo induced absorption is almost instantaneous and is basically

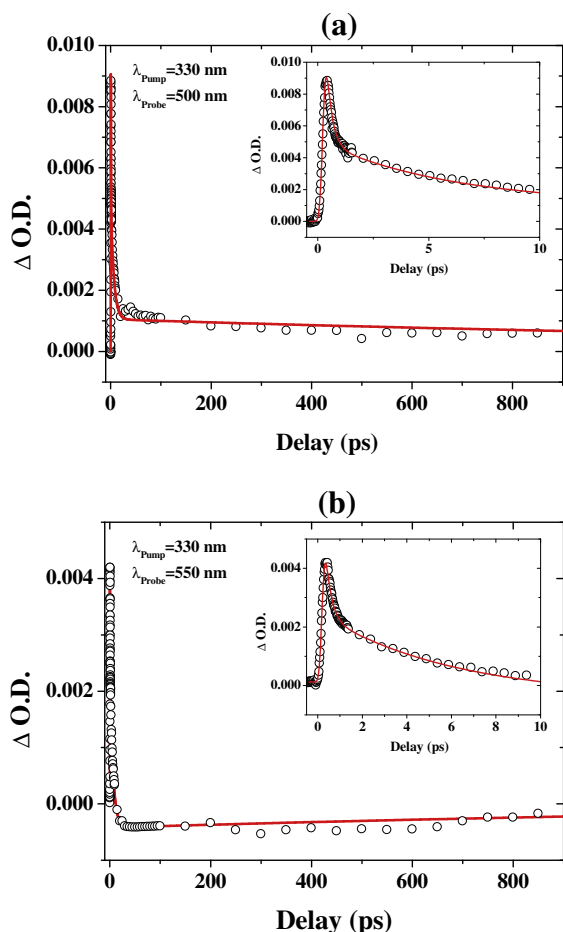


Figure 5. Evolution of the differential absorption recorded at $\lambda \sim 500$ nm (a) and $\lambda \sim 550$ nm (b) after the excitation of a $[\text{Fe}(\text{2 CH}_3\text{-phen})_3]^{2+}$ solution by a 100 fs laser pulse centered at 330 nm. The respective inset graphs show the evolution of the signal record on the 10 ps time scale.

limited by the integral overlap between the pump and the probe pulses. Then the absorption rapidly decreases. A fit of the data with indicates the fast relaxation proceeds with two time constant (so lid lines Figure 5a and b). The first time constant $t_2 = 250 \pm 40$ fs at $\lambda = 550$ nm and $t_2 = 200 \pm 30$ fs at $\lambda = 500$ nm. The second time constants are $t_3 = 7.0 \pm 0.5$ ps at 550 nm and $t_3 = 5.1 \pm 0.3$ ps at 500 nm. After few picoseconds and in agreement with Figure 4, we record a residual absorption (resp. bleaching) at 500 nm (resp. 550 nm). This latter absorption or bleaching relaxes on the nanosecond time scale. We were able to fit all these relaxations with a constant time $t_4 = 3.6 \pm 0.1$ ns.

6. Discussion

We can clearly state that for both $[\text{Fe}(\text{2 CH}_3\text{ phen})_3]^{2+}$ and $[\text{Fe}(\text{phen})_3]^{2+}$ complexes, the excitation at $\lambda_p = 480$ nm around the maximum of the MLCT absorption band selectively induces the LS \rightarrow HS photo switching. We have also shown that such a LS \rightarrow HS photo switching can be recorded by an excitation of the $[\text{Fe}(\text{phen})_3]^{2+}$ complex at both $\lambda_p = 355$ nm or $\lambda_p = 320$ nm in the blue edge of the MLCT absorption spectrum of this compound. The mechanism responsible for the LS \rightarrow HS state photo switching for these complexes results from the following cascade on the excited state hyper surface: $^1\text{MLCT} \rightarrow ^3\text{MLCT} \rightarrow ^5\text{T}_2$.

The analysis of the nanosecond, picosecond and femtosecond relaxation kinetics of $[\text{Fe}(\text{2 CH}_3\text{ phen})_3]^{2+}$ complex excited in the blue edge of its MLCT absorption spectrum of this compound

is very difficult for two reasons: firstly both complex in HS and LS state can be photo excited and, secondly, many different photo induced processes are taking place. Hence, to simplify the analysis of the signal we have made the following assumption. Since we could reproduce the transient absorption spectrum presented in Figure 4 neglecting the LS \rightarrow HS photo switching we decided to discard this contribution to the signal presented in Figure 5. In other words, we considered that at the used excitation wavelength, most of the signal we recorded is related to the 80% of the complex initially in the HS state. Under this approximation,

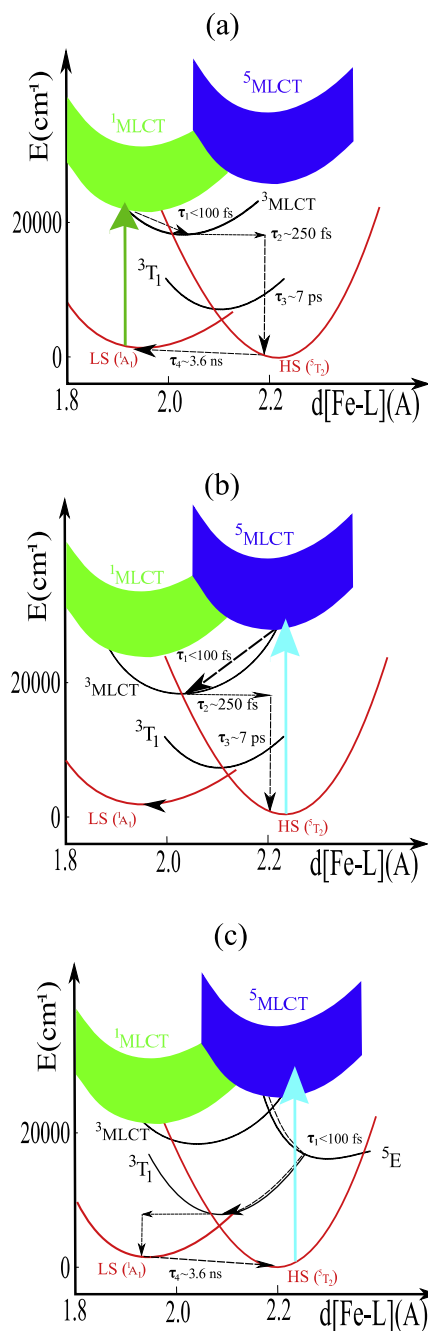


Figure 6. Energy levels and non-radiative relaxations paths identified for the $[\text{Fe}(\text{2 CH}_3\text{-phen})_3]^{2+}$ complex dissolved in acetonitrile. The solid and dashed arrows represent the allowed and forbidden optical transitions, respectively. (a) Relaxations path identified after photo-excitation of the LS state. (b) Primary relaxation path after photo-excitation of the HS state. According to this path the complex never reaches the LS state. (c) Suggested relaxation path identified after photo-excitation of the HS state. According to this relaxation path the complex reaches the LS state and then relaxes back to the HS state.

and upon laser excitation, we should record a ${}^5T_2(\text{HS}) \rightarrow {}^5\text{MLCT}$ transition. Now, according to computation performed on a similar compound by Graaf and Sousa, this ${}^5\text{MLCT}$ state is efficiently coupled to the ${}^3\text{MLCT}$ triplet state. Hence upon excitation, this triplet state can be very efficiently populated. It will therefore largely contribute to the transient absorption on the femtosecond time scale. As previously shown [13,15,17,18], the population of the ${}^3\text{MLCT}$ state happens on a time scale ~ 30 fs and therefore occurs within the pump probe pulse time overlap (~ 100 fs). Once in ${}^3\text{MLCT}$ state, the complexes relax very rapidly toward the HS (5T_2) state where they are lived in a highly excited vibrational state denoted ${}^5T_2^*$. We attributed the relaxation recorded with a ~ 220 fs time constant for the probe wavelengths $\lambda = 500$ and $\lambda = 550$ nm to the ${}^3\text{MLCT} \rightarrow {}^5T_2^*$ transition. Finally, we attributed the 7 ps time constant recorded at $\lambda = 500$ nm to the relaxation of the vibrationally excited molecules in the HS state. These processes are summarized in Figure 6b.

According to the latter relaxation kinetics, after few picoseconds, the $[\text{Fe}(\text{2 CH}_3 \text{ phen})_3]^{2+}$ complex should be back in the HS state and the absorption of the solution should remain unchanged. Figures 4 and 5 indicates this is clearly not the case. Therefore, while the relaxation kinetics presented in Figure 6b is very likely and may largely contribute to the signal at the early stage, it cannot account for the population of the LS state or the bleaching of the HS state. Hence, one has to consider another relaxation channel. A relaxation channel that is compatible with the energy level diagram proposed by Graaf and Sousa can be the following [28]: ${}^5\text{MLCT} \rightarrow {}^5E \rightarrow {}^3T_1 \rightarrow {}^1A_1$. In other words, one should also consider that upon excitation, part of the photo excited complexes relaxes through a d-d ligand field state. This latter assumption is interesting since, in other iron(II) compounds, the most likely candidate for the photo dissociative state are d-d the ligand field states [27]. Therefore, once in the 5E or 3T_1 state, the complex may be dissociated or brought in the LS state. According to the computation we made to simulate the transient spectrum in Figure 4b, 80% of the complex in the 5E or 3T_1 state should be dissociated and 20% should relax towards the LS state. According to our experimental data, it is difficult for to evaluate the branching ratio between the two relaxation channels (${}^5\text{MLCT} \rightarrow {}^5E \rightarrow {}^3T_1 \rightarrow {}^1A_1$ and ${}^5\text{MLCT}_a \rightarrow {}^3\text{MLCT} \rightarrow {}^5T_2^* \rightarrow {}^5T_2$). The weak amplitude of the signal recorded in Figure 4 indicates that the photo dissociation of the complex or photo induced population of the LS state have a weak quantum efficiency. While we could evaluate the constant time associated to the HS \rightarrow LS photo switching kinetics, we can clearly state that the 3.6 ns time constant we recorded in Figures 4 and 5 can be attributed to the time it takes for the $[\text{Fe}(\text{2 CH}_3 \text{ phen})_3]^{2+}$ complexes to reach the thermal equilibrium. It is likely related to ${}^1A_1 \rightarrow {}^5T_2$ relaxation process. Such an assignment is in good agreement with the measurements presented in Figures 2 and 3 where the complex was excited at $\lambda_p = 500$ nm. This implies that the recombination of the photo dissociated 2 CH₃ phen ligand occurs on a longer time. This assumption does well agree with the long lasting absorption presented in Figure 4 at $\lambda = 400$ nm, a wavelength corresponding to this ligand absorption band (Figure 1b). The ${}^5\text{MLCT} \rightarrow {}^5E \rightarrow {}^3T_1 \rightarrow {}^1A_1 \rightarrow {}^5T_2$ relaxation process is summarized in Figure 6c.

7. Conclusions

In conclusion, by means of ultrafast pump probe optical spectroscopy we have put into light both the LS \rightarrow HS as well as the

HS \rightarrow LS photo switching of the $[\text{Fe}(\text{2 CH}_3 \text{ phen})_3]^{2+}$ complex dissolved in acetonitrile. We have demonstrated that a selective switching from the LS state to the HS state is possible. We have also shown that it is possible to increase the population of the LS state exciting these complexes by near UV pulses. Finally we have proposed different relaxation processes that account for our measurements.

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