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Theoretical Study of the Light-Induced Spin Crossover Mechanism in $[\text{Fe}(\text{mtz})_6]^{2+}$ and $[\text{Fe}(\text{phen})_3]^{2+}$

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ABSTRACT: The deactivation pathway of the light-induced spin crossover process in two Fe(II) complexes has been studied by combining density functional theory calculations for the geometries and the normal vibrational modes and highly correlated wave function methods for the energies and spin–orbit coupling effects. For the two systems considered, the mechanism of the photoinduced conversion from the low-spin singlet to the high-spin quintet state implies two intersystem crossings through intermediate triplet states. However, for the $[\text{Fe}(\text{mtz})_6]^{2+}$ complex, the process occurs within few picoseconds and involves uniquely metal-centered electronic states, whereas for the $[\text{Fe}(\text{phen})_3]^{2+}$ system the deactivation channel involves both metal to ligand charge transfer and metal-centered states and takes place in a femtosecond time scale.

INTRODUCTION

The interest in molecular based materials with photoswitchable properties has increased in the last years due to their potential use in technological applications, such as sensors or optical memory devices.^{1–4} Among these materials, spin crossover (SCO) systems based on transition metal molecular complexes have been extensively studied because their properties can be optically switched in an extremely short time scale.⁵ In fact, at low temperatures the spin state of the metal can be changed from a low-spin (LS) ground state to a high-spin (HS) metastable state by light irradiation. This phenomenon is known as light-induced excited spin state trapping (LIESST)⁶ and was initially found in Fe(II) complexes^{6–10} and later observed in systems containing Fe(III)^{11–14} and Ni(II).^{15–17} A broad range of Fe(II)-based materials have been investigated both in solution and in the solid state, where cooperative effects are of interest. Particularly, six-coordinated iron(II) complexes with nitrogen-donor ligands in a nearly octahedral geometry have been the subject of intense research because these systems provide the largest structural changes under spin conversion and, therefore, favor cooperative transitions in the solid state. As a matter of fact, the spin crossover process in Fe(II)–N₆ complexes from the LS (¹A₁) ground state to the HS (⁵T₂) state is accompanied by an enlargement of the Fe–N distance of around 0.2 Å due to the occupation of the antibonding e orbitals in the quintet HS state.¹⁸ The study of the light-

induced spin crossover process in Fe(II) complexes from the singlet LS ground state to the quintet HS state has received much attention. The mechanism of the process has been qualitatively described by Hauser.⁶ After irradiation of the system into the LS absorption bands at low temperatures, the HS state is populated through a double intersystem crossing involving intermediate triplet states. In this photocycle, electronic states of different nature may be involved. Those include states centered on the metal (metal-centered, MC), states centered on the ligand (ligand-centered, LF), or states that involve excitations from one to the other or vice versa, i.e., metal to ligand charge transfer (MLCT) or ligand to metal charge transfer (LMCT) states. Hence, the photophysics of the spin conversion is an intricate problem that results from the interplay of several factors: electronic states of different character play a role, important structural changes go along the conversion, and various nonradiative processes are involved, such as internal conversion (IC), that is, transitions between electronic states of the same spin; intersystem crossing (ISC), which involves electronic states of different spin multiplicities; and intramolecular vibrational redistribution (IVR), where the vibrational energy is redistributed between different vibrational

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modes. For these reasons, together with the extremely short time scale of the spin conversion, a detailed interpretation of the photophysics of the process has not been possible until recently. The development of ultrafast spectroscopic techniques in the last 15 years opened the possibility to explore phenomena on the time scale of molecular vibrations.^{5,19} Progress on optical and X-ray techniques, as pump–probe transient absorption spectroscopy,^{20,21} ultrafast X-ray absorption and emission spectroscopies,^{22–24} and ultrafast fluorescence,²⁵ has been crucial to get insight into the mechanisms of photophysical and photochemical processes in transition metal complexes with resolution in the femtosecond scale. Although the experimental information acquired by these techniques is of key importance, the in depth understanding of these processes is only possible in combination with state-of-the-art computational methodologies.

A paradigmatic system that has been extensively studied, both by experiment and by means of computational approaches, is the iron(II) tris(bipyridine) complex in aqueous solution, $[\text{Fe}(\text{bpy})_3]^{2+}$. It is observed that by irradiating with visible light, the system is excited to the $^1\text{MLCT}$ state and afterward, it decays into the HS MC $^5\text{T}_2$ state in a femtosecond time scale with almost unity quantum yield. A large number of studies have been performed to ascertain the steps of the mechanism and the time scale of the photoinduced SCO process. From these studies, different interpretations have been proposed. Some authors claim that a first step involves singlet to triplet conversion within the MLCT manifold and subsequently a direct deactivation from the $^3\text{MLCT}$ to the $^5\text{T}_2$ state takes place.^{19,21,24,26,27} Alternatively, mechanisms involving either intermediate Fe-centered triplet states^{25,28–30} or $^5\text{MLCT}$ states³¹ have also been suggested.

In this work, we study the light-induced spin crossover process in two Fe(II) systems by means of ab initio computational methods. The computational approach is based on a combination of density functional theory (DFT) calculations for the geometries and vibrational frequencies of the relevant electronic states, with multiconfigurational wave function calculations that allow us to compute accurate electronic energies and spin–orbit coupling matrix elements of the spin states involved.^{28,29,32,33} From these data, intersystem-crossing rate constants can be derived from a time-dependent approach based on Fermi's golden rule.³⁴

Two different Fe(II)– N_6 isolated complexes have been studied (Figure 1). First, the $[\text{Fe}(\text{mtz})_6]^{2+}$ complex, where mtz refers to the 1-methyltetrazole monodentate ligand. In fact, this system is a model compound of the $[\text{Fe}(\text{ptz})_6]^{2+}$ complex, with ptz = 1-propyltetrazole, which has been shown to undergo light-induced spin crossover both in neat solid state compounds, like $\text{Fe}(\text{ptz})_6(\text{BF}_4)_2$,¹⁰ and in diluted systems, as $\text{Zn}_{1-x}\text{Fe}_x(\text{ptz})_6(\text{BF}_4)_2$.³⁵ From these studies, it was concluded that after excitation into the absorption bands of the singlet LS state, the quintet HS state is populated via two intersystem crossings involving the intermediate MC $^3\text{T}_1$ state. The intersystem crossing rate constants were estimated to be in the range 10^{10} to 10^{12} s^{-1} with a branching ratio from the $^3\text{T}_1$ state to the $^1\text{A}_1$ ground state and $^5\text{T}_2$ state of approximately 1:4. Recently, the intermediate states of the LIESST and reverse-LIESST pathways in the $\text{Fe}(\text{ptz})_6(\text{BF}_4)_2$ SCO compound have been elucidated. In both processes, triplet states centered on the iron are involved. In particular, the lifetime of the $^3\text{T}_2$ intermediate state of the LIESST process was estimated to be of

Figure 1. Molecular complexes investigated in this study. Fe is in the center of the complexes, represented by a light brown sphere, black spheres represent C, blue is N and pink is H.

1.2 ps, whereas the $^3\text{T}_1$ plays a role in the reverse-LIESST with a decay time of 39 ps.³⁶

The second material studied is a bidentate Fe(II) system, the $[\text{Fe}(\text{phen})_3]^{2+}$ complex, with phen = 1,10-phenanthroline (Figure 1). The photoinduced spin conversion of this system in solution has been studied by transient absorption spectroscopy.³⁷ After initial excitation of the system to the singlet MLCT band, the experimental data suggest a very fast transition to the triplet MLCT band, within less than 100 fs, and subsequently the system decays into a vibrationally excited quintet HS state in about 220 fs. Vibrational cooling within the $^5\text{T}_2$ state is estimated to be around 8.6 ps and the final HS to LS relaxation is completed in ~ 1 ns (800 ps in water solution and 1.1 ns in acetonitrile). Hence, these authors suggested the following relaxation scheme: $^1\text{MLCT} \rightarrow ^3\text{MLCT} \rightarrow ^5\text{T}_2^* \rightarrow ^5\text{T}_2$, where $^5\text{T}_2^*$ refers to a vibrational excited state. The same mechanism has been proposed in an analogous study of a similar system, the $[\text{Fe}(\text{2CH-3phen})]^{2+}$ complex.³⁸

Here, the photocycle of the LS to HS conversion for these two complexes will be studied. It will be shown that the deactivation channel of the $[\text{Fe}(\text{phen})_3]^{2+}$ complex involves both MLCT and MC states and takes place in a femtosecond time scale, whereas the light-induced SCO in the $[\text{Fe}(\text{mtz})_6]^{2+}$ system occurs within a few picoseconds and involves exclusively MC electronic states.

METHODOLOGY

The accurate theoretical description of the light-induced SCO process requires the computation of several components. On one hand, optimized equilibrium geometries and vibrational frequencies for all the electronic states involved in the photocycle are needed. On the other hand, potential energy curves along the reaction coordinate that connects the LS with the HS state give insight in the deactivation mechanism. In addition, energy differences between the various electronic states and spin–orbit coupling matrix elements are needed to estimate the intersystem crossing rate constants between electronic states of different spin multiplicity. To achieve this goal, a combined computational approach using both DFT and wave function based methods has been proposed. This procedure has been successfully applied in a previous study of the deactivation process in the $[\text{Fe}(\text{bpy})_3]^{2+}$ complex²⁹ and the Fe(III) complex $[\text{Fe}(\text{qsal})_2]^+$, with $\text{Hqsal} = 2-[(8\text{-quinolinylimino)methyl}]phenol$.³⁹

Optimized geometries and vibrational frequencies have been computed within the DFT framework using the Perdew–Becke–Ernzerhof (PBE0) hybrid functional⁴⁰ and a triple- ζ valence plus polarization basis set,⁴¹ as implemented in the TurboMole 6.3 package.^{42,43} The geometry optimizations of the lowest singlet, triplet, and quintet states were performed using the standard unrestricted DFT formalism, and the vibrational frequencies were computed analytically within the harmonic approximation. Instead, the geometries of the excited states have been determined by time-dependent DFT (TD-DFT)^{44,45} calculations and the harmonic frequencies computed numerically. No symmetry restrictions were imposed in the DFT calculations.

The energies of the different spin states have been computed by means of a multiconfigurational wave function based method, the CASSCF/CASPT2 approach. One-dimensional CASPT2 potential energy curves along the reaction coordinate, defined as a linear interpolation between the HS and LS PBE0 optimized structures, have been computed. The effects of spin–orbit coupling on the relative energies between the different electronic states are only minor and have not been included. This approach has proved to accurately describe thermal and optical SCO processes in several materials.^{28,30,32,46–49} The CASSCF/CASPT2 method⁵⁰ is a two-step approach in which a second-order perturbation treatment is applied on a complete active space self-consistent field (CASSCF) reference wave function. This methodology is implemented in the MOLCAS 7.4 software.^{51,52} Atomic natural orbital basis sets, specifically derived to allow for relativistic effects, have been used^{53,54} with the following contraction scheme: (7s, 6p, 5d, 4f, 3g, 2h) for Fe, (4s, 3p, 1d) for the N atoms bonded to the Fe, (3s, 2p) for the remaining N and C atoms, and (2s) for H. The active space used to construct the CASSCF wave functions contains ten electrons distributed among 15 orbitals, the five 3d Fe orbitals, two e-like σ -bonding ligand orbitals, three ligand virtual orbitals of π^* character, and a second set of diffuse Fe-3d orbitals to account for the large electron correlation effects in the 3d-shell. This active space assures a proper and balanced description of the different MC and MLCT states.^{32,46,55} CASPT2 accounts for the remaining electron correlation by correlating all the electrons except the deep core electrons ($1s^2$ for N and C and $1s^2, 2s^2, 2p^6$ for Fe). In the second-order perturbative CASPT2 method, the standard zeroth-order Hamiltonian has been used.⁵⁶ Scalar relativistic effects were included using a Douglas–Kroll–Hess Hamiltonian^{57,58} whereas the spin–orbit coupling matrix elements between the various electronic states were computed by the spin–orbit state interaction approach using the CASSCF wave functions.^{59,60} For the $[\text{Fe}(\text{mtz})_6]^{2+}$ and $[\text{Fe}(\text{phen})_3]^{2+}$ systems studied here, the CASSCF/CASPT2 calculations were performed within the C_i and C_2 symmetry point groups, respectively. However, because the local geometry around the central atom is quasi octahedral, the electronic states were labeled according to the O symmetry group.

Intersystem crossing rate constants, k_{ISC} , have been determined by applying a procedure based on Fermi's golden rule and a time-dependent approach as implemented in the VIBES program.^{34,61} This methodology has been successfully applied to different kind of systems.^{29,62–64} Within this approximation, ISC rate constants can be calculated as

$$k_{\text{ISC}} = |\langle \Phi_{\text{I}} | \hat{H}_{\text{SO}} | \Phi_{\text{F}} \rangle|^2 \int_{-\infty}^{\infty} dt G(t) e^{it(\Delta E_{\text{IF}} + (1/2)\text{Tr} \Omega_{\text{I}})} \quad (1)$$

where Φ_{I} and Φ_{F} refer to the initial and final electronic states, ΔE_{IF} is the energy difference between both states, $\hat{H}^{\text{SO}}$ is the spin–orbit coupling operator, $G(t)$ is a time-dependent correlation function that contains information about the vibrational frequencies and normal coordinates, and Ω_{I} is a diagonal matrix formed by the vibrational frequencies of the initial state. The explicit formula of $G(t)$ is rather lengthy and the interested reader is referred to ref 34 for more detailed information. Here, we only remark that $G(t)$ contains, apart from the diagonal matrices Ω_{I} and Ω_{F} , also the Duschinsky matrix $\mathbf{J}$ and the translation vector $\mathbf{D}$ that are used to express the normal coordinates of the final state $\mathbf{Q}_{\text{F}}$ in those of the initial state $\mathbf{Q}_{\text{I}}$ by the so-called Duschinsky transformation $\mathbf{Q}_{\text{F}} = \mathbf{J}\mathbf{Q}_{\text{I}} + \mathbf{D}$. The combination of energy difference between initial and final state, the size of the off-diagonal matrix elements of $\mathbf{J}$, and the norm of the translation vector $\mathbf{D}$ determines how large the final vibrational overlap between the different electronic states will be. Here, the relative energies of the different electronic states, ΔE_{IF} , and the spin–orbit coupling matrix elements have been computed within the CASSCF/CASPT2 approach. Vibrational frequencies and normal coordinates within the harmonic approach have been obtained from PBE0 DFT calculations.

RESULTS AND DISCUSSION

Light-Induced SCO in the $[\text{Fe}(\text{mtz})_6]^{2+}$ Complex. The geometries of the $^1\text{A}_1$ ground state and the metastable $^5\text{T}_2$ HS state of the $[\text{Fe}(\text{mtz})_6]^{2+}$ complex have been computed by means of DFT calculations in previous works.^{33,49} It was shown that although interatomic distances, and particularly, Fe–N distances, were in accordance with experiment, all DFT functionals considered lead to unphysical rotation angles of the methyltetrazole ligands, $\sim 45^\circ$, to minimize steric effects. This results from the lack of environment effects of the rest of the crystal that counterbalance the steric repulsion. Taking into account such effects through an embedded two-center complex, the rotation angles are well reproduced, with an average angle for the active site around 12° . To take into account this geometrical parameter, the CASPT2 potential energy curves of all the relevant electronic states have been computed along a reaction coordinate corresponding to the symmetric stretching mode of the Fe–N₆ coordination sphere fixing the rotation angle of the ligands at 10° . At each scan of the reaction coordinate, the geometry of the ligands has been optimized by PBE0 and the energy computed by CASPT2. The computed vertical excitation energies for the lowest transitions from the LS and HS states are collected in Table 1. These excitations involve electronic states centered in the Fe(II) atom, other excitations involving MLCT or LMCT states lie at higher energies for this particular system. As can be seen from Table 1, the $[\text{Fe}(\text{mtz})_6]^{2+}$ complex accurately reproduces the exper-

Table 1. Vertical CASPT2 Excitation Energies (cm^{-1}) for the $[\text{Fe}(\text{mtz})_6]^{2+}$ Complex and Experimental Data for $\text{Fe}(\text{ptz})_6(\text{BF}_4)_2$ ¹⁰

transition	CASPT2	experiment
$^1\text{A}_1 \rightarrow ^1\text{T}_1$	17509	18200
$^1\text{A}_1 \rightarrow ^3\text{T}_1$	9646	10280
$^1\text{A}_1 \rightarrow ^3\text{T}_2$	14361	14330
$^5\text{T}_2 \rightarrow ^5\text{E}$	12682	11760

imental data corresponding to the $\text{Fe}(\text{ptz})_6(\text{BF}_4)_2$ system, meaning that the different substituents (methyl or propyl) of the tetrazole rings have a negligible effect on the optical transitions centered on the metal. Particularly, the first step in the LIESST process, the excitation from the $^1\text{A}_1$ ground state to the first excited singlet, $^1\text{T}_1$, is well reproduced.

The CASPT2 one-dimensional potential energy curves for the lowest singlet, triplet, and quintet states are plotted in Figure 2. Because all these electronic states arise from the

Figure 2. CASPT2 potential energy curves of the lowest electronic states of $[\text{Fe}(\text{mtz})_6]^{2+}$ as a function of the Fe–N distance.

different distributions of the $3d^6$ electrons in the $\text{Fe}(\text{II})$ atom, the standard active space of 10 electrons in 12 orbitals⁵⁵ suffices and there is no need to add extra occupied or virtual ligand orbitals. As can be seen in Figure 2, the Fe–N equilibrium distance for the LS state is 1.95 Å and the corresponding value for the HS state is 0.2 Å larger, as expected in $\text{Fe}(\text{II})\text{--N}_6$ complexes. The excited singlet, $^1\text{T}_1$, and the intermediate triplet states, $^3\text{T}_2$ and $^3\text{T}_1$, show a minimum at an intermediate Fe–N distance, around 2.05 Å, due to the occupation of an antibonding e orbital in a $(t_2^5e^1)$ configuration. The Jablonski diagram of the electronic states involved in the spin conversion (Figure 2) shows that after light irradiation, the excited $^1\text{T}_1$ state is populated. This state crosses with the final HS $^5\text{T}_2$ in the Franck–Condon region, and the intermediate triplet states also interact with the HS state. To quantify these interactions, inclusion of spin–orbit coupling is necessary. In Table 2 the square of the spin–orbit coupling matrix elements for the possible interactions are presented. These elements have been computed at the geometry corresponding to the LS state, i.e., in the Franck–Condon region. Nevertheless, it has been demonstrated that spin–orbit coupling does not significantly change with the Fe–ligand distance, especially when MC states are involved.³² As can be seen in Table 2, all the values of the SO term are of similar orders of magnitude (between 10^4 and 10^5 cm^{-2}) except for the $^3\text{T}_2 \rightarrow ^1\text{A}_1$ transition. The spin–orbit

Table 2. Intersystem Crossing Rates between the Relevant Electronic States of $[\text{Fe}(\text{mtz})_6]^{2+}$ ^a

Φ_i	Φ_f	SO term (cm^{-2})	vibr term ($\text{cm}^{-2} \text{ s}^{-1}$)	$k_{\text{ISC}} (\text{s}^{-1})$	t
$^1\text{T}_1$	$^3\text{T}_2$	1.2×10^5	2.3×10^5	2.8×10^{10}	36 ps
$^3\text{T}_2$	$^1\text{A}_1$	5.3×10^2	1.6×10^6	8.5×10^8	1.2 ns
$^3\text{T}_2$	$^5\text{T}_2$	9.8×10^4	9.4×10^5	8.2×10^{10}	12 ps
$^1\text{T}_1$	$^3\text{T}_1$	1.6×10^4	5.3×10^1	8.5×10^5	>100 ns
$^3\text{T}_1$	$^1\text{A}_1$	9.8×10^4	1.0×10^8	9.8×10^{12}	102 fs
$^3\text{T}_1$	$^5\text{T}_2$	2.4×10^5	2.1×10^7	5.0×10^{12}	200 fs

^aThe spin–orbit and vibrational contributions (cf. eq 1) are separately given. t denotes the deactivation time.

coupling matrix element between these two states is strictly zero in the O_h point group by symmetry reasons. Here, due to the nearly octahedral symmetry of the compound, this term is not zero but of small value, $\sim 10^2 \text{ cm}^{-2}$. Regarding the SO term, the $^1\text{T}_1$ state populated after absorption shows important interactions with the lowest $^3\text{T}_2$ and $^3\text{T}_1$ intermediate states whereas there is no direct SO coupling between the singlet $^1\text{T}_1$ and the quintet $^5\text{T}_2$ state. To understand the photocycle and to quantify the time scale of the process, apart from the spin–orbit coupling term, the vibrational contribution as defined in eq 1 is needed. The results of this term along with the ISC rate constants are presented in Table 2. Inclusion of the vibrational contribution reveals that from the photoexcited $^1\text{T}_1$ state the system can cross to the $^3\text{T}_2$ state in 36 ps, whereas deactivation to the lower-lying $^3\text{T}_1$ state is not favored because the vibrational contribution is 4 orders of magnitude smaller. Because the geometrical structures of the two triplet states are very similar, the large difference in the vibrational term is explained by the larger energy difference between the $^1\text{T}_1$ and $^3\text{T}_1$ states. From the $^3\text{T}_2$ state, the complex could eventually decay either into the initial LS or into the HS, thus completing the spin conversion. Our results show that the decay to the $^5\text{T}_2$ HS is preferred because the ISC rate constant is 2 orders of magnitude larger than the corresponding deactivation to the initial LS state. On the basis of these results, the photoinduced spin conversion can be explained as follows: after populating the $^1\text{T}_1$ by light irradiation, the $^3\text{T}_2$ state is reached in 36 ps, and throughout a second ISC the $^5\text{T}_2$ is populated within 12 ps. According to this interpretation, the whole process takes place within 50 ps with a high quantum efficiency and involves two ISC, $^1\text{T}_1 \rightarrow ^3\text{T}_2 \rightarrow ^5\text{T}_2$. These results are in agreement with previous experimental studies, indicating that the process takes place in few picoseconds¹⁰ and with a recent study that pointed to the $^3\text{T}_2$ state as intermediate state in the LIESST process.³⁶

Examining the results in Table 2, it should be noticed that the highest ISC rate constants correspond to the deactivation from the lowest triplet state, $^3\text{T}_1$, to the LS and HS states. Both processes occur in the range of hundreds of femtoseconds. This fast channel can only be of importance if after excitation to the $^1\text{T}_1$ state, the $^3\text{T}_1$ state is populated. However, as previously commented, the direct $^1\text{T}_1 \rightarrow ^3\text{T}_1$ transition is not favored. An alternative path involving internal conversion from the $^3\text{T}_2$ to the $^3\text{T}_1$ state opens this possibility. Unfortunately, the time scale of the internal conversion within the two triplet states cannot be estimated, but previous studies gave evidence that this process is expected to be fast.²⁹ Under this assumption, a possible deactivation path involving two ISC and a IC is as follows: $^1\text{T}_1 \rightarrow ^3\text{T}_2 \rightarrow ^3\text{T}_1 \rightarrow ^5\text{T}_2$. This mechanism takes place in picoseconds, as experimentally measured; however, it leads

to a branching ratio that favors the LS ground state, with a value of 2:1 for the $^3T_1 \rightarrow ^1A_1$ and $^3T_1 \rightarrow ^5T_2$ conversions. This is contrary to the observed quantum efficiency that favors the HS state, and therefore, this fact plays against this proposal. However, the possibility that the two mechanisms commented here take place simultaneously cannot be ruled out.

Light-Induced SCO in the $[\text{Fe}(\text{phen})_3]^{2+}$ Complex. As a first step, a full geometry optimization of the ground state of the $[\text{Fe}(\text{phen})_3]^{2+}$ complex in vacuo has been performed by means of DFT PBE0 calculations. The resulting optimized geometry possesses D_3 symmetry with all Fe–N distances equal to 2.003 Å, which is in good agreement with the experimental average value of 1.983 Å.⁶⁵ The optimized structures for the rest of the electronic states involved in the light-induced spin conversion have been determined either by standard DFT calculations (lowest triplet and quintet states, 3T_1 and 5T_2) or by the TD-DFT methodology (singlet excited states, 1T_1 and $^1\text{MLCT}$). Only the lowest state of a given nearly degenerated manifold of states has been computed. It is assumed that the other states of the manifold have the same geometry and vibrational frequencies. For the 3T_1 and 5T_2 the optimized geometries slightly deviate from the D_3 point group. Average PBE0 optimized Fe–N distances for the 1T_1 and 3T_1 states are 2.101 and 2.109 Å, respectively, whereas for the quintet 5T_2 state it is 2.206 Å. As in the previous Fe(II) system, the Fe–N distance increases regularly ~ 0.1 Å when one electron is promoted from the nonbonding t_2 orbitals to an antibonding e orbital. It is important to notice that the average optimized Fe–N distance for the $^1\text{MLCT}$ state is 1.987 Å, that is, very close to the Fe–N distance in the 1A_1 ground state, in line with the fact that no antibonding e -like orbital is occupied in the lower $^1\text{MLCT}$ states. To obtain the optimal geometric parameters at the CASPT2 level of calculation, a hybrid DFT/CASPT2 approach as described before, has been applied. A scan of the Fe–N distance around the equilibrium distance has been performed, and at each point the geometry of the ligands was optimized by PBE0 calculations. In this way, the CASPT2 optimized Fe–N distance for the ground state turns out to be 1.92 Å, which is somewhat shorter than the value corresponding to a full PBE0 optimization. Equivalently, the Fe–N distances corresponding to the CASPT2 minimum for the 5T_2 and 3T_1 are 2.15 and 2.04 Å, respectively.

The vertical absorption spectrum from the 1A_1 ground state has been computed by means of CASPT2 calculations. At the LS geometry, the lowest excited singlet state is a MC state lying about 2.4 eV above the 1A_1 . However, for the $[\text{Fe}(\text{phen})_3]^{2+}$ complex, and at difference of the $[\text{Fe}(\text{mtz})_6]^{2+}$ system, the singlet MLCT states lie in the same energy region as the lowest singlet MC ligand field states. Indeed, the lowest $^1\text{MLCT}$ states span the energy range 2.5–3.0 eV. This is slightly higher, but very close, to the peak measured in the absorption spectrum of $[\text{Fe}(\text{phen})_3]^{2+}$ in acetonitrile, at approximately 2.5 eV.⁶⁶ The $^3\text{MLCT}$ states form a band in the same energy region as the $^1\text{MLCT}$ states and with the same Fe–N equilibrium distance. The $^5\text{MLCT}$ states, instead, appear at much higher energies and spread over 3.8–4.6 eV above the LS state, and therefore, these states are not involved in the LIESST process. Finally, the lowest triplet Fe-centered state, 3T_1 , appears at 1.4 eV above the 1A_1 state; however, a singlet–triplet transition is not allowed by the dipole selection rule. Hence, the first state populated in the $[\text{Fe}(\text{phen})_3]^{2+}$ complex by light irradiation is the $^1\text{MLCT}$ state, as found in a similar bidentate ligand

complex, the $[\text{Fe}(\text{bpy})_3]^{2+}$ system. This 1A_1 to singlet $^1\text{MLCT}$ excitation carries intensity because it is symmetry allowed in a perfect octahedral geometry, whereas the ligand field 1A_1 to 1T_1 transition is symmetry forbidden and only displays a weak signal in the absorption spectrum.

To elucidate the relaxation mechanism, all states that can be involved in the process have to be taken into account to analyze all the possible deactivation paths. Spin–orbit coupling matrix elements involving all low-lying electronic states have been calculated. These include the 16 lowest singlet, triplet, and quintet states, which leads to 144 spin states and the corresponding 144×144 spin–orbit matrix. The results of the spin–orbit contribution, together with the vibrational term and the rate constant for the intersystem crossings between the relevant electronic states, are reported in Table 3. Deactivation

Table 3. Intersystem Crossing Rates between the Relevant Electronic States of $[\text{Fe}(\text{phen})_3]^{2+}$ ^a

Φ_i	Φ_f	SO term (cm^{-2})	vibr term ($\text{cm}^2 \text{s}^{-1}$)	k_{ISC} (s^{-1})	t
$^1\text{MLCT}$	$^3\text{MLCT}$	1.1×10^5	2.6×10^8	2.8×10^{13}	36 fs
$^1\text{MLCT}$	3T_2	1.3×10^4	8.3×10^4	1.1×10^9	
$^1\text{MLCT}$	3T_1	1.4×10^4	6.0×10^7	8.1×10^{11}	>1 ps
$^3\text{MLCT}$	1A_1	2.5×10^3	4.7×10^4	2.6×10^8	
$^3\text{MLCT}$	5T_2	2.7×10^3	5.0×10^7	1.4×10^{11}	>1 ps
1T_1	3T_2	2.8×10^5	4.6×10^3	1.3×10^9	
3T_2	1A_1	2.0×10^4	6.0×10^0	1.2×10^5	
3T_2	5T_2	7.7×10^5	6.3×10^2	4.9×10^8	
1T_1	3T_1	1.7×10^4	2.6×10^7	4.5×10^{11}	>1 ps
3T_1	1A_1	8.2×10^5	5.7×10^4	4.7×10^{10}	
3T_1	5T_2	1.9×10^6	5.1×10^6	9.8×10^{12}	102 fs

^aThe spin–orbit and vibrational contributions (cf. eq 1) are separately given. t denotes the deactivation time.

times are also detailed when pertinent. In light of our results, after population of the $^1\text{MLCT}$ state by irradiation, the system most probably deactivates to the $^3\text{MLCT}$ manifold. As can be seen in Table 3, this process is favored both by a large spin–orbit coupling term and by vibrational terms, resulting in a large rate constant, $2.8 \times 10^{13} \text{ s}^{-1}$, and a deactivation time of 36 fs. This result is in agreement with transient absorption spectroscopy measures of $[\text{Fe}(\text{phen})_3]^{2+}$ in solution, which estimated the relaxation time toward the $^3\text{MLCT}$ state in less than 100 fs.³⁷ Other deactivation routes from the $^1\text{MLCT}$ to triplet MC states are 2 orders of magnitude slower, and therefore, less optimal. Once the $^3\text{MLCT}$ state is reached, this state can directly relax to either the 1A_1 LS ground state or the 5T_2 HS state. Relaxation back to the LS state is very slow, because the two contributions, vibrational and spin–orbit, are small. Alternatively, direct deactivation to the 5T_2 is favored by a large vibrational term; however, the small spin–orbit coupling between $^3\text{MLCT}$ – 5T_2 , $2.7 \times 10^3 \text{ cm}^{-2}$, hinders this path. This small direct SO coupling can be justified by the fact that the orbital occupation of the two electronic states differs by a double electron transfer, from a $t_2^4 e^1 L^1$ configuration of the $^3\text{MLCT}$ to a $t_2^4 e^2$ configuration in the 5T_2 . Nevertheless, on the basis of the present calculations, we cannot exclude the possibility that indirect spin–orbit terms, that is, SO mediated by other spin electronic states, could be of importance and make this channel viable. A different path to explain the relaxation from the $^3\text{MLCT}$ state to the HS state can involve

the Fe-centered 3T_1 state. The results in Table 3 show that the deactivation from the 3T_1 to the 5T_2 state is very effective and takes place in around 100 fs, whereas relaxation back to the 1A_1 is 2 orders of magnitude slower. A fast population of the 3T_1 state is only possible by internal conversion from the 3MLCT states, because the other possibilities, from either the 1MLCT or the 1T_1 states, exhibit deactivation times 1 order of magnitude larger than the measured ones. As a consequence, a plausible deactivation path could involve both MLCT and MC states as follows: $^1MLCT \rightarrow ^3MLCT \rightarrow ^3T_1 \rightarrow ^5T_2$, in which the first intersystem crossing implying singlet and triplet MLCT states takes place in 36 fs and the second ISC involving iron-centered states, 3T_1 and 5T_2 , occurs in 102 fs. As commented before, we have not estimated the time scale of the internal conversion between the 3MLCT and 3T_1 states, but this spin-allowed transition is expected to be very fast. In summary, the time scale of the deactivation process based on our results is in overall accord with the experimental observation that the process takes place in around 300 fs via 3MLCT states.

SUMMARY AND CONCLUSIONS

The mechanism of the photoinduced spin crossover process in two Fe(II) complexes has been studied by means of a combination of theoretical methods. Density functional theory calculations allow us to compute optimized geometries and vibrational spectra, multiconfigurational CASSCF and CASPT2 calculations give sufficiently accurate energies, spin–orbit coupling matrix elements, and relative energies, and intersystem crossing transition rate constants are derived by a time-dependent approach based on Fermi's golden rule. This integrated strategy permits us to describe the essential features of the light-induced spin conversion and helps to elucidate the mechanism of the process, in conjunction with the experimental information available. Specifically, the electronic states involved in the process can be assessed and the rates of the intersystem crossings quantified.

In this work, this methodology has been applied to two Fe(II) complexes, $[Fe(mt_z)_6]^{2+}$ and $[Fe(phen)_3]^{2+}$. The light-induced spin conversion in the $[Fe(mt_z)_6]^{2+}$ complex starts by populating the 1T_1 metal-centered state by photoirradiation. Metal to ligand charge transfer bands are too high in energy to be accessed. From the 1T_1 state, the HS state is reached within 50 ps with a high quantum efficiency following the path $^1T_1 \rightarrow ^3T_2 \rightarrow ^5T_2$. This interpretation implies two intersystem crossings between metal-centered states and sets the time scale of the process on the order of picoseconds. Both characteristics are in agreement with the experimental data available for the similar $[Fe(ptz)_6]^{2+}$ system.

In the $[Fe(phen)_3]^{2+}$ complex, irradiation of the LS state populates the singlet metal to ligand charge transfer band, 1MLCT . The 1MLCT and 3MLCT states show similar geometries and lie in the same energy region; therefore, a first deactivation step $^1MLCT \rightarrow ^3MLCT$ is favored and occurs within 36 fs. From this state, the process can proceed in two ways: either through an internal conversion to the Fe-centered 3T_1 state, that is, $^1MLCT \rightarrow ^3MLCT \rightarrow ^3T_1 \rightarrow ^5T_2$, or by a direct deactivation from the 3MLCT manifold to the final HS state, $^1MLCT \rightarrow ^3MLCT \rightarrow ^5T_2$. The first path requires that the internal conversion takes place in the femtosecond time scale and the second route is only possible if second-order spin–orbit coupling is of importance.⁶⁷

The different time scale of the LIESST process in the two complexes derives from the initial step in the deactivation. The $^1MLCT \rightarrow ^3MLCT$ intersystem crossing for $[Fe(phen)_3]^{2+}$ is extremely fast, whereas the $^1T_1 \rightarrow ^3T_2$ crossing for $[Fe(mt_z)_6]^{2+}$ is much slower. The subsequent steps occur on similar time scales in both complexes.

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