Photoinduced Low-Spin → High-Spin Mechanism of an Octahedral Fe(II) Complex Revealed by Synergistic Spin-Vibronic Dynamics

Mátýás Pápai*

ABSTRACT: The Fe(II) low-spin (LS; \(1A_1g, t_{2g}^6 e_{g}^0\)) → high-spin (HS; \(5T_{2g}, t_{2g}^4 e_{g}^2\)) light-induced excited spin state trapping (LIESST) mechanism solely involving metal-centered states is revealed by synergistic spin-vibronic dynamics simulations. For the octahedral [Fe(NCH)\(_6\)]\(^{2+}\) complex, we identify an initial \(\sim 100\) fs \(1T_{1g} \rightarrow 3T_{2g}\) intersystem crossing, controlled by vibronic coupling to antisymmetric Fe–N stretching motion. Subsequently, population branching into \(3T_{1g}, 5T_{2g}\) (HS), and \(1A_{1g}\) (LS) is observed on a subpicosecond time scale, with the dynamics dominated by coherent Fe–N breathing wavepackets. These findings are consistent with ultrafast experiments, methodologically establish a new state of the art, and will give a strong impetus for further intriguing dynamical studies on LS → HS photoswitching.

Photoinduced low-spin (LS) → high-spin (HS) transition in transition-metal complexes, known as light-induced excited spin state trapping (LIESST), has attracted great interest since its discovery in 1984. LIESST is an intriguing phenomenon both from the point of view of the fundamentals of excited-state processes and revolutionary applicational areas, such as molecular data storage. It is known that the LS-to-HS transition can also be triggered by varying the temperature, pressure, and magnetic field; in fact, the first discovery of these so-called spin-crossover (SCO) complexes is dated way back to 1931.

In the past two decades, the LIESST mechanism has been a very "hot" research topic; this is motivated by the fact that the gained knowledge may allow control of excited-state pathways and thus can lead to the design of improved functional molecules and technologies. In the case of switchable hexacoordinated complexes with a Fe\(^{II}\)N\(_6\) core, which by far dominate the known LIESST-exhibiting systems, irradiation of light converts the singlet ground state \([1A_{1g}(LS), t_{2g}^6 e_{g}^0]\) into a quintet metastable state \([5T_{2g}(HS), t_{2g}^4 e_{g}^2]\); thus, a \(\Delta S = 2\) net change of the spin momentum occurs. The LIESST mechanism was first investigated in 1991 by Hauser\(^5\) for the 1-propyltetrazole [Fe(ptz)\(_6\)]\(^{2+}\) pseudo-octahedral SCO Fe(II) complex, promoted to the lowest singlet metal-centered (MC) state. Utilizing UV/vis/near-IR absorption spectroscopy, he identified a triplet intermediate state, which at 10 K decays via branching into a quintet metastable state \([5T_{2g}(HS), 75\%]\) and the ground state \([1A_{1g}(LS), 25\%]\), occurring via intersystem crossing (ISC), as illustrated in Figure 1. More recently, for the Zn-doped crystal [Zn\(_{0.9}\)Fe\(_{0.1}\)(ptz)\(_6\)]\(^{2+}\), probed at 125 K by time-resolved absorption spectroscopy, Hauser and co-workers identified the upper triplet \(5T_{2g}\) as the intermediate state, which is formed from \(1T_{1g}\) in <150 fs and decays into the \(5T_{2g}\) HS state in 1.2 ps. The HS state is metastable at low temperatures (\(T < 50\) K), and its lifetime is determined by quantum-mechanical tunneling.

Despite these valuable mechanistic insights, several unknowns remain, in most cases, because of the ambiguities in the interpretation of the experimental data. An excellent example is the more complicated case of [Fe(bipy)\(_3\)]\(^{2+}\) (bipy = 2,2′-bipyridine), a LS Fe(II) complex, which became the LS ↔ HS photoswitching prototype for time-resolved investigations. [Fe(bipy)\(_3\)]\(^{2+}\) is converted to the HS state in <100 fs, initiated

Received: June 17, 2021
Published: September 9, 2021
by irradiation into the optically active singlet metal-to-ligand charge-transfer (MLCT) band. This <100 fs time scale and the HS lifetime (ca. 650 ps in aqueous solution) are consistent for various experimental studies, but it is strongly debated how the HS state is populated.⁷⁻⁹ A final consensus is yet to be established; in order to achieve this goal, theory, which has the potential to complement and support time-resolved experiments, has a crucial role. However, the computational art of the singlet-to-quintet transitions has so far been limited to analysis of the static potential energy surfaces (PESs)¹⁰/couplings¹¹ and estimation of the excited-state lifetimes by Fermi’s golden rule.¹²⁻¹⁴ Albeit often useful, these approaches face severe shortcomings when it comes to fast electronic relaxation such as LIESST, with a time scale comparable to that of nuclear motion. In fact, this nuclear–electronic coupling, leading to a dynamic mixing of the electronic states, is among the main sources for the complexity of the obtained time-resolved experimental data, which theory is intended to alleviate.

In this Communication, we present the first theoretical dynamics study on LS → HS photoswitching with excitation into 1MC states (1T₁g, [Fe(ptz)₆]²⁺ prototype; Figure 1). In order to achieve feasibility at a high computational level, we investigate the excited-state dynamics of [Fe(NCH)₆]²⁺, a well-established model¹⁴⁻¹⁷ for metastable Fe(II)-based SCO systems. Its validity, with a special emphasis on LIESST, is discussed in the Supporting Information (SI). Employing a synergistic spin-vibronic approach,¹⁸⁻¹⁹ we achieve an invaluable mechanistic understanding, whose adequacy is assessed and confirmed by its consistency with the above-discussed experiments.

Herein, we employ a synergistic approach, which exploits the complementary character of trajectory surface hopping (TSH; full dimensionality) and quantum dynamics (QD; fully quantum description). We utilize full-dimensional TSH on potentials computed on-the-fly to select the dominant nuclear degrees of freedom and QD on high-level ab initio (CASPT2) precomputed surfaces along the selected modes for the accurate simulation of LIESST excited-state dynamics. A brief methodological description is provided in the Computational Methods section, with details given in the SI.

Figure 2 presents the normal-mode activity of the vibrational motion, obtained from the excited-state TSH trajectories. As is clear from the figure, three modes, ν₁₁₅, ν₁₄₄, and ν₁₅₁, dominate the excited-state nuclear motion. As shown in Figure 3, all three modes have Fe–N stretching character, but while the 2-fold-degenerate ν₁₁ and ν₁₄ modes are antisymmetric, ν₁₅ is a totally symmetric (breathing) mode. These three Fe–N stretching modes are in excellent agreement with the natural choice of coordinates upon the occupation of e₈* antibonding orbitals, shown in Figure 1, in MC excited states.

Figure 4 shows the PESs along modes ν₁₅ and ν₁₄; the PESs along ν₁₁ are shown in Figure S7. While the ν₁₁ breathing mode is crucial to connect the LS (1A₈g) and HS (3T₂g) states (Figure 4a), it maintains the octahedral symmetry and does not allow the different singlet and triplet MC components to cross. The reason for this is that, in the singlet and triplet excited states, a single e₈* orbital is populated, which activates antisymmetric Fe–N stretching modes, while the ν₁₄ breathing mode is totally symmetric. Indeed, as seen in Figure 4b, the excited-state potentials split along ν₁₄, allowing the possibility of singlet–triplet ISC and triplet internal conversion (IC) via the intersection of the corresponding MC PESs.

**Figure 2.** Dynamic normal-mode activity, as determined from the standard deviation of nuclear displacements, projected onto the ground-state normal modes. This was obtained from the singlet–triplet TSH simulations. The labels of the three dominant normal modes, ν₁₁₅, ν₁₄₄, and ν₁₅₁, are depicted. As illustrated in Figure 3, the character of these three modes is Fe–N stretching.

**Figure 3.** Illustration of the three dominant modes of [Fe(NCH)₆]²⁺, ν₁₁₅ (antisymmetric Fe–N stretching), ν₁₄₄ (antisymmetric Fe–N stretching), and ν₁₅₁ (symmetric Fe–N stretching), identified by the TSH simulations. Also shown are the O₈ symmetry labels of the modes.

In Figure 5, we present the electronic population dynamics, as obtained from the three-dimensional QD simulation utilizing the selected modes and all relevant singlet–triplet–quintet states. As shown in the figure, the 1T₁₈ population decay has two components, characterized by the 39 and 168 fs exponential time constants. These time scales are in excellent agreement with the experimentally observed <150 fs ISC.⁶ As proposed by Marino et al.,⁶ the 1T₁₈ states indeed deactivate via the 3T₂g states. Subsequently, the excited-state population flows on a subpicosecond time scale to 3T₁₄ by triplet IC and to the 3T₂g manifold via triplet–quintet ISC; as a minor component, the ground state 1A₈g is recovered. The 3T₁₄ population is stable on the 1 ps time duration of the simulation, which is consistent with its 39 ps⁶ lifetime detected experimentally.⁵⁰ Crucially, the simulated dynamics captures all important aspects of the LIESST mechanism revealed by experiments: very fast singlet–triplet ISC, the role of 3T₂g states as intermediates, and branching into the HS/LS states. This consistency supports the presented results, which for certain aspects, such as the singlet–triplet ISC, reach even a quantitative agreement with experiment.⁶
Finally, we reveal fine details of the LIEST mechanism based on the time evolution of excited-state nuclear wavepackets. We now analyze the singlet \(-\) triplet ISC along \(\nu_{14}\), which is the natural choice for the involved \(^3T_{1g}/^3T_{2g}\) states (occupation of a single \(e_g^*\) orbital). Figure 6a shows snapshots of the excited-state singlet wavepacket along \(\nu_{14}\) for the initial 200 fs. The \(^1T_{1g}\) wavepacket immediately starts to propagate away from \(q_{14} = 0\), entering the \(^1T_{1g}/^3T_{2g}\) crossing region. This, combined with a sizable spin–orbit coupling (\(\sim 175\) and \(250\) cm\(^{-1}\)), allows efficient ISC to the \(^3T_{2g}\) manifold, which is indeed what is observed in Figure 5. On the 100–200 fs time scale, the wavepacket becomes more diffuse, which is the reason why the ISC is slower for >100 fs. These results highlight the importance of vibronic motion, as confirmed by the discrepancy between the 36 ps \(^1T_{1g}\) \(\rightarrow\) \(^3T_{2g}\) ISC time constant of ref 13 for \([Fe(mtz)_6]^{2+}\), based on Fermi’s golden rule, and the <150 fs experimental and simulated 39/168 fs values obtained in this work.

In Figure 6b, we analyze the wavepacket motion in the intermediate \(^3T_{2g}\) state along \(\nu_{15}\). Clearly, a coherent wavepacket oscillation is induced, with a period of \(\sim 110\) fs. The \(^3T_{2g}\) wavepacket dephases and spreads, and, importantly, the Gaussian full width at half-maximum (fwhm, green) does not reach the crossings with the \(^5T_{2g}\) and \(^1A_{1g}\) states (dashed lines in Figure 6b). This is to say that the \(^3T_{2g}\) wavepacket only slightly leaks into the crossing region, which is the reason why the quintet population rises relatively slowly (in \([Fe(bipy)_3]^{2+}\), the HS state is...
populated in <100 fs\textsuperscript{18}). Although the wavepacket gains more access to the $T_\text{2g}$/$T_\text{2e}$ intersection along $\nu_{14}$, this channel does not allow significant net population flow to the $S_{\text{2g}}$ states. This is due to very efficient $T_\text{2g} \rightarrow S_{\text{1e}}$ deactivation, favored by the energetics and easy access to the crossing region (located just at the $S_{\text{2g}}$ minimum) along $\nu_{14}$, as is clear from Figure 4b.

In this Communication, we revealed the Fe(II) LIESST mechanism of Fe(NCH)\textsubscript{6}\textsuperscript{2+} using synergistic spin-vibronic dynamics simulations. The obtained mechanistic picture is consistent with the experimental findings and includes assignment of the principal intermediate $T_\text{2g}$, whose dynamics are controlled by the key antisymmetric ($\nu_{14}$) and symmetric ($\nu_{15}$) Fe–N stretching vibrations. Importantly, the present work establishes a new theoretical state of the art for LS $\rightarrow$ HS photo switching and will certainly motivate intriguing dynamical studies, both experimental and theoretical ones.

**Computational Methods.** The TSH simulations are based on Tully’s fewest switches,\textsuperscript{21} a three-step propagator technique\textsuperscript{22} (with transformations between the adiabatic–spin diabatic and diagonal representations), and local diabatization.\textsuperscript{23} The QD simulations are based on a diabatic vibronic-coupling\textsuperscript{24,25} Hamiltonian and the multiconfigurational time-dependent Hartree (MCTDH) method.\textsuperscript{30} Our methodology follows the following implementations: TSH, SHARC2.1\textsuperscript{31} interfaced to ORCA4.2,\textsuperscript{32,33} utilizing time-dependent density functional theory (TD-DFT; B3LYP\textsuperscript{34,35} singlet–triplet states), MCTDH8.4\textsuperscript{31} and CAPT2 (12 electrons/14 orbitals: five–five Fe 3d/4d-based, two-$\pi$Fe–N bonding and a pair of Fe 3s/4s correlating active orbitals), OpenMolcas20.10.\textsuperscript{36} Further details of the utilized methodology are described in the SI.

### ASSOCIATED CONTENT

* Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.1c01838.

Validity of the [Fe(NCH)\textsubscript{6}]\textsuperscript{2+} model, normal-mode frequencies and characters, methodological and computational details of the TSH and QD simulations, and optimized ground-state geometries (PDF)

### AUTHOR INFORMATION

**Corresponding Author**

Máté Pépí – Wigner Research Centre for Physics, Budapest H-1525, Hungary; orcid.org/0000-0002-4819-0611; Email: papai.matyas@wigner.hu

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.inorgchem.1c01838

**Notes**

The author declares no competing financial interest.

### ACKNOWLEDGMENTS

The research leading to the presented results has received funding from the Hungarian National Research, Development and Innovation Fund (Grant NKFIH PD 134976). The author acknowledges support from the János Bolyai Scholarship of the Hungarian Academy of Sciences. The author is grateful to Tamás Rozgonyi for fruitful discussions. Guest access to the central HPC cluster of the Technical University of Denmark is acknowledged.

### REFERENCES

(1) Decurtins, S.; Göltlich, P.; Köhler, C.; Spiering, H.; Hauser, A. Light-induced excited spin state trapping in a transition-metal complex: The hexa-1-propyltetrazole-iron (II) tetrafluoroborate spin-crossover system. Chem. Phys. Lett. 1984, 105, 1–4.

(2) Létard, J.-F.; Guionneau, P.; Goux-Capes, L. Spin Crossover in Transition Metal Compounds III; Springer: Berlin, 2004; pp 221–249.

(3) Bousseksou, A.; Molnár, G.; Matouzenko, G. Switching of Molecular Spin States in Inorganic Complexes by Temperature, Pressure, Magnetic Field and Light: Towards Molecular Devices. Eur. J. Inorg. Chem. 2004, 2004, 4353–4369.

(4) Cambi, L.; Szegő, L. Über die magnetische Suszeptibilität der komplexen Verbindungen. Ber. Dtsch. Chem. Ges. B 1931, 64, 2591–2598.

(5) Hauser, A. Intersystem crossing in the [Fe(ptz)]\textsuperscript{2+}(BF\textsubscript{4})\textsuperscript{2} spin crossover system (ptz = 1-propyltetrazole). J. Chem. Phys. 1991, 94, 2741–2748.

(6) Marino, A.; Chakraborty, P.; Servol, M.; Lorenz, M.; Collet, E.; Hauser, A. The Role of Ligand-Field States in the Ultrafast Photophysical Cycle of the Prototypical Iron(II) Spin-Crossover Compound [Fe(ptz)]\textsuperscript{2+}(BF\textsubscript{4})\textsuperscript{2}. Angew. Chem., Int. Ed. 2014, 53, 3863–3867.

(7) Zhang, W.; Alonso-Mori, R.; Bergmann, U.; Bressler, C.; Chollet, M.; Galler, A.; Gawelda, W.; Hadt, R.; Harts cock, R.; Kroll, T.; et al. Tracking excited-state charge and spin dynamics in iron coordination complexes. Nature 2014, 509, 345–348.

(8) Aubock, G.; Chergui, M. Sub-50-fs photoinduced spin crossover in [Fe(bpy)]\textsuperscript{2+}. Nat. Chem. 2015, 7, 629–633.

(9) Mogulevski, A.; Wilke, M.; Grell, G.; Bokarev, S. I.; Aziz, S. G.; Engel, N.; Raehem, A. A.; Kühn, O.; Kiyani, I. Y.; Aziz, E. F. Ultrafast Spin Crossover in [Fe\textsuperscript{2+}(bpy)]\textsuperscript{2+}: Revealing Two Competing Mechanisms by Extreme Ultraviolet Photoemission Spectroscopy. ChemPhysChem 2017, 18, 465–469.

(10) Vankó, G.; Bordage, A.; Papai, M.; Haldrup, K.; Glatzel, P.; March, A. M.; Douny, G.; Britz, A.; Galler, A.; Assela, T.; et al. Detailed Characterization of a Nanosecond-Lived Excited State: X-ray and Theoretical Investigation of the Quintet State in Photoexcited [Fe(terpy)]\textsuperscript{2+}. J. Phys. Chem. C 2015, 119, 5888–5902.

(11) Sousa, C.; Llunell, M.; Domingo, A.; de Graaf, C. Theoretical evidence for the direct 3MLCT-HS deactivation in the light-induced spin crossover of Fe(II)–polypyridyl complexes. Phys. Chem. Chem. Phys. 2018, 20, 2351–2355.

(12) Sousa, C.; de Graaf, C.; Rudovskiy, A.; Broer, R.; Tatchen, J.; Etinski, M.; Marian, C. M. Ultrafast Deactivation Mechanism of the Excited Singlet in the Light-Induced Spin-Crossover of [Fe(2,2′-bipyridine)]\textsuperscript{2+}. Chem. - Eur. J. 2013, 19, 17541–17551.

(13) Sousa, C.; de Graaf, C.; Rudovskiy, A.; Broer, R. Theoretical Study of the Light-Induced Spin-Crossover Mechanism in [Fe(mtz)]\textsuperscript{2+} and [Fe(ptz)]\textsuperscript{2+}. J. Phys. Chem. A 2017, 121, 9720–9727.

(14) Kepenekian, M.; Robert, V.; Le Guennic, B.; De Graaf, C. The energetics of Fe(NCH)\textsubscript{6}\textsuperscript{2+} via CASPT2 calculations: A spin-crossover perspective. J. Comput. Chem. 2009, 30, 2327–2333.

(15) Droghetti, A.; Alfe, D.; Sanvito, S. Assessment of density functional theory for iron(II) molecules across the spin-crossover transition. J. Chem. Phys. 2012, 137, 124303.

(16) Lawson, L.; Aquilante, F.; Robinson, T. W.; Hauser, A. Accurate Spin-State Energetics of Transition Metal Complexes. 1. CCSD(T), CASPT2, and DFT Study of [M(NCH)\textsubscript{6}]\textsuperscript{2+} (M = Fe, Co). J. Chem. Theory Comput. 2012, 8, 4216–4231.

(17) Fumana, M.; Wagner, L. K.; Sanvito, S.; Droghetti, A. Diffusion Monte Carlo Perspective on the Spin-State Energetics of Fe(NCH)\textsubscript{6}\textsuperscript{2+}. J. Chem. Theory Comput. 2016, 12, 4323–4341.

(18) Capano, G.; Penfold, T. J.; Chergui, M.; Tavagnelli, I. Photophysics of a copper phenanthroline elucidated by trajectory and wavepacket-based quantum dynamics: a synergetic approach. Phys. Chem. Chem. Phys. 2017, 19, 19590–19600.

(19) Gómez, S.; Heindl, M.; Szabadi, A.; González, I. From Surface Hopping to Quantum Dynamics and Back. Finding Essential Electronic
and Nuclear Degrees of Freedom and Optimal Surface Hopping Parameters. *J. Phys. Chem. A* 2019, 123, 8321–8332.

(20) The $T_{1g}$ lifetime was measured through the reverse LIESST process, in which the HS state is converted to the LS state by irradiation with 830 nm light.

(21) Tully, J. C. Molecular dynamics with electronic transitions. *J. Chem. Phys.* 1990, 93, 1061–1071.

(22) Mai, S.; Marquetand, P.; González, L. A general method to describe intersystem crossing dynamics in trajectory surface hopping. *Int. J. Quantum Chem.* 2015, 115, 1215–1231.

(23) Granucci, G.; Persico, M.; Zoccola, A. Including quantum decoherence in surface hopping. *J. Chem. Phys.* 2010, 133, 134111.

(24) Cederbaum, L. S.; Köppel, H.; Domcke, W. Multimode vibronic coupling effects in molecules. *Int. J. Quantum Chem.* 1981, 20, 251–267.

(25) Köppel, H.; Domcke, W.; Cederbaum, L. S. *Advances in Chemical Physics*; John Wiley & Sons, Ltd., 1984; pp 59–246.

(26) Capano, G.; Chergui, M.; Rothlisberger, U.; Tavernelli, I.; Penfold, T. J. A Quantum Dynamics Study of the Ultrafast Relaxation in a Prototypical Cu(I)–Phenanthroline. *J. Phys. Chem. A* 2014, 118, 9861–9869.

(27) Eng, J.; Gourlaouen, C.; Gindensperger, E.; Daniel, C. Spin-Vibronic Quantum Dynamics for Ultrafast Excited-State Processes. *Acc. Chem. Res.* 2015, 48, 809–817.

(28) Pápai, M.; Vankó, G.; Rozgonyi, T.; Penfold, T. J. High Efficiency Iron Photosensitiser Explained with Quantum Wavepacket Dynamics. *J. Phys. Chem. Lett.* 2016, 7, 2009–2014.

(29) Penfold, T. J.; Gindensperger, E.; Daniel, C.; Marian, C. M. Spin-Vibronic Mechanism for Intersystem Crossing. *Chem. Rev.* 2018, 118, 6975–7025.

(30) Beck, M.; Jäckle, A.; Worth, G.; Meyer, H.-D. The multi-configuration time-dependent Hartree (MCTDH) method: a highly efficient algorithm for propagating wavepackets. *Phys. Rep.* 2000, 324, 1–105.

(31) Mai, S.; Marquetand, P.; González, L. Nonadiabatic Dynamics: The SHARC Approach. *Wiley Interdiscip. Rev.: Comput. Mol. Sci.* 2018, 8, No. e1370.

(32) Neese, F. The ORCA program system. *Wiley Interdiscip. Rev.: Comput. Mol. Sci.* 2012, 2, 73–78.

(33) Neese, F. Software update: the ORCA program system, version 4.0. *Wiley Interdiscip. Rev.: Comput. Mol. Sci.* 2018, 8, No. e1327.

(34) Reiher, M.; Salomon, O.; Artur Hess, B. Reparameterization of hybrid functionals based on energy differences of states of different multiplicity. *Theor. Chem. Acc.* 2001, 107, 48–55.

(35) Reiher, M. Theoretical Study of the Fe(phen)$_2$(NCS)$_2$ Spin-Crossover Complex with Reparametrized Density Functionals. *Inorg. Chem.* 2002, 41, 6928–6935.

(36) Fdez Galván, I.; Vacher, M.; Alavi, A.; Angeli, C.; Aquilante, F.; Autschbach, J.; Bao, J. J.; Bokarev, S. I.; Bogdanov, N. A.; Carlson, R. K.; et al. OpenMolcas: From Source Code to Insight. *J. Chem. Theory Comput.* 2019, 15, 5925–5964.