

Significant Variation of the Singlet–Quintet Intersystem Crossing Rate Constant in an Iron(II) High-Spin Complex as a Function of Temperature**

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In experimental physical sciences, a given physical quantity is determined as a function of external parameters, such as temperature, pressure, or concentration. In general, the range of the parameters over which the quantity is experimentally accessible is limited and the variation of the quantity over that range usually does not exceed a few orders of magnitude. For example, the electroluminescence intensity as a function of temperature for Si/Ge nanostructures decreases by four orders of magnitude between 25 and 1000 K;^[1] the field-effect transistor carrier mobility changes by up to five orders of magnitude between 70 and 500 K;^[2] whilst the self-diffusion coefficient of water confined to nanopores decreases by four orders of magnitude between room temperature and 220 K.^[3] Important thermal variations of up to seven orders of magnitude have been observed for the thermal conductivity and heat capacity of crystalline and amorphous solids, such as SiO₂, between 0.01 and 300 K.^[4] In solution, the accessible temperature range for measuring a given quantity, for example the rate constant of a chemical reaction, is restricted to the range between the melting and the boiling point of the solvent; thus, rate constants typically span three to five orders of magnitude according to van't Hoff's rule.

With regard to photophysical processes, the presence of several excited states within a comparatively small energy interval most often results in a competition between different processes, such as internal conversion, intersystem crossing, fluorescence, phosphorescence, and light-induced energy and electron transfer.^[5] As each of these processes has a specific temperature and pressure dependence, a given process dominates over a limited temperature or pressure interval only, and thus its rate constant can only be determined over this temperature or pressure range. Of course, if the temper-

ature or pressure range over which a given rate constant can be determined is large enough, activation parameters can be extracted and in principle be used to estimate the rate constant outside the experimentally accessible range. However, this method assumes that the rate law follows, for example, Arrhenius or absolute rate theory behavior, and this is not necessarily justified for photophysical and photochemical processes in particular at low temperatures, at which quantum mechanical tunneling may become important.^[6] To experimentally verify such deviations from classical behavior unambiguously, rate constants have to be determined over as large a range of temperature or pressure as possible.

Spin-crossover systems, that is, octahedral complexes with a central transition metal having d⁴–d⁷ electronic configuration,^[7] are ideal for studying the dynamics of intersystem crossing. These complexes show reversible optical bistability between the high-spin and low-spin state, which have maximum and minimum spin multiplicity, respectively, when subjected to various perturbations, such as temperature variation, external pressure,^[8] magnetic fields,^[9] and light irradiation.^[10] In the case of iron(II)-based systems, the thermal spin transition^[7] takes place from the ¹A₁ low-spin (LS) state as the quantum mechanical ground state at low temperatures to the ⁵T₂ high-spin (HS) state at higher temperatures and is largely entropy-driven. This behavior is governed by the zero-point energy difference between the two spin manifolds.

Apart from the phenomenon of a thermal spin transition, it is also possible to control the HS and LS populations by irradiating with light of the appropriate wavelength. In the so-called light-induced excited spin-state trapping (LIESST)^[10,11] effect, irradiation into d–d or metal–ligand charge transfer (MLCT) bands of the LS species in the UV/Vis range below the thermal transition temperature results in a quantitative population of the HS state with high quantum efficiency. The subsequent relaxation back to the LS ground state can then be followed by spectroscopic methods as a function of temperature up to the thermal transition temperature. At elevated temperatures, the HS→LS relaxation is thermally activated, as expected for the large horizontal and the small vertical relative displacements of the potential wells of the two states and the ensuing energy barrier between them. At low temperatures however, deviations from the classical behavior towards a temperature-independent rate constant indicate quantum mechanical tunneling in the form of a non-adiabatic multiphonon process.^[12] For the model complex [Fe(ptz)₆]²⁺ (ptz = 1-propyltetrazole) doped into [Zn(ptz)₆](BF₄)₂, for

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instance, the observed HS→LS rate constant increases by nine orders of magnitude from $2 \times 10^{-6} \text{ s}^{-1}$ ($\tau = 10 \text{ d}$) at 40 K to $3 \times 10^3 \text{ s}^{-1}$ ($\tau = 0.3 \text{ ms}$) at 130 K; that is, at just above the thermal transition temperature and thus the highest accessible temperature for irradiation into LS bands.^[13] Similarly, the low-temperature tunneling rate constant for another classical iron(II) complex, namely $[\text{Fe}(\text{mepy})_3\text{tren}]^{2+}$ ((mepy)₃tren = tris[4-(6-methylpyrid-2-yl)-3-aza-3-butenyl]-amine), doped into $[\text{Zn}(\text{mepy})_3\text{tren}](\text{PF}_6)_2$ increases from 10^{-1} s^{-1} ($\tau = 10 \text{ s}$) to $5 \times 10^8 \text{ s}^{-1}$ ($\tau = 20 \text{ ns}$) on applying an external pressure of 28 kbar.^[14]

At 10 K, the trapped HS state can also be converted back into the LS state by selective irradiation into the very weak d–d absorption band of the HS species in the NIR region.^[10,15] However, this reverse-LIESST effect is much less efficient. For the above-mentioned $[\text{Fe}(\text{ptz})_6]^{2+}$ complex, about 85 % of the LS population can be recovered with a quantum efficiency of about 10 %, but for systems having intense ¹MLCT transitions at lower energy with tails reaching into the NIR, a maximum LS population of only 10 % can be recovered because of the competition with LIESST.^[16]

For systems very close to the spin-crossover point, but HS down to cryogenic temperatures, it is also possible to populate the LS state, now in turn as a metastable state, by irradiation in the NIR range.^[17] A detailed low-temperature relaxation study on the 1-ethyltetrazole derivative, $[\text{Fe}(\text{etz})_6](\text{BF}_4)_2$, revealed the importance of cooperative effects resulting in a light-induced hysteresis.^[18]

Because the light-induced HS→LS conversion has a) a low quantum efficiency, b) is only possible for irradiation into the weak d–d absorption band of the HS species, and c) only results in at best a partial population of the LS state, studies of the LS→HS relaxation have to date been restricted to low temperatures and high enough concentrations to work with the weak d–d transitions of both the HS and the LS species.^[15–19] Herein we overcome these limits by studying the very dilute mixed-crystal system $[\text{Fe}_x\text{Zn}_{1-x}(\text{bbtr})_3](\text{ClO}_4)_2$, $x = 0.02$ (bbtr = 1,4-di(1,2,3-triazol-1-yl)butane), using the weak ⁵T₂→⁵E transition at 830 nm^[20] of the HS species for pumping and the intense ¹MLCT transition in the UV of the LS species for probing. In this system, the triazole-based ligand acts as a bridging ligand between two neighboring iron(II) centers, each of which is surrounded by six ligands. The complexes thus form a hexagonal 2D structure with the counteranions between the layers. The iron-only compound shows a complete and abrupt spin transition at 108 K with a 13 K wide hysteresis.^[20,21] At room temperature in the HS state, the compound is colorless, and the absorption spectrum shows the above mentioned ⁵T₂→⁵E transition at 830 nm ($\epsilon = 4 \text{ L mol}^{-1} \text{ cm}^{-1}$) and a rise below 345 nm corresponding to the tail of a more intense ⁵MLCT transition. At 10 K, the compound is red, and the NIR band has disappeared and is replaced by the ¹A₁→¹T₁ d–d band of the LS species centered at 550 nm ($\epsilon = 38 \text{ L mol}^{-1} \text{ cm}^{-1}$) and furthermore, a rise below 420 nm corresponding to the tail of an even more intense ¹MLCT transition and with a shoulder at 380 nm corresponding to the higher energy ¹A₁→¹T₂ d–d band.^[20]

The dilute mixed crystals $[\text{Fe}_x\text{Zn}_{1-x}(\text{bbtr})_3](\text{ClO}_4)_2$, $x = 0.02$, used in the present study were prepared in the same

way as the iron-only compound,^[21] using an appropriate ratio of the metal ions in the solution from which hexagonal crystals of approximate dimensions $100 \times 100 \times 100 \mu\text{m}^3$ were grown. Figure 1 shows the 10 K single-crystal absorption spectrum after very slow cooling with a rate of 0.1 K min^{-1} below 100 K (full line). All d–d bands are too weak to be observable at an iron(II) and a crystal thickness of $100 \mu\text{m}$. Instead, the band in the UV centered at 315 nm corresponding to the ¹MLCT transition, which in the concentrated material appears as a rise towards the UV, is now fully discernible.

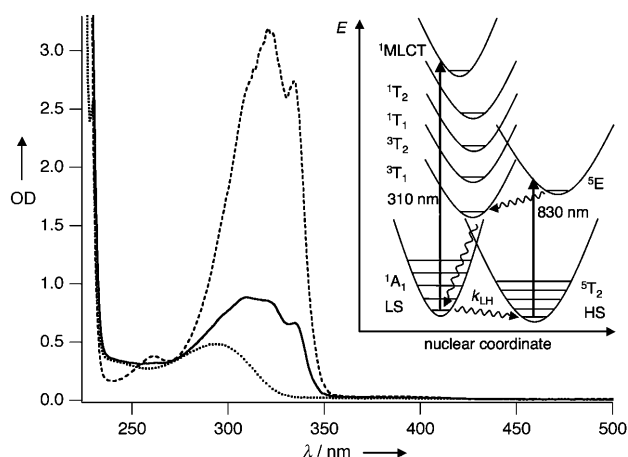


Figure 1. Single-crystal absorption spectra of $[\text{Fe}_x\text{Zn}_{1-x}(\text{bbtr})_3](\text{ClO}_4)_2$ at 10 K after slow cooling (—), after irradiation at 532 nm (.....) and 830 nm (-----). Inset: Energy levels and mechanism for reverse LIESST, indicating pump and probe wavelengths. The extinction coefficient of the ⁵T₂→⁵E transition at $\lambda_{\text{pump}} = 830 \text{ nm}$ is $4 \text{ L mol}^{-1} \text{ cm}^{-1}$, and that of the ¹MLCT transition at $\lambda_{\text{probe}} = 310 \text{ nm}$ is about $10000 \text{ L mol}^{-1} \text{ cm}^{-1}$.

The question arises regarding the populations of the two states obtained upon slow cooling. As there are no reference spectra available for comparison, and as Mössbauer spectroscopy and magnetic susceptibility measurements are not feasible for the low iron(II) concentration, we chose to answer this question by using LIESST and reverse LIESST. Figure 1 includes the single-crystal absorption spectra at 10 K following irradiation at 532 (dotted line) and 830 nm (broken line). Irradiation at 532 nm, that is, into the spin-allowed d–d band of the LS species, converts the system quantitatively into the HS state. The band centered at 295 nm thus corresponds to the ⁵MLCT transition of the HS species. Irradiation at 830 nm, that is, into the spin-allowed d–d transition of the HS species, results in a steady state with a saturation value of the LS fraction, γ_{LS} , of 85 %.^[20] The ¹MLCT transition at 315 nm ($\epsilon \approx 10000 \text{ L mol}^{-1} \text{ cm}^{-1}$) is considerably more intense and at slightly lower energy than the ⁵MLCT transition because of the better overlap between metal-centered and ligand orbitals resulting from the typically 0.2 \AA ^[22] smaller metal–ligand bond length in the LS state. The two spectra following irradiation may serve as reference spectra. Therefore, in the dilute system, the thermal spin transition is only partial, with a low-temperature LS fraction, γ_{LS} , of about 20 % at 10 K, and above 100 K the LS fraction becomes negligible. This result is

in accordance with expectation when compared to the neat compound, which shows a very cooperative spin transition. In the dilute zinc matrix, transition curves are much more gradual and generally shifted to lower temperatures.^[23] Therefore, in the present system, we may conclude that the zero-point energy difference between the two states is very close to zero, with a component of the HS multiplet as the quantum mechanical ground state (Figure 1, inset).

At 10 K, all relaxation processes are too slow to be measured within a reasonable timeframe, but above 40 K they become fast enough to be studied. The inset of Figure 2 shows two relaxation curves at 55 K obtained after irradiation at 532 and 830 nm. They are single exponentials with an observed rate constant $k_{\text{obs}} = 2 \times 10^{-5} \text{ s}^{-1}$ ($\tau = 14 \text{ h}$), and they meet at the thermal equilibrium value of the LS fraction $\gamma_{\text{LS}} = 0.2$ at 55 K.

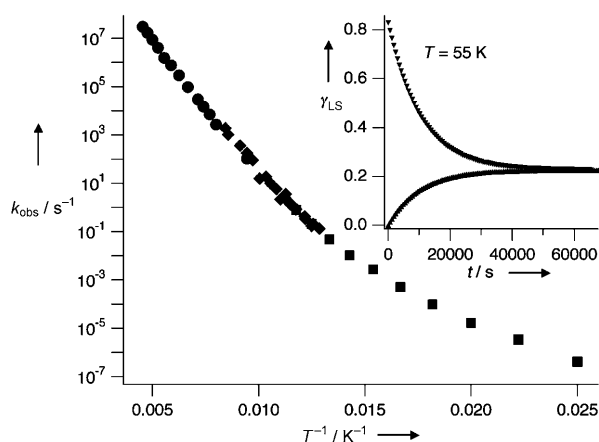


Figure 2. The relaxation rate constant k_{obs} plotted on a logarithmic scale versus $1/T$ from 40 to 220 K using the three different setups for the appropriate temperature ranges (●, ◆, ■; see the Experimental Section). Inset: relaxation curves at 55 K for irradiation at 830 nm (▼) and 532 nm (▲).

With such a slow relaxation process, the excitation rate is not important, because with a CW laser of a few mW power, the saturation value of γ_{LS} of 85% is reached within a few minutes. However, with increasing temperature, the relaxation rate constant also increases rapidly, and at elevated temperatures a pulsed laser system has to be employed (see Experimental Section). Despite the small quantum efficiency of the light-induced population of the LS state and the low value of the extinction coefficient of only $4 \text{ L mol}^{-1} \text{ cm}^{-1}$ at the pump wavelength, the LS→HS relaxation can be easily monitored at the wavelength of the very intense ¹MLCT transition of the LS species (Figure 1, inset). Indeed, an initial light-induced population of the LS state of only 2% is necessary to determine the rate constant of the single-exponential relaxation decay precisely. In Figure 2, the corresponding observed rate constant, k_{obs} , is given on a logarithmic scale as a function of inverse temperature. In principle $k_{\text{obs}} = k_{\text{HL}} + k_{\text{LH}}$; that is, k_{obs} is the sum of the rate constants of the HS→LS and the LS→HS processes. Above

100 K, where the equilibrium LS fraction is negligible, k_{obs} is equal to k_{LH} , and even below that temperature, $k_{\text{LH}} > k_{\text{HL}}$.

The most striking feature of the temperature dependence of the observed rate constant is the range of 14 orders of magnitude, increasing from $4 \times 10^{-7} \text{ s}^{-1}$ ($\tau = 30 \text{ d}$) at 40 K to $3 \times 10^7 \text{ s}^{-1}$ ($\tau = 30 \text{ ns}$) at 220 K. Above 100 K, the process follows the classical Arrhenius behavior, and a least-squares fit yields values for the activation energy E_a of $1842(21) \text{ cm}^{-1}$ and pre-exponential factor A of $7.3(5) \times 10^{12} \text{ s}^{-1}$. The value of the activation energy is still below the classical height of the barrier estimated on the basis of the characteristic metal–ligand bond length difference of 0.2 Å ^[22] between the two states. However, the value approaches the high-temperature limit predicted for a non-adiabatic multi-phonon process.^[24] Similarly, it is evident that below 100 K there are substantial deviations from classical thermally activated behavior. According to Buhks et al.,^[12] these deviations, with the relaxation rate constant approaching a limiting value at $T \rightarrow 0$, are characteristic for nuclear tunneling.

In conclusion, in the diluted $[\text{Zn}_{1-x}\text{Fe}_x(\text{bbtr})_3](\text{ClO}_4)_2$ system, in which the iron complexes are predominantly in the HS state at all temperatures, and making use of the very different transition dipole moments of the transitions used for pumping and probing, it was possible to determine the LS→HS intersystem crossing rate constant over a substantially larger temperature interval than usually accessible for the HS→LS relaxation in spin-crossover systems. As there are no other competing processes over the whole temperature range, the dynamics of the same process could be measured exclusively over the full range. The upper temperature limit of 220 K and the corresponding lifetime of 30 ns are dictated by the quantum efficiency of the light-induced population of the LS state, which begins to decrease above 160 K. The 14 orders of magnitude range for an experimentally observed process that is observed by only varying the temperature is unique.

Experimental Section

Samples were prepared as described in reference [21]. Variable-temperature single-crystal absorption spectra were recorded on a Cary 5000 dual-beam spectrometer with the crystal mounted on a small aperture in a copper plate inside a closed cycle cryostat (Janis-Sumitomo SHI-4.5) using silver contact glue to ensure efficient heat exchange.

The large variation in the rate constant required the use of different excitation light sources and monitoring set-ups for the different regimes. At low temperatures, where the relaxation is slow, irradiation at 830 and 532 nm was performed with a laser diode and a DPSS laser, respectively, with a power of a few mW; full absorption spectra as a function of delay after the laser was switched off were recorded with the spectrometer. At intermediate temperatures, the output of a titanium sapphire laser at 830 nm was passed through a chopper for excitation, and the light of a xenon lamp at 320 nm using a single monochromator (Spex 270M), a photomultiplier (Hamamatsu R928), and an digital oscilloscope (Tektronix TDS 540B) were used for monitoring the decay of the light-induced LS state. At higher temperatures, the idler wave of a MOPO (Opotek Magic Prism, pumped by the third harmonic of a pulsed Nd:YAG laser) at 830 nm was used for excitation.

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