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Low-Temperature Tunneling in the Spin-State Relaxation Dynamics of Iron(III) Spin-Crossover Compounds

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Some 13 years ago Buhks et al.[1] suggested that the spin conversion in spin-crossover compounds should be treated as a nonadiabatic process within the theory of radiationless multiphonon relaxation. They predicted a thermally activated high-spin → low-spin (HS → LS) relaxation at elevated temperatures and a nonvanishing tunneling rate at cryogenic temperatures. Although Buhks et al. refer to spin-crossover complexes in solution, the theory is equally valid for the solid state,[2] with the low-frequency lattice vibrations playing the role of the heat bath instead of solvent librations.

For the HS($^5T_2$) → LS($^1A_1$) relaxation in Fe(II) compounds, Xie and Hendrickson subsequently found the predictions to be true,[3] and Hauser et al. demonstrated the validity of the inverse energy gap law in the strong vibronic coupling limit.[4] This served to explain the extremely long-lived light-induced HS states with low-temperature lifetimes of 10^2–10^6 s in these compounds.[4,5]

Lawthers and McGarvey showed a perturbation of the LS($^2T_2$) ⇔ HS($^6A_1$) equilibrium in Fe(III) compounds to be possible with pulsed laser excitation, too.[6] Despite this and the fact that at ambient temperatures the HS → LS relaxation rate constants for Fe(III) spin-crossover compounds are typically only an order of magnitude larger than for Fe(II) systems, i.e., $10^{8\pm1}$ s^{-1} versus $10^{7\pm1}$ s^{-1},[7] no reports of long-lived metastable states at low temperatures for the former have appeared in the literature so far.

The Fe(III) spin-crossover compound [Fe(acpa)$_2$]PF$_6$ (Hacpa = *N*-(1-acetyl-2-propylidene)-*N*-(2-pyridylmethyl)amine)[8] is ideally suited for a photophysical investigation of the HS → LS relaxation down to low temperatures. Figure 1 shows the temperature dependence of the absorption spectrum between 150 and 300 K in propriononitrile/butyronitrile (4:5). The LMCT band at 14 600 cm^{-1}, characteristic of the LS species, disappears at elevated temperatures and is replaced by the characteristic HS band at 17 600 cm^{-1}. The transition temperature $T_{1/2}$ of ~200 K is slightly higher than the ~180 K in the solid state.[9] Pulsed laser excitation within the LS band (ν = 14 400 cm^{-1}, 3 mJ/pulse, 7-ns pulse width) results in a transient bleaching at 14 800 cm^{-1} and a corresponding increase in absorption at 18 450 cm^{-1}, indicating that we are indeed looking at a light-induced population of the HS state followed by HS → LS relaxation. The inset in Figure 2 shows the relaxation curves at 60 K for [Fe(acpa)$_2$]PF$_6$ dispersed in KBr. They are slightly nonexponential, probably due to small laser-induced temperature gradients and inhomogeneities in the matrix rather than to the physics of the relaxation process as such. Mean relaxation rate constants are plotted as ln[$k_{HL}(T)$] versus $1/T$ in Figure 2. Evidently, the same type of behavior as for the HS → LS relaxation in Fe(II) spin-crossover systems is observed, namely, more or less temperature independent tunneling below 100 K, and a thermally activated process at elevated temperatures. For [Fe(acpa)$_2$]PF$_6$ in KBr, the low-temperature tunneling rate constant $k_{HL}(T \rightarrow 0)$ is ~10^2 s^{-1}, the activation energy for the thermally activated process E_a is ~730(40) cm^{-1}. Above 200 K the relaxation rate constant is >5 × 10^6 s^{-1}, in accordance with the observed line broadening of Mössbauer spectra.[9]

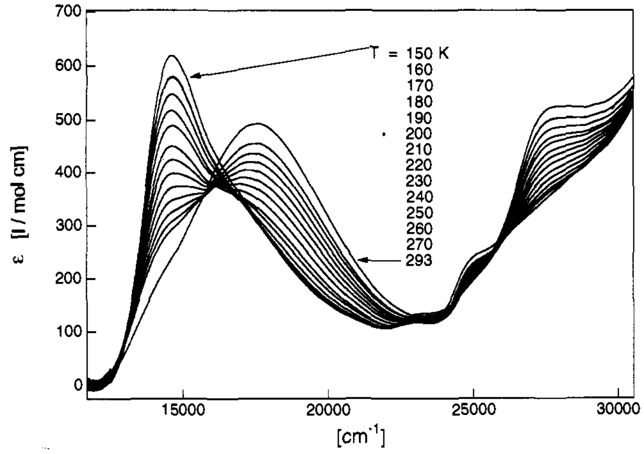

Figure 1. Absorption spectrum of [Fe(acpa)$_2$]PF$_6$ in propriononitrile/butyronitrile (4:5) between 150 and 300 K.

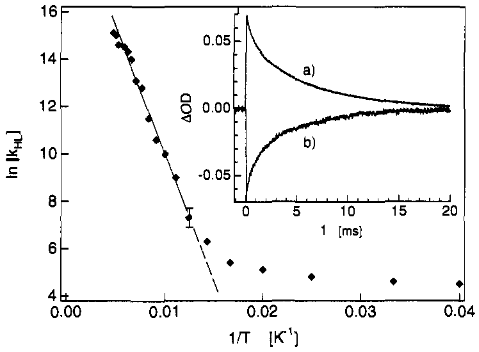

Figure 2. ln[$k_{HL}(T)$] versus $1/T$ for the HS → LS relaxation in [Fe(acpa)$_2$]PF$_6$ in KBr. Effective activation energy at high temperatures E_a = 730(40) cm^{-1}. Inset: transient absorption of [Fe(acpa)$_2$]PF$_6$ in KBr at 60 K monitored at (a) 18 450 and (b) 14 800 cm^{-1} after pulsed laser excitation at 14 400 cm^{-1}.

How does the value of 10^2 s^{-1} for the low-temperature tunneling rate constants compare to the 10^{-6}–10^{-2} s^{-1} typically observed for Fe(II) spin-crossover compounds?[4,5] According to the equation[2]

$$k_{HL}(T \rightarrow 0) = \frac{2\pi}{\hbar^2 \omega} g_f \beta_{HL}{}^2 |\langle \chi_p | \chi_o \rangle|^2 = \frac{2\pi}{\hbar^2 \omega} g_f \beta_{HL}{}^2 \frac{S^p \mathrm{e}^{-S}}{p!} \quad (1)$$

where β_{HL} is the electronic matrix element given by spin–orbit coupling, g_f the electronic degeneracy of the final state, and $|<\chi_p|\chi_o>|^2$ a Franck–Condon factor, $k_{HL}(T \rightarrow 0)$ depends critically upon the relative vertical and horizontal displacements of the potential wells of the initial and the final state. The former is conveniently expressed by the reduced energy gap $p = \Delta E^0_{HL}/\hbar\omega$, the latter by the Huang–Rhys factor $S = {}^1/_2 f \Delta Q^2/\hbar\omega$, where ΔQ is the difference in equilibrium position in the

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accepting mode, f and $\hbar\omega$ are the corresponding force constant and vibrational frequency, respectively, and ΔE^0_{HL} is the zero-point energy difference.

For Fe(II) compounds with an [FeN$_6$] core, a value of S of ~45 has been estimated from the difference in the metal–ligand bond length between the HS and the LS state Δr_{HL} of ~0.16–0.21 Å,[10] an average force constant f of $\sim 2 \times 10^5$ dyn/cm, and a vibrational frequency $\hbar\omega$ for the totally symmetric mode of ~250 cm^{-1}.[4] For Fe(III) systems with an [FeN$_4$O$_2$] core, this is not as straightforward. However, with an average value of Δr_{HL} of ~0.12 Å,[9] a 50% larger vibrational frequency, and a correspondingly larger force constant, a value for S of ~25 is a reasonable estimate. For spin-crossover compounds with $T_{1/2}$ between 100 and 200 K, the reduced energy gap p is ~1, both for Fe(II) and Fe(III) systems. Thus with the electronic matrix element for Fe(II) being ~150 cm^{-1} and for Fe(III) ~40 cm^{-1},[1] the relation

$$\frac{k^{III}_{HL}(T\rightarrow 0)}{k^{II}_{HL}(T\rightarrow 0)} \approx 10^6\text{–}10^7 \qquad (2)$$

holds, which is in good agreement with observation. Of course, this is only a very crude estimate, but it shows that basically due to the smaller value of Δr_{HL} for Fe(III) the much larger low-temperature tunneling rate constants can be rationalized at least semiquantitatively. At elevated temperatures the ratio of $k(T)^{III}_{HL}$ to $k(T)^{II}_{HL}$ becomes smaller, and for a meaningful estimate the actual vibrational frequencies and the exact bond length and zero-point energy differences of the complexes in hand would have to be explicitly considered.

Further work, both experimental and theoretical, is needed to understand the HS → LS relaxation in spin-crossover compounds, and thus intersystem crossing dynamics in the strong vibronic coupling limit, at the required level.

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