Cooperative formation of high-spin species in a photoexcited spin-crossover complex

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Cooperative formation of high-spin species in a photoexcited spin-crossover complex

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The dynamics of the photoinduced phase transition was investigated in a prototypical spin crossover complex, \([\text{Fe(ptz)}_3\text{][BF}_4\text{]_2}\) (ptz = 1-propyltetrazole), under photoexcitation at 77 K near the transition temperature \((T_c = 130 \text{ K})\). When the excitation power \(I\) exceeds \(\approx 1 \text{ mW/mm}^2\), we observed an “acceleration” of the creation rate of the density \(n_{\text{HS}}\) of the high-spin (HS) species after a characteristic incubation period. The “acceleration” is interpreted in terms of the negative pressure effect; the photocreated HS species with a larger ionic radius expands the volume to cause the structural phase transition.

\[ \frac{dn_{\text{HS}}}{dt} = \Pi(1 - n_{\text{HS}} - n_{\text{HS}}k_0 \exp(-\alpha n_{\text{HS}})), \]  

(1)

where \(\Pi\), \(k_0\), and \(\alpha\) are the conversation efficiency, the bare relaxation rate, and the avalanche factor, respectively. Thus, the dynamics of the PIPT process is still controversial even in the spin crossover complex.

Here, our strategy to extract the cooperative effect in the PIPT process is to enhance the intersite interaction by approximating the energy level of the metastable state to that of the ground state. For this purpose, we have investigated the PIPT process in the most prototypical spin crossover complex, \([\text{Fe(ptz)}_3\text{][BF}_4\text{]_2}\), near \(T_c\) for the LS-HS phase transition. As we had expected, we observed an “acceleration” of the creation rate of the density \(n_{\text{HS}}\) after a characteristic incubation period when \(I\) exceeds \(\approx 1 \text{ mW/mm}^2\). Based on the quantitative analysis of the \(n_{\text{HS}}\)-t curves, we propose that the photocreated HS species with a larger ionic radius induces a negative pressure to cause the structural phase transition.

Single crystals of \([\text{Fe(ptz)}_3\text{][BF}_4\text{]_2}\) were prepared in the manner of the procedure described in Ref. 23. The typical size of the crystals was \(4 \times 4 \times 0.05 \text{ mm}^3\). We measured the temperature dependence of magnetic susceptibility, and confirmed that our crystal shows the thermally induced LS-HS phase transition at \(T_c = 130 \text{ K}\). At the phase transition, the color of the crystal changes from transparent purple (the LS phase) to transparent and colorless (the HS phase). We emphasize that the cell volume discontinuously increases by 3% at the LS-HS phase transition, reflecting the fact that the ionic radius \((r_{\text{HS}} = 0.78 \text{ Å})\) of the HS Fe\(^{2+}\) ion is larger than...
that \((r_{LS}=0.61 \text{ Å})\) of the LS Fe\(^{2+}\) ion. The density \(n_{HS}\) of the HS species can be precisely estimated from the intensity of the intra-atomic absorption of the LS species located at \(\approx 2.3 \text{ eV}\). We used an Ar\(^{2+}\) laser (514.5 nm) and a cw yttrium aluminum garnet (YAG) laser (532 nm) as the excitation and probe light sources, respectively. The intensity of the excitation light was continuously controlled with a circular neutral density filter. The excitation light illuminated the sample so that the excitation light (3 mm\(^2\)) completely overlaps the probe light (1 mm\(^2\)). The intensity of the transmitted probe light was digitally recorded as a function of time. In order to make the measurement efficient, the magnitude of \(I\) as well as the on/off action of the excitation light was controlled by a personal computer. We further measured the temperature at the sample surface under photoexcitation, and confirmed that the temperature rise is less than 2 K even at the maximum excitation condition \((I=7.0 \text{ mW/mm}^2)\).

We show in Fig. 1(a) the prototypical \(n_{HS}\)-time curves of [Fe(ptz)\(_6\)](BF\(_4\))\(_2\) measured at 77 K. \(n_{HS}=1\) means that all the Fe\(^{2+}\) sites take the HS state. In the strong excitation condition (for example, see the 2.0 mW/mm\(^2\) data), \(n_{HS}\) superlinearly increases with time, and then becomes almost constant. Hereafter, we describe this constant value as \(\langle n_{HS}\rangle\). We note that \(\langle n_{HS}\rangle\) is not necessarily in unity in the photoexcited steady state, because the photocreation process of the HS species balances with their thermal relaxation processes of them. Actually, the relaxation speed [see Fig. 1(b)] is comparable with the creation speed. This makes a sharp contrast with the low temperature experiment reported by Enachescu et al.,\(^{20}\) in which \(n_{HS}\) seems to approach unity in every excitation condition (see Fig. 2 of Ref. 20). In the intermediate case (for example, see the 1.6 mW/mm\(^2\) data), \(n_{HS}\) nonlinearly increases after the characteristic incubation period, and then becomes constant. In Fig. 2, we show the microscope image of the [Fe(ptz)\(_6\)](BF\(_4\))\(_2\) single crystal taken at one-second intervals after the photoexcitation of 1.7 mW/mm\(^2\). The color shows negligible change until 3 s after the photoexcitation [Fig. 2(a)–2(c)], but drastically brightens up at \(t=4\) s [Fig. 2(d)] and \(t=5\) s [Fig. 2(e)]. Such an incubation behavior implies that some cooperative interaction dominates the PIPT process.

In Fig. 3, we plotted \(\langle n_{HS}\rangle\) in the photoexcited steady state against \(I\). The increasing (decreasing) speed of each \(I\)-step was about 1 s. The magnitudes of \(\langle n_{HS}\rangle\) were measured 30 s after the increase (decrease) of \(I\). In the weak excitation region \((I<1 \text{ mW/mm}^2)\), \(\langle n_{HS}\rangle\) increases linearly with \(I\), reflecting the fact that the creation rate of the HS species is proportional to \(I\). With further increases of \(I\) beyond \(\approx 1 \text{ mW/mm}^2\), however, \(\langle n_{HS}\rangle\) steeply increases to reach \(\sim 1\). We interpreted this threshold behavior in terms of the dynamical phase transition\(^{21}\) of the photoexcited steady state from the \(n_{HS}=0\) state \((I<2 \text{ mW/mm}^2)\) to the \(\langle n_{HS}\rangle\sim 1\) \((I\geq 2 \text{ mW/mm}^2)\) state. We further observed optical hysteresis\(^{26}\) between the \(I\)-increasing run and the \(I\)-decreasing run, perhaps due to the significant structural change at the PIPT of [Fe(ptz)\(_6\)](BF\(_4\))\(_2\).\(^{25}\)

Now, let us qualitatively analyze the experimentally obtained \(n_{HS}\)-\(T\) curve (see Fig. 1) with a simple rate equation [Eq. (1)]. The first term, \(\dot{I}'(1-n_{HS})\), represents the photocrea-
The rate equation with the effective parameters, that is, $\Gamma \equiv 4 \times 10^{-3}$ mW/mm$^2$/s, $k_0 = 2$ s$^{-1}$, and $\alpha = 3.9$, cannot reproduce the overall temporal behavior of $n_{HS}$. This is because the creation rate $I \Gamma$ [order of 0.01 s$^{-1}$; see Fig. 4(a)] is too slow to reproduce the experimentally-observed fast increase of $n_{HS}$ [order of 10 s; see Fig. 1(a)], even if we neglect the relaxation process. In contrast, the PIPT process of $[\text{Fe}(2\text{-pic})_3]\text{Cl}_2 \cdot \text{EtOH}$ at a low temperature $\approx 4$ can be quantitatively reproduced by the same rate equation [Eq. (1)]. We, therefore, conclude that an extra creation process of the HS species dominates the present PIPT process near $T_c$, where the HS state and the LS ground state are nearly degenerate.

Spiering and co-workers have systematically investigated the second coordination effect by a chemical substitution in $[\text{Fe}(2\text{-pic})_3]\text{Cl}_2 \cdot \text{EtOH}$ and $[\text{Fe}(\text{ptz})_6]\text{[BF}_4]_2$. They have found that the chemical substitution significantly modifies the LS-HS transudation temperature, and have ascribed the chemical impurity effect to the strain effect. For example, $T_c$ of $[\text{Fe}_{1-x}\text{Zn}_x(\text{ptz})_6]\text{[BF}_4]_2$ decreases in proportion to the concentration $x$ of the Zn$^{2+}$ impurity as $T_c \approx 130 - 30x$. Here, note that the ionic radius ($r_{\text{Zn}} = 0.74$ Å) of the Zn$^{2+}$ ion is larger than that ($r_{\text{Fe}} = 0.61$ Å) of the LS Fe$^{2+}$ ion, and hence, the Zn$^{2+}$ impurities expand the lattice to stabilize the HS phase with larger cell volume. We think that a similar strain is induced by the photocreared HS species, because its ionic radius ($r_{\text{Fe}} = 0.78$ Å) is larger than that ($r_{\text{Fe}} = 0.61$ Å) of the LS Fe$^{2+}$ ion. Then, the photocreared HS species also suppress $T_c$ via the stress effect, analogously to the case of the Zn$^{2+}$ impurity. In other words, the photocreared HS species induces the negative pressure within the system. In an extreme case, the system would reach the phase boundary between the LS phase and the HS phase, and show the structural phase transition.

In Fig. 5, we show the creation rate $d n_{HS}/dt$ against $n_{HS}$ at several excitation conditions. We found that the $d n_{HS}/dt$-$n_{HS}$ curves show broad maxima at $n_{HS} \approx 0.3$, irrespective of $I$. [Note that the scale of the horizontal axis of Fig. 5 is two orders larger than that of Fig. 4.] This suggests that the critical density, where the system reaches the phase boundary, is located at $\approx 0.3$. Here, we emphasize that the physical impurity has a dynamic nature, and migrates in the crystal via the creation/relaxation process. Then, the HS-rich regions are spontaneously created in the crystal due to the intrinsic spatial fluctuation of $n_{HS}$. Such HS-rich regions

FIG. 4. (a) Initial creation rate of $n_{HS}$ of $[\text{Fe}(\text{ptz})_6]\text{[BF}_4]_2$ at 77 K against the excitation power $I$. A straight line stands for the result of the least-square-fitting. (b) Relaxation curve of $n_{HS}$ after photoexcitation stops ($I=5.8$ mW/mm$^2$) together with the calculation (broken curve) based on the rate equation.

FIG. 5. Creation rate of $n_{HS}$ of $[\text{Fe}(\text{ptz})_6]\text{[BF}_4]_2$ at 77 K against $n_{HS}$ at several excitation conditions.
could show the phase transition before the spatial average of $n_{\text{HS}}$ reaches the critical value. This may be the origin for the gradual increase of $\text{d}n_{\text{HS}}/\text{d}t$, as observed in Fig. 5. We, however, cannot observe any trace of the spatial fluctuation in the microscopic images (see Fig. 2), whose spatial resolution is $\sim 10 \mu\text{m}$. This suggests that the size of the spatial fluctuation is much less than $\sim 10 \mu\text{m}$.

In summary, we have systematically investigated the temporal behavior of $n_{\text{HS}}$ of the photoexcited $[\text{Fe(ptz)}_6](\text{BF}_4)_2$ near $T_c$ for the LS-HS phase transition, as a function of excitation power $I$. We observed an acceleration of the creation rate $\text{d}n_{\text{HS}}/\text{d}t$ after the characteristic incubation period when $I$ exceeds $\sim 1 \text{ mW/mm}^2$. We interpreted the acceleration in terms of the negative pressure effect induced by the photo-created HS species.

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27. The quantum efficiency ($\Phi=0.3 \text{ sites/photon}$) is different from the value ($=0.8 \text{ sites/photon}$) reported in Ref. 34. This is because we have derived $\Phi$ from the initial creation ratio $\text{d}n_{\text{HS}}/\text{d}t$ at $n_{\text{HS}}=0$, not from the fitting of the overall $n_{\text{HS}}$--$I$ behavior. We emphasize that the quantum efficiency ($\Phi=13 \text{ sites/photon}$) would become an unphysical value, if we reproduced the magnitude of $\langle n_{\text{HS}} \rangle$ within the frame of Eq. (1).
35. We observed no trace of the spatial fluctuation of $n_{\text{HS}}$ in our microscope image. This suggests that the size of the fluctuation would be less than few $\mu\text{m}$.