

# Evidence of four light-induced metastable states in iron-nitrosyl complexes

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## Abstract

Thermodynamic measurements on irradiated  $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}] \cdot 2\text{H}_2\text{O}$  reveal the existence of four light-induced long-lived metastable states, which decay exponentially in time. The activation energies and frequency factors of the four independent states are determined from isothermal calorimetric and differential scanning calorimetric measurements.

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## 1. Introduction

Two light-induced long-lived metastable states, denoted as SI and SII, are established in crystals, glassy matrices or cooled liquids with the general chemical composition  $X_n[\text{ML}_5(\text{NO})] \cdot y\text{H}_2\text{O}$  [1,2]. The central transition metal atom M (e.g., Fe, Ni, Ru, Os, Mo) is surrounded by any ligands L, e.g., F, Cl, Br, I, CN,  $\text{NH}_3$ , OH, CO, CH, etc., including hemoproteins and metalloporphyrins [3–12].  $X_n$  represents various cations or anions, depending on the formal charge of the complex and  $y$  denotes the water content. Recently, SII has been discovered in a compound containing  $\text{N}_2$  instead of NO as the active ligand [13], so that the metastable states are established as a general fundamental physical property. The best analyzed system among all these substances is sodium nitroprusside  $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}] \cdot 2\text{H}_2\text{O}$  (SNP), in which SI and SII can be accessed by irradiation with light in the spectral range 350–600 nm having a life time  $\tau \geq 10^6$  s at temperatures below  $T = 190$  K (SI) and  $T = 140$  K (SII),

respectively [14]. However, up to now the fundamental question about the number of metastable states, which can be accessed by light-illumination, is not answered conclusively. Based on differential scanning calorimetric (DSC) measurements a third metastable state was proposed [14] and four metastable states were used to describe the DSC curve in Ref. [1]. This inconsistency is especially disturbing since the nature of the metastable states is still a matter of discussion [15]. To finally clarify this issue and to detect all possible energy minima in the potential landscape we performed isothermal calorimetric and DSC measurements as an extension to the results of Zöllner et al. [14], whereby the isothermal calorimetric measurements extend the accessible time scale of the decay time to  $50\text{--}10^4$  s.

## 2. Experimental

The DSC (Mettler DSC 30) is equipped with two quartz windows inside and outside of the cryostat for light irradiation. Single crystals of orthorhombic sodium nitroprusside (SNP)  $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}] \cdot 2\text{H}_2\text{O}$ , space group  $Pnmm$ ,

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four molecules per unit cell [16,17], were grown from aqueous solution, doubly recrystallized, and cut perpendicular to the crystallographic axes. The high quality of the single crystals was checked by X-ray diffraction and optical methods. The SNP crystals of 15.34 mg, 0.4 mm thickness, polished to optical quality, lying in an Al-crucible, are irradiated by the light of a metal halide lamp (Osram HMI 575 W), narrowed by a set of broad band interference filters plus color glasses (GG 400, BG 39) to  $\Delta\lambda = 400\text{--}500\text{ nm}$  with an intensity of  $I = 200\text{ mW/cm}^2$ . The electric field vector vibrates parallel to the  $c$ -axis of the crystal, in order to obtain maximal population. The total exposure  $Q = \int I dt$  on the crystal to reach saturation in SI (about  $50\text{ kJ/mol}$ ) is  $Q = 3000\text{ J/cm}^2$ . In order to achieve maximal population of SII the crystal is subsequently irradiated with unpolarized light in the spectral range  $\Delta\lambda = 1100\text{--}1200\text{ nm}$  using a broad band interference filter, an intensity of  $I = 100\text{ mW/cm}^2$  and a total exposure of  $Q = 200\text{ J/cm}^2$ . For the dynamic measurements linear heating rates  $\beta = dT/dt = \text{const.}$  between  $0.2$  and  $0.7\text{ K/min}$  are used and the spectrum of the unirradiated sample is subtracted, so that the baseline is horizontal, lying at zero and only the heat release of the metastable states is determined. The isothermal decay is detected at those temperatures where the life time of SI or SII is long enough for the measurement with DSC, because after the irradiation at  $T = 110\text{ K}$  we need about three minutes to reach the desired temperature and temperature control by the DSC. The heat released during the decay of the metastable states is given by  $\Delta H_{\text{tot}} = \int (dQ/dt) dt$ . The activation energy  $E$  and frequency factor  $Z$  are obtained from the isothermal measurements by fitting the temperature dependence of the life times  $\tau$  with the Arrhenius law

$$\tau^{-1} = Z \exp\left(-\frac{E}{k_B T}\right), \quad (1)$$

while they are obtained from the dynamic measurements with

$$\frac{dQ}{dt} = \Delta H_{\text{tot}} Z \exp\left(-\frac{E}{k_B T} - \frac{Z}{\beta} \int_{T_0}^T \exp\left(-\frac{E}{k_B T'}\right) dT'\right), \quad (2)$$

which describes the DSC curve of a single Arrhenius-like decay.  $k_B$  denotes the Boltzmann constant,  $\beta$  the heating rate, and  $T_0$  the starting temperature for the integration. The temperature was calibrated by the onset of the phase transition temperatures of In ( $T = 156.6^\circ\text{C}$ ), Ga ( $T = 29.8^\circ\text{C}$ ), Hg ( $T = -38.9^\circ\text{C}$ ), hexane ( $T = -95.0^\circ\text{C}$ ),  $n$ -pentane ( $T = -129.7^\circ\text{C}$ ), ammonium dihydrogen phosphate ( $T = -123.3^\circ\text{C}$ ), and potassium dihydrogen phosphate ( $T = -151.3^\circ\text{C}$ ) resulting in a temperature accuracy of  $\pm 0.8\text{ K}$ . Calibration of the enthalpy was made with respect to the phase transitions of In ( $H = 28.45\text{ J/g}$ ) and Hg ( $H = 11.4\text{ J/g}$ ).

### 3. Results and discussion

First, the time dependencies of the isothermal decays obtained after exposure to light were recorded, exemplarily shown at the temperatures  $T = 183\text{ K}$  for SI and  $T = 132\text{ K}$  for SII in Fig. 1. In both cases the heat flow  $dQ/dt$ , i.e., the time derivative of the heat, has to be fitted by the sum of two exponential functions with significant differences in the life times. From the temperature dependence of  $\tau$ , given in Fig. 2, we obtain the activation energies  $E$  and frequency factors  $Z$ , which are named isothermal in Table 1. We have to point out, that the uncertainties of the frequency factors  $Z$  are generally in the range of one order of magnitude due to the small available temperature range. The fundamental new result is

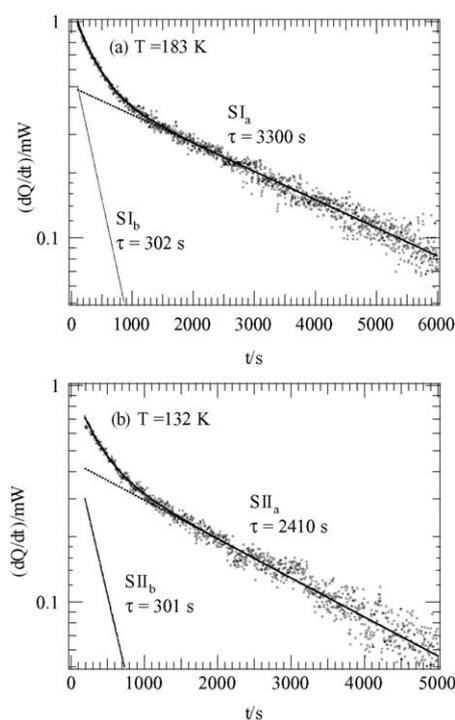


Fig. 1. Isothermal decays of the light-induced metastable states: (a) SI at  $T=183\text{ K}$  and (b) SII at  $T=132\text{ K}$ .

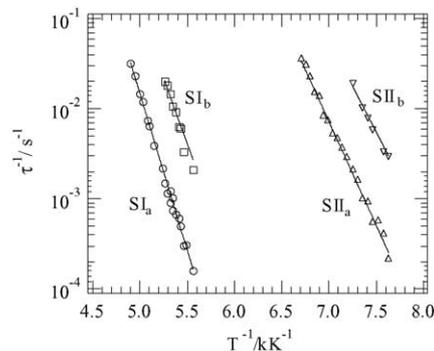


Fig. 2. Temperature dependence of the life times  $\tau$  of the four metastable states  $SI_{a,b}$  and  $SII_{a,b}$ .

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