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

D. Schaniel[a,*], Th. Woike[a], L. Tsankov[b], M. Imlau[c]

[a] *Institut für Mineralogie und Geochemie, Universität zu Köln, Zülpicherstr. 49b, 50674 Köln, Germany*
[b] *Department of Nuclear Engineering, Sofia University, Boul. J. Bourchier 5, 1164 Sofia, Bulgaria*
[c] *Fachbereich Physik, Universität Osnabrück, Barbarastr. 7, 49069 Osnabrück, Germany*

Abstract

Thermodynamic measurements on irradiated $Na_2[Fe(CN)_5NO]\cdot2H_2O$ 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.
© 2004 Elsevier B.V. All rights reserved.

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 $X_n[ML_5(NO)]\cdot yH_2O$ [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, 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 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 $Na_2[Fe(CN)_5NO]\cdot2H_2O$ (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 50–10^4 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) $Na_2[Fe(CN)_5NO]\cdot2H_2O$, space group *Pnnm*,

* Corresponding author. Tel.: +49 221 4706355; fax: +49 221 4705199.
E-mail address: dominik.schaniel@uni-koeln.de (D. Schaniel).

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 $\Delta\lambda = 400$–500 nm with an intensity of $I = 200$ 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 kJ/mol) is $Q = 3000$ J/cm^2. In order to achieve maximal population of SII the crystal is subsequently irradiated with unpolarized light in the spectral range $\Delta\lambda = 1100$–1200 nm using a broad band interference filter, an intensity of $I = 100$ mW/cm^2 and a total exposure of $Q = 200$ J/cm^2. For the dynamic measurements linear heating rates $\beta = dT/dt = \text{const.}$ between 0.2 and 0.7 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 $T = 110$ 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 τ with the Arrhenius law

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

while they are obtained from the dynamic measurements with

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

which describes the DSC curve of a single Arrhenius-like decay. k_B denotes the Boltzmann constant, β 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 ($T = 156.6\,°C$), Ga ($T = 29.8\,°C$), Hg ($T = -38.9\,°C$), hexane ($T = -95.0\,°C$), n-pentane ($T = -129.7\,°C$), ammonium dihydrogen phosphate ($T = -123.3\,°C$), and potassium dihydrogen phosphate ($T = -151.3\,°C$) resulting in a temperature accuracy of ± 0.8 K. Calibration of the enthalpy was made with respect to the phase transitions of In ($H = 28.45$ J/g) and Hg ($H = 11.4$ 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 $T = 183$ K for SI and $T = 132$ 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 τ, 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
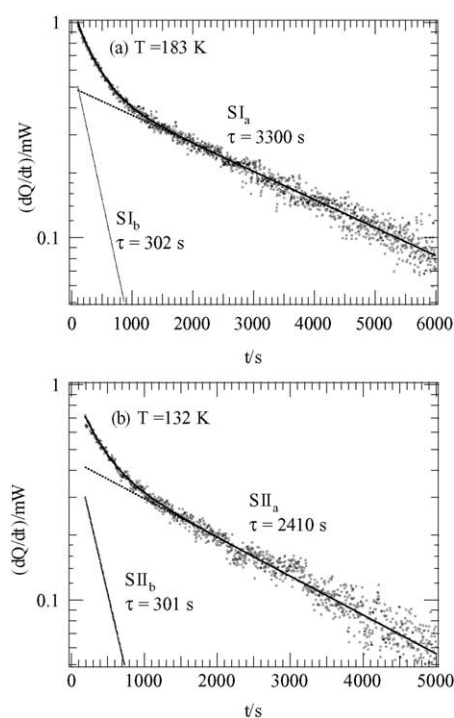

Fig. 1. Isothermal decays of the light-induced metastable states: (a) SI at T=183 K and (b) SII at T=132 K.
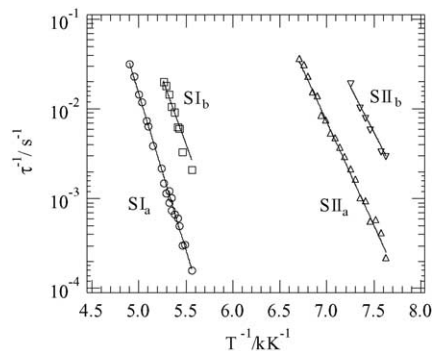

Fig. 2. Temperature dependence of the life times τ of the four metastable states SI$_{a,b}$ and SII$_{a,b}$.
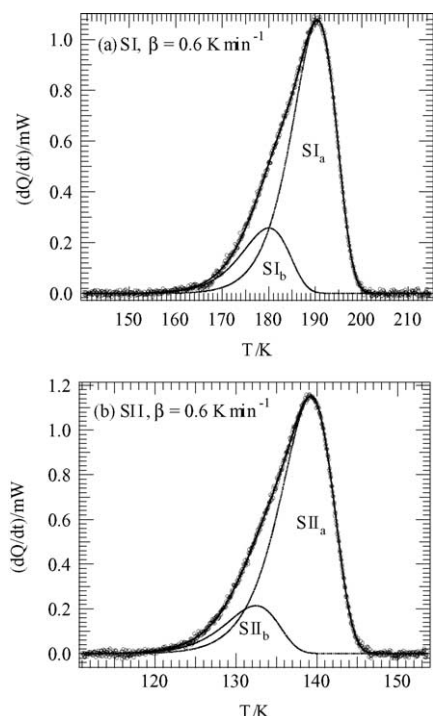
Fig. 3. Dynamic decay spectra of the metastable states, detected with the heating rate $\beta = 0.6$ K/min: (a) SI and (b) SII.

that not only two but four light-induced long-lived metastable states (SI_a, SI_b, SII_a and SII_b) are detected in the temperature range 180–210 and 130–150 K.

Second, we performed dynamic measurements with different heating rates $\beta = 0.2$–0.9 K/min in order to investigate the complete temperature range of the decay. Fig. 3 shows a typical decay of SI and SII for $q = 0.6$ K/min. Due to the exponential decay in time, we can evaluate the dynamic curves as a sum of two Arrhenius decays (Eq. (2)), thereby likewise obtaining the activation energy E and the frequency factor Z. In addition we receive the total enthalpy ΔH_{tot}, whereby $\Delta H_{tot} = \Delta H_a + \Delta H_b$ is the integrated area of the whole detected decay composed by parts a and b. It is obvious that for every state SI or SII there are two decays (a and b), which have to be fitted with different temperature maxima and ar-
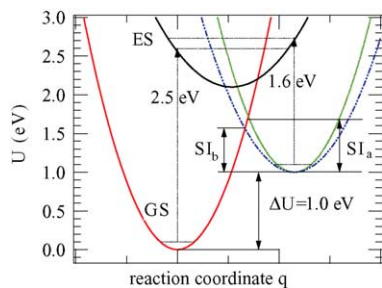

Fig. 4. Harmonic potential scheme for the states GS, SI_a, SI_b, and the excited intermediate state ES. The population of the metastable states $SI_{a,b}$ occurs via optical excitation to ES and subsequent relaxation into the $SI_{a,b}$ basin. The life time of $SI_{a,b}$ is determined by E_A and Z, as given in Table 1.

eas. From several independent measurements with different heating rates we obtain the mean values for $E_{a,b}$ and $Z_{a,b}$, presented in Table 1 as dynamic, together with the total enthalpies ΔH_a, ΔH_b. These results are in excellent agreement with those from the isothermal measurements.

Third, we prepared and investigated the states SI_a and SII_a separately by thermal de-excitation of SI_b and SII_b, which is an unambiguous proof that the new states are independent from each other and do not result from, e.g., tunneling processes or the existence of a saddle point in the energy landscape. Such investigations are possible since the four states have different life times at a given temperature. For example, after the irradiation at $T = 110$ K we heated the crystal up to $T = 134$ K, where SII_a has a life time of 1800 s and SII_b of 160 s. Here, the crystal was kept during five life times of SII_b (800 s) so that SII_b decayed completely, whereas SII_a decayed only partially for 0.44τ, which could be precisely detected afterwards in the area of the signal. The resulting signal can then be fitted with a single Arrhenius decay yielding the activation energy and frequency factor in accordance with the results from the dynamic measurements given in Table 1. Note that the area of the state SII_a is decreased according to its life time, indicating that no molecules are transferred from state SII_b to SII_a. We performed this third experiment at different temperatures and received always the expected reduction in the area of the state SII_a. The same is true for SI_a, especially the activation energy and frequency factor of the pure state SI_a are in accordance with the dynamic results given in Table 1.

The isothermal calorimetric and dynamic DSC measurements show clearly that at least four metastable states can be generated by irradiation with light in SNP. The population ratios of 4:1 (SI_a:SI_b) and 5:1 (SII_a:SII_b) may explain, why they were only detected partially in a few experiments up to now [1,14]. The use of high-quality single crystals of SNP in our experiments ensures that the four states do not result from different structural phases or defects in the material, but are an intrinsic property of these light-induced metastable states. This is further confirmed by the third experiment, where we show that the states SI_a and SII_a can be prepared separately. This selective depopulation of SI_b and SII_b shows that the four states are independent. If further metastable states exist they can be populated only to lower than 0.5 kJ/mol, as this is the detection limit of the used DSC machine.

Summarizing the obtained thermodynamic data and the results from Mössbauer and absorption spectroscopy [18,19] one can construct a potential scheme in harmonic approximation. Mössbauer spectroscopy yields the proportionality between enthalpy $\Delta H_{a,b}$ (kJ/mol) and the number of excited molecules n (%).

Therefore the energetic increase ΔU (eV) of the metastable states with respect to the ground state can be calculated via

$$\Delta U \text{ (eV)} = \left(\frac{1}{n}\right) (\%) \, \Delta H (\text{kJ/mol})$$

$$\times \, 1.036 \times 10^{-2} \text{ (eV mol/kJ)}, \tag{3}$$

Table 1
Activation energy E, frequency factor Z, and enthalpies $\Delta H_{a,b}$ of the four metastable states $SI_{a,b}$ and $SII_{a,b}$ with respect to the ground state obtained from dynamic and isothermal measurements

	SI_a			SI_b			SII_a			SII_b		
	E (eV)	Z (s^{-1})	ΔH_a (kJ/mol)	E (eV)	Z (s^{-1})	ΔH_b (kJ/mol)	E (eV)	Z (s^{-1})	ΔH_a (kJ/mol)	E (eV)	Z (s^{-1})	ΔH_b (kJ/mol)
Isothermal	0.69(3)	3×10^{15}		0.58(3)	4×10^{13}		0.46(3)	1×10^{14}		0.41(3)	1×10^{13}	
Dynamic	0.67(3)	1×10^{15}	42.9	0.56(3)	1×10^{13}	11.0	0.48(3)	6×10^{14}	31.4	0.42(3)	4×10^{13}	5.9

The values for the dynamic measurements correspond to mean values from several measurements.

yielding $\Delta U = 1.0(1)$ eV for $SI_{a,b}$ and $SII_{a,b}$. The population of $SI_{a,b}$ occurs via an excited state ES (antibonding $\pi^*(NO)$ in the orbital picture), from where the system relaxes either into the ground state (GS) or into one of the metastable states $SI_{a,b}$. The performed experiments show that about 50% of the molecules relax back into GS, about 40% into SI_a, and the remaining 10% into SI_b. For the optical excitation GS$\rightarrow \pi^*(NO)$ about 2.5 eV are needed [19]. Since SI_a and SI_b have equal energetic positions ΔU but significantly different activation energies (0.68 and 0.57 eV), the form of the potential well has to be different. Either the two states are located at different reaction coordinates q or they vary in the width of the potential well. As illustrated in Fig. 4 exemplarily for SI, the activation energy is determined by the intersection of the parabola of GS with those of SI_a and SI_b. Assuming that the harmonic potentials of SI_a and SI_b have the same width, and therefore the same force constants, the minima are located at different positions q_a, q_b. This implies that in the potential surface of the metastable states two minima occur, indicating two different structural configurations for each of the states SI and SII, which could not be detected so far [20,15]. On the other hand, also the force constants of the states SI_a and SI_b could differ, which can be detected in vibrational spectroscopy. Indeed infrared spectra exhibit additional weak lines in the range of the N−O stretch vibration at 1836 cm^{-1}, which were then assigned to isotopes of N and O [21,22]. Different force constants of SI_a and SI_b, reflected in a different width of the potential wells, are supported by the frequency factors obtained from the calorimetric measurements, where $Z(SI_a)$ is one order of magnitude larger than $Z(SI_b)$ (see Table 1), yielding a narrower harmonic potential well for SI_a, as depicted in Fig. 4. Optical depopulation of the states $SI_{a,b}$ is possible with light of about 1.6 eV [19], again exciting into the $\pi^*(NO)$ orbital, from where a relaxation into GS or SII occurs. The same considerations as discussed above hold for the states $SII_{a,b}$ for which a similar potential picture can be drawn.

While a decay of SI_b into SI_a can be excluded from our measurements (third experiment), the decay of SI_a into SI_b is generally possible, though during the DSC measurements the state SI_b obtained in this manner would immediately decay into the GS. The detection of such a two-step decay requires time-resolved measurements. Such experiments using a pulsed light-source for the generation of the metastable states are under way. The same considerations hold for the decay of SI and SII. From our measurements we can exclude a decay of SII into SI, while SI may decay back into the GS via SII.

The existence of four independent metastable states requires the re-analysis and re-investigation of all experimental data on the metastable states obtained with various methods up to now, to decide whether they are compatible with this finding or not, after the population ratios of 4:1 (SI_a:SI_b) and 5:1 (SII_a:SII_b) have been taken into account. Especially the geometrical interpretation of the metastable states as linkage isomers *isonitrosyl* Fe−ON for SI and a 90° *side-on* config-

uration of the NO for SII), based on X-ray diffraction results [7,20], will be challenged. This model is supported by DFT calculations [23] but always remained in contradiction to the results of neutron diffraction experiments [15,24,25].

The metastable states are connected with an electronic re-arrangement at the Fe−NO bond [26], which results in an energetic increase of SI and SII of about 1 eV above the ground state [27]. This light-induced activation of the NO may be used to ease the release of NO from these molecules and therefore they may be used as NO-carriers in biomed-ical applications, as was similarly proposed for ruthenium amine nitrosyl complexes [28]. In those complexes the life time of the metastable states at 300 K is $\tau = 1.8$ s (SI) and $\tau = 0.024$ s (SII) [29].

4. Conclusions

Experimental evidence for four independent long-lived light-induced metastable states, SI_a, SI_b, SII_a and SII_b, in SNP with population ratios of 4:1 (SI_a:SI_b) and 5:1 (SII_a:SII_b) are reported. Activation energies and frequency factors de-scribing the Arrhenius behavior of the thermal decay of all the metastable states were determined. We further demon-strated that the states SI_a and SII_a can be prepared separately by selective depopulation of SI_b and SII_b, thereby proving the independence of the four states.

Acknowledgments

References

[1] P. Gütlich, Y. Garcia, Th. Woike, Coord. Chem. Rev. 219–221 (2001) 839.
[2] P. Coppens, I. Novozhilova, A. Kovalevski, Chem. Rev. 102 (2002) 861.
[3] H. Zöllner, W. Krasser, Th. Woike, S. Haussühl, Chem. Phys. Lett. 161 (1989) 497.
[4] T. Woike, H. Zöllner, W. Krasser, S. Haussühl, Solid State Commun. 73 (1990) 149.
[5] Th. Woike, S. Haussühl, Solid State Commun. 86 (1993) 333.
[6] K. Ookubo, Y. Morioka, H. Tomizawa, E. Miki, J. Mol. Struct. 379 (1996) 241.
[7] P. Coppens, D.V. Fomitchev, M.D. Carducci, K. Culp, J. Chem. Soc., Dalton Trans. 6 (1998) 865.
[8] S.C. DaSilva, D.W. Franco, Spectrochim. Acta A 55 (1999) 1515.
[9] Y. Morioka, A. Ishikawa, H. Tomizawa, E.I. Miki, J. Chem. Soc., Dalton Trans. 5 (2000) 781.
[10] D. Fomitchev, I. Novozhilova, P. Coppens, Tetrahedron 56 (2000) 6813.
[11] S. Ferlay, H.W. Schmalle, G. Francese, H. Stoeckli-Evans, M. Imlau, D. Schaniel, Th. Woike, Inorg. Chem. 43 (2004) 3500.
[12] T. Woike, S. Dahaoui, D. Schaniel, S. Ponou, N.K. Hansen, V. Petricek, Z. Krist. 219 (2004) 558.
[13] D. Fomitchev, K.A. Bagley, P. Coppens, J. Am. Chem. Soc. 122 (2000) 532.
[14] H. Zöllner, Th. Woike, W. Krasser, S. Haussühl, Z. Krist. 188 (1989) 139.
[15] D. Schaniel, J. Schefer, M. Imlau, T. Woike, Phys. Rev. B 68 (2003) 104108.
[16] P.T. Manoharan, W.C. Hamilton, Inorg. Chem. 2 (1963) 1043.
[17] F. Bottomley, P.S. White, Acta Crystallogr. B35 (1979) 2193.
[18] T. Woike, M. Imlau, V. Angelov, J. Schefer, B. Delley, Phys. Rev. B 61 (2000) 12249.
[19] D. Schaniel, J. Schefer, B. Delley, M. Imlau, T. Woike, Phys. Rev. B 66 (2002) 85103.
[20] M.D. Carducci, M.R. Pressprich, P. Coppens, J. Am. Chem. Soc. 119 (1997) 2669.
[21] J.A. Guida, O.E. Piro, P.J. Aymonino, Solid State Commun. 57 (1986) 175.
[22] J.A. Guida, P.J. Aymonino, O.E. Piro, E.E. Castellano, Spectrochim. Acta 49A (1993) 535.
[23] B. Delley, J. Schefer, Th. Woike, J. Chem. Phys. 107 (1997) 10067.
[24] M. Rüdlinger, J. Schefer, G. Chevrier, N. Furer, H.U. Güdel, S. Haussühl, G. Heger, P. Schweiss, T. Vogt, T. Woike, H. Zöllner, Z. Phys. B 83 (1991) 125.
[25] J. Schefer, T. Woike, S. Haussühl, M.D. Fernandez Diaz, Z. Krist. 212 (1997) 29.
[26] T. Woike, M. Imlau, V. Angelov, J. Schefer, B. Delley, Phys. Rev. B 61 (2000) 12249.
[27] T. Woike, W. Krasser, H. Zöllner, W. Kirchner, S. Haussühl, Z. Phys. D 25 (1993) 351.
[28] E. Tfouni, M. Krieger, B.R. McGarvey, D.W. Franco, Coord. Chem. Rev. 236 (2003) 57.
[29] D. Schaniel, T. Woike, C. Boskovic, H.-U. Güdel, Chem. Phys. Lett. 390 (2004) 347.