Possible reaction coordinates in the metastable states of sodiumnitroprusside $Na_2[Fe(CN)_5NO]2H_2O$: a discussion based on neutron diffraction- and spectroscopic measurements

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Abstract. The metastable states of sodiumnitroprusside $Na_2[Fe(CN)_5NO]2H/D_2O$ are extremely stable at temperatures below 200 K. It is possible to allocate structural changes measured by neutron diffraction to measured spectroscopic parameters, but the amount of the structural change is relatively small for a reaction co-ordinate as the metastable states have an extremely long lifetime. New hypotheses for related systems try to explain such a phenomena in two ways: The first way is a 90° bending of the NO-bond in the metastable state, the second one an exchange of the oxygen and nitrogen atoms in the NO-bond (which can be regarded as an 180° bending). As such changes would be possible also from our density functional calculations, we re-investigated our neutron diffraction data using the new models. However, our results are not compatible with one of these models. On the contrary, the neutron diffraction data show partially opposite tendencies. We compare both models with EXAFS measurements, with vibrational spectroscopic results and the data found by Mössbauer spectroscopy. We propose a potential scheme for all three states (GS, MS_I and MS_{II}) extracted from absorption and thermodynamic data to explain the electronic and energetic rearrangement, and the population dynamics.

PACS. 61.80.Hg Neutron radiation effects – 61.50.Lt Crystal binding; cohesive energy – 33.45.+x Mössbauer spectra

1 Introduction

Long-lived metastable states are of fundamental interest for information storage and investigations of the correlation amongst electron density, chemical bond and structural behavior. If the lifetime is long enough, structural analysis and determination of the electron density can be performed. As an example, single crystals of sodiumnitroprusside (SNP, $Na_2[Fe(CN)_5NO]2H_2O$) can be transformed into two extremely long-lived metastable states MS_I and MS_{II} with a lifetime greater than 10^{10} s at temperatures below 200 K (MS_I) and 150 K (MS_{II}), respectively. This is of special interest as such systems can be used for holographic data storage yielding storage densities of up to 1 TByte/cm^3 [1].
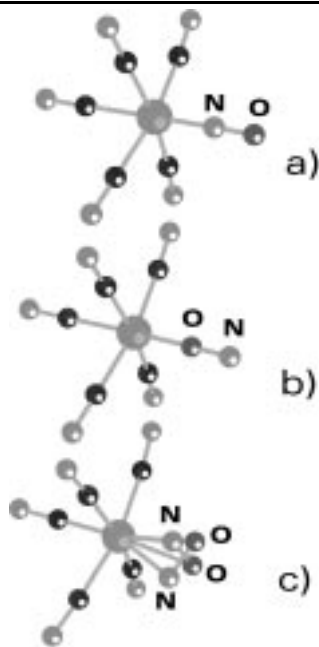
Up to date, we could only observe small structural changes with population of the metastable states, for example see [2] for MS_I and [3] for MS_{II}. These changes could be related to the observed spectroscopic data [4] by a pseudo di-atomic potential [5] only dependent on the position of the two involved atoms in the periodic table.

In the meantime, new models have been proposed assuming a significant change in the structure and by this a long searched explanation for the stability of the metastable states. One model used for MS_I is an exchange of the nitrogen and oxygen atoms in the NO-bond, going from Fe-N-O to Fe-O-N, and for MS_{II} a bending of the NO-bond by 90°, based in principle on the interpretation of anomalous temperature factors of the N and O atoms. However, published data show this only for related systems [6]. According to the authors it exists also in the SNP-system [7]. As such changes would be in agreement with our present calculations using a local spin density functional [8], we decided to re-investigate the existing neutron data using the new models. This is motivated especially, as the oxygen and nitrogen scattering lengths are rather different (9.36 fm and 5.803 fm, respectively [9]).On the other hand, if the NO-bond would be bent by 90°, this should be easily detected in the neutron data as the scattering is done on the nucleus and not on the electron shell. In the second part we further discuss the explanations and propose a potential scheme extracted from optical and thermodynamic data.

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Table 1. Refinement parameters for MS_I using different models. The occupation number n is given in [%] of the maximal possible occupation of this site. For better interpretation: The scattering lengths of nitrogen is 9.36 fm and of oxygen is 5.803 fm. N(O) is indicating a nitrogen on the oxygen position of the NO-bond, O(N) an oxygen on the nitrogen position.

	NO-exchange	N and O occupation not restricted	published data [2]
n (N1)	0.94(1)	1.13 (1)	1.0 fixed
n (N (O))	0.06(1)	0.0	0.0
n (O)	0.94(1)	1.024(9)	1.0 fixed
n (O (N1)]	0.06(1)	0.0	0.0
NO-exchange	6%	none	0%
R	7.2%	7.1%	7.2%
Rw	10.6%	10.3%	10.7%
χ^2	3.55	3.44	3.56

Table 2. Refinement parameters for MS_{II} using different models. The sites of N1 is 0.206, 0.658, 0.4687 and the position of O tilted (0.047, 0.245, 0.479). A refinement of this (x, y, z) parameters is not possible due to the low occupation number.

	NO-tilted 90°	N and O occupation not restricted	published data [2]
n (N1)	0.995(3)	0.990(5)	1.0 fixed
n (N1') (N1' ≈ N1)	0.005(3)	none	0.0
n (O straight)	0.995(3)	1.008(9)	1.0 fixed
n (O tilted 90°)	0.005(3)	none	0.0
			0%
R	5.2%	5.2%	5.2%
Rw	7.1%	7.1%	7.1%
χ^2	2.43	2.43	2.43

Fig. 1. The different models of the Prusside molecule compared in this paper: The standard molecule without an exchange in the NO-binding (a), with the exchange (b) and with the 90° tilted NO-bond (c).

2 Results and discussion

All our calculations are based on previous collected data published in [2] for MS_I and [3] for MS_{II}.

Figures 1a to c show the different models compared. Refinement parameters are listed in Tables 1 (MS_I) and 2 (MS_{II}). We tested the proposed exchange of the NO atoms in two ways: N and O are completely exchanged in the metastable state (*e.g.* N(O) in Tab. 1 a nitrogen in the metastable state is refined at the place of the oxygen in the ground state and O(N) *vice versa*). Therefore, we should be able to fit the number g of the NO-exchange,

which is expected to be about 50% at the used illumination parameters. Table 1 clearly shows, that the refined value g of the exchange model is only approximately 6% (column 1). In a second calculation (column 2) not fixing the sum of occupation numbers of both atoms in the NO-bond, and expecting the chemically reasonable value of 1 (full occupation of both sites), we get an over-occupation of the nitrogen position, exactly the opposite tendency of the proposed NO-exchange (the scattering length of nitrogen is larger than the value for oxygen).

The occupation number of the oxygen closely matches the expected value of 1. The agreement factors show practically no change for all models. The results are compared to the published data with no exchange of N and O, showing small changes in the structure (column 3). We conclude from these results that the proposed model of an NO-exchange does not explain our data for MS_I, even as such an exchange is not excluded by our density functional calculations [8].

The second model, an 90° tilt of the NO-bond, is diverging if used for MS_I, therefore, no results are shown in Table 1. Further, using the results of the normal coordinate analysis [10], in which we have shown that the N-O stretching vibration is mainly a N-O valence vibration (86%) with about 13% Fe-N valence vibration, we can use the pseudo potential in a good approximation as described by the badger-rule [5] for the increase of the NO-bond length in MS_I (0.02 Å) and MS_{II} (0.06 Å), which is very small. This evaluation does not depend on the exchange of nitrogen against oxygen, since we are comparing only the ratios of force constants. The general validity of the Badger-rule is shown by Harris [11]. The validity of our calculation can be proved by determining the increase of the NO-bond length in optically excited CpNiNO (C_5H_5NiNO, Cyclopentadienylnitrosylnickel), in which the metastable states are measured by EXAFS (extended X-Ray absorption fine structure) results [12,13]. The N-O stretching vibration shifts from 1824 cm^{-1} to

1387 cm^{-1}, so that we get $\Delta r = 0.11$ Å, which is also very small and in agreement with the EXAFS results, assuming that only the bond lengths Fe-N and N-O increase, but no exchange of N and O takes place. The difference in the Debye-Waller factor of Ni-N, Ni-C and Ni-O over the temperature range of 4 to 278 K is simply explained by the authores by the different vibrations.

The second model, a 90° tilt of the NO-bond, is used for MS$_{II}$. Using the same space group Pnnm, two NO-groups must be present simultaneously, statistically distributed in the crystal, in order to conserve the mirror plane m. As shown in Figure 1c in one anion the N-atom lies above and the O-atom below m and in the next anion the opposite arrangement is present. The $(N-C)_{trans-}$Fe axis trans to the N-O lies in the mirror plane m and the equatorial N-C-Fe axes build an angle of 45° with the a-b-mirror plane m. We observe a rather poor explanation of our data as shown in Table 2, column 1: Only half of a percent of the molecules would occupy these positions instead of the expected 32% [3]. The refinement is compared to the published data [3] in column 3. However, Figure 1c shows, that this model assumes a statistical distribution of the NO over two sites due to symmetry with a relative high Fe-N distance of 1.90 Å (compared to 1.68 Å in the ground state), which may be not the correct assumption. Column 2 shows in addition, that a NO-exchange does not match the data either. This is in good agreement with the Mössbauer parameters [4], especially with the asymmetry parameter η, where $\eta < 0.02\,(MS_I)$ and $\eta \leq 0.1\,(MS_{II})$, so that the quasi $4m$ symmetry of the anion is unaffected by the excitation of MS$_I$ or MS$_{II}$. A further hint for the existence of quasi $4m$ symmetry of the anions in MS$_{II}$ is found by polarized infrared spectroscopy. All 33 internal vibrational modes of the anion are distributed among the symmetry species of the $4m$ point group as $\Gamma = 8A_1 + A_2 + 4B_1 + 2B_2 + 9E$. All $8A_1$ and $9E$ modes are infrared active. A_1 modes can be detected with polarization along the crystallographic a- and b-axis and the E modes along the a-, b-, c-axis in SNP. Therefore, they can be clearly assigned to the measured absorption bands. If, however, the N-O ligand is tilted by 90°, the symmetry of the anion is reduced to m and the internal vibrational modes are represented by $\Gamma = 19a' + 14a''$. This shows that all degenerate modes (E) under $4m$ symmetry must split in m symmetry. However, no such splitting of E modes could be found, either the $\nu(CN)$ stretching at 2133 cm^{-1} in MS$_{II}$ or the $\delta(FeCN)$ deformation mode at 595 cm^{-1} in MS$_{II}$, detected with a resolution of 2 cm^{-1} [14,15]. Assuming that the quasi $4m$ symmetry of the anion is unchanged in the metastable states and considering the results of absorption spectroscopy [16,17] and differential scanning calorimetry [18,19], the behavior of the metastable states can be summarized in a potential scheme given in Figure 2.

Starting from the HOMO, mainly $3d_{xy}$ orbital, of the formally Fe^{2+}-central atom, the empty antibonding π^*-NO orbital can be reached by irradiation with light in the range of 350 to 580 nm. In Figure 2 we have only shown the transition $3d_{xy} \rightarrow \pi^*$-NO at about 2.5 eV. From the
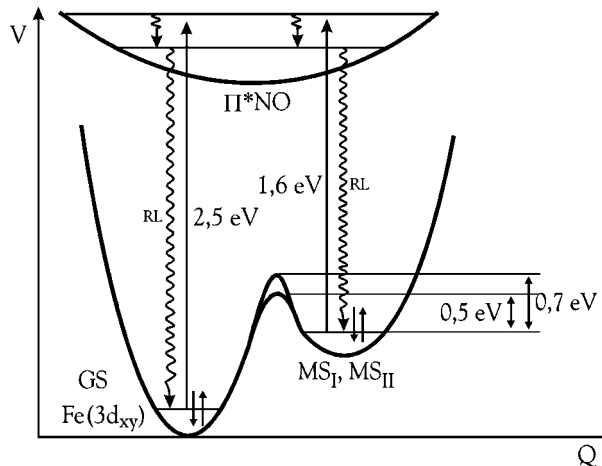
Fig. 2. Potential scheme of the ground and metastable states in $[Fe(CN)_5NO]^{2-}$.

excited π^*NO orbital the metastable states MS$_I$ and MS$_{II}$ are populated by radiationless transitions (RL), so that MS$_I$ and MS$_{II}$ are not the excited π^*NO orbital, as often assumed [20–22], since the crystal is diamagnetic in GS, MS$_I$ and MS$_{II}$.

Güdel [21] has proposed the quintet state $((t^2g)^4\pi^*NO)^2$ for MS$_I$ in order to explain the lifetime of MS$_I$ in analogy to the spin-crossover compounds [23]. This, however, is in clear contradiction to the very weak temperature dependence of the quadrupole splitting of the central atom, detected by Hauser *et al.* [24], and the diamagnetism. A second explanation for the existence of MS$_I$, given by Guida [22] proposed an increase of electron density in the $3d_{z^2}$-orbital, which is again in clear contradiction to the Mössbauer results. Since the quadrupole splitting given by $QS = const[(nd_{x^2-y^2} - nd_{z^2}) + (nd_{xy} - n/2d_{xz,yz})]$ increases in MS$_I$ and MS$_{II}$, however, a higher population of $3d_{z^2}$ decreases QS. This lower value of QS can not be compensated by decreasing the electron density of the $d_{xz,yz}$ orbital. Because of its degeneracy it is weighted by a factor of two with respect to nd_{z^2}. It is possible that we need a sufficient lifetime in the excited Π^*NO orbital for the rearrangement of the energetic position of the ground state. In the given orbital scheme we have not shifted the Π^*NO orbitals. Deexcitation can be performed by irradiation with light in the red spectral range (600-900 nm) exciting again the empty Π^*NO orbital, followed by the radiationless transition into the ground state. The maximum of the absorption band in MS$_I$ lies at 1.6 eV and for the transition Fe$(3d_{xy}) \rightarrow \Pi^*$NO at 2.5 eV. In the red spectral range only depopulation is possible. In the blue-green spectral region both population and depopulation of MS$_I$ take place with an equilibrium of 50% of transfered anions at 450 nm. A second de-excitation path is the thermal decay above the potential barriers of 0.7 eV (MS$_I$) and 0.5 eV (MS$_{II}$), which explains the stability below the characteristic temperatures of 200 K (MS$_I$) and 150 K (MS$_{II}$). The lifetimes at $T = 100$ K and

a frequency factor of $Z = 10^{15}$ are: $\tau(MS_I) = 1.9 \times 10^{20}$ s and $\tau(MS_{II}) = 1.6 \times 10^{10}$ s, calculated by the Arrhenius law.

The potential barrier between MS_I and MS_{II} is higher than 0.7 eV, since MS_I can not be populated by the thermal decay of MS_{II} as detected by Differential Scanning Calorimetry [19]. MS_I and MS_{II} are lying energetically about 1 eV above the ground state, since about 50 kJ/mol is given up from 50% of the molecules to the lattice [19]. This energy loss has to be distributed over the orbitals involved with the changed electron density. The given orbital scheme has to be fulfilled by the lower lying mainly $Fe(3d_{xz,yz})$ orbital and the energetic behavior of the Π^*NO orbital, which will be performed by absorption spectroscopic measurements [25]. The main problem is the clear description of the reaction coordinate Q.

3 Summary

In summary, we have again confirmed that the structural changes of the metastable electronic excited states are rather small. An exchange of the NO-atoms in the NO-bond from Fe-N-O to Fe-O-N for MS_I could not be observed as a 90° bending of the NO-bond for MS_{II} neither. We have summarized all spectroscopic and thermodynamic data in a potential scheme, which explains the gigantic lifetimes of MS_I and MS_{II} and the wavelength dependent population and depopulation process.

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