

**Experiment title:**

Photo-excited states of the nitroprusside ion studied with valance emission spectroscopy

Experiment number:

CH-1665

Beamline:

ID16

Date of experiment:

from: 30/11/2004 to: 6/12/2004

Date of report:

1/3/2004

Shifts:

18

Local contact(s):

S. Huotari

*Received at ESRF:***Names and affiliations of applicants** (* indicates experimentalists):

György VANKÓ* — ESRF ID16;

Szilvia KÁRPÁTI*, Zoltán NÉMETH* — Eötvös Univ. Budapest, Hungary;

Franz RENZ* — Gutenberg Univ. Mainz, Germany;

Gábor MOLNÁR — CNRS Toulouse, France;

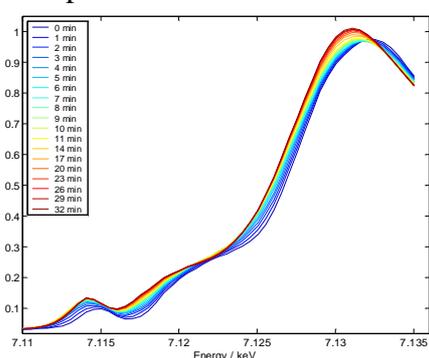
Report:

At low temperatures, the nitroprusside ion ($[\text{Fe}(\text{CN})_5\text{NO}]^-$) can have two long-lived metastable states. These states, denoted as MS_1 and MS_2 , form when the nitroprusside (NP) is irradiated with light in the spectral range of 350–590 nm. Deexcitation to the ground state (GS) can be achieved by illumination with red or near infrared light, or heating above the decay temperatures (150 K for MS_1 and 200 K for MS_2). MS_1 and MS_2 can be (partly) interconverted with the appropriate irradiation.[1]

The scheme on the right, which summarises the possible transitions, is rather complicated because none of the excitations/de-excitations is a simple process: they all involve the passing through higher energy transient states and the yields depend on the branching ratios of the involved relaxations. Nevertheless, these transitions make the NP materials an intriguing class of photoswitchable compounds.[2] Furthermore, according to light scattering experiments, they have strong potentiality in high-capacity holographic information storage systems [3].

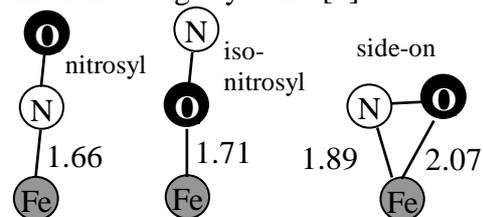
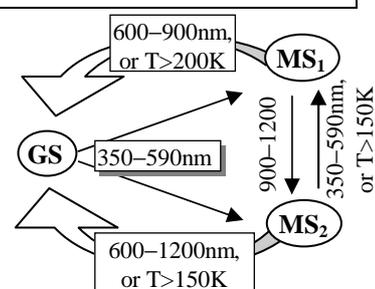
The nature of the MS_1 and MS_2 states are far from being understood. The first structural works suggested that the metastable states preserve the nitrosyl-like structure of the GS, and only the Fe–N bond length, and the tilt of the NO group varies a small amount. A later X-ray diffraction study, however, assigned MS_1 to isonitrosyl, and MS_2 to ‘side-on’ bonding.[4] These isomers are further supported by theoretical calculations,[5] moreover, vibrational spectra of the excited states can be readily interpreted in terms of such arrangements of NO,[6,7] thus this became the prevailing description of these states.[1] However, neutron diffraction, the only method directly sensitive to the atomic positions, repeatedly reports nitrosyl-like bondings in agreement with the first observations.[8,10]

We chose X-ray emission spectroscopy to contribute to the elucidation of the structures of the metastable states. The $\text{K}\beta''$ and $\text{K}\beta_{2,5}$ emission peaks originate in electron transitions from the highest energy molecular orbitals with (at least some) p -character to the $1s$ hole of the metal. It has been clearly demonstrated on Mn compounds that these features convey valuable chemical information due to the involvement of the appropriate



p and s orbitals of the ligand in the molecular orbitals.[11,12] Most important to our study is the $\text{K}\beta''$, where the contribution from the ligand $2s$ orbitals is dominant, thus its energy position correlates with the $2s$ binding energy while its intensity varies exponentially with the bond length. Consequently, this spectral region can be used to *identify the ligands* and estimate their distance.

First we studied polycrystalline sodium-nitroprusside (SNP) to examine its sensitivity to radiation, and to collect some reference emission data. The total fluorescence yield XANES, shown on the left, revealed very fast decomposition in the beam. To minimize radiation damage we defocused the beam, and



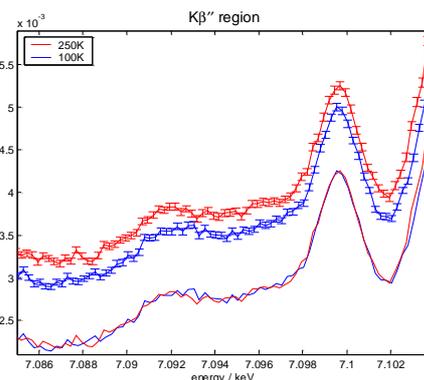
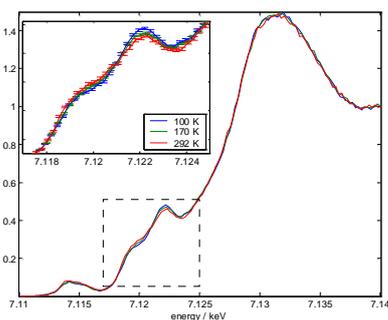
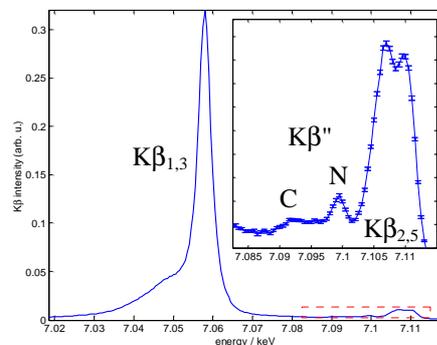
limited the exposure to 1 minute over each spot of the samples by taking rapid scans with appropriate sample displacements in between. The spectra shown in this report are sums of a great number of such rapid scans.

The full $K\beta$ emission spectrum of polycrystalline SNP is shown on the right. The main $K\beta_{1,3}$ line reflects the low-spin character of the iron. The inset displays the valence emission part, which reveals a relatively significant peak and a broader one with much smaller intensity below in the $K\beta''$ region, i.e., at energies below the $K\beta_{2,5}$. To interpret this, first we note that our previous X-ray emission study on a spin-crossover iron complex of pseudo-octahedral geometry indicated that a Fe–N bond length of 2.0 Å or smaller is needed to make the $K\beta''$ contribution discernible.[9] With bond lengths below 2 Å, the intensity is expected to increase exponentially along with the shortening of the metal-ligand distance, as the $K\beta''$ features reflect hybridisation with the 2s orbitals of the ligand. In the SNP, the five C atoms of the cyanide ligands are rather far from the iron (1.93–1.94 Å), while the donor atoms relevant to our study are significantly closer (≈ 1.7 Å; cf. the second scheme on the previous page). Consequently, one can expect intense N or O peaks from the nitrosyl or isonitrosyl structures, respectively. Thus the larger peak should be assigned to the contribution from the N of the NO ligand, while the broad one to the C of the CN.: the Fe–N bond is relatively short, thus it is expected to give an intense peak.

Upon excitation, the following variations are expected for the isonitrosyl and the side-on structures: if an isonitrosyl bond is formed, in analogy with the Mn-compounds, the contribution from O is expected to show up with significant intensity (due to the short distance) at an energy about 5 eV smaller than the N $K\beta''$ peak. The ‘side-on’ structure, having longer Fe–N and Fe–O bonds as well as one shortened Fe–C bond (1.82 Å), should also be in principle easily recognised by the enhanced C and the smaller N contributions. Moreover, in both cases a diminution of the N peak, proportional to the excitation yield, should be observed.

Two SNP crystals were irradiated with LED diodes of 455 nm for 24h at 80K. Upon excitation their colour has changed from reddish to dark (see picture on the right, taken under liquid N_2). Mössbauer spectroscopy studies showed about 20% conversion to the excited states under such conditions. The main $K\beta_{1,3}$ line, remained identical in all states showing no difference in the spin state of the iron. The partial fluorescence yield XANES spectra (on the left), taken on the maximum of the $K\beta_{1,3}$ line, show small variations with increasing temperature in the pre-edge region. Although there seems to be a trend, which might be related to the de-excitation steps, the minor extent of the changes, and the statistical limitation of the data do not permit us to draw deep conclusions.

With both crystals, the valence emission spectra revealed no changes when the temperature passed the decay temperatures of the excited states (c.f. spectra on the right). The absence of the above-described variations can only be explained if there’s no major variation in the bonding pattern in the metastable states. This finding is in agreement with the neutron diffraction results, which claims that the only change concerning the first neighbours of the iron is the minor difference in the Fe–N bond length and the small alteration of the C–Fe–N angles, and suggests that isonitrosyl and side-on linkage isomers presented by Carducci *et al.*, though intuitively attractive, do not adequately represent the photo-excited metastable states of the nitroprusside ion.



- [1] P. Coppens *et al.*, Chem. Rev. **102** (2002) 861.
- [2] P. Gülich *et al.*, Coord. Chem. Rev. **219** (2001) 839.
- [3] M. Imlau *et al.*, Phys. Rev. Lett. **82** (1999) 82860.; M. Imlau *et al.*, Europhys. Lett. **53** (2001) 471.;
- [4] M. D. Carducci *et al.*, J. Am. Chem. Soc. **119** (1997) 2669.
- [5] B. Delley *et al.*, J. Chem. Phys. **107** (1997) 10067.; T. Ishikawa *et al.*, J. Chem. Phys. **122** (2005) 074314.
- [6] T. Woike *et al.*, Phys. Rev. Lett. **53** (1984) 1767.; Y. Morioka *et al.*, Chem. Phys. Lett. **292** (1998) 625.
- [7] H. Paulsen *et al.*, J. Am. Chem. Soc. **124** (2002) 3007.
- [8] M. Rüdlinger *et al.*, Z. Phys. B **83** (1991) 125.; J. Schefer *et al.*, Eur. J. Phys. B **3** (1998) 349.
- [9] G. Vankó, T. Neisius, S. Kárpáti, G. Molnár, F. Renz, F. de Groot, to be published.
- [10] D. Schaniel *et al.*, Phys. Rev. B **68** (2003) 104108.
- [11] U. Bergmann *et al.*, Chem. Phys. Lett. **302** (1999) 119.
- [12] U. Bergmann *et al.*, J. Chem. Phys. **116** (2002) 2011.; P. Glatzel *et al.*, Coord. Chem. Rev. **249** (2005) 65.