

**Experiment title:**

Characterization of the long-lived metastable states of the nitroprusside anion

Experiment number:

CH-947

Beamline:

ID18

Date of experiment:

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12

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Report:

Nuclear inelastic scattering (NIS) measurements have been performed on a guanidium nitroprusside ((CN₃H₆)₂[Fe(CN)₅NO], GNP) monocrystal at 77 K after the sample has been illuminated with blue light (450 nm) at 50 K to populate the two metastable states, MS₁ and MS₂, of the nitroprusside anion. A second measurement has been performed at 77 K after warming up the illuminated crystal to 250 K where the metastable states decay to the groundstate (GS, Fig. 1).

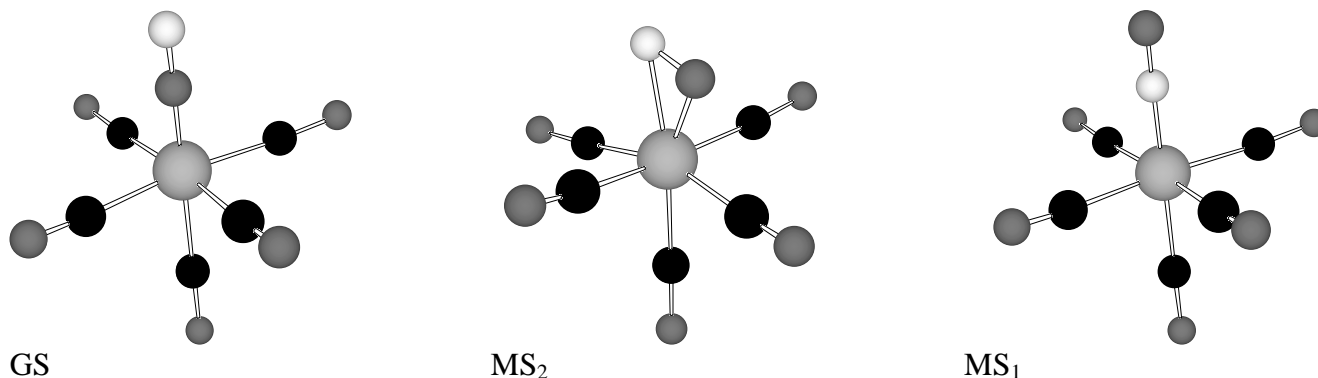


Figure 1. Geometry of ground state and metastable states of the NP anion as retrieved from DFT calculations.

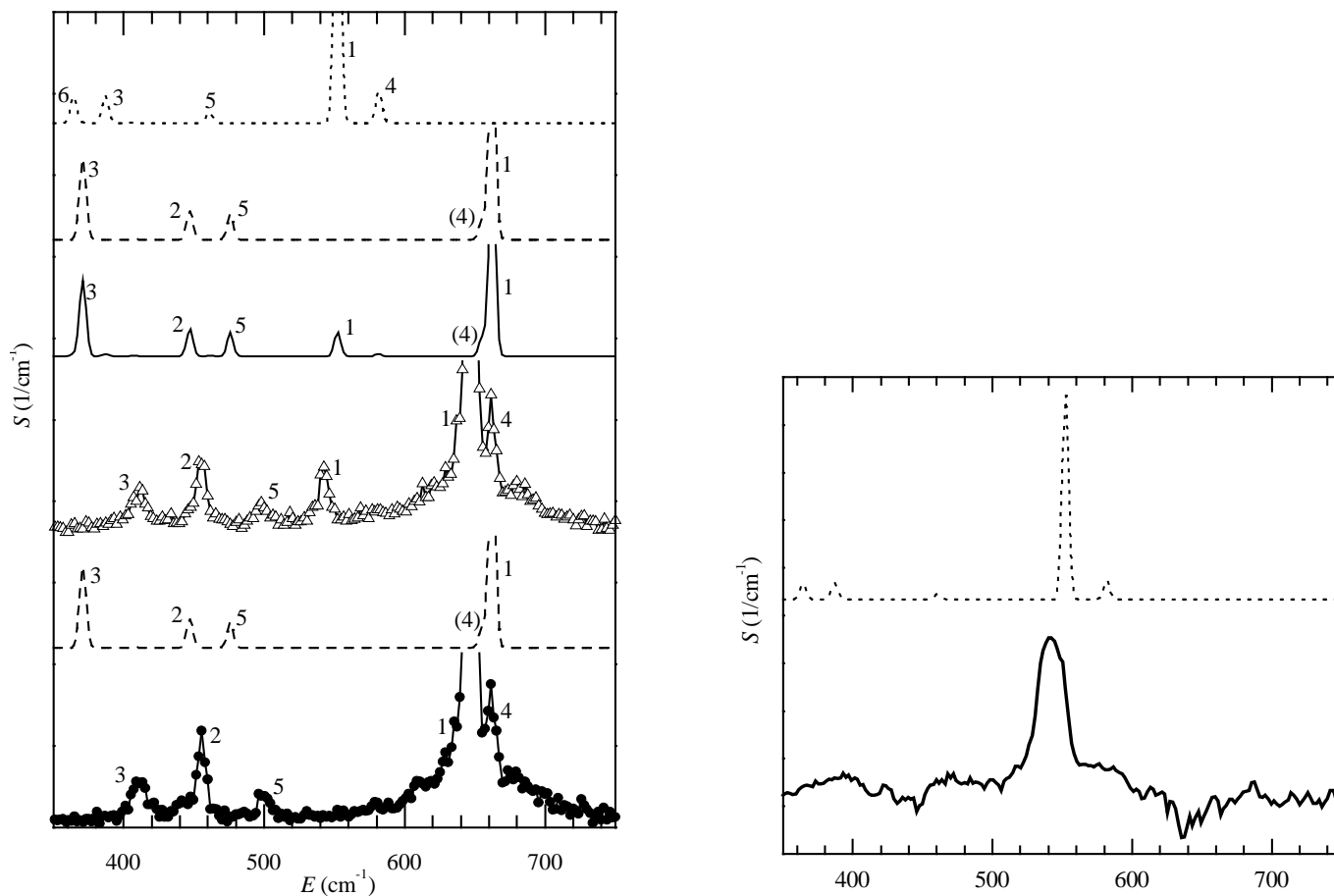


Figure 2. Left panel: experimental NIS spectra at 77 K before (Δ) and after (\bullet) warming up to 250 K and cooling down again. The dashed and the dotted lines represent the simulated spectra for GS and MS_1 . The solid line is a superposition of GS (93 %) and MS_1 (7 %). Right panel: difference of the experimental NIS spectra before and after warming up (solid line). The dotted line represents the simulated spectrum for MS_1 .

Comparison of the experimental NIS spectra (Fig. 2), which have been recorded under conditions excluding and including the metastable MS_1 state, with simulated NIS spectra using density functional theory (DFT), strongly supports the isonitrosyl structure of the metastable MS_1 state as proposed by Carducci et al. [1] (Fig. 1). A possible explanation for the remaining discrepancy between the conclusions derived from X-ray, NIS, and DFT studies on one side and from neutron scattering studies on the other side might be related with possible surface effects that play a role when illuminating the sample to populate the metastable states. NIS is very sensitive to surface properties, due to the limited escape depth of the 6.4 keV fluorescence radiation. Hence, the NIS measurement will not be adversely affected if only in the surface layer of the sample the MS_1 states are populated, for instance due to a temperature gradient in the sample or due to insufficient penetration of the sample by the illumination with light. The results of this study have been published in Ref. [2].

References

- [1] M. D. Carducci, M. R. Pressprich, P. Coppens, *J. Am. Chem. Soc.* **119** (1997) 2669.
- [2] H. Paulsen, V. Rusanov, R. Benda, C. Herta, V. Schünemann, C. Janiak, Th. Dorn, A. I. Chumakov, H. Winkler, A. X. Trautwein, *J. Am. Chem. Soc.* **124** (2002, in press).