

Metastable Isonitrosyl Structure of the Nitroprusside Anion Confirmed by Nuclear Inelastic Scattering

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Abstract: Nuclear inelastic scattering (NIS) measurements were performed on a guanidium nitroprusside ((CN₃H₆)₂[Fe(CN)₅NO], GNP) monocrystal at 77 K after the sample was 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 was performed at 77 K after warming up the illuminated crystal to 250 K where the metastable states decay to the groundstate. The measured spectra were compared with simulated NIS spectra that were calculated by using density functional methods. Comparison of measured and simulated spectra provides strong evidence for the isonitrosyl structure of the metastable MS₁ state proposed by Carducci et al. (Carducci, M. D.; Pressprich, M. R.; Coppens, P. *J. Am. Chem. Soc.* **1997**, *119*, 2669–2678).

Introduction

Sodium nitroprusside dihydrate (Na₂[Fe(CN)₅NO]·2H₂O, in short SNP·2H₂O) as well as many other nitroprusside species have become a promising basis for holographic information storage devices with extreme high capacity¹ since the existence of long-lived metastable states was discovered by Mössbauer spectroscopy in 1977.² In the following years extensive spectroscopic studies have given further insight: there are two metastable states, MS₁, which is stable up to 195 K, and MS₂, which decays above 150 K.³ Both metastable states can be populated reversibly from the ground state by illumination with light at low temperature. The population is not performed directly but via transient states of higher energy.⁴ There is no apparent dependency on the counterions or on the crystalline environment, which means that the metastability of the states must be a purely molecular phenomenon.⁵ From the longevity of the metastable states Güdel⁶ concluded that they have to be explained either by a structural change or by multielectron

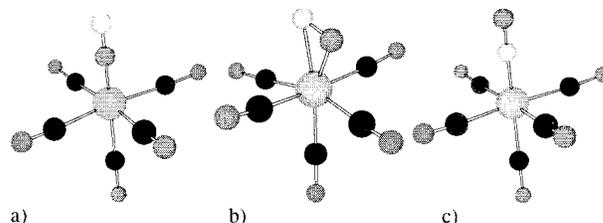


Figure 1. Optimized geometry of (a) the ground state, (b) the side-on bonding (MS₂), and (c) the isonitrosyl (MS₁) structure of the NP anion as retrieved from BLYP/6-311+G(2d,p) DFT calculations.

promotion. But despite all efforts the nature of the metastable states remained in the dark for almost 20 years.

In 1997, in their pioneering X-ray study, Carducci et al.⁷ gave for the first time an explanation for the metastable states that is consistent with almost all the available experimental data. According to their explanation, MS₁ corresponds to an isonitrosyl geometry of the nitroprusside (NP) anion and MS₂ corresponds to a side-on bonding of the nitrosyl group (Figure 1). Electronic structure calculations applying density functional theory (DFT) by Delley et al.⁸ yielded local minima on the energy hypersurface for the isonitrosyl structure and for the side-on structure. Later studies applying different DFT methods confirmed these results.^{9,10} From the DFT calculations the

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geometry, the vibrational frequencies, and the electric field gradient (efg) at the nuclear positions for the ground state (GS), MS₁, and MS₂ could be retrieved and compared with experimental data gained by Mössbauer spectroscopy,^{1,2} IR and Raman spectroscopy,¹ and X-ray diffraction.^{3,7} Additional information has been gained by investigating experimentally and theoretically the shift of vibrational frequencies upon isotope substitution (¹⁵NO, ⁵⁴Fe, ¹⁸O).^{11,12} In general, there is good agreement between the calculated and the measured quantities. An exception is the efg at the iron nucleus in the metastable state MS₂. It is supposed that this disagreement is due to the fast rotation of the nitrosyl group about the approximately 4-fold symmetry axis of the remaining part of the anion within the lifetime of the excited state of the ⁵⁷Fe nucleus.^{8,9}

In summary, the combination of spectroscopic experiments (IR, Raman, Mössbauer) and DFT calculations supports the structures that have been proposed by Carducci et al. on the basis of X-ray diffraction experiments. Nevertheless, the question about the nature of the metastable states of the NP anion is still not unequivocally clear, because the only method that could directly determine the nuclear positions, neutron scattering, does not confirm the isonitrosyl structure.^{13,14} Instead the neutron diffraction data indicate an Fe–N–O bonding structure for both, the ground state and the metastable MS₁ state.

We have applied the relatively new technique of nuclear inelastic scattering (NIS) of synchrotron radiation¹⁵ in the present study to further elucidate the nature of the metastable states in the NP anion. The NIS method aims at the dynamics of the Mössbauer nucleus alone and allows the extraction of those normal modes that are connected with a mean-square displacement (msd) of this nucleus. The basic idea of the NIS method is to detune the energy E_{phot} of the incoming photons of the synchrotron beam from the resonance energy E_{res} of the Mössbauer nucleus by an energy $E = E_{\text{phot}} - E_{\text{res}}$ that is sufficient to excite a molecular vibration.¹⁵ In the isotropic case the absorption probability $S(E)$ of an NIS spectrum is a function of the energy difference E , in the anisotropic case it depends also on the wavevector \mathbf{k} of the incoming synchrotron radiation. In the low-temperature approximation this function can be written as¹⁶

$$S(E, \mathbf{k}) \propto \sum_i \delta(E - E_i) \langle (\mathbf{k} \cdot \mathbf{u}_i)^2 \rangle \quad (1)$$

where E_i is the energy of the i th molecular vibration. The term $\langle (\mathbf{k} \cdot \mathbf{u}_i)^2 \rangle$ describes the contribution of the i th vibration to the total msd of the iron nucleus projected on the wavevector \mathbf{k} . By definition $S(E)$ is normalized, i.e., $\int S(E) dE = 1$. Different from vibrational spectra detected with other methods, NIS

spectra depend solely on the eigenfrequencies and eigenvectors of the vibrations, but not on other properties such as the polarizability of the molecule.

NIS spectra for different cuts of a guanidinium nitroprusside ((CN₃H₆)₂[Fe(CN)₅NO]) monocrystal in the ground state have been recorded and interpreted with the help of DFT calculations.¹⁶ Recently, we have demonstrated for a monocrystal of a spin-crossover complex that single molecular vibrations could be resolved by anisotropic nuclear inelastic scattering.¹⁷ To apply this technique to the problem of the metastable states, guanidinium nitroprusside (GNP) has been chosen among other nitroprussides for the following reasons: (i) In a GNP monocrystal the symmetry axes of all NP anions are approximately parallel. This allows information to be gained about the anisotropy of the molecular vibrations.^{16,18} (ii) It has been demonstrated in a conventional Mössbauer experiment that due to the alignment of the molecular axes a population of metastable states up to 26% could be achieved by using light emitting diodes (LEDs) instead of a laser,¹⁸ which considerably simplifies the experimental setup at the synchrotron beamline.

In this study NIS measurements on a GNP monocrystal at 77 K are described. Before measuring the first spectrum, the metastable states MS₁ and MS₂ were populated by illumination with light from blue LEDs. A second spectrum was measured after depopulating the metastable states by warming up the crystal to 250 K to let the metastable states decay to the ground state. The resulting NIS spectra are compared with theoretical simulations based on DFT calculations for the NP anion in vacuo. While calculations for the complete crystal should, in principle, lead to an increased accuracy, the calculation for the free anion is the more general approach that allows explanations that are independent of the crystalline environment. This is of importance since it is generally accepted that the metastable states of the nitroprusside anion are a molecular phenomenon that is hardly influenced by the crystalline environment.^{5,7,8} The metastable states have been observed not only in various nitroprussides with different counterions and solvent molecules,^{5,19} but also in glassy materials such as frozen solutions of nitroprusside anions²⁰ and in analogous nitrosyl complexes with different ligands²¹ or with Ru²² or Os²³ as the central metal ion. The bond distances of the NP anion as determined by X-ray diffraction exhibit only a weak dependence on the type of counterions (Table 1).^{7,24,25} Neither in SNP·2H₂O nor in GNP do the distances between hydrogens and electronegative atoms (>3.1 Å for GNP) permit the formation of hydrogen bonds.^{24,25} Mössbauer measurements on 25 different nitroprussides demonstrate that the quadrupole splitting (1.722 mm/s < ΔE_Q < 1.931 mm/s) and the isomer shift (0.049 mm/s < δ < 0.086

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Table 1. Calculated and Measured Bond Distances (Å)

bond	NP anion (calcd) ^a	SNP·2H ₂ O (calcd) ^a	SNP·2H ₂ O (exptl) ^b	GNP (exptl) ^c	BaNP (exptl) ^c
Fe–N	1.65	1.66	1.67	1.65	1.66
Fe–C _{ax}	1.96	1.91	1.92	1.95	1.94
Fe–C _{eq}	1.96	1.93	1.93	1.94	1.93
N–O	1.17	1.14	1.13	1.13	1.13
C–N _{ax}	1.17	1.17	1.16	1.15	1.14
C–N _{eq}	1.17	1.17	1.16	1.14	1.14

^a Using BLYP/6-311+G(2d,p), present work.

mm/s) at 77 K are almost independent from the crystalline environment.²⁶ IR spectra of SNP, SNP dihydrate, SNP in aqueous solution, and SNP in acetonitrile solution give differences of the N–O and C–N bond stretching vibrations of 1% on average (maximum 2%).²⁷ Similar observations have been made for the IR spectra of nitroprussides with different counterions.²⁸ The small influence of the counterions on the molecular properties of the nitroprusside anion is also reflected in theoretical calculations of bond distances (Table 1) and electric field gradients for the free NP anion and for the SNP crystal.^{8,9} The comparison between experiments and calculations indicates that the observed deviations arise only to a small extent from the neglect of the crystalline environment. The major source of errors is most probably the approximations on which the employed density functionals are based.

Experimental Section

Sample Preparation. Guanidinium nitroprusside with an isotope enrichment in ⁵⁷Fe of 25% was synthesized starting from 0.2 g of ⁵⁷Fe metal (95.3% isotope purity) blended with 0.6 g of normal iron metal, using a high-yield, millimolar-scale synthesis that is described in detail by Janiak et al.²⁹ GNP was eventually prepared from sodium nitroprusside, Na₂[Fe(CN)₅NO], by 2-fold cation exchange via silver nitroprusside. Monocrystals of GNP could be grown by slow solvent evaporation from a saturated aqueous GNP solution in the presence of a saturated NaCl solution.²⁹ The largest crystals had approximately cubic shape and dimensions of 3 × 4 × 4 mm³. The purity of the GNP product and of the intermediates has been ascertained to be better than 98% by ⁵⁷Fe Mössbauer spectroscopy and by ⁵⁷Fe NMR spectroscopy.²⁹ One of the GNP monocrystals was oriented by using X-ray diffraction and cut perpendicular to the crystallographic c-axis. The resulting sample, called the c-cut crystal, has one triangular shaped surface where the c-axis is the surface normal. This means that the axis of molecular symmetry is perpendicular to this surface within a cone of ±9° for all NP anions.

Nuclear Inelastic Scattering. NIS spectra were recorded at the Nuclear Resonance Beamline ID 18 of the European Synchrotron Radiation Facility (ESRF) in Grenoble, France. The incident beam was monochromatized by a Si(111) double-crystal to a bandwidth of 20 000 cm⁻¹. A further decrease of bandwidth down to 5 cm⁻¹ was obtained with a high-resolution monochromator (HRM).³⁰ This beam was used to excite the 14.413 keV nuclear level of the ⁵⁷Fe nuclei in the GNP sample. The decay of the excited nuclear state (lifetime 141 ns) to the ground state occurs with 90% probability by the emission of a

conversion electron. To detect the subsequent 6.4 keV K-fluorescence radiation, which is delayed compared to electronic scattering, an avalanche photodiode with a time resolution of less than 1 ns is used.³¹

The c-cut crystal was mounted on a sample holder surrounded by two LEDs of 450 nm wavelength and of 200 mcd (milliCandela) intensity. The sample holder was mounted on a coldfinger in the vacuum of a closed-cycle cryostat. After the sample was cooled to 50 K, it was illuminated by the two LEDs for 24 h. Afterward the sample was warmed to 77 K and the sample holder together with the coldfinger was mechanically shifted downward by a few millimeters, thus placing the crystal in the synchrotron beam but keeping its c-axis parallel to the wavevector **k**. To record NIS spectra the energy of the HRM was detuned stepwise from the nuclear resonance energy. In the beginning, 18 scans were performed, sampling the energy range from –600 to +800 cm⁻¹ in steps of 2 cm⁻¹. To increase the statistics in the most relevant energy region, an energy range from +320 to +725 cm⁻¹ was chosen for 9 additional scans. After warming the sample to 250 K for 90 min, 16 scans in the same energy range were performed, followed by 12 scans from –320 to +800 cm⁻¹.

Density Functional Calculations. Electronic structure calculations applying density functional theory (DFT) were performed for the NP anion in vacuo. The geometries of the ground state structure, the side-on bonding structure, and the isonitrosyl structure were optimized and subsequently the normal modes of molecular vibrations were calculated. From the normal modes the NIS spectra at 77 K were simulated according to the procedure described elsewhere.¹⁶ Roughly the same simulated spectra were obtained if the approximation given by eq 1 was used.

Several different density functional methods were used: (i) Perdew and Wang's exchange functional and their gradient corrected correlation functional³² (PW91), (ii) Becke's exchange functional³³ together with Perdew's gradient corrected correlation functional³⁴ (BP86), (iii) Becke's exchange functional³³ using the correlation functional of Lee, Yang, and Parr³⁵ (BLYP), and (iv) Becke's three-parameter hybrid functional³⁶ using Lee, Yang, and Parr's correlation functional³⁵ (B3LYP). We used the following basis sets: (i) the 6-311+G(2d,p) basis for H, C, and N and the Wachters-Hay double- ζ basis for Fe³⁷ (6-311+G(2d,p) for short), and (ii) the Dunning–Huzinaga all electron double- ζ basis for H, C, and N and the Los Alamos effective core potential plus double- ζ basis set on Fe³⁸ (LANL2DZ). The calculations for the anion were performed with the program packages Gaussian 98³⁹ and Turbomole.⁴⁰

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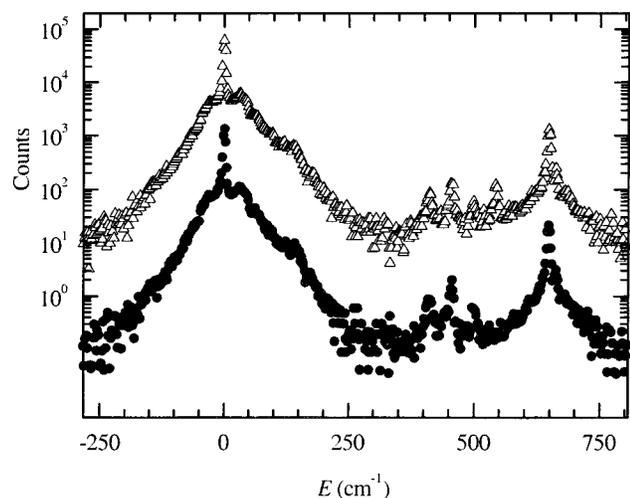


Figure 2. Experimental NIS spectra at 77 K after illumination (Δ) and after warming up to 250 K for 90 min and cooling to 77 K again (\bullet).

Results

To show the elastic and the inelastic parts of the measured NIS spectra simultaneously, the logarithm of the count rates has been plotted (Figure 2). The logarithmic presentation illustrates the bipartition of the central peak at zero energy: a sharp peak with a line width comparable to the energy resolution of the high-resolution monochromator is superimposed on a broad peak with a line width (full width at half-maximum) of about 90 cm^{-1} . The broad, inelastic peak is attributed to the creation and annihilation of acoustical phonons, whereas the sharp, elastic peak is due to the recoilless scattering of the incoming photon, a process that does not change the vibrational state of the crystal.

The simulated NIS spectrum for the ground state (Figure 3, dashed line) using the normal modes calculated with BLYP/6-311+G(2d,p) is in qualitative agreement with the measured spectrum after warming. The simulated spectrum for the isonitrosyl structure (Figure 3, dotted line) differs from the simulated ground state spectrum in exhibiting its strongest peak at 564 cm^{-1} (MS_1) compared to 667 cm^{-1} (GS).

Apart from the central peak, significant count rates can be observed in the range from 350 to 750 cm^{-1} . Here, inelastic peaks are observed which can be attributed to the creation of optical phonons, or in molecular terms, to the excitation of molecular vibrations.^{16,17} For the comparison of measured and simulated NIS spectra, the normalized probability density S has been plotted (Figure 3). When judging the relative intensities of the modes 2, 3, and 5 one should keep in mind that these modes have a very low intensity in comparison to mode 1 and are more susceptible to small errors of the calculated eigenvectors. The measured NIS spectra before and after warming up the crystal to 250 K are practically identical except for a peak at about 540 cm^{-1} . This peak appears in the spectrum that was recorded after illuminating the sample with light, and in the spectrum that was recorded after warming up the sample, it is missing.

Previous NIS measurements and density functional calculations for the ground state of monocrystalline guanidinium nitroprusside¹⁶ have shown that from the 33 normal modes of vibration of the NP anion there are 18 in the energy range from 350 to 750 cm^{-1} . From these 18 modes, 4 modes that correspond

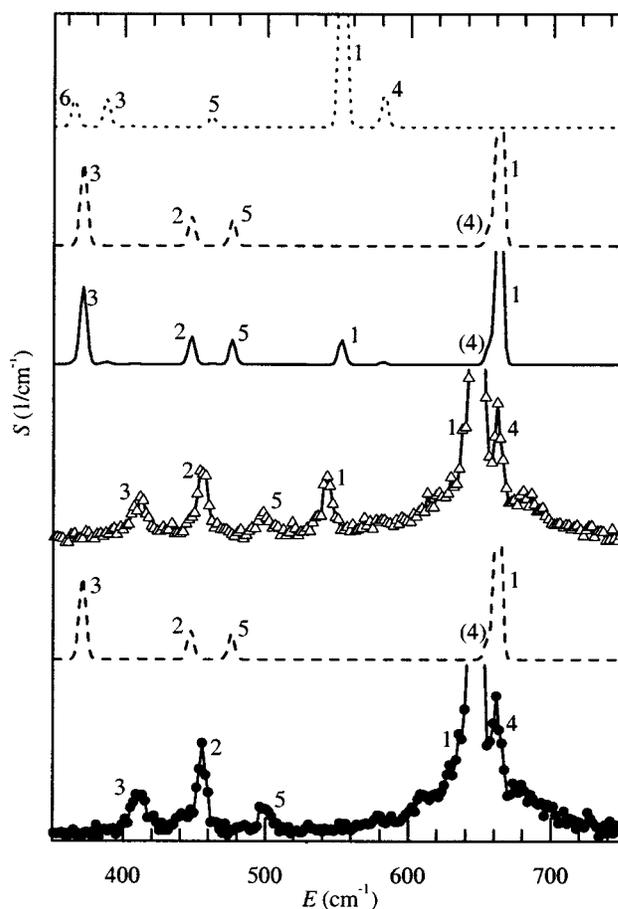


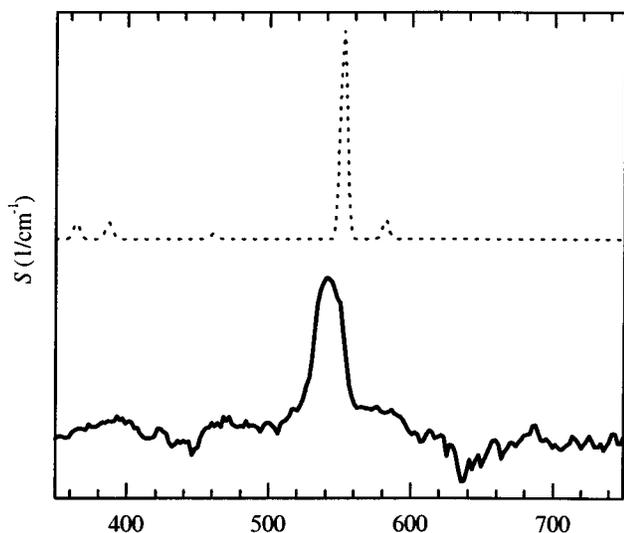
Figure 3. Experimental NIS spectra at 77 K before (Δ) and after (\bullet) warming up to 250 K for 90 min and cooling again. The dashed and the dotted lines represent the simulated spectra for GS and MS_1 , respectively. The solid line is a superposition of GS (93%) and MS_1 (7%). The peaks are labeled according to Table 2.

to the irreducible representations A_2 , B_1 , and B_2 (using the approximate C_{4v} symmetry of the anion) are principally invisible in the NIS spectrum, because of the vanishing msd of the Mössbauer nucleus that is located on the 4-fold symmetry axis. Another 5 modes have low intensity and can hardly be observed. The remaining 9 modes (3 modes of A_1 symmetry and 3 doubly degenerate E modes) can be observed in an isotropic NIS spectrum (e.g. a powder sample). However, if the wavevector \mathbf{k} of the incident synchrotron radiation is parallel to the crystallographic c -axis, only 3 A_1 modes can be observed in the NIS spectrum: an Fe–N bond-stretching mode at 662 cm^{-1} (mode 1, Table 2), an Fe–C–N bending mode at 447 cm^{-1} (mode 2), and an Fe– C_{ax} bond-stretching mode at 371 cm^{-1} (mode 3). The E modes can be observed if the wavevector \mathbf{k} is perpendicular to the c -axis. In practice, the molecular symmetry axis of the NP anion is not exactly parallel to the c -axis but inclined by 9° , and the surface normal of the sample is inclined by the wavevector \mathbf{k} of the synchrotron radiation by approximately 10° , therefore, also the 3 doubly degenerate E modes (4, 5, and 6, see Table 2) contribute to the NIS spectrum to some extent. The contribution of mode 6, however, is masked by mode 3. To account for this the NIS spectra were simulated with an inclination of 20° between the molecular symmetry axis and the wavevector \mathbf{k} . By comparing the measured intensities of the peaks that are attributed to the Fe–X ($X = \text{N}, \text{O}$)

Table 2. Selected Normal Modes of Vibration of the NP Anion As Calculated with BLYP/6-311+G(2d,p) with IR and Raman Frequencies¹² for SNP Given in Brackets^a

sym. spec.	mode ^b	GS		MS ₁	
		<i>E</i> (cm ⁻¹)	msd ^c (pm ²)	<i>E</i> (cm ⁻¹)	msd ^c (pm ²)
1	A ₁ Fe–X ^c <i>s</i>	662 (658)	2.16	552 (565)	2.98
2	A ₁ Fe–C–N θ	447 (443)	0.26	428 (442)	0.01
3	A ₁ Fe–C _{ax} <i>s</i>	371 (413)	0.51	387 (408)	0.24
4	<i>E</i> Fe–X–Y ^c γ	655 (667)	0.99	582 (581)	1.63
5	<i>E</i> Fe–C–N γ'	476 (463)	1.23	461 (458)	0.56
6	<i>E</i> Fe–C _{eq} <i>s</i>	370 (502)	1.23	364 (492)	1.37
	Fe–C–N θ				

^a Slightly different frequencies are reported by other groups.¹¹ ^b The letter *s* denotes the stretching modes and small greek letters denote bending modes (using the convention of ref 16). ^c Contributions of the individual vibrational modes to the total msd of the iron nucleus, projected on the crystallographic *c*-axis (A₁ modes) or on the *a*-axis (*E* modes), which are proportional to the intensity of these modes in the NIS spectra.¹⁷ ^e XY = NO (GS) or XY = ON (MS₁).

**Figure 4.** Difference of the experimental NIS spectra before and after warming up to 250 K (solid line). The difference has been subjected to a 5-point smooth. The dotted line represents the simulated spectrum for MS₁.

stretching mode in the ground state and in the metastable state MS₁ with the simulated peaks, about 7% population of MS₁ can be estimated. From the estimation for MS₁, a population of about 2% for MS₂ could be expected, which, however, is too small to be retrieved from the measured data. The metastable state MS₂ is therefore disregarded here.

To filter out the spectrum for MS₁, a difference spectrum has been calculated (Figure 4) by subtracting the spectrum recorded after warming up the sample to 250 K (scaled down by a factor of 0.93) from the spectrum recorded before warming up the illuminated sample. Ideally, this procedure should reveal the NIS spectrum of the MS₁ state (with 7% estimated population). Comparison of this experimental difference with the simulated spectrum for MS₁ supports this assumption (Figure 4).

Using different basis sets in the DFT calculations leads to only minor differences in bond lengths (<1 pm) or frequencies (<10 cm⁻¹). A larger influence has been found for the choice of the DFT method. Here differences of more than 3 pm for the Fe–N bond distance and of more than 50 cm⁻¹ for the Fe–N bond stretching vibrations are observed using B3LYP, BLYP,

and BP86 and the 6-311+G(2d,p) basis set. Comparing observed and calculated frequencies, no trend has been noticed, i.e., the calculated frequencies could not be corrected by applying a simple scaling factor. In summary the frequencies calculated with BLYP tend to be smaller than the measured ones, while the opposite is valid for the frequencies calculated with B3LYP. Comparison of the calculated bond lengths for the NP anion with calculated values for the SNP dihydrate crystal⁸ and with experimental data for crystals of GNP,²⁵ BaNP²⁵ (Ba[Fe(CN)₅NO]), and SNP dihydrate⁷ (Table 1) shows that the influence of the crystal environment on the bond lengths of the NP anion is rather small.

Our combined NIS and DFT studies (the latter independently of the method or basis set chosen) reveal that only the Fe–(NO) stretching mode (mode 1) and the Fe–N–O bending mode (mode 4) exhibit a significant shift if the NP anion is transferred from the ground state to the metastable state MS₁. This result is in agreement with IR and Raman studies and with earlier DFT calculations.^{8,12} The comparison between the normal modes of vibration in the ground state and in the metastable state MS₂ is more difficult because of the substantial change in the character of the modes by going from GS to MS₂.

The observed peaks in the NIS spectrum, which was recorded at 77 K after illumination, could be interpreted with the help of simulated NIS spectra for the ground state and for the metastable state MS₁ (assuming 7% population for MS₁, Figure 3). After warming the sample up to 250 K the metastable states decayed to the ground state. The corresponding experimental NIS spectrum (Figure 3) indeed lacks the intense mode at 550 cm⁻¹, which was attributed to the Fe–O stretching mode of MS₁.

Conclusions

Comparison of experimental nuclear inelastic scattering (NIS) spectra, which have been recorded under conditions excluding and including the metastable MS₁ state, with simulated NIS spectra using density functional theory strongly supports the isonitrosyl structure of the metastable MS₁ state as proposed by Carducci et al.⁷ A possible explanation for the remaining discrepancy between the conclusions derived from X-ray, IR, Raman, NIS, and DFT studies on one side and from neutron scattering studies on the other side might be related to 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 (about 0.3 mm in case of GNP compared with a penetration length of estimated 10 mm for neutrons with $\lambda = 0.85$ Å). Hence, the nuclear inelastic scattering measurement will not be adversely affected, if the MS₁ states are populated only in the surface layer of the sample, for instance due to a temperature gradient in the sample or to insufficient penetration of the sample by the illumination with light.

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