

The Structure of the FeNO Group in Two Metastable States (MS1 and MS2) of the Nitroprusside Anion in Na₂[Fe(CN)₅NO]·2H₂O. Infrared Spectra and Quantum Chemistry Calculations for the Normal and the ¹⁵N and ¹⁸O Isotopic Substituted Substance^{||}

M. E. Chacón Villalba,[†] Jorge A. Güida,^{*,†,‡} Eduardo L. Varetti,^{†,§} and Pedro J. Aymonino^{†,§}

CEQUINOR (Centro de Química Inorgánica) (CONICET-UNLP) and LANAIS EFO (CONICET-UNLP), Departamento de Química, Facultad de Ciencias Exactas, Universidad Nacional de La Plata, 47 esq. 115, C.C. 962, 1900 La Plata, R. Argentina, and Departamento de Ciencias Básicas, Universidad Nacional de Luján, 6700 Luján, R. Argentina

Received October 8, 2002

Low temperature infrared spectra of light induced metastable states MS1 and MS2 of the nitroprusside anion in Na₂[Fe(CN)₅NO]·2H₂O, isotopically normal and substituted with ¹⁵N and ¹⁸O, are presented and discussed. As a consequence of the relatively high population of the MS2 state achieved by further irradiation with 1064 nm light of samples previously irradiated with 488.0 nm light, new bands were seen for the first time, and others, previously reported, were confirmed. The comparison of the spectral data obtained for the FeNO moiety of the isotopically normal as well as of the ¹⁵N and ¹⁸O substituted anion with the results of quantum chemical (DFT) calculations support the assignment of the bands which appear after successive irradiations to MS1, the linear Fe(η^1 -ON) linkage isomer, and to MS2, the side-bound Fe(η^2 -NO) isomer.

Introduction

The nitroprusside anion, [Fe(CN)₅NO]²⁻ (NP), other anions of general formula [ML₅NO]²⁻, with M = Fe, Ru, Os; L = CN, halogens, OH, NO₂, and [NiNO(η^5 -Cp)] can be photoexcited at low temperatures to two long living metastable states, MS1 and MS2.¹ These states are mainly characterized by the relative values of the NO stretching wavenumbers: $\nu(\text{NO})_{\text{GS}} > \nu(\text{NO})_{\text{MS1}} > \nu(\text{NO})_{\text{MS2}}$ (GS: ground state).

MS1 has been generated for the first time in Na₂[Fe(CN)₅NO]·2H₂O (SNP) and revealed by Mössbauer spectroscopy.² To disclose the properties of the new state, this kind of study has been extended to other spectroscopies^{3,4} as well as to differential scanning calorimetry.⁵ Other transition metal

nitrosyls were also studied.^{6–12} A second metastable state was put into evidence for the first time by infrared spectra of irradiated single crystal plates of SNP and Ba[Fe(CN)₅NO]·3H₂O.⁴ Infrared and UV–vis measurements were made on irradiated [NiNO(η^5 -Cp)] at low temperature, disclosing also the second excited state (MS2) in this organometallic compound,^{13a} although mention of its metastable character was made more recently.^{13b} The relationship between the photoexcitation process in SNP and in [NiNO(η^5 -Cp)] has been suggested very recently.^{14a,b} DFT calcula-

* To whom correspondence should be addressed. E-mail: guida@quimica.unlp.edu.ar.

[†] CEQUINOR (Centro de Química Inorgánica) (CONICET-UNLP), Universidad Nacional de La Plata.

[‡] Universidad Nacional de Luján.

[§] LANAIS EFO (CONICET-UNLP), Universidad Nacional de La Plata.

^{||} Dedicated to Prof. Dr. Achim Müller in his 65th anniversary.

- (1) Coppens, P.; Novozhilova, I.; Kovalevsky, A. *Chem. Rev.* **2002**, *102*, 861 and references therein.
- (2) Hauser, U.; Oestreich, V.; Rohrweck, H. D. *Z. Phys.* **1977**, *A280*, 17; **1977**, *A280*, 125; **1978**, *A284*, 9.
- (3) Woike, Th.; Krasser, W.; Bechthold, P. S.; Haussühl, S. *Solid State Commun.* **1983**, *45*, 499; **1983**, *45*, 503.

- (4) Güida, J. A.; Piro, O. E.; Aymonino, P. J. *Solid State Commun.* **1986**, *57*, 175.; **1988**, *66*, 1007.
- (5) Zöllner, H.; Woike, Th.; Krasser, W.; Haussühl, S. *Z. Kristallogr.* **1989**, *188*, 139. Zöllner, H.; Krasser, W.; Woike, Th.; Haussühl, S. *Chem. Phys. Lett.* **1989**, *161*, 497.
- (6) Woike, Th.; Zöllner, H.; Krasser, W.; Haussühl, S. *Solid State Commun.* **1990**, *73*, 149.
- (7) Woike, Th.; Haussühl, S. *Solid State Commun.* **1993**, *86*, 333.
- (8) (a) Ookubo, K.; Morioka, Y.; Tomizawa, H.; Miki, E. *J. Mol. Struct.* **1996**, *379*–241. (b) Kawano, M.; Ishikawa, A.; Morioka, Y.; Tomizawa, H.; Miki, E.; Ohashi, Y. *J. Chem. Soc., Dalton Trans.* **2000**, 2425.
- (9) Güida, J. A.; Piro, O. E.; Aymonino, P. J. *Inorg. Chem.* **1995**, *34*, 4113.
- (10) Güida, J. A.; Piro, O. E.; Schaiquevich, P. S.; Aymonino, P. J. *Solid State Commun.* **1997**, *101*, 471.
- (11) Fomitchev, D. V.; Coppens, P.; Li, T.; Bagley, K. A.; Chen, L.; Richter-Addo, G. B. *Chem. Commun.* **1999**, 2013.
- (12) Da Silva, S. S.; Franco, D. W. *Spectrochim. Acta* **1999**, *A55*, 1515 and references therein.

tions carried out for $[\text{NiNO}(\eta^5\text{-Cp}^*)]$ predicted the existence of the isonitrosyl isomer (MS1, with linear NiON structure),^{14b} but the detection of such a state in $[\text{NiNO}(\eta^5\text{-Cp})]$ was possible later by infrared spectroscopy.^{14c}

As the new metastable states have generally long lives at low temperatures ($\tau > 2$ months for SNP below 200 K), the nitrosyl compounds that show these states were proposed as high density optical storage materials.¹⁵

At the beginning of these studies, metastable states were believed to be electronic excited states originating in the transition $2b_2(d_{xy}) \rightarrow 7e(\pi^*\text{NO})$,^{2,3} but according to this assumption, the FeNO moiety should show bent structures in the excited states. However, the infrared dichroic behavior observed for thin crystal plates of SNP (using cuts along the main crystallographic planes) leads to the conclusion that the FeNO groups keep the linearity when the nitroprusside anions are excited to MS1 and MS2.¹⁶ On the basis of those results, alternative electronic states were proposed [cf. refs 2, 3 with refs 9, 10]. Moreover, the electronically excited anion should be ESR active, a characteristic not proved by the measurements.¹⁷

More recently, an alternative explanation for the nature of the metastable states was proposed on the basis of the refined analysis of X-ray diffraction results obtained from irradiated single crystals of SNP.^{14a} According to this new interpretation, the metastable states correspond to NO linkage isomers, with the linear $\text{Fe}(\eta^1\text{-ON})$ structure for MS1 and the side-bound $\text{Fe}(\eta^2\text{-NO})$ structure for MS2. However, these results were not confirmed by the reinterpretation of neutron diffraction data.^{15,18} The proposed structure for MS1 is in agreement with the results obtained from the infrared dichroic behavior of crystal plates;¹⁶ although this technique is unable to distinguish between the linear FeNO and FeON configurations, it can be used to estimate the FeNO (or FeON) bond angle.

Very recently, the FeON linear configuration of MS1 was confirmed by the analysis of the infrared shifts observed for bands of SNP isotopically substituted with ¹⁵NO, N¹⁸O, and ⁵⁴Fe, supported by quantum chemistry calculations.¹⁹ Independent Raman measurements were made for SNP isotopically substituted with ¹⁵NO, suggesting the mentioned arrangement.²⁰ Isotopic substitution with ¹⁵NO and ¹⁵N¹⁸O was also used to characterize the MS1 state in iron nitrosyl

porphyrins.²¹ Nuclear inelastic scattering studies made on guanidinium nitroprusside confirmed the FeON linear configuration for MS1.²²

In our previous infrared studies,¹⁹ the low concentration of MS2 attained allowed the detection of only a few bands attributed to that state, from which no conclusions could be obtained about the corresponding structure. In order to increase the population of the MS2 state, in the present work the cooled samples of normal or isotopically substituted SNP were irradiated either with the 488.0 or the 514.5 nm light of an Ar⁺ laser to generate mainly MS1, and then, further irradiation was performed with the 1064 nm line of a Nd:YAG laser to convert MS1 into MS2.¹⁵ Therefore, it was possible to follow by infrared spectroscopy the GS \rightarrow MS1 \rightarrow MS2 processes. Results obtained for the three species were then interpreted with the help of DFT calculations. The present study gives new evidence in favor of the side-bound $\text{Fe}(\eta^2\text{-NO})$ structure of MS2 and confirms our previous findings for MS1.¹⁹

Experimental Section and Calculations

¹⁵NO and N¹⁸O isotopically substituted samples of SNP were prepared according to published techniques.^{23,24}

Infrared spectra were recorded with a FTIR Bruker 113v spectrophotometer equipped with a mid-IR DTGS detector and working at 2 cm⁻¹ resolution. Nujol mulls of powdered samples spread between CsI disks were mounted on an Oxford OX8ITL cryostat and kept at 77 K. The samples were then irradiated either with the 488.0 or the 514.5 nm lines of an Ar⁺ laser (Spectra Physics #166) at ca. 30 mW cm⁻² power for about 2 h. Infrared spectra were scanned to monitor the growing MS1 population. Samples were irradiated afterward with the 1064 nm light of a Nd:YAG laser (Quantum Forte 1064-SLM) for 1–5 h with a power of 150–200 mW cm⁻² until almost complete conversion of MS1 to MS2 was attained. Difference spectra were also obtained to improve the definition of very weak bands and to reveal the new ones overlapped with those of GS or MS1.

The vibrational properties of GS, MS1, and MS2 were calculated by means of the density functional theory (DFT) approach, using the B3LYP functional.²⁵ The LanL2DZ, 6-311+G, and 6-311+G-(2d) basis sets were used for all the atoms, as provided with the Gaussian 98 programs.²⁶ The optimized parameters obtained previously for the nitroprusside anion²⁷ were used to define the initial molecular geometries. After optimization of the geometries for GS, MS1, and MS2, the wavenumbers of the corresponding normal modes of vibration were calculated for the different isotopomers.

Results

Spectroscopic Results. The vibrational spectra of the compounds irradiated at low temperature show two new sets of bands at wavenumbers downshifted with respect to the

- (13) (a) Crichton, O.; Rest, A. J. *J. Chem. Soc., Dalton Trans.* **1977**, 986. (b) Chen, L. X.; Bowman, M. K.; Wang, Z.; Montano, P. A.; Norris, J. R. *J. Phys. Chem.* **1994**, *98*, 9457.
- (14) (a) Carducci, M. D.; Pressprich, M. R.; Coppens, P. *J. Am. Chem. Soc.* **1997**, *119*, 2669. (b) Fomitchev, D. V.; Furlani, T. R.; Coppens, P. *Inorg. Chem.* **1998**, *37*, 1519. (c) Schaiquevich, P. S.; Güida, J. A.; Aymonino, P. *J. Inorg. Chim. Acta* **2000**, *303*, 277.
- (15) Gülich, P.; Garcia, Y.; Woike, Th. *Coord. Chem. Rev.* **2001**, *219–221*, 839 and references therein.
- (16) Güida, J. A.; Aymonino, P. J.; Piro, O. E.; Castellano, E. E. *Spectrochim. Acta* **1993**, *49A*, 535.
- (17) Terrile, C.; Nascimento, O. R.; Moraes, I. J.; Castellano, E. E.; Piro, O. E.; Güida, J. A.; Aymonino, P. *J. Solid State Commun.* **1990**, *73*, 481.
- (18) Schefer, J.; Woike, Th.; Haussühl, S.; Fernández Díaz, M. T. *Z. Kristallogr.* **1997**, *212* 29. Schefer, J.; Woike, Th.; Imlau, M.; Delley, B. *Eur. Phys. J.* **1998**, *B3*, 349.
- (19) (a) Chacón Villalba, M. E.; Güida, J. A.; Piro, O. E.; Aymonino, P. *J. 32nd International Conference on Coordination Chemistry, Santiago, Chile, August 24–29, 1997*. (b) Chacón Villalba, M. E.; Güida, J. A.; Varette, E. L.; Aymonino, P. *J. Spectrochim. Acta* **2001**, *A57*, 367.

- (20) Morioka, Y.; Takeda, S.; Tomizawa, H.; Miki, E. *Chem. Phys. Lett.* **1998**, *292*, 625.
- (21) Cheng, L.; Novozhilova, I.; Kim, C.; Kovalewsky, A.; Bagley, K. A.; Coppens, P.; Richter-Addo, G. B. *J. Am. Chem. Soc.* **2000**, *122*, 7142.
- (22) Paulsen, H.; Rusanov, V.; Benda, R.; Herta, C.; Schünemann, V.; Janiak, C.; Dorn, T.; Chumakov, A. I.; Winkler, H.; Trautwein, A. X. *J. Am. Chem. Soc.* **2002**, *124*, 3007.
- (23) Chacón Villalba, M. E.; Varette, E. L.; Aymonino, P. *J. Vib. Spectrosc.* **1997**, *14*, 275.
- (24) West, D. X. *J. Inorg. Nucl. Chem.* **1968**, *30*, 1263.
- (25) (a) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648. (b) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev.* **1988**, *B37*, 785.

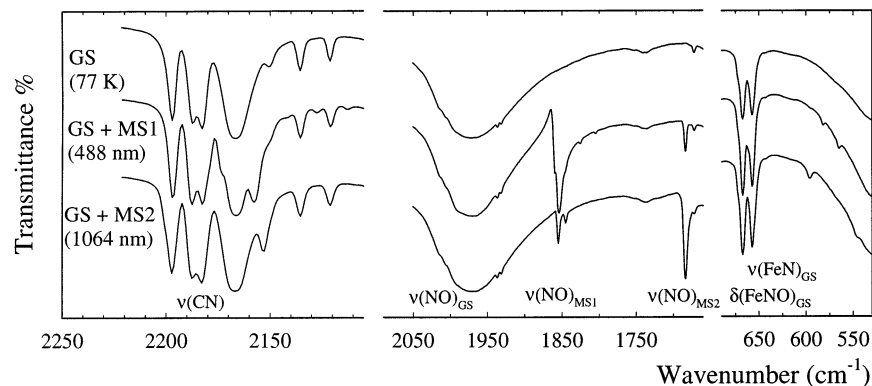


Figure 1. Low temperature (77 K) infrared spectra of $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}] \cdot 2\text{H}_2\text{O}$ before (GS) and after sequential irradiation with 488.0 nm light (GS + mainly MS1) and 1064 nm light (GS + mainly MS2).

ground state bands. These shifts are larger for the FeNO modes than for the $\text{Fe}(\text{CN})_5$ moiety. In fact, the sets of MS1 and MS2 bands of SNP are characterized by $\nu(\text{NO})$ downshifts of 110 and 280 cm^{-1} , respectively, which are reduced to 9–13 cm^{-1} for the $\nu(\text{CN})$ modes.^{3,4} These spectroscopic observations provide clear evidence that changes generated by the irradiation are mainly located in the FeNO group. The new states are very stable at low temperature but decay into the ground state at different onset temperatures by heating the samples⁵ or by irradiation with light of appropriate wavelength (usually, red light).¹⁵

Figure 1 shows selected regions of the infrared spectra obtained at 77 K, with the same sample for isotopically normal SNP (1) in the ground state, (2) after 2 h irradiation with 488.0 nm light, and (3) after the conversion of MS1 into MS2 by further irradiation with 1064 nm light. Difference spectra between irradiated (488.0 and 1064 nm light) and ground state samples are shown in Figure 2 for isotopically normal samples as well as for the ^{15}NO and N^{18}O substituted species. These spectra show the most relevant bands resulting from the irradiation procedures. Figure 3 reproduces a sequence of selected spectral regions taken during the irradiation with 1064 nm light of a N^{18}O -SNP sample which was previously irradiated with 488.0 nm light to populate the MS1 state. It can be clearly seen how the original MS1 bands are replaced by a new set of bands, assigned to MS2.

Wavenumbers and assignments for GS, MS1, and MS2 bands of isotopically normal and ^{15}NO and N^{18}O substituted samples are collected in Table 1. These results confirm previous reports referred to isotopically normal single crystal plates of SNP.^{4,16}

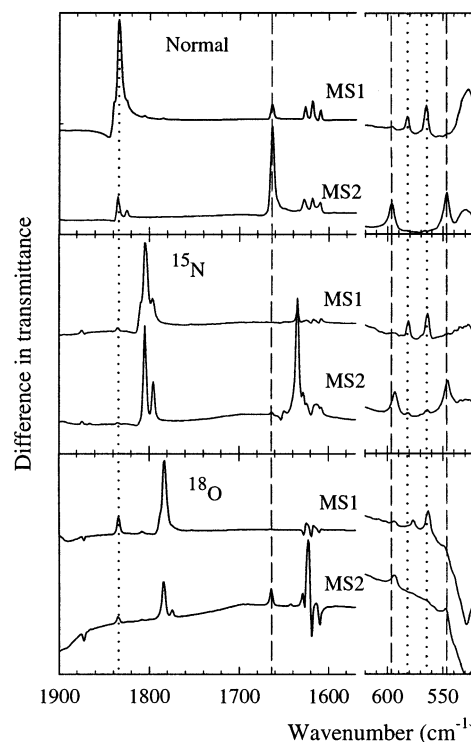


Figure 2. Difference infrared spectra between metastable states and GS of the nitroprusside anion in SNP, with normal isotopic composition and in the ^{15}NO substituted or N^{18}O substituted substance. The vertical lines mark the position of relevant bands in the normal substance (dotted lines correspond to MS1 and dashed lines to MS2 bands).

Calculation Results. The optimized structures obtained with the 6-311+G(2d) basis set are represented in Figure 4. The structure predicted for MS2 shows that the side-bound NO group eclipses an equatorial NCFeCN group. Bond distances and angles calculated for the three species agree with the results obtained by Gorelsky and Lever with their B3LYP/6-311++G(3df,p) calculation,^{28,1} with differences in distances not exceeding 0.004 Å.

Results of the wavenumber calculations are collected in Table 2, where values obtained from three calculations with increasing quality of the basis sets are included for comparison purposes. Only the modes of vibration more relevant for the present study are considered. It can be seen that the LanL2DZ calculation predicts rather well the wavenumbers

- (26) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Baboul, A. G.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.7; Gaussian, Inc.: Pittsburgh, PA, 1998.
- (27) Chacón Villalba, M. E.; Varetto, E. L.; Aymonino, P. J. *Spectrochim. Acta* **1999**, *A55*, 1545.

- (28) Gorelsky, S. I.; Lever, A. B. P. *Int. J. Quantum Chem.* **2000**, *80*, 636.

Table 1. Wavenumbers (77 K) and Assignments of IR Bands of GS, MS1, and MS2 States of the Nitroprusside Anion Isotopomers in Na₂[Fe(CN)₅NO]·2H₂O

		wavenumber (cm ⁻¹)									
		normal			¹⁵ NO			N ¹⁸ O			
GS	MS1	MS2	GS	MS1	MS2	GS	MS1	MS2	assignments		
2177	2168 ^a	2180 ^a	2177	2167 ^a	2180 ^a	2177	2167 ^a	2180 ^a	$\nu(\text{CN})_{\text{ax/eq}}$		
2168	2159 ^a	2165 ^a	2168	2159 ^a	2165 ^a	2168	2159 ^a	2165 ^a	$\nu(\text{CN})_{\text{ax}}$		
2163	2153(sh)	2149 ^a	2163	2154(sh)		2163	2153(sh)	2150 ^a	$\nu(\text{CN})_{\text{eq}}$		
2146	2138	2133	2147	2138	2134	2146	2138	2133	$\nu(\text{CN})_{\text{eq}}$		
2131			2131			2131			$\nu(^{13}\text{CN})_{\text{ax}}$		
2116	2107		2116	2107		2116	2107		$\nu(^{13}\text{CN})_{\text{eq}}$		
2101	2092		2101	2092		2101	2092		$\nu(^{13}\text{CN})_{\text{eq}}$		
1960 ^b	1835 ^b	1664	1917 ^b	1805	1635	1912 ^b	1784	1622 ^c	$\nu(\text{NO})$		
				1754			1753		$\nu(^{15}\text{N}^{18}\text{O})$		
667	582 ^c	596 ^c	658	581 ^c	593 ^c	664	577 ^c	594 ^c	$\delta(\text{FeXY})$		
657	565 ^c	547 ^c	653	564 ^c	546 ^c	649	563 ^c	547 ^c	$\nu(\text{Fe}-\text{XY})$		

^a Obtained from difference spectra. ^b Value corresponding to the isotopically isolated species (see Discussion). ^c Value measured in difference spectra.

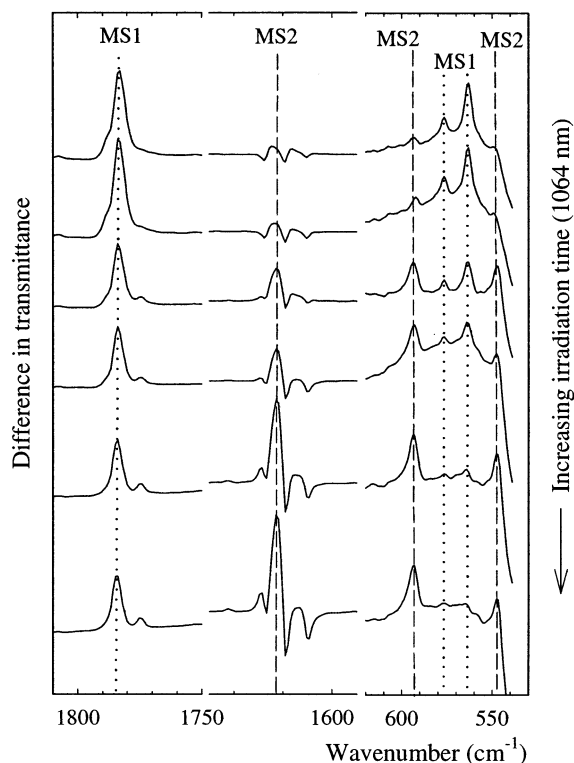


Figure 3. Difference infrared spectra (between each of the excited spectra and GS spectrum) showing the growth of MS2 bands at the expense of the MS1 bands during irradiation of a N¹⁸O substituted sample with 1064 nm light. The uppermost spectrum corresponds to the original sample after irradiation with 488 nm light. The following spectra correspond to increasing irradiation times from 1 h each up to 5 h. The GS bands are practically not affected.

for the different modes, with the NO stretching being a notable exception. Results obtained with the 6-311+G basis set are not better than the former, specially for the CN and NO stretchings. The introduction of polarized functions in the 6-311+G(2d) basis set gives better results only for the NO stretching, while values for the CN stretchings are about 60 cm⁻¹ larger than the experimental ones. The present predicted wavenumbers, as well as results obtained by other authors using more sophisticated procedures,^{28,29} show that the FeNO moiety cannot be appropriately modeled by the most usual calculation methods and levels. The band shifts

(29) Delley, B.; Schefer, J.; Woike, T. *J. Chem. Phys.* **1997**, *107*, 10067.

and infrared intensities calculated with the best basis set (III in Table 2) were used in the subsequent discussion (see later).

Vibrational modes are described by the corresponding sets of atomic displacement vectors. Such descriptions of the FeNO vibrational modes of the nitroprusside anion in GS and MS1 are straightforward due to the linear FeNO or FeON arrangements, respectively. In the case of MS2, however, more complex vibrations arise from the side-bound Fe(η^2 -NO) structure. Thus, the mode designated as $\nu(\text{FeX})$ for MS2 in Table 2 comprises the FeN and FeO stretchings and also the FeNO deformation. In the same way, the mode designated as $\delta(\text{FeXY})$ for MS2 has contributions from the FeNO and FeON deformations and from the FeN and FeO stretching vibrations. Not negligible contributions from the rest of the anion atoms are observed for these MS2 modes.

Discussion

NO Stretching in GS, MS1, and MS2. The NO stretching bands of MS1 and MS2 are easily recognized by their large intensities and shifts. They appear for isolated anions at 1835 cm⁻¹ for MS1 and at 1664 cm⁻¹ for MS2 in isotopically normal samples (Figures 1 and 2), while for GS this band is located at 1960 cm⁻¹ for isotopically isolated anions (which are not affected by vibrational coupling between them) and at 1943 cm⁻¹ for bulk samples.

$\nu(\text{NO})_{\text{GS}}$ undergoes a considerable shift upon isotopic substitution with ¹⁵N (one unit of mass increase) to 1917 cm⁻¹ at 77 K ($\Delta\nu(^{14/15}\text{NO})_{\text{GS}} = 43 \text{ cm}^{-1}$) for isolated substituted anions and to 1908 cm⁻¹ for almost complete substitution where vibrational coupling operates. For ¹⁸O substitution (two units of mass increase), $\nu(\text{N}^{18}\text{O})$ shifts, also at 77 K, to 1912 cm⁻¹ ($\Delta\nu(\text{N}^{16/18}\text{O})_{\text{GS}} = 48 \text{ cm}^{-1}$) for isolated groups and to 1898 cm⁻¹ for bulk. The shifts observed for ¹⁸O are scarcely greater than for ¹⁵N, a fact that could be explained qualitatively by the displacement vectors depicted in Figure 2 of ref 19b. As for FeXY (XY = NO or ON), linear arrangements X shows larger displacement vectors than Y, greater shifts are expected when X is isotopically substituted than when Y is substituted.

For MS1, where the FeXY groups are linearly arranged, $\Delta\nu(\text{N}^{16/18}\text{O})_{\text{MS1}} = 51 \text{ cm}^{-1}$ in SNP; therefore $\Delta\nu(\text{N}^{18}\text{O})_{\text{GS}} (48 \text{ cm}^{-1}) < \Delta\nu(\text{N}^{18}\text{O})_{\text{MS1}} (51 \text{ cm}^{-1})$. The opposite behavior

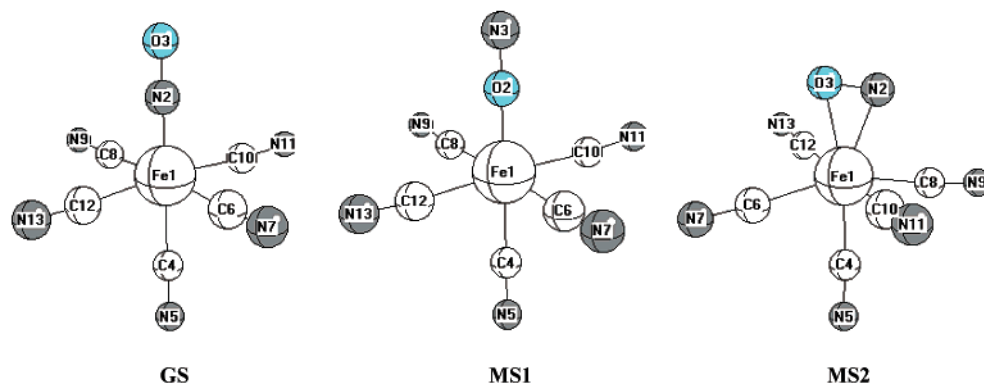


Figure 4. The optimized structures for the GS ($\eta^1(\text{N})$), MS1 ($\eta^1(\text{O})$) and MS2 ($\eta^2(\text{NO})$) isomeric states of the nitroprusside anion as obtained from B3LYP/6-311+(2d) calculations.

Table 2. DFT Calculated Wavenumbers of the More Relevant Modes of Vibration in the Ground State (GS) and Metastable States (MS1 and MS2) of the Nitroprusside Anion, Using the B3LYP Functional and Different Basis Sets with Calculated IR Intensities (km mol^{-1}) in Parentheses

calcd I: LanL2DZ					calcd II: 6-311+G					calcd III: 6-311+G(2d)					exptl (77 K)							
GS	MS1	$\Delta 1^a$	MS2	$\Delta 2^a$	GS	MS1	$\Delta 1$	MS2	$\Delta 2$	GS	MS1	$\Delta 1$	MS2	$\Delta 2$	GS	MS1	$\Delta 1$	MS2	$\Delta 2$	mode		
2160	2149	11	2154	6	2151	2139	12	2147	4	2232	2221	11	2227	5	2177	2167	10	2165	12	$\nu(\text{CN})$		
										(6.2)	(7.4)		(28.7)								$\nu(\text{CN})$	
2153	2139	14	2147	7	2143	2130	13	2140	3	2225	2214	11	2222	3	2168	2159					$\nu(\text{CN})$	
										(17.3)	(15.9)		(14.2)									$\nu(\text{CN})$
2151	2136	15	2141	10	2138	2126	12	2136	2	2220	2209	11	2216	4	2163	2153 sh	10				$\nu(\text{CN})$	
										(0)	(0)		(76.7)									$\nu(\text{CN})$
2148	2132	15	2139	9	2135	2123	12	2130	5	2216	2205	11	2212	4	2146 br	2138	8	2133	13		$\nu(\text{CN})$	
										(88.3)	(74.3)		(5.4)									$\nu(\text{CN})$
2148	2132	15	2135	13	2135	2123	12	2125	10	2216	2205	11	2206	10	2146 br	2138	9	2133	13		$\nu(\text{CN})$	
										(88.3)	(74.3)		(72.3)									$\nu(\text{CN})$
1806	1768	38	1466	340	1780	1755	25	1439	341	1920	1937	-17	1664	256	1960 ^b	1835	116	1663	287		$\nu(\text{NO})$	
										(1057)	(742)		(364)		1866 ^c		31	202			$\nu(\text{NO})$	
684	600	84	617	67	671	594	77	635	36	697	615	82	648	49	667 ^b	582 ^b	85	596 ^b	71		$\delta(\text{FeXY})$	
										(22.4)	(5.6)		(46.1)									$\delta(\text{FeXY})$
29	3		61		44	13		79		16	19		92		10	17		49			Δ^d	
713	603	110	556	157	715	607	108	556	159	713	596	117	556	157	657 ^b	565 ^b	92	547 ^b	110		$\nu(\text{FeX})^e$	
										(4.6)	(10.8)		(22.4)									$\nu(\text{FeX})^e$

^a $\Delta 1 = (\nu(\text{GS}) - \nu(\text{MS1}))$; $\Delta 2 = (\nu(\text{GS}) - \nu(\text{MS2}))$. ^b Corresponds to isotopically isolated modes. ^c Extrapolated wavenumber of NO stretching for null interaction.³¹ ^d $\Delta = \delta(\text{FeXY}) - \nu(\text{FeX})$. ^e $\nu(\text{FeX})$: X = N for GS, X = O for MS1; see text for MS2.

Table 3. Observed and Calculated Isotopic Shifts (^{15}NO and N^{18}O) at 77 K of FeNO Vibrational Modes of the Nitroprusside Anion in the Ground, MS1, and MS2 States

GS				MS1				MS2				
^{15}N		^{18}O		^{15}N		^{18}O		^{15}N		^{18}O		
exptl	calcd ^a	exptl	calcd ^a	exptl	calcd ^a	exptl	calcd ^a	exptl	calcd ^a	exptl	calcd ^a	assignments
43	39/39	48	36/41	30	28/32	51	52/55	29	27/30	42	37/42	$\nu(\text{NO})$
9	14/15	3	3/3	1	1/1	5	12/15	3	7/9	2	3/5	$\delta(\text{FeXY})^b$
4	4/3	8	13/13	1	4/5	2	4/5	1	2/2	0	0/1	$\nu(\text{FeX})^b$

^a The pairs of calculated values were obtained using the LanL2DZ and 6-311+G(2d) basis sets, respectively. ^b X = N, O; Y = O, N.

is observed for the replacement of ^{14}N by ^{15}N because in this case $\Delta\nu(^{14/15}\text{NO})_{\text{GS}} (43 \text{ cm}^{-1}) > \Delta\nu(^{14/15}\text{NO})_{\text{MS1}} (30 \text{ cm}^{-1})$ (see Table 3). This behavior is observed also for MS1 in $\text{Na}_2[\text{Ru}(\text{CN})_5\text{NO}] \cdot 2\text{H}_2\text{O}^{10}$ and $\text{K}_2[\text{RuCl}_5\text{NO}]$.³⁰

In those cases and in SNP, $\Delta\nu(\text{NO}) = \nu(^{15}\text{NO}) - \nu(\text{N}^{18}\text{O})$ increases from GS to MS1 (see Figure 2 and Table 1) from 3–5 cm^{-1} to 18–20 cm^{-1} , respectively. $\Delta\nu(\text{NO})_{\text{MS2}} = \nu(^{15}\text{NO}) - \nu(\text{N}^{18}\text{O}) = 13 \text{ cm}^{-1}$ observed for SNP lies between those shifts.

Also, $\nu(\text{NO})_{\text{MS2}}$ behaves differently than in the cases of the FeXY linear arrangements (GS, MS1). The band appears at 1635 cm^{-1} for ^{15}NO ($\Delta\nu = 29 \text{ cm}^{-1}$) and at 1622 cm^{-1} for N^{18}O ($\Delta\nu = 42 \text{ cm}^{-1}$). A simple diatomic model predicts

shifts to 1634 and 1620 cm^{-1} , respectively, very close to the observed wavenumbers. For GS, wavenumbers measured are 1917 and 1912 cm^{-1} , respectively, while values calculated with the same model are 1925 and 1908 cm^{-1} , respectively. For MS1, corresponding wavenumbers are 1805 and 1784 cm^{-1} (measured), and 1801 and 1786 cm^{-1} (calculated), respectively. In these last cases, differences between measured and calculated wavenumbers are significant, specially for $^{14/15}\text{N}$ replacement. These observations suggest a different structure for MS2, as it is the side-on one.

The $\nu(\text{NO})$ wavenumbers predicted by the calculations are of similar quality as those obtained by other authors.^{28,29} Calculations I and II (Table 2) predict a weak softening of this mode when going from GS to MS1 (38 and 25 cm^{-1} , respectively), and similar results were obtained by Delley

(30) Güida, J. A.; Ramos, M. A.; Piro, O. E.; Aymonino, P. J. *J. Mol. Struct.* **2002**, *609*, 39.

et al.²⁹ and Gorelsky and Lever²⁸ in their calculations. Moreover, these last authors obtained a shift to a *larger* wavenumber using the B3LYP/6-311++G(3df,p) level of calculation, a result which is reproduced by our calculation III (-17 cm^{-1}) (Table 2). Gorelsky and Lever suggested that such discrepancy is probably due to the neglect of the environmental effects on the NO stretching frequency. In fact, as an extrapolated value of 1866 cm^{-1} has been obtained for an ideally isolated GS nitroprusside anion,³¹ the experimental shift referred to that value is more in line with the calculated ones, as shown also in Table 2. The experimental NO stretching shifts corresponding to the GS \rightarrow MS2 isomerization agree better with the calculated values.

FeX Stretching and FeXY Deformations Vibrations. The bands due to the FeN stretching and FeNO deformation of GS suffer large shifts upon excitation of the nitroprusside anion. The relative shifts ($\Delta\nu(\text{FeX})/\nu(\text{FeX})$ and $\Delta\delta(\text{FeXY})/\delta(\text{FeXY})$) are larger than those observed for $\nu(\text{NO})$, as pointed out in ref 16. These bands, located originally at 657 and 667 cm^{-1} , respectively, are downshifted to 582 and 565 cm^{-1} for MS1 and to 596 and 547 cm^{-1} for MS2 in isotopically normal samples. As these bands are quite weak (Figure 1), it was necessary to resort to difference spectra with respect to the GS spectrum to measure them properly. Figure 3 shows the behavior of these bands (for N^{18}O substituted SNP) during irradiation with 1064 nm light of a sample previously populated with the mixture of MS1 and MS2 (mainly MS1). It can be clearly seen how the couple of bands located at 582 and 565 cm^{-1} , separated by 17 cm^{-1} , and assigned to MS1,^{16,19} are replaced almost completely by the 596 and 547 cm^{-1} bands, separated by 49 cm^{-1} , attributed to the MS2 species. Our highest level calculation (III in Table 2) predicts separations of 19 and 92 cm^{-1} , respectively. The relative intensities of MS1 and MS2 bands are predicted correctly, the lowest wavenumber band being the more intense for MS1 and the less intense for MS2.

It is to be noted that the calculated isotopic shifts are in general somewhat larger than the measured ones (Table 3). The agreement between experimental and calculated values is particularly poor for the shifts suffered by the FeO stretching and the FeON deformation in MS1 after substitution with ^{18}O , as was previously reported.¹⁹ Possible causes of the differences are the limitations of the calculation method and the basis sets used to model the FeNO moiety, as already mentioned. In fact, when the isotopic shifts are calculated with a force field scaled to reproduce the experimental wavenumbers of the GS species, the experimental shifts are very well reproduced.²⁷ Such force fields could not be obtained for MS1 and MS2 because complete sets of wavenumbers are not available.

Despite these discrepancies, the semiquantitative agreement between observed and calculated isotopic shifts seem to support the isomeric forms proposed by Coppens and co-workers^{14a} for the nitroprusside anion excited to MS1 and MS2.

CN Stretching Region. This region is dominated by the intense bands of GS, because of the relatively low concentrations obtained for MS1 and MS2. Only two new bands can be easily seen in this region after irradiation. One band is located at 2138 cm^{-1} in the spectra corresponding to MS1 (Figure 1, Table 1) and should be assigned to the CN_{eq} stretching of species E (under the ideal C_{4v} symmetry of an isolated nitroprusside anion), which appears as a very broad band centered at 2147 cm^{-1} in the GS spectrum. That band was therefore downshifted by 9 cm^{-1} , not far from the calculated shift of 11 cm^{-1} (calculation III in Table 2). This band disappears upon 1064 nm irradiation and is replaced by a new band located at 2133 cm^{-1} in the spectra of MS2 (Figure 1, Table 1). This new band should be one of the components resulting from the splitting of the mentioned E band, as a consequence of the diminished anion symmetry (C_s), shifted also to lower wavenumbers. In fact, the largest shift for the CN stretching bands due to the GS \rightarrow MS2 isomerization is predicted for one of the bands arising from the splitting of the E band, which should also be the most intense one. The second band should be considerably less downshifted and should be relatively weak, according to calculation III (Table 2).

Concluding Remarks

Samples of sodium nitroprusside dihydrate were irradiated with blue or green laser light at low temperature to generate mainly the well characterized MS1, isonitrosyl, isomeric state of the nitroprusside anion. The population enhancement of MS2 by the MS1 \rightarrow MS2 conversion process promoted by further irradiation with near-IR light was subsequently employed to obtain well defined infrared bands pertaining to the second metastable state.

The main changes observed in the infrared spectra of SNP as consequences of the two irradiation procedures can be reasonably explained in a semiquantitative way by isotopic substitutions and quantum chemistry calculations using DFT techniques. These facts confirm our previous infrared identification of MS1 as the linear $\text{Fe}(\eta^1\text{-ON})$ linkage isomer¹⁹ and provide additional evidence to support the side-bound $\text{Fe}(\eta^2\text{-NO})$ arrangement for MS2, as proposed by Carducci et al. on the basis of experimental X-ray diffraction data.^{14a}

Acknowledgment goes to Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET) R. Argentina, for financial support through CEQUINOR (CONICET, UNLP) and for Grant PIP #4752/97, to the Agencia Nacional de Promoción Científica y Tecnológica (ANPCYT), R. Argentina, for Grant PICT #00118, to Comisión de Investigaciones Científicas de la Provincia de Buenos Aires, R. Argentina (CICPBA), for financial help, to Alexander von Humboldt-Foundation (Germany) for the donation of the Nd-YAG laser used in this work, and to Universidad Nacional de La Plata for an incentive for research work. J.A.G. also acknowledges partial support from Universidad Nacional de Luján, R. Argentina.

(31) Estrin, D. A.; Baraldo, L. M.; Slep, L. D.; Barja, C.; Olabe, J. A.; Paglieri, L.; Corongiu, G. *Inorg. Chem.* **1996**, *35*, 3897.