

## Infrared evidence of NO linkage photoisomerization in $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}]\cdot 2\text{H}_2\text{O}$ at low temperature.

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### Introduction:

NO effects in biological systems like action in cardiovascular and central nervous system and the genitourinary tract, among others, increase the interest in metal-nitrosyls as NO source [1]. Special interest is centred in sodium nitroprusside dihydrate ( $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}]\cdot 2\text{H}_2\text{O}$ , SNP) which is one of the most studied metal-nitrosyls and used as hypotensive agent [1].

Sodium nitroprusside dihydrate as other pentaligandnitrosyl anions  $\{[\text{ML}_5\text{NO}]^{2-}$  (M=Ru, Os; L=CN, halogens, OH,  $\text{NO}_2$ ), can be transformed reversibly into two very long living metastable states (MSI and MSII) by irradiation with light in the 400-500 nm range at low temperature [2]. Infrared spectra of both excited species show respectively new sets of bands which are characterized by  $\nu(\text{NO})$  downshifts of 110 (MSI) and 280  $\text{cm}^{-1}$  (MSII) [3]. Upon heating the samples, metastable states decay into the ground state at about 150 and 200 K for MSII and MSI, respectively.

For more than one decade, the metastable states were considered as due to the population of two excited, very stable, electronic states [2]. However, recently, as results of new single crystal X-ray diffraction measurements, geometrical isomerism have been proposed, with linear geometry (FeON) for MSI and T shaped (side-on) coordination for MSII [4]. The geometrical interpretation for MSI from the diffraction results is in accordance with a linear FeNO group predicted from polarized infrared spectra measurements performed on single crystals plates of SNP [3], but disagree with the geometry of the MSII state, for which the linear geometry is also predicted. More recently, the reinterpretation of previous neutron diffraction data did not confirm those results [5].

In this presentation we discuss additional information on the geometry of the excited states analysing, by infrared spectroscopy, the metastable states of  $^{15}\text{N}(\text{O})$ ,  $^{18}\text{O}$  and  $^{54}\text{Fe}$  substituted species in SNP.

## Results and Discussion:

All MSI bands of  $[\text{Fe}(\text{CN})_5\text{NO}]^{2-}$  ion shift to lower wavenumbers respects the ground state modes (GS), but those directly related to the FeNO group moves the most ( $\Delta\nu(\text{NO})=-110$ ,  $\Delta\delta(\text{FeNO})=-84$  and  $\Delta\nu(\text{FeN})=-93$ ),  $\Delta\nu(\text{CN})=-10$ ,  $\Delta\nu(\text{FeC})=-5 \text{ cm}^{-1}$ ). This fact is clear evidence that, after excitation to the MSI and MSII states, the changes are mainly localized in the FeNO bonds.

Table 1 compares the GS with the MSI shifts when FeNO group of the  $[\text{Fe}(\text{CN})_5\text{NO}]^{2-}$  ion is alternatively substituted by  $^{15}\text{N}$ ,  $^{18}\text{O}$  and  $^{54}\text{Fe}$  isotopes.

Table 1: Isotopic shifts ( $\text{cm}^{-1}$ ) respect normal ground and MSI states for  $\nu(\text{NO})$ ,  $\delta(\text{FeNO})$  and  $\nu(\text{FeN})$  vibrational modes in  $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}]\cdot 2\text{H}_2\text{O}$ .

	$\Delta\nu(\text{NO})$ ,		$\Delta\delta(\text{FeNO})$		$\Delta\nu(\text{FeN})$	
	GS	MSI	GS	MSI	GS	MSI
$^{15}\text{NO}$	-39	-30	-10	0	-4	-1
$\text{N}^{18}\text{O}$	-43	-50	-3	-4	-8	-2
$^{54}\text{Fe}$	+1	0	+6	+5	+4	+5

One of the most surprising results observed in Table 1 is the almost unshifted  $\Delta\delta(\text{FeNO})$  and  $\Delta\nu(\text{FeN})$  MSI modes when the  $^{15/14}\text{N}(\text{O})$  isotopic substitutions take place as compared with the GS shifts. MSI shifts for  $^{18}\text{O}$  isotopic substitution are in reverse order in comparison with those of the GS (Table 1). The different behaviour of the  $\delta(\text{FeNO})$  and  $\nu(\text{FeN})$  bands for the GS and MSI could be explained as due to the fact that in the ground state the NO group is directly bonded to iron through the nitrogen while in MSI is through the oxygen, suggesting a Fe-O-N bond. Normal coordinate analysis for MSI state both for the isotopically normal and  $^{15}\text{N}$ ,  $^{18}\text{O}$  and  $^{54}\text{Fe}$  substituted nitroprussides support the FeON structure rather than the conventional FeNO.

## References:

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