

Vibrational properties of nitroprusside and related anions in solids

Pedro J. Aymonino

Programa QUINOR, Química Inorgánica, Departamento de Química, Facultad de Ciencias Exactas, Universidad Nacional de La Plata, C.C. 962, 1900 La Plata, República Argentina.

Abstract - Structural and vibrational properties of the nitroprusside, $[\text{Fe}(\text{CN})_5\text{NO}]^{2-}$, anion, including the vibrational interaction between the NO groups of neighbouring anions in structurally propitious crystals are briefly reviewed. The discussion extends to pentacyanonitrosylmanganate(3-) anions in the potassium salt. The vibrational behaviour of electronically excited (metastable) nitroprusside anions is also considered. Finally, the vibrational manifestations of the strong coupling existing along the NCMnOMnCN axis of the linear μ -oxo bis(pentacyanomanganate)(6-) anion, and the correct assignment of its electronic absorption bands are also reviewed.

The nitroprusside anion, or pentacyanonitrosylferrate(2-), $[\text{Fe}(\text{CN})_5\text{NO}]^{2-}$, (Npr^{2-}), is an old member of the vast series of pentacyanometalates.

Its structure is a pseudo-octahedron containing the NCFeNO grouping in the polar axis and four CN groups in the equator, slightly bended towards the axial cyanide. Ideal symmetry is C_{4v} but in crystals it is always lower. In $\text{SrNpr} \cdot 4\text{H}_2\text{O}$ (ref. 1), for instance, bond lengths of ligands are nearly equal to bond lengths of the free groups, nitric oxide and cyanide (1.17 and 1.15 for NO and 1.13 and 1.14 for CN^- , respectively ref. 2).

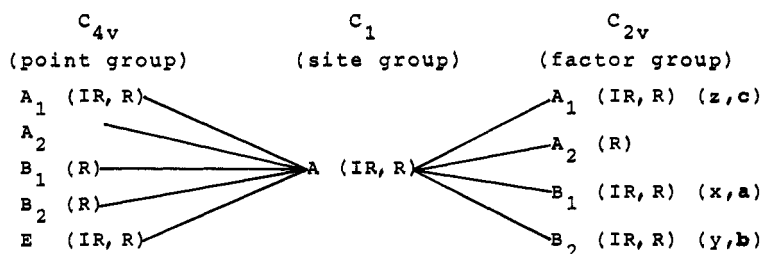
Wavenumbers of the stretching vibrations of the bonded ligands are 2152 cm^{-1} and about 1960 cm^{-1} for CN and NO, respectively, in $\text{BaNpr} \cdot 3\text{H}_2\text{O}$ (ref. 3), not far from values reported for free CN^- and NO (2080 and 1880 cm^{-1} , respectively, ref. 4). In fact, ν_{CN} is greater than in the Fe^{III} complex $[\text{Fe}(\text{CN})_6]^{3-}$, which has its CN stretching bands between 2135 and 2118 cm^{-1} (ref. 4). Therefore, although ν_{NO} is somewhat shifted towards the value reported for NO^+ (2273 cm^{-1} ref. 4), Fe^{III} and NO^{O} oxidation states seem to apply better than the commonly accepted Fe^{II} and NO^+ (cf. ref. 5). It is to be noted that XPS (ESCA) results point to a +0.35 fractional charge on the NO group of $\text{Na}_2\text{Npr} \cdot 2\text{H}_2\text{O}$ (ref. 6) but on the contrary, SINDO calculations (ref. 7) result in a -0.254 charge, a seemingly overestimated value (ref. 7). A strong charge separation is recognized in the NO group, specially as result of the SINDO calculations ($q_{\text{N}} = +0.503$, $q_{\text{O}} = -0.757$) (ref. 7). The high polarity of the group and the big change it experiences when the bond vibrates (ref. 6) ($(\text{dm}/\text{ds})_{\text{O}} = 3.35 \text{ a.u.}$ (ref. 6)) are important characteristics of the group.

Other characteristic vibrations of Npr^{2-} are δ_{FeNO} (666 cm^{-1}) and ν_{FeN} (650 cm^{-1}). To the FeN bond is recognized a strong π contribution amounting 1.693 (ref. 7 and references therein). The FeCN deformation and FeC stretching bands appear below 500 cm^{-1} and are fairly intermingled. The strong band at 419 cm^{-1} is usually assigned to a FeC stretching and a FeCN deformation (ref. 8a,b).

The strong polarity of the NO group in Npr^{2-} perhaps determines that in monoclinic $\text{SrNpr} \cdot 4\text{H}_2\text{O}$ (ref. 1) and orthorhombic $\text{BaNpr} \cdot 3\text{H}_2\text{O}$ (ref. 9) the anions pile up along the c crystallographic axes, forming double rowed chains separated about 7\AA . In the chains the anions are intercalated in an antiparallel ($\text{SrNpr} \cdot 4\text{H}_2\text{O}$) or nearly antiparallel ($\text{BaNpr} \cdot 3\text{H}_2\text{O}$) fashion with the NO groups faced up (and opposed), the interanionic distances being about 4\AA (4.2\AA in $\text{BaNpr} \cdot 3\text{H}_2\text{O}$ (ref. 9a, b)). The polar axes of the anions are parallel to the a

axes (see Fig. 1 of ref. 10). This arrangement brings up a strong infrared dichroism in single crystal plates, as proved both for $\text{SrNpr.4H}_2\text{O}$ (ref. 11) and $\text{BaNpr.3H}_2\text{O}$ (ref. 3).

The correlation diagram presented below will help to understand the vibrational behaviour of the barium salt (ref. 3) which belongs to the Pca_21 (C_{2v}^2 , $\text{N}^\circ 29$) space group ($Z = 4$) (cf. ref. 9).



As shown in (ref. 3), (001) (c-cut) plates display in the NO stretching region a very strong and broad absorption band centered at about 1960 cm^{-1} when transmitted light is analyzed along a (B_1 mode), and a sharp and narrow band at 1936 cm^{-1} (B_2) when $\mathbf{E} // \mathbf{b}$. An a-cut (100) plate shows two sharp bands at 1976 and 1936 for $\mathbf{E} // \mathbf{b}$. The last band is again due to the B_2 mode and the band of highest wavenumber is assigned to the longitudinal B_1 mode which appears due to experimental defects as it occurs also when $\mathbf{E} // \mathbf{c}$. Finally, the b-cut (010) shows the strongest dichroic behaviour.

The intensity of the B_1 band is so strong that even in the thinnest obtainable plates it absorbs the radiation completely. In order to obtain the real position of the absorption maximum, it is possible to resort to specular reflection spectroscopy. Thus, when light is thrown onto an (ab) face (c-cut) at 15° incidence in the (bc) plane and the polarization analyzer is oriented parallel to the a axis ($\text{TE}_{\text{reflectance}}$) the TO B_1 mode appears as a sharp and defined feature at 1968 cm^{-1} (ref. 12).

This spectrum contains the necessary information to simulate the absorption spectrum of a plate as thin as necessary to transmit light in the NO stretching region. It can be deduced in this way that thickness of the crystal plate should be reduced at least to $0.2 \mu\text{m}$ to see the ν_{NO} peak (see Fig. 6 of ref. 11). This peak appears at 1962 cm^{-1} . It is to be noted the 26 cm^{-1} difference existing between this value, corresponding to the B_1 mode, and 1936 cm^{-1} , assigned to B_2 . Such a strong (Davydov) correlation splitting should be traced to a strong dipolar coupling between neighbouring NO groups in the chains along the c crystallographic axis.

From the wavenumbers of the B_1 and B_2 modes it is possible to obtain the values of the interaction force constant (f_1) and of the dipole moment derivative ($(\text{dm}/\text{ds})_0$) which are, respectively, 0.172 mdyne/\AA and 13 D/\AA (ref. 10). The high value of f_1 confirms the strong interaction between neighbouring vibrating NO groups. Interestingly, f_1 is about one hundredth of the (bonded) NO stretching force constant ($f_{\text{NO}} = 15.91 \text{ mdyne/\AA}$ (ref. 13)).

This interaction can be broken by isotopic substitution in the NO groups. Thus, when exchanging ^{16}O with ^{18}O , at low substitution degree a band assignable to the stretching of isolated N^{18}O groups can be seen in the low temperature powder spectrum (ref. 13). At higher ^{18}O concentrations, a feature that can be assigned to the isolated N^{16}O stretching can be seen in the spectrum. A simplified GF matrix treatment of the triatomic FeNO grouping allows the calculation of the vibrational frequencies of isolated groups and clusters of increasing number of isotopically identical groups. Results describe fairly well the contours of the absorption bands for different degrees of substitution (see Figure 4 of ref. 14). Wavenumbers of isolated N^{16}O and N^{18}O groups are 1947 and 1904 cm^{-1} , while for complete substitution they are 1968 and 1924 cm^{-1} , respectively.

A further (indirect) proof of the existence of the strong NO coupling in $\text{BaNpr.3H}_2\text{O}$ and $\text{SrNpr.4H}_2\text{O}$ is provided by the spectrum of partially ^{18}O substituted $[\text{Fe}(\text{o-phen})_2][\text{Fe}(\text{CN})_5\text{NO}].2\text{H}_2\text{O}$ which shows sharp and narrow bands at 1893 and 1853 cm^{-1} (ref. 14). These bands are to be compared with the broad and complex bands found for $\text{BaNpr.3H}_2\text{O}$ (ref. 13). In this compound the bulky cations "isolate" the anions and do not allow any appreciable interaction between their NO groups (ref. 14).

A simpler interactive case is provided by $K_3[Mn(CN)_5NO] \cdot 2H_2O$, where the anions are in one set of C_1 sites and due to interaction give place to only two bands in the NO stretching region (ref. 15), at 1745 and 1732 cm^{-1} , splitting amounts 13 cm^{-1} therefore. A two-dimensional treatment of the interaction using the value 12 D/Å given in (ref. 6) for $((dm/ds)_0)$, predicts a splitting of 16 cm^{-1} .

Recently, an excited electronic metastable state of nitroprusside was obtained by irradiating $Na_2Npr \cdot 2H_2O$ single crystals at low temperature (lower than 160 K) with the green line (514 nm wavelength) of an Ar^+ -laser (ref. 16), and it was characterized by Mössbauer (ref. 16) and Raman (ref. 17) spectroscopies. The apparently same excited state has been detected also when irradiating a K_2Npr solution with powerful CW or pulsed lasers (ref. 18 a,b).

In orthorhombic $Na_2Npr \cdot 2H_2O$ the anions are disposed as in the strontium and barium salts, in (ab) planes but their polar axes are not parallel to the crystal a axis but form with it an angle of 30° (ref. 16, 17).

When a thin a-cut plate of $Na_2Npr \cdot 2H_2O$ is irradiated at boiling air temperature with the 514 nm line of the Ar^+ -laser new bands appear (ref. 19). For instance, a band assigned to the NO stretching of the metastable species shows up at 1839-1834 cm^{-1} , with the same polarization behaviour as the ground state band, which appears at 1954-1942 cm^{-1} . This band has its counterpart in the Raman spectrum of the irradiated crystal again at 1838-1834 cm^{-1} (ref. 17). The downshift of the NO stretching band upon excitation has been explained by a population increase of the antibonding π^* orbitals of the NO group (ref. 16, 17, 18), which apparently does not suffer the expected bending (ref. 17, 19, 20). Other new bands appear in both spectra but in the infrared spectrum there are bands not reported in Raman, most of which show a strong dichroic behaviour.

The most conspicuous of them is perhaps the band located at 1665 cm^{-1} , in a region that turns difficult its assignment, although it is tempting to trace it to a strongly shifted NO stretching. This and its companion bands disappear at about 90 K while the other set of bands (common to infrared and Raman) do it at about 140 K, when heating the irradiated crystal. This different behaviour, which has also been proved for $BaNpr \cdot 3H_2O$ (ref. 20), is presently unexplained.

At the beginning of this lecture, the strong π contribution to FeN bonding in nitroprusside was mentioned. Interestingly, a strong bond of this sort exists in the μ -oxobis (pentacyanomanganate)(6-) anion, which is one of the few cases where oxygen is linearly bonded due, precisely, to strong π bonding, with complete $p\pi$ donation to the metallic nuclei. The oxygen-to-manganese double bonding and the σ , π bonding between manganese and axial cyanides bring up high electronic conjugation and polarizability to the anion along the NCMnOMnCN (polar) axis.

In the double potassium salt with cyanide, $K_7[Mn_2(CN)_{10}O] \cdot CN$, the axes of the anions are normal to the c crystallographic axis and therefore to the long axes of the needle-like crystals bringing about a strong electronic and vibrational dichroism (ref. 21, 22).

Among the infrared features shown by an ordered array of needles are to be pointed out the strongly polarized bands at 2158 and 408 cm^{-1} which have been assigned to the antisymmetric axial CN and MnC stretchings (ref. 22), respectively. The corresponding, symmetric, Raman modes appear at 1881 and 527 cm^{-1} , respectively. The extraordinarily big differences existing between infrared and Raman wavenumbers point to a strong coupling between the two $Mn(CN)_5$ moieties through the oxygen bridge.

These modes, together with the $MnOMn$ symmetric stretching (all A_1) give place to a strong Raman resonance effect. Band progressions are seen at 2133, 1888, 527 and 258.5 cm^{-1} , all due to the axial MC symmetric stretching coupled with equatorial and axial CN stretchings, with itself (overtones) and with the $MnOMn$ symmetric stretching, respectively (ref. 22, 23).

The experimental excitation profiles fit quite well to the theoretical curves (ref. 23, 24) and confirm in part the assignment proposed for the electronic bands (ref. 25). Our results point to a metal-to-ligand (cyanide) charge transfer (ref. 22, 23) better than to the proposed d-d transition (ref. 25) for the band at 509 nm.

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