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Polarized and Low Temperature Infrared Spectra of Barium Nitroprusside Dihydrate, $Ba[Fe(CN)_5NO].2H_2O$

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The infrared spectra of barium nitroprusside dihydrate were studied and the observed bands were assigned either to the internal modes of the nitroprusside ion or to the intornal and librational modes of the hydration water. The data were obtained from monocrystals (measuring in this case the polarized light) and from the polycrystalline substance (both normal and deuterated). The existence of two kinds of hydration water was evident from the infrared spectra, in good accordance with X-ray studies. The water molecules seem to form weak hydrogen bonds with neighbor nitroprusside ions; an orientation for these bonds in the lattice is proposed.

Introduction

Detailed studies of the IR spectra of the nitroprusside ion have been restricted to the sodium salt. In fact, several papers have been published about sodium nitroprusside in the past few years; these deal with: a) the assignmentof bands due to the nitroprusside ion [1-6], b) the force field of this ion[3,5] and c) the bands arising from the water of hydration in the crystal[4,6].

As a contribution to the understanding of the IR spectra of this class of compounds, this paper reports on the spectra of barium nitroprusside dihydrate (BNP) both in the form of the powder (normal and deutorated) and the monocrystal. In the case of the latter the polarization of the light transmitted through oriented crystal sections was measured.

The crystal structure of BNP was determined by Lanfranconi and Alvarez[7] and their data were used as a basis for the interpretation of the spectra.

Experimental Section

Materials. Aqueous solutions of BNP were prepared by the reaction between equivalent amounts of silver nitroprusside and barium chloride solution; the silver chloride which formed was removed by filtration. Single crystals were obtained by slow evaporation of this solution at 30°C in a thermostat. Large crystals were grown from small ones suspended in saturated solutions which were thermostated and concentrated as above. In this way prisms elongated along the c axis and measuring up to 16 × 6 × 3.5 mm were obtained. The orientation and identification of the crystallographic axes were performed by standard X-ray methods. Thin sections of the monocrystals were cut normal to each axis with a string saw, using water as solvent. One face of each section was polished on cotton cloth with a suspension of alumina in alcohol, then fastened to a CsI plate with paraffin, and the section worked with fine (n° 600) waterproof emerypaper and alcohol, and finally with alumina-alcohol until the desired thickness (between 10 and 50 microns) was obtained. The sample was then covered with another CsI plate before measurement of the spectra.

Partial deuteration of BNP was accomplished by dissolving the substance in D_2O (Fluka, 99.7% nominal) and evaporating over calcium chloride in a desiccator. A higher degree of deuteration was attained by three succesive crystallizations from D_2O, with evaporation of the solvent under reduced pressure at room temperature. Powder spectra were run as mulls (in Nujol or Halocarbon oils) between CsI plates.

Instrumentation. The IR spectra were recorded on a Perkin-Elmer 457 spectrophotometer fitted with a common beam, wire-grid polarizer. When running polarized spectra, the axes of the crystal sections were positioned at 45_2 from the monochromator slits and the polarizer was set such that the electric vector was oriented parallel to each of these axes in succesive spectra. IR data was obtained in the range 4000-250 cm^{-1}. The spectrophotometer was calibrated using water, carbon monoxide and indene bands[8,9]. Frequency accuracy was estimated to be

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Table I. Observed bands in the infrared spectra of barium nitroprusside dihydrate and their assignment. Units are cm^{-1}

Mull spectra		Polarized spectra[a]			
Room. temp.	ca. 20°K	a	b	c	Assignment
—	—	—	3890 (br)	—	3553+375 = 3928
3868	38873	3865	—	—	2×1955 = 3910
3625	3632	ca. 3625 (sh)	ca. 3625 (sh)	3620	H_2O, antisym. stretching
3588	3595	—	3590 (sh)	ca. 3590 (sh)	H_2O, antisym. stretching
3553	3535	3548	3553	—	H_2O, simmetric stretching
3500 (sh)	3470	ca. 3510 (sh)	ca. 3500 (sh)	3500	H_2O, simmetric stretching
3205	3223	3212	3212	3212	2×1613 = 3226
		—	2668	2668	2172+503 = 2675
		2589	—	—	2150+441 = 2591
		—	2570	2570	2159+428 = 2579
		2403	—	—	1955+468 = 2423
		—	2198 (sh)	2198 (sh)	1613+595 = 2208
	2172 (sh)	2172	2172	2172	CN (equat.) stretching
2152	2160	2159	2159	2159	CN (axial) stretching
		—	2155 (sh)	2155 (sh)	CN (equat.) stretching
	2149	2150	2150	2150	CN (equat.) stretching
		2127	2127	2127	$C^{15}N$ stretching
2110	2117	2112	2112	2112	^{13}CN stretching
		—	2015 (br)	2015 (br)	?
		—	—	1976	1613+375 = 1988
1960	1965	1955 (br)	—	—	NO stretching
1936 (sh)	1939 (sh)	—	1936	—	
		1903	—	—	?
1613	1626	—	1619	1619	H_2O bending
	1612	1613	—	—	
		1323	—	—	2×663 = 1326
		—	1245 (br)	—	1613—375 = 1238
		1164	—	—	663+503 = 1166
		988	—	—	2×503 = 1006; 663+324 = 987
664	666	—	664	660	FeNO deformation
648	650	649	—	—	FeN stretching
565 (br)	594 (br)	595 (br)	—	—	H_2O libration
			—	550 (br)	
502	505	—	503	503	[b]
475 (sh)	476	475 (sh)	—	—	H_2O libration
	462 (sh)	468 (sh)	468 (sh)	468 (sh)	[b]
441	446,439	—	441	435 (sh)	[b]
419	421	—	420	420	[b]
		415	415	415	[b]
380 (br)	375	375 (br,sh)	375 (br)	375 (br)	H_2O libration
322	323	—	323	323	[b]
		—	280	280 (sh)	[b]

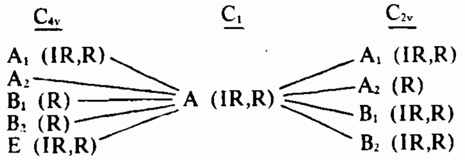
[a] Letters indicate the crystal axis to which the analyzer is parallel. [b] FeC stretching and FeCN deformations (see text). br: broad; sh: shoulder.

± 2 cm^{-1} for sharp bands and ± 3 cm^{-1} for broad, poorly defined bands or shoulders.

Low temperature spectra were obtained at ca. 20°K using a Cryo-Tip cryostat (model AC-3L-110) and at liquid nitrogen temperature with a RIIC variable temperature cell (model VLT-2).

Results and Discussion

BNP belongs to the orthorhombic system, space group C^5_{2v} – Pca2$_1$ (n° 29). The unit cell contains four molecules of formula Ba[Fe(CN)$_5$NO] . 2H$_2$O[7]. According with the X-ray study of BNP[7] the deviation of the nitroprusside ion from C_{4v} symmetry is not large, and therefore we have adopted such symmetry as the effective symmetry of the anion in the lattice. The 33 normal modes of the nitroprusside ion are then classified as 8A$_1$ (IR and Raman active) + 1A$_2$ (inactive) + 4B$_1$ (Raman active) + 2B$_2$ (Raman active) + 9E (IR and Raman active). In the crystal lattice these ions occupy sites with C_1 symmetry with consequent complete activation and removal of degeneracy of all modes. According to the forementioned site and space groups, the activities of the crystal vibrations should be as follows:



Therefore, each IR-active mode of the anion should be split into three components in the BNP lattice. This splitting is most apparent in the NO stretching band and in the bending band of water (see Table I and later discussion). Most other bands show, at best, only a small splitting which points out that there exists little interaction between the components of the crystal lattice. Consequently, we have adopted the oriented gas model as a first order approximation in the interpretation of the observed dichroism in the spectra of monocrystalline samples.

Frequencies of the IR bands observed in mulls and in polarized spectra, as well as their assignment, are reported in Table I.

Polarized spectra. Section parallel to 100 planes (called bc sections, 010 planes (ac sections) and 001 planes (ab sections) were cut from single crystals. A projection of the crystal lattice on the 001 plane is shown in Fig. 1; the corresponding parameters appear in Table II. The NCFeNO axis of the nitroprusside ions forms an angle of about 10° with the crystallographic a axis and is nearly parallel to the 001 plane (the NO group is slightly out of line and forms an angle of about 5° with this plane). Taking into account such geometry, the following dichroic behavior must be expected for the vibrational modes of the nitroprusside ion. These modes with transition moments parallel to the axis of the ion (A_1 modes) should appear in the spectra of the ab and ac sections, when the light is analyzed parallel to the a axis; the modes with transition moment normal to the ion axis (all modes except A_1), should be always active in the spectra of the bc section, and active in the spectra of ab and ac sections when the light is analyzed parallel to b and c axes, respectively.

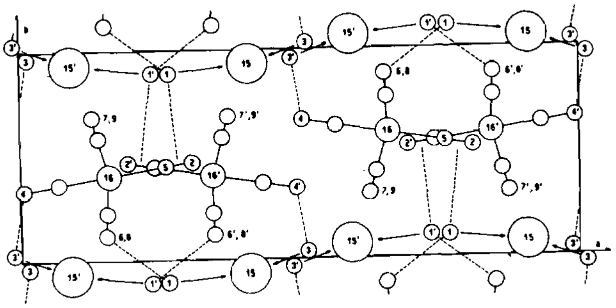


Figure 1. Projection of the BNP lattice on the 001 plane (slightly more than two unit cells are shown). Arrows indicate the coordination of water to the Ba ions; dashed lines indicate the probable hydrogen bonds. See Table II for the atomic parameters. Unit cell parameters[7] are: a = 19.471 Å, b = 7.631 Å. c = 8.609 Å.

Table II. Parameters for relevant atoms in the unit cell of BNP.[7]

Atom	x/a	y/b	z/c[a]	
O1	.258	.890	.164	(B-water)
O2	.302	.463	.164	(NO group)
O3	.009	—.025	—.035	(A-water)
N4	.005	.330	.164	
N5	.245	.454	.153	
N6	.158	.147	—.090	
N7	.132	.678	—.065	
N8	.157	.112	.412	
N9	.128	.691	.421	
Ba15	.398	.928	.172	
Fe16	.160	.415	.176	

[a] Values for unprimed atoms in Figure 1. For primed atoms these figures must be decreased in 0.5 z/c.

The dichroism of the water bands cannot be predicted in advance because the position of the hydrogen atoms is not known from the X-ray study. However, some conclusions about their nature and relative position in the lattice can be obtained through the study of the polarized spectra and the spectra of deuterated powder samples, as will be discussed later.

The assignment of bands due to the nitroprusside ion.

a—*CN stretching bands.* An intense band at 2152 cm^{-1} and a weak one at 2110 cm^{-1} are observed in the CN stretching region when the spectrum of BNP is run in a Nujol mull. The first band is resolved into two components at 2150 and 2159 cm^{-1}, both in the low temperature spectrum of the powdered sample and in polarized spectra (Table I and Fig. 2). A shoulder appears at 2172 cm^{-1} in some spectra, and more clearly at low temperatures.

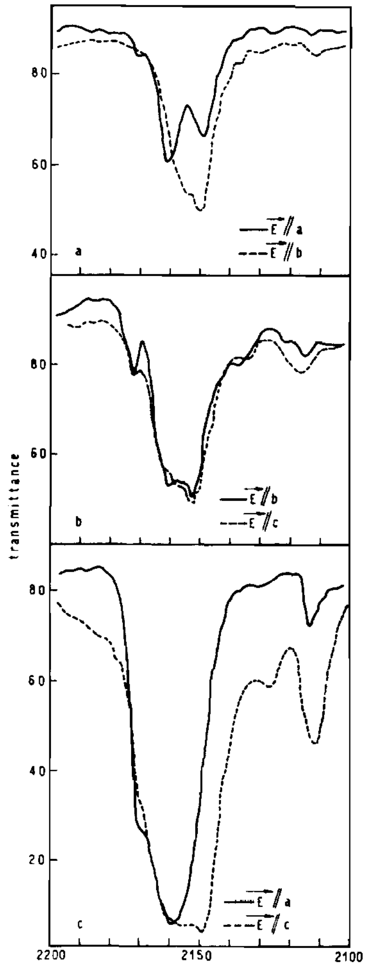


Figure 2. Polarized spectra of BNP in the CN stretching region. a and b spectra were run at liquid nitrogen temperature; c spectrum at room temperature. Sample tickness in c spectrum is ca. 15 microns.

The band at 2150 cm^{-1} is active when the electric vector of light is parallel to the b and c axes. This fact and the relatively large intensity of this band leads to its assignment to the E stretching mode. The breadth of this band suggests the superposition of at least one more band, nevar resolved in our spectra, which is centered around 2155 cm^{-1}. This second band could be assigned to the equatorial non-totally symmetric stretching mode, B_1, activated in IR by the lack of symmetry of the crystal site. The 2159 cm^{-1} band shows the dichroic behavior expected for an A_1 mode. It is therefore assigned to the axial CN stretching. The weak shoulder at 2172 cm^{-1} seems to behave in the same manner as the 2159 cm^{-1} band in the polarized spectra, suggesting its assignment to the equatorial A_1 stretch. This mode gains activity in the IR mainly because of the departure from 90° of the N-Fe-C_{equat} angle (mean value for BNP is 95°[7]) and it can therefore be expected to be weak.

The weak band at 2112 cm^{-1} is assigned to the stretching of naturally occurring ^{13}CN groups. This assignation was made initially by comparison with sodium nitroprusside[1,4] and confirmed by calculation of the expected frequency shift for ^{13}CN groups located in equatorial and axial positions. This calculations was made in the diatomic approximation and give values of 2112 cm^{-1} for equatorial ^{13}CN, and 2114 cm^{-1} for axial ^{13}CN groups. The observed values in the polarized spectra of ab and ac sections were 2111 cm^{-1} (analyzer normal to a axis) and 2113 cm^{-1} (analyzer parallel to a axis), respectively. In the same way (diatomic approximation) we calculate a frequency of 2124 cm^{-1} for the stretching of a $C^{15}N$ group. The shoulder at 2127 cm^{-1} is then assigned to such isotopically substitued groups in BNP.

b- *NO and FeNO vibrational bands.* The strong and broad band at 1960 cm^{-1} in the spectra of polycrystalline BNP is due to NO stretching. It shows a shoulder at 1936 cm^{-1} which is well resolved in the polarized spectra along the b axis (Fig. 3), whereas a broad band centered at ca. 1955 cm^{-1} is active when analyzing along the a axis. We assign both bands as components of the factor group split NO stretching mode. A third component could be expected to be active along c and in fact a band appears at 1976 cm^{-1} in the spectra of the bc section (Fig. 3, b). However, such a band is not observed in the spectrum of the ac section, when analyzing along c (Fig. 3, c). We think that such a third component is probably weak enough (because of the parallelism of the NO group with the 001 plane) as to be non observable, and we prefer to assign the 1976 cm^{-1} band to a combination of bonding and librational vibrations of water molecules (Table I).

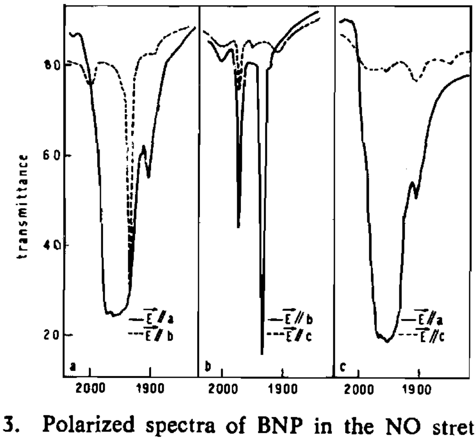


Figure 3. Polarized spectra of BNP in the NO stretching region, run at room temperature. Sample tickness: 10-15 microns.

The bands at 662 and 649 cm^{-1} are associated with the Fe-NO moiety, as was shown in sodium nitroprusside dihydrate by means of IR and Raman polarization data[1,2] and by ^{15}N isotopic substitution[5]. The 649 cm^{-1} band shows activity when the spectrum is analyzed along the a axis (Fig. 4, a and c) and therefore is assigned to the Fe-N stretching (A_1). The 662 cm^{-1} feature, in accordance with its activity along b and c axes, is assigned to the deformation mode (E).

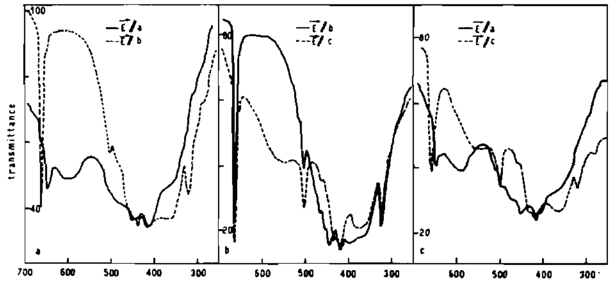


Figure 4. Polarized spectra of BNP in the low frequency region, run at room temperature.

c- *Fe-C stretchings and Fe-CN deformations.* The bands originated by these vibrations appear between 550 and 250 cm^{-1}, a region of considerable complexity, aumented by the librational bands of water.

The assignment of bands of the nitroprusside ion by different authors in this region are not always consistent and there exists also a lack of agreement regarding the bands to be assigned as fundamentals. On the other hand, there is still much controversy about the assignment of bands in this region taking as a basis the comparison with the spectra of hexacyano complexes. (see Ref. 10 and 11). Lacking additional experimental arguments, we have preferred not to assign bands in this region to definite modes. Rather, we have attempted to determine, when feasible, the symmetry of the mode associated with each observed band.

Definite bands at 503, 441, 420, 415 and 323 cm^{-1} and shoulders at ca. 468 cm^{-1} and ca. 280 cm^{-1}, due to the nitroprusside ion, were observed in this low frequency region. The bands at 503, 441, 420 and 323 cm^{-1} are possibly due to E modes because of their behaviour in polarized spectra (Fig. 4). The dichroic activity of the features at 468 and 415 cm^{-1} is doubtful and their assignment to A_1 modes was made by comparison with the results of Tosi[4]. Using the same criterion, the shoulder at 280 cm^{-1}, observed

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(10) D.W. James and M.J. Nolan in "Progress in Inorganic Chemistry", (Ed.: F.A. Cotton), Vol. 9, p. 262, Interscience, N.Y., 1968.

(11) I. Nakagawa and T. Shimanouchi, *Spectrochim. Acta, 18*, 101 (1962).

in some of the spectra, is assigned to a mode of E symmetry.

d- *C-Fe-C and C-Fe-N deformations.* These modes, which should absorb below 250 cm^{-1}, are out of the range of our instrument.

The fundamental bands due to the nitroprusside ion are summarized in Table III.

Table III. Bands due to fundamental vibrations of the nitroprusside ion.

Specie	Frequency (cm^{-1})	Assignment
A_1	2172	CN (equat.) stretching
	2159	CN (axial) stretching
	1955	NO stretching
	649	FeN stretching
	468 415	FeC stretching and FeCN deformations
B_1	2155	CN (equat.) stretching
E	2150	CN (equat.) stretching
	662	FeNO deformation
	503 441 420 323 280	FeC stretching and FeCN deformations

The assignment of bands due to water. Two crystallographically distinct types of water molecules are present in crystalline barium nitroprusside dihydrate[7]. In the X-ray study, only the oxygen atoms were located and therefore the position of the hydrogen atoms must be inferred from other data. An effort to establish the location of the hydrogen atoms was made during the present work.

The existence of two crystallographically distinct kinds of water molecules in the crystal lattice is reflected in the IR spectra of BNP mulls, both at room and low temperatures. The relevant features in these spectra are: a) A broad band in the O-H stretching region, characterized by the presence of well defined peaks at 3625 and 3553 cm^{-1}. Such frequencies are comparable with those observed for water bands of sodium nitroprusside dihydrate (3625 and 3545 cm^{-1})[6] and suggest the existence of a weakly bonded water molecule. The other features (more prominent at low temperatures) as well as the "tailing" towards lower frequencies indicates that a second type of more strongly H-bonded water molecules could exist; b) Three broad bands are observed in the low frequency region, at 565, 475 and 375 cm^{-1} (measured at room temperature), whose intensity is greatly enhanced by lowering of the sample temperature and which dissapear on dehydration of the sample. These bands are due to librational vibrations of more than one crystallographically distinct kind of water of hydration (two bands are expecsted for each kind of water molecule in this spectral region[12]).

More information about the water molecules in BNP was obtained through deuteration (following the technique proposed by Falk and collaborators[13,6]). Several crystalline samples with increasing deuterium content were prepared and their spectra were measured in the form of mulls at room and liquid nitrogen temperatures. In the low temperature spectra, the bands were more clearly resolved and, in some cases, were more intense.

The polarized spectra of monocrystalline sections provided some useful data about the probable orientation of the hydrogen bonds.

In the following, we will discuss the data obtained from these two experimental approaches in the stretching, bonding and librational regions of the spectra, respectively. The observed bands due to the hydration water in BNP are summarized in Table IV.

Table IV. Bands due to the hydration water in BNP (measured in Nujol mulls).

Vibration	Frequency (cm^{-1}) Room temp.	 Low temp.[a]	Assignment
stretchings	3625	3632	A-H_2O
		3598	A-HOD (isolated OH)
	3588	3595	B-H_2O
		3562	A-HOD (isolated OH)
	3553	3535 (sh)	A-H_2O
		3524	B-HOD (isolated OH)
		3483	B-HOD (isolated OH)
	3500 (sh)	3470	B-H_2O
	2697	2700	A-D_2O
		2673	B-D_2O
	2665 (sh)	2650	A-HOD (isolated OD)
	2647	2625	A-HOD (isolated OD)
	2622	2604	B-HOD (isolated OD)
		2587	A-D_2O
	2604		
		2573	B-HOD (isolated OD)
	2570 (sh)	2546	B-D_2O
bendings	1613	1626 1612	HOH
	1427	1433 1421 [b]	HOD
	1193	1200 1190	DOD
librations	565	594	B-H_2O (A axis)
	475 (sh)	476	A-H_2O (A axis)
	375 (sh)	375	A-H_2O (C axis)
	360 (sh)	362	A-D_2O (A axis)
	290 (sh)	287	A-D_2O (C axis)

[a] Liquid nitrogen temperature; [b] measured in Halocarbon mull. sh: shoulder.

a- *The stretching regions.* The changes brought about as a result of increasing the deuterium content in the samples were more clearly seen in the O-D stretching region, between 2700 and 2500 cm^{-1}. Four bands at 2650, 2625, 2604 and 2573 cm^{-1} are clearly seen in the spectrum of a sample with a relatively small degree of deuteration (Fig. 5, a). As the deuterium content increases four new bands appear at 2700, 2673, 2587 and 2546 cm^{-1} (Fig. 5, b, c). We assign the first set of four bands to the uncoupled O-D stretchings of HOD molecules, whereas

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(12) J. van der Elsken and D.W. Robinson, *Spectrochim. Acta, 17,* 1249 (1961).

(13) V. Seidl, O. Knop and M. Falk, *Can. J. Chem., 47,* 1361 (1969)

the second set should be originated by DOD molecules.

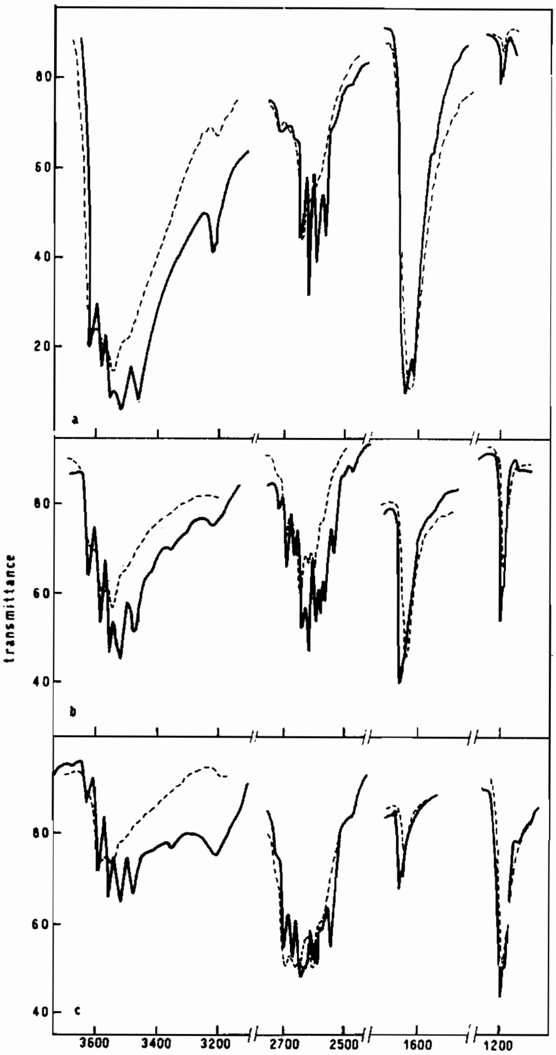

Figure 5. Spectra of partially deuterated samples of BNP in the stretching and bending regions of water, measured in Nujoll mulls. – – – –: room temperature; ————: liquid nitrogen temperature. Deuterium content is estimated to be 5% in a, 30% in b, and 70% in c.

The four bands assigned to HOD point immediately to the existence of two crystallographically nonequivalent kinds of water molecules in the lattice, and to crystallographically nonequivalent O-H bonds in each water molecule. These observations are consistent with predictions based on the space group found for BNP, C^5_{2v}[7], which locates the eight water oxygen atoms in the unit cell in two set sof our C_1 sites each, and the sixteen water hydrogen atoms in four sets of four C_1 sites each.

By comparison with the data obtained for sodium nitroprusside dihydrate in this region[6] and taking into account the expected shift toward lower wavenumbers due to hydrogen bond formation[14], the bands at 2700, 2650, 2625 and 2587 cm^{-1} were assigned to the most weakly hydrogen-bonded water molecules (which will be called A-water), and the bands at 2673, 2604, 2573 and 2546 cm^{-1} were assigned to the other, more strongly hydrogen-bonded water molecule (B-water).

Unfortunately, the spectra were much less well-defined in the O-H stretching region, due to the intense background and to band overlapping. The counterparts of the O-D bands were located, in some cases as shoulders, at 3632, 3598, 3562 and 3535 cm^{-1} for the A-water, and at 3595, 3524, 3483 and 3470 cm^{-1} for the B-water (all frequencies correspond to low temperature spectra).

The frequency raties (OH/OD) for the uncoupled stretchings were:

$$\frac{3598}{2650} = 1.358 \quad \text{and} \quad \frac{3562}{2625} = 1.357, \text{ for A-water}$$

$$\frac{3524}{2604} = 1.353 \quad \text{and} \quad \frac{3483}{2573} = 1.354, \text{ for B-water}$$

The similarity among these ratios supports the assignment of doublet components to nonequivalent O-H bonds.

The water bands in the stretching region show appreciable dichroism in the polarized spectra (Fig. 6). Such spectra must be interpreted on the basis of the most probable orientation for the water molecules in the lattice.

Both kinds of hydration water (whose oxygen atoms are labelled O1 and O3 in the X-ray study[7]) are coordinated to barium ions and are probably oriented so as to maximize the interaction of the hydrogen atoms with neighboring nitroprusside ions by formation of H-bonds. At the same time, they should tend to minimize the interaction of the hydrogen atoms with the barium ions (because of cation-proton repulsion). In the following discussion, we use the numbering of atoms given in Ref. 7 and reproduced in Fig. 1.

The atoms in the vicinity of O3 which could be involved in H-bonding are the following: a) N4′ at 3.50 Å from O3, conforming a Ba-O3-N4 angle of 122.8°; b) N7 at 3.27 Å from O3 and forming a Ba-O3-N7 angle equal to 140.8°; c) N6 at 3.21 Å from O3 and forming a Ba-O3-N6 angle of 131.9°. We believe that none of these atoms are adequately positioned to constitute a well defined hydrogen bond due to the relatively large distances or angles. As described below, the O1-water seems to be in better position to form two definite hydrogen bonds. These considerations, together with the large isotropic temperature factor observed for O3 (this factor is 4.27 for O3 and 1.15 for O1[7]), suggest that the O3 atom belongs to the most weakly hydrogen bonded water and must therefore be identified with the A-water mentioned above.

The bands at 3625 cm^{-1}, originated by the antisymmetric O-H stretching, and at 3553 cm^{-1} due to the symmetric O-H stretching, are assigned to such A-water. Looking at the behavior of these bands in the polarized spectra of bc and ac sections (Fig. 6, b, c) it can be seen that the band at 3625 cm^{-1} is

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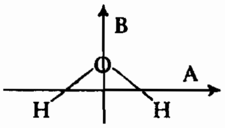
(14) G.C. Pimentel and A.L. McClellan, "The Hydrogen Bond", W.H. Freeman, San Francisco, 1960.

always more intense when the light is analyzed with its electric vector parallel to the c axis, whereas its intensity decreases in the ab section (Fig. 6, a). This observation can be rationalized admitting that the A inertial axis of the water molecule: forms a relatively small angle with the crystallographic c axis. The 3553 cm^{-1} band shows higher intensity when analyzing along the b axis in the bc section, and along the a axis in the ac section, whereas its intensity remains almost the same along both a and b axes in the ab section, indicating that the B inertial axis of this water molecule forms an angle which is not far from 45° with the a and b crystal axes. Such orientation of the inertial axes of the A-water could be explained by the existence of a weak H-bond between N4 and O3. This oxygen atom is coordinated to a barium ion probably through one if its lone electron pairs.



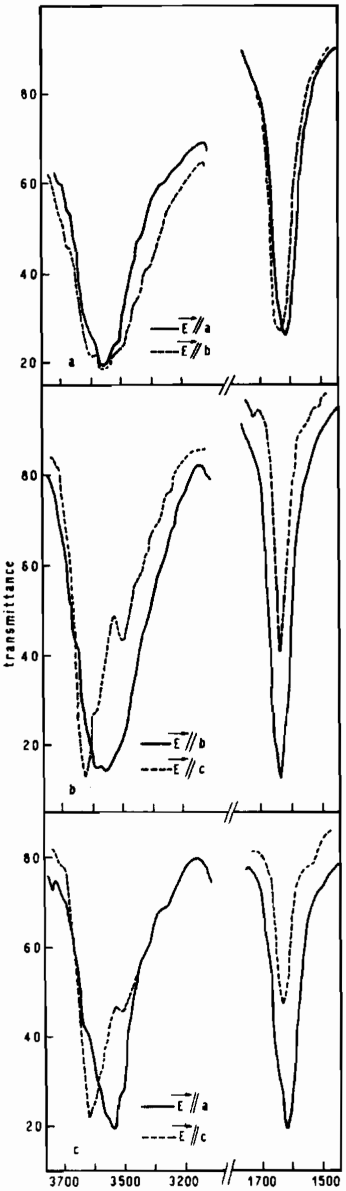


Figure 6. Polarized spectra of BNP in the stretching and bending regions of water, run at room temperature.

The best candidates for hydrogen bond formation in the neighborhood of the O1 atoms are the N8 atom(distance O1-N8 equal to 3.36 Å, angle Ba-O1-N8 equal to 120.3°), the N6 atom (distance O1-N6 equal to 3.50 Å, angle Ba-O1-N6 equal to 120.6°), and the nitrosyl group, N5-O2 (distance O1-O2 equal to 3.37 Å and angle Ba-O1-O2 equal to 81.6°; distance O1-N5 equal to 3.34 Å and angle Ba-O1-N5 equal to 100.5°). Being the Ba-O-N angles practically equal, we think that the N8 atom is favored over the N6 one for H-bond formation because of the shorter distances O1-N8. The angle N5-O1-N8 is equal to 118.4°. According to such a geometry, each hydrogen attached to the O1 atom can form a relatively weak H-bond, one of them pointing towards the N8 atom and the other towards the N5 atom or to the π electron system of the NO group. The O1 atom is then probably coordinated to a barium ion through one lone electron pair. Accepting that the B inertial axis of this water molecule is approximately coincident with the bisector of the N5-O1-N8 angle, we find that such B axis forms angles of 37° with (its projection on) the 001 plane, 40° with the 100 plane and 28° with the 010 plane. The line between O1 and the NO group, and therefore, the axis of one of the H-bonds, are almost parallel to the 001 plane.

The stretching bands of this O1-water (which should be identified with the B-water of the deuterated spectra) are located at lower frequencies than those corresponding to the A-water molecules and are more difficult to study because of severe overlapping. Some changes in their intensity can be appreciated in the polarized spectra of the bc section (Fig. 6, b), where the 3588 cm^{-1} band (antisymmetric O-H stretching) becomes more intense when the analyzer is rotated from the c axis to the b axis; at the same time the intensity of he 3500 cm^{-1} band (symmeric O-H stretching), decreases (the behavior of this last band is best seen in low temperature polarized spectra, not shown here). The dichroism shown by these two bands is in accordance with the forementioned spatial arrangement of the B-water molecules. No definite conclusions could be obtained from the dichroism of these bands in the other crystal sections.

b– *The bending regions.* The bands due to the bending mode of H$_2$O and D$_2$O are broad singlets at room temperature, but each of them split in two components at low temperature. The magnitude of the splitting depends on the degree of isolation of the water molecules, when the sample is deuterated.

In undeuterated BNP the bending fundamental of H$_2$O shows two main components separated by 14 cm^{-1} when the sample is cooled; we explain that splitting as being originated by correlation effects, arising from dynamical interaction of molecules within the same unit cell. In fact, in BNP, the water molecules are aligned parallel to the crystallographic c axis, with a separation of 4.3 Å between them. A similar distance between water molecules exists in sodium nitroprusside dihydrate, in which the bending bands show correlation splitting[4].

In partially deuterated BNP one of the components of the splitted bands reduces to a shoulder separated by about 8 cm^{-1} from the main peak, and with larger isotopic dilution that splitting is reduced to about 5 cm^{-1}. The decreasing separation between the components of the bonding bands with increasing isotopic dilution can be appreciated in Fig. 5.

The double peaks observed for the bending fundamentals of isotopically diluted H_2O and D_2O are explained as arising from the crystallographic nonequivalence of the water molecules in the lattice.

The HOD bending fundamental (not shown in Fig. 5) is also a broad singlet at room temperature which splits in two components separated by 12 cm^{-1} at liquid nitrogen temperature. In fact, one could expect to observe four components for this band, arising from the two kinds of water molecules having crystallographically nonequivalent OH(OD) bonds. Probably we ar eobserving a splitting which is mainly a consequence of the nonequivalence of the OH(OD) bonds, an effect which should be specially important in the case of the HOD band. The minor splitting due to the kinds of water molecules (5 cm^{-1} for the H_2O and D_2O bending bands, as reported above) seems to be non observable in the HOD bending band.

The bands due to the bending vibration of H_2O molecules show relatively larger intensity when light is analyzed along a and b axes in the polarized spectra of the monocrystalline sections ac and bc (Fig. 6, b, c). Such behavior is to be expected if the B inertial axes of the water molecules are more nearly parallel to the 001 crystal plane than to the 010 and 100 planes; this geometry coincides with the spatial configuration of both kinds of water molecules, proposed in the discussion of their stretching bands.

These broad and featureless deformation bands observed in the polarized spectra also show frequency shifts when the analyzing direction is changed during the study of the ab and ac sections (Fig. 6, a, c). Such shifts probably arise from two effects: the correlation splitting, with components active along different axes and the existence of two kinds of water molecules in the crystal giving rise to two somewhat shifted bands with again different activity along each crystal axis.

c– *The librational region.* Three broad bands appear at 594, 476 and 375 cm^{-1} which are assigned to the librational movements of the water molecules. Two new bands at 362 and 287 cm^{-1} appear on deuteration, whose intensity is markedly enhanced at liquid nitrogen temperature. It seems evident that these last two bands correspond to the 476 and 375 cm^{-1} bands of the nondeuterated samples, the frequency ratios being: $476/362 = 1.317$ and $375/287 = 1.306$ (all mentioned frequencies were measured at liquid nitrogen temperature). The 594 cm^{-1} band should be consequently shifted to 420-460 cm^{-1} by deuteration, in which case it is probably buried in the complex band centered at ca. 430 cm^{-1} in our spectra.

The librational bands show marked dichroism in the polarized spectra (Fig. 4). Such dichroic behavior could be interpreted by taking the inertial axes of the free water molecule as the librational axes, an hypothesis which seems justified in a first approximation because the water molecules are not too strongly bonded in the crystal lattice. Accepting also the spatial orientation of the water molecules proposed in relation with their stretching vibrations, the assignment of the 476 and 375 cm^{-1} bands to the librations around the A and C inertial axes, respectively, of the A-water, and the 594 cm^{-1} band to the libration around the A inertial axis of the B-water logically follows. It can be seen in Fig. 4 (a and c) that the 476 and 375 cm^{-1} bands behave as if originated by mutually normal transition moments. a fact which reinforces the assignment of both bands to the same kind of molecule.

Two different frequencies are measured in the polarized spectra for the third band: 594 cm^{-1} when analyzing along the a crystal axis and 550 cm^{-1} along the c axis; such a shift could be ascribed to the interaction between neighboring molecules (i.e., factor group or correlation effect).

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