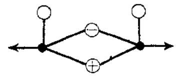
(ReCl) and ν(ReI)/ν(ReBr) (Table II); these fall, respectively, in the ranges 0.68–0.71 and 0.80–083. For a diatomic M–X system in which only the reduced mass changes in passing along the sequence X = Cl, Br, I, the calculated ratios are ν(ReBr)/ν(ReCl) = 0.72 and ν(ReI)/ν(ReBr) = 0.86.

Appendix

Under its full point group symmetry (C_{2v}), structure III should give rise to five infrared-active ν(CO) ($2\ A_1 + 2\ B_1 + B_2$) and five infrared-active ν(ReX) ($2\ A_1 + 2\ B_1 + B_2$) bands. In the case of the CO vibrations, it is likely that interaction between the halves of the anion will be negligible. As a consequence, the two out-of-plane ν(CO) vibrations (A_1^a and B_1^a) should be degenerate. Two of the in-plane ν(CO) vibrations (A_1^b and B_1^b) should also be degenerate. We therefore expect that III will give rise to three infrared bands in the CO stretching region: ($A_1^a + B_1^a$), ($A_1^b + B_1^b$), and B_2. The same conclusion is reached by the method of local symmetry in which the ν(CO) frequencies are considered to arise from an $Re(CO)_3X_3$ group having C_s symmetry.

By a similar argument, the two terminal ν(ReX) vibrations (A_1^a and B_1^a) should be degenerate. The three remaining ν(ReX) frequencies are vibrations of the bridging halogen atoms. The A_1^b mode may be drawn as below.[15] It does not involve a change in



dipole moment but must obtain intensity by coupling with the A_1^a vibration. If the coupling is appreciable, the degeneracy of the A_1^a and B_1^a vibrations will be lifted and the spectrum should show five bands in the ReX stretching region. If the coupling is weak the A_1^b vibration will not have much intensity and the A_1^a and B_1^a vibrations will remain nearly degenerate. In this case, only three ν(ReX) frequencies might be observed.

Consideration of the full point group symmetry (C_s) for structure VI predicts five infrared-active ν(ReX) frequencies ($3\ A' + 2\ A''$). None of these is expected to be degenerate, and examination of the symmetry modes indicates that they are all associated with a change in dipole moment.

Acknowledgments.—We thank Miss B. Prescott for running the far-infrared spectra and Mr. C. R. Sprinkle for experimental assistance.

[15] R. P. Bell and H. C. Longuet-Higgins, *Proc. Roy. Soc.* (London), **A183**, 357 (1945).

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Laser Raman Spectra of a Single Crystal of Sodium Nitroprusside and the Vibrational Frequencies of the $Fe(CN)_5NO^{2-}$ Ion[1a]

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Received March 10, 1969

The Raman spectra of an oriented single crystal of sodium nitroprusside excited by 6328-Å radiation from an He–Ne laser have been investigated in detail. The infrared absorption spectra of the polycrystalline sample have also been recorded at room temperature as well as at liquid N_2 temperature. The analysis of the data in the light of the crystal structure and earlier spectral data has enabled us to assign many of the vibrational frequencies of the $Fe(CN)_5NO^{2-}$ ion.

Introduction

There has been considerable interest, during the past few years, on the study of the vibrational spectra of the coordination complexes of transition metals. Among a large number of reports, mention may be made of the works on the infrared and Raman spectra of some metal cyanide complexes of the types $M(CN)_2$, $M(CN)_4$, $M(CN)_6$, and $M(CN)_8$.[2–6] From the analysis of the spectra several interesting conclusions on the nature of the metal–ligand bond and its correlation with the CN bond strengths were drawn. The assignments of the infrared-active vibrational frequencies reported in most of the above studies tend to be somewhat ambiguous because of insufficient data. One reason is that most of the transition metal cyanides are highly colored; consequently, their Raman spectra excited by the conventional Hg-arc sources are incomplete. However, with the availability of the laser sources (particularly, the He–Ne laser giving intense monochromatic radiation of λ 6328 Å), the Raman spectra of many colored substances can be recorded routinely. Also, the collimated and the polarized nature of the laser beam allows excitation of the Raman spectra of a properly oriented single crystal giving the different polarizability (derivative) components for a normal

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[1] (a) This work was sponsored, in part, by the U. S. Atomic Energy Commission. (b) University of Maryland, College Park, Md. 20742. (c) Los Alamos Scientific Laboratory, University of California, Los Alamos, N. M. 87544.

[2] (a) L. H. Jones, *Spectrochim. Acta*, **19**, 1675 (1963); (b) L. H. Jones, *J. Chem. Phys.*, **26**, 1578 (1957); **27**, 468 (1957).

[3] I. Nakagawa and T. Shimanouchi, *Spectrochim. Acta*, **18**, 101 (1962).

[4] D. M. Sweeny, I. Nakagawa, S. Mizushima, and J. V. Quagliano, *J. Am. Chem. Soc.*, **78**, 889 (1956).

[5] R. L. McCullough, L. H. Jones, and G. A. Crosby, *Spectrochim. Acta*, **16**, 929 (1960).

[6] J. P. Mathieu and H. Poulet, *Proc. Intern. Meeting Mol. Spectr., 4th, Bologna, 1959*, **3**, 1016 (1962).

vibration. The resulting data can enable us to identify the phonons of different symmetry types allowed by the symmetry of the crystal. The Raman-active phonons of $K_3Fe(CN)_6$ have been analyzed in this fashion by Deveze and Krauzman.[7] (We refer to phonon as the factor group fundamental and the mode as the fundamental of one complex ion unit.)

We have investigated the Raman spectra of an oriented single crystal of sodium nitroprusside [$Na_2Fe(CN)_5NO \cdot 2H_2O$] excited by 6328-Å radiation from an He–Ne laser. The infrared spectra of the polycrystalline sample have also been recorded at room temperature as well as at liquid N_2 temperature. The partially D_2O-substituted compound (both single crystal and powder) was studied also, in order to identify any H_2O vibrations. The analysis of the data in the light of the reported crystal structure of sodium nitroprusside[8] has enabled us to assign many of the normal mode frequencies of the $Fe(CN)_5NO^{2-}$ ion. A discussion of the results is presented in this report.

Experimental Section

Single crystals of sodium nitroprusside were grown by slow evaporation of an aqueous solution of the sample. Specimens were cut and polished with the edges coinciding with the crystallographic axes. The orientations were checked (a) by comparing the morphology of the grown crystal with the data reported by Spijkerman, *et al.*,[9] (b) with the help of a polarizing microscope, and (c) by measuring the cell lengths from the Weissenberg photographs taken on an X-ray diffraction unit and comparing with the literature values.

The Raman spectra were recorded on a Cary 81 Raman spectrophotometer equipped with a Spectra Physics 125 He–Ne laser (output ~60 mW at 6328 Å). The geometry of the experimental arrangement to obtain the Raman spectrum with a polarizability (derivative) component α'_{ij} is described by the notation $X(ij)\bar{X}$, originally due to Damen, *et al.*[10a] X and $\bar{X}$ denote the directions of propagation of the incident and the scattered beams, and i and j refer to their respective directions of electric vectors. In order to avoid the effect of the preferential sensitivity of the monochromator for the radiation with a particular polarization direction, the analyzer was kept fixed and the direction of polarization of the laser beam was changed by inserting a 45° cut half-wave plate in its path.

The infrared spectra of the polycrystalline sample (Nujol mull) were recorded on a Perkin-Elmer 621 infrared spectrophotometer in the region 4000–200 cm^{-1} and on a Fourier transform FS620 interferometer in the region 200–60 cm^{-1}. The infrared spectra at low temperature were obtained by attaching the substrate plates containing the sample (sandwiched between them) to the cold finger of a double-walled dewar flask evacuated to ~10^{-5} mm. Liquid N_2 was used as the coolant.

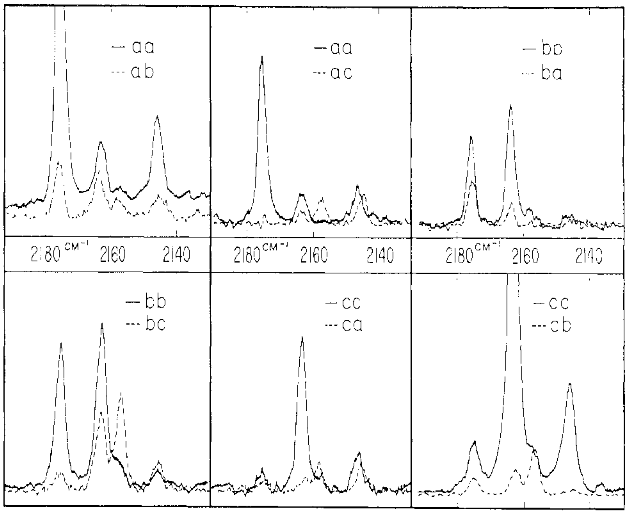

Figure 1.—Polarized Raman spectra of a single crystal of $Na_2Fe(CN)_5NO \cdot 2H_2O$ in different orientations. In the notation of Damen, *et al.*,[10a] the 12 spectra are described from left to right top and then left to right bottom as: ———, $c(aa)\bar{c}$, $b(aa)b$, $c(bb)c$, $a(bb)\bar{a}$, $b(cc)b$, $a(cc)\bar{a}$; – – – –, $c(ab)\bar{c}$, $b(ac)b$, $c(ba)c$, $a(bc)\bar{a}$, $b(ac)b$, $a(cb)\bar{a}$.

Table I

Raman-Active Phonon Frequencies of $Na_2Fe(CN)_5NO \cdot 2H_2O$

	A_g			B_{1g}	B_{2g}	B_{3g}	Site group	Isolated ion
ν, cm^{-1}	I_{aa}	I_{bb}	I_{cc}	I_{ab}	I_{ac}	I_{bc}	C_s	C_{4v}
2174	95[a]	57	12	23	4	4	A′	A_1
2162	17	63	120	13	3	3	A′	A_1
2156.5	...	2	2	...	19	37	A″	B_1
2145	25	4	32	...	...	...	A′	E
2143.5	...	...	...	...	26	7	A″	
1947	12	...	...	4	...	...	A′	A_1
665	34	44	...	32	9	2	A′ + A″	E
656	260	44	...	62	4	2	A′	A_1
500	18	...	...	...	...	...		
493	...	...	24	...	...	...	A′	A_1
472	220	130	30	40	3	8	A′	A_1
429	...	...	...	3	...	...		
422	...	...	...	2	3	...		
415	10	...	...	...	8	30	A′ + A″	E
410	...	...	...	...	...	25	A″	B_1
408	19	90	100	...	...	...	A′	A_1
374	...	...	...	...	...	2		E
320	6	...	...	...	1	...	A′ + A″	E
165	...	200	...	...	...	28		
160	300	...	...	19	...	...		
157.5	...	...	280	...	...	...		
154	...	80	...	...	...	14		
136	...	125	...	...	...	18		
134	...	...	...	25	...	...		
123–125	470	290	...	38	8	42	A′ + A″	A_1 + B_1
110	...	...	...	11	...	...		
104	...	...	4	...	15	...		
97	...	16	30	...	...	200		
81	...	...	45	40	420	90		
77	330	180	...	...	...	...		
71	...	...	...	90	...	...		
60	82	36	40	...	...	200		
42	...	...	11	...	6	100		

[a] Numbers under columns marked I_{aa}, etc., are the relative intensities of the phonons in various α'_{ij} traces on the scale 0–500, measured at the maxima. They are believed to be accurate to 10%.

The traces of the Raman spectra, in the region of CN stretching vibrations, with different polarizability (derivative) components α'_{ij} are reproduced in Figure 1. Table I gives the Raman-active phonon frequencies of $Na_2Fe(CN)_5 \cdot 2H_2O$ and their relative intensities in the spectra with different α'_{ij} components. A recent article by Tosi, *et al.*,[10b] reported similar Raman studies of a single crystal of $Na_2Fe(CN)_5NO \cdot 2H_2O$. For the most part our results, given in Table I, are similar to theirs. However, we observe a small splitting of some of the peaks which they reported as one; that is, we find slightly different frequencies for the different α'_{ij}. The frequencies they reported, which we observe

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(7) J. Deveze and M. Krauzman, *Compt. Rend., A, B*, **263B**, 864 (1966).

(8) P. T. Manoharan and W. C. Hamilton, *Inorg. Chem.*, **2**, 1043 (1963).

(9) J. J. Spijkerman, D. K. Snediker, F. C. Ruegg, and J. R. DeVoe, National Bureau of Standards Technical Note 260-13, U. S. Government Printing Office, Washington, D. C., 1967.

(10) (a) T. C. Damen, S. P. S. Porto, and B. Tell, *Phys. Rev.*, **142**, 570 (1966); (b) L. Tosi, H. Poulet, and J. P. Mathiew, *Compt. Rend.*, **268**, 249 (1969).

as split (parentheses), are (cm^{-1}): 2143 (2145, 2143.5), 496 (500, 493), 412 (415, 410), 162 (165, 160), 155 (157.5, 154), 135 (136, 134), and 77 (81, 77).

The infrared spectrum of the Nujol-mulled sample at liquid N_2 temperature is reproduced in Figure 2. The frequencies of the absorption maxima in the infrared spectra of $N_2Fe(CN)_5NO\cdot 2H_2O$ and its deuterated analog are given in Table II. Infrared and Raman frequencies are accurate to at least ± 1 cm^{-1}. The resolution is about 2.5 cm^{-1} for most of the Raman data and 1 cm^{-1} for the infrared data.

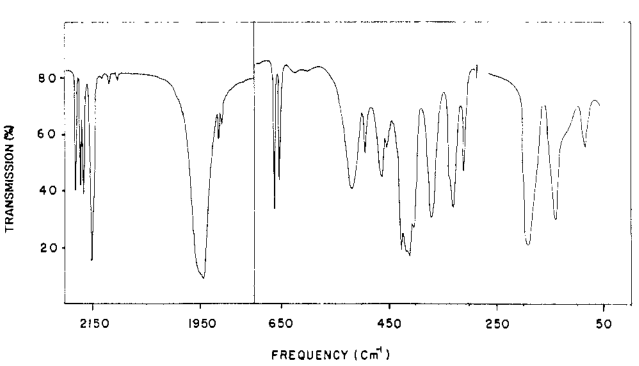

Figure 2.—Infrared spectrum of Nujol mull of $Na_2Fe(CN)_5NO\cdot 2H_2O$ at liquid N_2 temperature.

Discussion

Sodium nitroprusside belongs to the orthorhombic system, space group $D_{2h}{}^{12}$-P_{nnm}.[8] The unit cell contains four formula units of the type $Na_2Fe(CN)_5NO\cdot 2H_2O$. The crystal structure is made up of Na^+, $Fe(CN)_5NO^{2-}$, and H_2O units. The 84 atoms in a unit cell lead to 252 vibrational modes distributed as follows: 132 internal vibrations of the four $Fe(CN)_5NO^{2-}$ complexes, 24 internal vibrations of the four water molecules, 36 rotatory lattice modes, 57 translatory lattice modes, and the 3 acoustical modes. Of the lattice modes, only those involving H_2O molecules are expected to be above 200 cm^{-1}. These can be sorted out by searching for isotope shifts in the D_2O-substituted crystals. The detailed structure analysis shows that the H_2O molecules are not involved in any appreciable hydrogen bonding with the $Fe(CN)_5NO^{2-}$ ion (the shortest H_2O–CN distances reported are 3.27 and 3.36 Å); they merely serve to fill the empty space in the lattice. The absence of any appreciable hydrogen bonding was also suggested in an earlier report on the infrared spectrum of the crystal.[11]

The observed peaks in the Raman and the infrared spectra can be interpreted in terms of the 252 modes mentioned above. The interpretation of the intramolecular H_2O bands in the infrared spectra of the sample is fairly straightforward and, in our work, has been checked against the data on the deuterated sample. The frequencies of the normal modes of $Fe(CN)_5NO^{2-}$ are expected to lie in the region 2200–200 cm^{-1} except for some of the skeletal bending modes whose frequencies may be below 200 cm^{-1} where lattice frequencies are also expected.

TABLE II

OBSERVED INFRARED ABSORPTION FREQUENCIES FOR MINERAL OIL MULLS OF $Na_2Fe(CN)_5NO\cdot 2H_2O$ AND ITS DEUTERATED ANALOG

—$Na_2Fe(CN)_5NO\cdot 2H_2O$—			$Na_2Fe(CN)_5NO\cdot 2\{D_2O, HDO, H_2O\}$ (80–90% D)	
300°K	100°K	Assignment	300°K	100°K
3870	3885 mw[a]	$2\nu_{NO}$	3870	3885 m
3627	3628 s	$\nu_3(H_2O)$	3627	3628 w
		$\nu_{OH}(HOD)$	3606	3608 m
		$\nu'_{OH}(HOD)$	3570	3564 m
3546	3542 s	$\nu_1(H_2O)$	3548	3543 w
	3526 vw, sh			
	3207 mw	$2\nu_2(H_2O)$		
		$\nu_3(D_2O)$	2695	2696 s
		$\nu_{OD}(HOD)$	2656	2657 mw
		$\nu'_{OD}(HOD)$	2632	2626 m
				2608 vvw
		$\nu_1(D_2O)$	2600	2596 ms
				2509 w
		$2\nu_2(D_2O)$		2358 w
2173	2177.0 m	$\nu^{A_1}{}_{CN}$(axial)	2173	2177.1 m
2160	2167.2 m	$\nu^{A_1}{}_{CN}$(radial)	2160	2167.5 m
2156	2163.5 m	$\nu^{B_1}{}_{CN}$	2156	2163.0 m
	2154 vw, sh			2154 vw, sh
2143	2146.5 s	$\nu^{E}{}_{CN}$	2143	2146.1 s
2125	2130.8 vw			
2113.5	2115.0 w	$\nu(C^{15}N)$ $+\nu(^{13}CN)$		2116 vw
2109				
2098	2100.8 w			2101 vw
1950	1952 s, sh			
1940	1945 vs	ν_{NO}	1940	1946 vs
	1912 vb, sh			
1905.5	1915.5 vw	$\nu^{15}N^{16}O$		
1900	1910.5 vw	$\nu^{14}N^{18}O$		
1624 w, sh	1626 ms			
1618 m	1619 ms	$\nu_2(H_2O)$		1619 w
1612 w, sh	1610 ms			
		$\nu_2(HOD)$		1431 w
				1418 m
				1198 m
		$\nu_2(D_2O)$	1193	1193 m
				1187 m
	666.5 s	$\nu_{FeNO}(E)$		667.2 m
	656.8 ms	$\nu_{FeN}(A_1)$		657.2 m
519 mw, vb	527 ms, b	$L(H_2O)$		
498	502.7 mw	$\nu_{FeCN}(A_1)$	498	503.0 mw
		$L(HOD, D_2O)$		493 w, b
475 vvw, vb	472 m	$L(H_2O)$		
468	463 w	$\nu^{A_1}{}_{FeC}$(axial)	467	463 w
		$L(HOD, D_2O)$		454 w, b
433	435 ms		433	435 ms
424	426 m, sh	$\nu^{E}{}_{FeC}$	423	428 s
	422 vs	$L(D_2O)$?		422 s
417	414 m	$\nu^{E}{}_{FeCN}(\theta)$	417	413 m
		$L(HOD, D_2O)$		390 w, b
				380 w, b
375 w, vvb	380 s	$L(H_2O)$		
		$L(D_2O)$		352 ms
342 w, vvb	342 s	$L(H_2O)$		
		$L(HOD, D_2O)$		331 w
321.5	321.5 ms	$\nu^{E}{}_{FeCN}(\lambda)$	321	321 m
				306 m
		$L(HOD, D_2O)$		291 w
				275 mw
190			190	
139 vb			139 vb	
118			118	
95			95	

[a] The relative intensities and shapes are indicated by: s, strong; m, medium; w, weak; b, broad; sh shoulder; v, very.

The $Fe(CN)_5NO^{2-}$ ion has a distorted octahedral structure (point group C_{4v}); the arrangement of the atoms in the structure is shown in Figure 3. The linear group ONFeC(5)N(5) contains the axial (lying on the C_4 axis of symmetry) NO, FeN, FeC(5), and C(5)N(5) bonds, and the radial FeC and CN bonds lie on the σ_v planes of symmetry. In the orthorhombic lattice, however, the local symmetry of the $Fe(CN)_5NO^{2-}$ ion is reduced to $C_s(\sigma_d)$ which contains the crystallographic axes a and b. The axial bonds lie on this

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(11) F. A. Cotton, R. R. Monchamp, R. J. M. Henry, and R. C. Young, *J. Inorg. Nucl. Chem.*, **10**, 28 (1959).

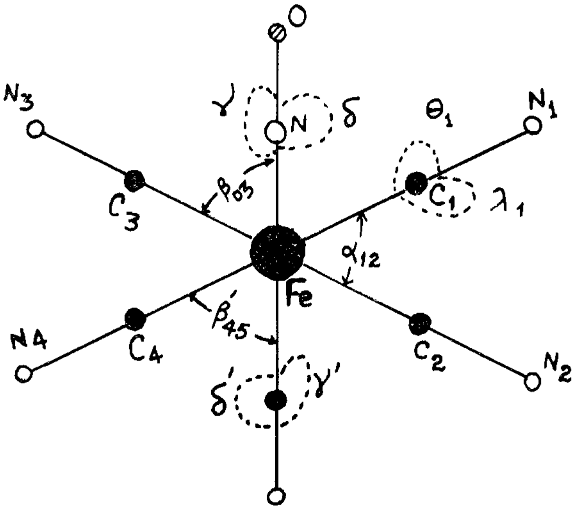
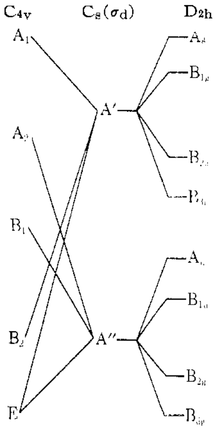


Figure 3.—Internal coordinates of $Fe(CN)_5NO^{2-}$.

TABLE III

CORRELATION CHART GIVING SITE AND FACTOR GROUP SPLITTINGS OF THE FUNDAMENTAL MODE



D_{2h}	Raman	Ir
A_g	α'_{aa}, α'_{bb}, α'_{cc}	. . .
B_{1g}	α'_{ab}	. . .
B_{2u}	. . .	T_b
B_{3u}	. . .	T_a
A_u	. . .	. . .
B_{1u}	. . .	T_c
B_{2g}	α'_{ac}	. . .
B_{3g}	α'_{bc}	. . .

plane at about 36° to a and 54° to b. (We have adopted Manoharan and Hamilton's notation:[8] a = 6.17 Å, b = 11.84 Å, and c = 15.43 Å.)

The following 36 internal coordinates have been employed to describe the normal modes of $Fe(CN)_5NO^{2-}$ ion: 4 FeC_{radial} stretches, 4 CN_{radial} stretches, 1 FeC_{axial} stretch, 1 CN_{axial} stretch, 1 FeN stretch, 1 NO stretch, 4 CFeC (radial) angle bends (α), 4 $NFeC_{radial}$ angle bends (β), 4 $C_{axial}FeC_{radial}$ angle bends (β'), 4 FeCN (radial) angle bends in the axial direction (θ), 4 FeCN (radial) angle bends in the directions perpendicular to above (λ), 2 FeNO linear bends (γ and δ), and 2 FeCN (axial) linear bends (γ' and δ'). These include 3 redundancy conditions involving the α, β, and β' bends.

The distribution of the 33 normal modes among the symmetry species of C_{4v} is: $\Gamma = 8 A_1 + A_2 + 4 B_1 + 2 B_2 + 9 E$. The selection rules indicate that the A_1 and E modes are both Raman as well as infrared active, B_1 and B_2 modes are only Raman active, and the A_2 mode is completely inactive. The correlation chart given in Table III shows that the reduced local symmetry C_s results in a lifting of the degeneracy of the E modes and all the modes become active in both infrared as well as Raman spectra. The presence of four such units in the unit cell results in a fourfold multiplicity of each mode as indicated in Table III. The last two columns of Table III give the selection rules for the Raman and the infrared activity of the phonons.

H_2O Bands.—The water bands are generally weak in the Raman spectrum and were not observed in the present studies. A single crystal of $Na_2Fe(CN)_5NO \cdot 2\{H_2O,HDO,D_2O\}$, with about 60 atom % D, showed no shifts in any of the observed Raman peaks from those of $Na_2Fe(CN)_5NO \cdot 2H_2O$. Thus, all observed Raman peaks in Table I can be assigned either to internal vibrations of $Fe(CN)_5NO^{2-}$ or to lattice vibrations not involving H_2O.

In the infrared spectrum several interesting water bands appear as noted in Table II. Since the H_2O molecules have[8] a site symmetry of C_1, each internal vibration may be split into three infrared-active vibrations (B_{1u}, B_{2u}, and B_{3u}). In the present study, this splitting is observed only for the bending vibration, ν_2. Thus, at liquid nitrogen temperature the H_2O compound shows peaks at 1626, 1619, and 1610 cm^{-1} while the D_2O compound (with 10–20% H) shows peaks at 1198, 1193, and 1187 cm^{-1}. As D is added to H (or H to D), this splitting decreases, the outer peaks diminish in intensity, and finally only one peak is observed (as 1619 cm^{-1} for H_2O in 10–20% H and 90–80% D). This shows that it is definitely correlation field splitting. At room temperature the water molecules are apparently less strongly oriented so the correlation field splitting is somewhat less.

The room-temperature stretching vibrations, ν_1 (symmetric) and ν_3 (antisymmetric), are observed at 3546 and 3627 and 2598 and 2694 cm^{-1} for H_2O and D_2O, respectively. There is a small downward shift of ν_1 at liquid nitrogen temperature but no correlation field splitting is observed, nor is there a significant shift in frequency of ν_1 or ν_3 as a function of isotopic content.

The HOD molecule in sodium nitroprusside is interesting in that there are two OH stretching, two OD stretching, and two HOD bending vibrations active in the infrared spectrum. This is a different type of field splitting as it is observed for the stretching vibrations as well as for the bending vibration. Neither the relative intensities nor the frequencies for the HOD doublets vary appreciably with isotopic concentration. At present we do not have the explanation for this splitting.

Several lattice vibrations of H_2O and D_2O are observed in the region 550–250 cm^{-1}, as noted from Table II, by their isotopic shift. These absorptions are very broad and very weak at room temperature but become quite prominent at low temperature, again suggesting rather loose orientation of the water molecules at room temperature. We are not able to assign the lattice modes of H_2O nor to relate with any confidence those of D_2O to those of H_2O. The picture is complicated somewhat by the presence of HOD in the D_2O sample.

CN and NO Stretching Vibrations.—Infrared absorption bands and Raman shifts in the region 2200–1900 cm^{-1} are due to the phonons involving CN and NO stretching vibrations. The 5 CN stretching modes of $Fe(CN)_5NO^{2-}$ ion are distributed among the symmetry species of C_{4v} as: $\Gamma_{CN} = 2\ A_1 + B_1 + E$. At the site $C_s(\sigma_d)$ in the lattice the A_1 modes are symmetric with respect to $\sigma_d(A')$, the B_1 mode is antisymmetric with respect to $\sigma_d(A'')$ and the E mode splits into $A' + A''$. The correlation coupling results in two infrared-active phonons (transition moments parallel to *a* and *b*) for each of the A′ modes and one infrared-active phonon (transition moment parallel to *c*) for each of the A″ modes. There are two Raman-active phonons for each of the A′ and A″ modes whose nonzero polarizability (derivative) components are given in Table III.

Bor[12] observed four bands (2173.4, 2161.6, 2156.7, and 2143.4 cm^{-1}) in the infrared spectrum of the polycrystalline sample. No specific assignments for the observed bands were given except that the appearance of four bands was considered to be consistent with the selection rules for C_{4v} symmetry. Gans, *et al.*,[13] observed some additional shoulders on the low-frequency side of the main bands which were interpreted as the components arising due to correlation field splitting. These were subsequently assigned correctly by Tosi[14] and Sabatini[15] to the ^{13}CN stretching modes.

The Raman spectra of the oriented single crystal provide valuable information on the phonon assignments. The Raman-active phonons at 2174, 2162, and 2145 cm^{-1} appear in the α'_{aa}, α'_{bb}, α'_{cc}, and α'_{ab} traces whereas those at 2157 and 2143.5 cm^{-1} appear in the α'_{bc} and α'_{ac} traces. The former three are, therefore, assigned to the A′ modes and the latter two are assigned to the A″ modes (site group species). The 2174-cm^{-1} phonon appears with maximum intensity in the α'_{aa} trace and is, clearly, due to the CN_{axial} stretching mode whereas the 2162-cm^{-1} phonon appears with maximum intensity in the α'_{cc} trace and is due to the CN_{radial} symmetric stretching mode. This follows because the axial CN groups are in the *ab* plane[4] and are lined up more along *a* than *b;* thus, α'_{aa} should be the largest α'_{ij} for the axial CN stretch while α'_{cc} should be the largest α'_{ij} for the radial A_1 CN stretch. Two possibilities exist for the assignment of the remaining three CN phonons. One is to regard the 2145- and 2143.5-cm^{-1} phonons as the two split components of E which requires the 2157-cm^{-1} phonon to be assigned to the B_1 mode. This agrees with the assignment proposed by Sabatini[15] from polarized infrared studies. The other possibility is to interchange the roles of 2157- and 2143.5-cm^{-1} phonons in the above description. The former assignment gives extremely small splitting (1.5 cm^{-1}) of the E mode suggesting, thereby, negligible distortion of the $Fe(CN)_5NO^{2-}$ ion from C_{4v} symmetry whereas the appearance of 2157-cm^{-1} phonon strongly in the infrared spectrum suggests otherwise if assigned to the normally inactive B_1 vibration of the isolated ion. It is, in fact, likely that the B_1 and E(A″) modes couple, resulting in enhanced intensity in infrared absorption of the B_1 mode. The polarized spectra of Sabatini[15] show that the A″ mode at ~2144 cm^{-1} is more intense than that at 2158 cm^{-1} which would be unreasonable if 2144 cm^{-1} is the B_1 mode. We conclude that the most logical explanation is that the unperturbed B_1 and E(A″) modes lie somewhat below 2157 cm^{-1} and somewhat above 2143.5 cm^{-1}, respectively. They interact and separate to 2157 and 2143.5 cm^{-1}. The spectrum of an aqueous solution of $Na_2Fe(CN)_5NO$ (as listed in Table IV) agrees qualitatively with such an interpretation. The Raman spectrum of a solution shows a strong peak at 2162 cm^{-1} with a shoulder at about 2150 cm^{-1}, probably arising from the A_1 and B_1 vibrations, respectively. In the infrared spectrum for the solution we see a strong peak at 2142 cm^{-1} and a shoulder at about 2158 cm^{-1}, probably arising from the E and A_1 vibrations, respectively.

TABLE IV

VIBRATIONAL FREQUENCIES (CM^{-1}) FOR AQUEOUS $Na_2Fe(CN)_5NO$

Ir	Raman
~2158 w, sh	2162 s
	~2150 w, sh
2142 s	
	123 w, b

The polarization character of the Raman-active phonon at 1947 cm^{-1} and the intensity of the infrared-active phonon at ~1940 cm^{-1} indicate their assignment to the NO stretching mode. There appears a shoulder on the high-frequency side of the NO stretch; however, this is not present in the D_2O compound. Thus it perhaps arises from a water combination band or an impurity.

The weak bands in the region 2140–2100 cm^{-1} of the infrared spectra are due to ^{13}CN stretching vibrations as indicated by their shifts from the ^{12}CN stretching frequencies. The observed shifts (~45 cm^{-1}) are almost exactly equal to the theoretical values calculated in the diatomic molecule approximation. The weak bands at 1906 and 1900 cm^{-1} in the infrared spectra appear to be due to $^{15}N^{16}O$ and $^{14}N^{18}O$ stretches, respectively. The shifts from $^{14}N^{16}O$ are about the same as those calculated for a linear Fe–N–O molecule.

Low-Frequency Vibrational Modes.—The FeC and FeN stretching modes have the same distribution among the symmetry species of C_{4v} as the corresponding CN and NO models; therefore, they are assigned on the same basis. The frequency of the FeN stretch (bond length $\simeq$1.63 Å) is expected to be higher than that of the FeC stretch (bond length $\simeq$1.90 Å). Thus, the 656-cm^{-1} Raman-active phonon (A_g, B_{1g}) is assigned

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(12) G. Bor, *J. Inorg. Nucl. Chem.*, **17**, 174 (1961).

(13) P. Gans, A. Sabatini, and L. Sacconi, *Inorg. Chem.*, **5**, 1877 (1966).

(14) L. Tosi, *Comp. Rend.*, *A*, *B*, **264B**, 1313 (1967).

(15) A. Sabatini, *Inorg. Chem.*, **6**, 1756 (1967).

to the former and the 472-cm^{-1} Raman-active phonon (also A_g, B_{1g}) is assigned to the FeC_{axial} stretch. Both of these phonons have maximum intensity in the α'_{aa} traces, as expected for the axial stretches. The 408-cm^{-1} Raman-active phonon has maximum intensity in the α'_{cc} trace and is, probably, due to the FeC_{radial} symmetric stretch. The 410-cm^{-1} Raman-active phonon (B_{3g}) is assigned to the FeC radial stretch (B_1). This latter assignment is in accord with the proximity of the A_{1g} and B_{1g} M–C stretches of the tetracyanoaurate ion.[16] All five FeC bond lengths are more or less equal as revealed by the X-ray studies. The higher frequency of the axial FeC stretch than that of the radial FeC stretch is, perhaps, due to significant coupling with the Fe–N vibration. The 665-cm^{-1} Raman-active phonon was assigned by Tosi, *et al.*,[10b] as a component of the FeN stretch. This is not realistic, as, if the two Raman-active FeN stretches are split, one should appear as A_g and the other as B_{1g}. This is not so. The fact that the B_{2g} and B_{3g} components are weak in the Raman spectrum does not dictate that the 665-cm^{-1} peak is not from an E mode; therefore, we prefer the assignment of Sabatini,[15] $\nu_{21}(\delta_{FeNO})$ 665 cm^{-1}.

The strong band at ~424 cm^{-1} shows three components (422, 426, 435 cm^{-1}) in the low-temperature infrared spectrum and is undoubtedly due to FeC_{radial} stretch (E), which should be quite intense in the infrared spectrum. Most of the other Raman-active phonons in the region 600–200 cm^{-1} are weak and the reported infrared spectra in this region lack the polarization data. Consequently, the assignments in this region are only tentative and have been made on the basis of somewhat speculative arguments. The axial A_1 MC stretch appears in the infrared spectrum also, at 468 cm^{-1}.

The other infrared bands in this region, namely, at 321, 417, and 498 cm^{-1}, and the Raman band at 374 cm^{-1} must arise from Fe–C–N bending vibrations. The A_1 bending vibration, ν_7, is probably the highest as it should couple with the axial stretches at 656 and 470 cm^{-1}. Therefore, we assign 493 cm^{-1} to ν_7. The 417-cm^{-1} peak is rather close to the MC stretch complex at 424 cm^{-1} for a vibration of the same symmetry; however, it does appear from the Raman spectrum to be an E vibration. We therefore have tentatively assigned it as ν_{19}. We assign 321 cm^{-1} to ν_{18} as we believe the λ FeCN bending vibrations should be lower than the θ FeCN bending vibrations, because of the short FeN bond and apparent strain on the radial $Fe(CN)_4$ plane. The A″ peak at 374 cm^{-1} may arise from $\nu_9(A_2)$, $\nu_{12}(B_1)$, or $\nu_{20}(E)$.

TABLE V

FUNDAMENTAL VIBRATIONAL FREQUENCIES OF $Fe(CN)_5NO^{2-}$ ION IN SOLID $Na_2Fe(CN)_5NO \cdot 2H_2O$

Species (C_{4v})	NO	Mode	Frequency, cm^{-1}	
A_1	ν_1	ν_{CN}(axial)	2174	(2173)[a]
	ν_2	ν_{CN}(radial)	2162	(2162)
	ν_3	ν_{NO}	1947	(1945)
	ν_4	ν_{FeC}(radial)	408	(408)
	ν_5	ν_{FeC}(axial)	472	(468)
	ν_6	ν_{FeN}	656	(653)
	ν_7	θ_{FeCN}	493	
	ν_8	$(\beta, \beta')_{CFeC}$	123	. . .
A_2	ν_9	λ_{FeCN}		
B_1	ν_{10}	ν_{CN}(radial)	2157	(2157)
	ν_{11}	ν_{FeC}(radial)	410	
	ν_{12}	θ_{FeCN}		
	ν_{13}	$(\beta, \beta')_{CFeC}$	125	?[b]
B_2	ν_{14}	λ_{FeCN}		
	ν_{15}	α_{CFeC}		
E	ν_{16}	ν_{CN}(radial)	2144	(2145)
	ν_{17}	ν_{FeC}(radial)	422	(424)
	ν_{18}	λ_{FeCN}		(321)
	ν_{19}	α_{FeCN}		(417)
	ν_{20}	$(\gamma', \delta')_{FeCN}$	415	
	ν_{21}	$(\gamma, \delta)_{FeNO}$	665	(663)
	ν_{22}	α_{CFeC}	104	?
	ν_{23}	β_{NFeC}		?(139)
	ν_{24}	β'_{C_5FeC}	100	?

[a] Numbers in parentheses are the frequencies observed in the infrared spectra. [b] A question mark indicates that the assignment is uncertain.

The CFeC radial bending frequencies are expected in the 100-cm^{-1} region which is complicated by the lattice vibrations. The Raman spectrum of the aqueous solution shows a weak band at ~123 cm^{-1} which is, most likely, due to the ν_{CFeC} bend (A_1). Such bending modes of the other species are expected in the same region. Thus, the 125-cm^{-1} Raman-active phonon is assigned to $\nu_{CFeC}(B_1)$ and the 97–110-cm^{-1} Raman-active phonons are assigned $\nu_{CFeC}(E)$. The 139-cm^{-1} infrared-active phonon is, perhaps, due to β_{NFeC}. The Raman-active phonons from 154 to 165 cm^{-1} very likely arise from lattice vibrations. They are really too high for the skeletal modes of $Fe(CN)_5NO^{2-}$ but too low for the other molecular modes. The assignments discussed above are listed in Table V. As mentioned before, many of the assignments are uncertain. Complete polarized infrared data would contribute substantially toward checking some of them. A study of isotopic shifts for ^{13}C, ^{18}O, and ^{15}N would be very valuable for confirmation of the assignments and for a normal-coordinate analysis. At present the oriented single-crystal Raman spectra yield the most conclusive frequency assignments.

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(16) L. H. Jones and J. M. Smith, *J. Chem. Phys.*, **41**, 2507 (1964).