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Transition dipole-dipole coupling between the NO stretching vibrations of nitroprusside ions in $Sr[Fe(CN)_5N(^{16}O,^{18}O)]\cdot 4H_2O$ and $Ba[Fe(CN)_5N(^{16}O,^{18}O)]\cdot 3H_2O$ isotopic mixtures

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The NO stretching band in the infrared absorption spectra of polycrystalline $Sr[Fe(CN)_5N(^{16}O,^{18}O)]\cdot 4H_2O$ and $Ba[Fe(CN)_5N(^{16}O,^{18}O)]\cdot 3H_2O$ isotopic mixtures exhibits a fine structure which is not present in the spectra of isotopically normal crystals. These features can be ascribed to isolated light and heavy nitroprusside ions and to clusters integrated by two, three, etc. isotopically alike adjacent complexes. The fine structure of the NO stretching band of ^{18}O-enriched crystals is described quantitatively in terms of a linear-chain model of $[Fe(CN)_5NO]^{2-}$ oscillators coupled through harmonic transition dipole-dipole interaction between the strongly polar NO vibrations of nearest-neighboring ions. ^{16}O- and ^{18}O-containing nitroprusside clusters are assumed to be statistically distributed along the chains. The theoretical frequencies and relative intensities obtained by this model are in fairly close agreement with the observed infrared spectra. In the case of $Ba[Fe(CN)_5N(^{16}O,^{18}O)]\cdot 3H_2O$ solid solutions, the vibrations of isolated $[Fe(CN)_5N\,^{18}O]^{2-}$ ions and pairs and triplets of them are spectroscopically resolved at low temperatures.

I. INTRODUCTION

The nature and magnitude of intermolecular coupling between the polar vibrations of the noncyanide ligands in some pentacyano-*L*-metallates, including $Sr[Fe(CN)_5NO]\cdot 4H_2O$, $Ba[Fe(CN)_5NO]\cdot 3H_2O$, and $K_3[Co(CN)_5N_3]\cdot 2H_2O$ have been studied on the basis of their crystallographic and spectroscopic data.[1,2] In the strontium and barium nitroprusside salts, the $[Fe(CN)_5NO]^{2-}$ ions are arranged with their NO ligands piled up in an alternating antiparallel fashion, forming linear chains along the crystal **c** axis.[3–5] The nitrosyl groups are approximately perpendicular to the chains and evenly spaced at short distances (of about 4 Å) from each other (see schematic diagram of Fig. 1). This packing gives rise to an appreciable intermolecular dipole-dipole coupling between the strongly polar NO stretching vibrations of neighboring nitroprusside ions in the crystals. In a previous article,[1] we brought into evidence measurable effects of this phenomenon on the vibrational structure in the NO stretching region, employing infrared spectroscopy. The main features of the fine structure exhibited by the NO stretching band in the infrared spectra of polycrystalline $Sr[Fe(CN)_5N(^{16}O,^{18}O)]\cdot 4H_2O$ isotopic mixtures and the dichroic behavior of the corresponding infrared absorption band in single crystals of $Ba[Fe(CN)_5NO]\cdot 3H_2O$ were explained on the basis of a one-dimensional model of nitrosyl groups vibrationally coupled via dipole-dipole forces, with interactions between first neighbors.

In the present work we are presenting further evidence for this dipole-dipole coupling by giving a fuller quantitative account of the fine structure of the NO stretching band in the already reported infrared spectra of $Sr[Fe(CN)_5N(^{16}O,^{18}O)]\cdot 4H_2O$ solid solutions[1] as well as the corresponding infrared band of

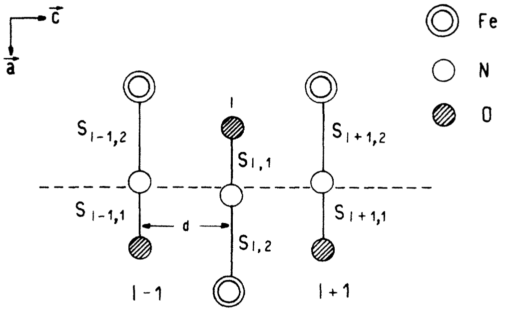

FIG. 1. Schematic illustration showing the arrangement of the FeNO molecular fragments of nitroprusside ions along a chain in the crystals. (i) $Sr[Fe(CN)_5NO]\cdot 4H_2O$: adjacent molecules on a chain are related through crystallographic inversion centers located at the middle points between NO ligands; distances from nitrosyl at crystal site l to neighboring NO groups at sites $l-1$ and $l+1$ are slightly different and their average is 4.3 Å. (ii) $Ba[Fe(CN)_5NO]\cdot 3H_2O$: contiguous molecules are related through glide planes perpendicular to **a**, with displacement along **c** in half of its length; the corresponding NO ligands are thus evenly spaced along the chains (at a distance $r_1 = 4.4$ Å). The angle between nearest-neighbor nitrosyls is 13.3°.

$Ba[Fe(CN)_5N(^{16}O,^{18}O)]\cdot 3H_2O$ isotopic mixtures with up to 45% of ^{18}O, in terms of the one-dimensional model referred to above. To this purpose, we shall use a suitable modification of the theory developed by Decius[6] to deal with the vibrational coupling present in nitrates and carbonates of the aragonite structure.

For the sake of comparison, the ir spectrum of a solid solution of $[Fe(o\text{-phen})_3][Fe(CN)_5N(^{16}O,^{18}O)]\cdot 2H_2O$ with 30% of $N^{18}O$ was obtained, where *o*-phen is an abbreviation for ortho-phenanthroline. In this salt the anions are separated from each other by the bulky cations[7] and no appreciable coupling is expected to occur.

II. EXPERIMENTAL

As reported before,[1] the equilibrium

$$[Fe(CN)_5NO]^{2-} + 2OH^- \rightleftharpoons [Fe(CN)_5NO_2]^{4-} + H_2O$$

was employed to exchange ^{18}O between pentacyanonitrosylferrate(II) and enriched water.[8] The procedure for the preparation of ^{18}O-enriched samples of strontium nitroprusside tetrahydrate was described in Ref. 1. In the present work a slight change was made to obtain samples of both strontium and barium nitroprussides with higher percentage of ^{18}O. Perchloric acid of higher concentration than before ($5M$) was used. The amounts of $Na_2[Fe(CN)_5NO]\cdot 2H_2O$ and of $4M$ NaOH remained unchanged while 0.02 cm^3 of $5M$ $HClO_4$ was used instead of 0.4 cm^3 of $1M$ $HClO_4$. Samples isotopically substituted with approximately 45% of $N^{18}O$ were obtained in this way for both salts. Subsequent dilutions were made by mixing them with the calculated amount of normal salts, dissolving the mixture in water and evaporating the solvent.

The isotopically substituted sample of $[Fe(o\text{-phen})_3][Fe(CN)_5N(^{16}O,^{18}O)]\cdot 2H_2O$ was precipitated by the addition of a stoichiometric amount of a concentrated solution of $[Fe(o\text{-phen})_3]Cl_2\cdot 7H_2O$ to a solution of ^{18}O-labeled nitroprusside.

The ir absorption spectra of ^{18}O-enriched samples as Nujol mulls sandwiched between CsI plates were recorded both at room temperature and at the boiling point of nitrogen with a Perkin-Elmer 580B infrared spectrophotometer. Wave number accuracy was estimated to be ±2 cm^{-1}. The low-temperature spectra were obtained from samples placed in a Research and Industrial Instruments Co. (RIIC) variable temperature cell (model VLT-2). They showed the expected increase of resolution, especially in the $N^{18}O$ bands corresponding to the strontium and barium salts. No fine structure was observed in the low-temperature spectrum of polycrystalline $[Fe(o\text{-phen})_3][Fe(CN)_5N(^{16}O,^{18}O)]\cdot 2H_2O$ in the NO stretching region.

III. THEORY

We shall consider the vibrational structure of $Sr[Fe(CN)_5NO]\cdot 4H_2O$ and $Ba[Fe(CN)_5NO]\cdot 3H_2O$ crystals associated with the NO and FeN stretching modes of the nitroprusside ion both, in the isotopic mixtures and as a limit in the case of the isotopic pure lattices. For this purpose we shall regard the solids as composed of linear, parallel, noninteracting chains (separated at distances greater than 7.5 Å) of coupled $[Fe(CN)_5NO]^{2-}$ ions (see Fig. 1).

The Lagrangian for a cluster of n isotopically alike ions coupled through the NO and FeN stretching vibrations of nearest-neighbor complexes is given by

$$L_n = \tfrac{1}{2}\sum_{\alpha=1}^{2}\sum_{l=1}^{n}\dot{q}_{l\alpha}^{2} - \tfrac{1}{2}\sum_{\alpha=1}^{2}\omega_\alpha^2\sum_{l=1}^{n}q_{l\alpha}^2 - \sum_{l=1}^{n-1}V_{l,l+1} , \qquad (1)$$

where q_{l1} and q_{l2} are the normal coordinates associated respectively with the NO and FeN stretching modes of the ion at the lattice site l. The first and second sums in Eq. (1) correspond to uncoupled anions, while the third one takes into account the vibrational intermolecular interaction which in the harmonic approximation has the quadratic form

$$\sum_{l=1}^{n-1}V_{l,l+1} = \sum_{l=1}^{n-1}[F_1 q_{l1}q_{l+1,1} + F_2 q_{l2}q_{l+1,2} + F_{12}(q_{l1}q_{l+1,2} + q_{l2}q_{l+1,1})] . \qquad (2)$$

Assuming that the interaction is due to transition dipole-transition dipole forces, there results the following expressions for the coupling constants:

$$F_1 = \frac{1}{r_1^3}\left[\frac{\partial m}{\partial q_1}\right]_0^2 h_1 , \qquad (3a)$$

$$F_2 = \frac{1}{r_2^3}\left[\frac{\partial m}{\partial q_2}\right]_0^2 h_2 , \qquad (3b)$$

$$F_{12} = \frac{1}{r_{12}^3}\left[\frac{\partial m}{\partial q_1}\right]_0\left[\frac{\partial m}{\partial q_2}\right]_0 h_{12} . \qquad (3c)$$

In Eqs. (3), r is the center-to-center distance between nearest interacting dipoles and m is the nitroprusside dipole moment. The factors h are angular functions of the form

$$h = (\sin\theta_l \sin\theta_{l+1}\cos\chi_{l,l+1} - 2\cos\theta_l\cos\theta_{l+1}) , \qquad (4)$$

where θ_l and θ_{l+1} are the angles that the pair of coupled dipoles at lattice sites l and $l+1$ subtend from the line joining their centers, and $\chi_{l,l+1}$ is the angle between the projections of the dipoles on a plane perpendicular to the line between centers.

From integrated infrared absorbances measured in polycrystalline $Sr[Fe(CN)_5NO]\cdot 4H_2O$ and $Ba[Fe(CN)_5NO]\cdot 3H_2O$, it results that the $(\partial m/\partial q_2)_0^2$ value corresponding to the FeN stretching mode is only 2.5% of the $(\partial m/\partial q_1)_0^2$ value associated with the strongly polar NO stretching mode. Consequently, the second term in Eq. (2) for the coupling of the FeN stretching vibrations is very small compared with the interaction energy of the NO stretching mode. The third contribution to Eq. (2), which gives rise to intermode mixing of NO and FeN stretching vibrations, is also small because it is proportional to $(\partial m/\partial q_2)_0$ and in addition it couples normal modes of very different frequencies.[9] Neglecting these two contributions to $V_{l,l+1}$ in Eq. (2), the Lagrangian (1) becomes

$$L_n=\frac{1}{2}\sum_{l=1}^{n}\dot{q}_{l1}^{2}-\frac{1}{2}\omega_1^2\sum_{l=1}^{n}q_{l1}^{2}-\sum_{l=1}^{n-1}F_1q_{l1}q_{l+1,1}+\left[\frac{1}{2}\sum_{l=1}^{n}\dot{q}_{l2}^{2}-\frac{1}{2}\omega_2^2\sum_{l=1}^{n}q_{l2}^{2}\right]. \tag{5}$$

In this equation, the contribution of the term in parentheses corresponds to the degenerated vibrations of uncoupled FeN stretching modes and will not be considered any further. Consequently, the subindex 1 will be dropped from the resulting Lagrangian to simplify the notation.

If in Eq. (5) we allow n to become very large, the Lagrangian for the isotopic pure lattice is obtained. The corresponding equations of motion can be solved to determine the dispersion relation $\omega(k)$ for the optic modes associated with the polar NO stretching vibration

$$\omega(k)=\omega_1\left[1+\frac{2F_1}{\omega_1^2}\cos\eta\right]^{1/2}, \tag{6}$$

where $\eta=2\pi kd$.

In Eq. (6), $\omega(k)$ is the angular frequency of optic modes, $d=c/2$ (see Fig. 1), and the wave vector k takes values within the first Brillouin zone: $-1/2d<k\leq 1/2d$.

As described in Ref. 1, the frequency of the infrared-active fundamental transition is obtained from Eq. (6) by setting the wave vector k value of the optic mode equal to $\pm 1/2d$,[10]

$$\omega_{\infty}=\omega_1\left[1-\frac{2F_1}{\omega_1^2}\right]^{1/2} \tag{7}$$

for the isotopically pure crystal of $Sr[Fe(CN)_5NO]\cdot 4H_2O$ (optic mode polarized approximately along the crystal **a** axis) and in the case of $Ba[Fe(CN)_5NO]\cdot 3H_2O$ by making $k=0$ and $k=\pm 1/2d$,

$$\omega_{\infty b}=\omega_1\left[1+\frac{2F_1}{\omega_1^2}\right]^{1/2}, \tag{8a}$$

$$\omega_{\infty a}=\omega_1\left[1-\frac{2F_1}{\omega_1^2}\right]^{1/2}, \tag{8b}$$

corresponding to optic modes polarized, respectively, along the crystal **b** and **a** axes (see Fig. 1).

In the case of a finite chain integrated by a cluster of n isotopically alike ions, the n normal-mode frequencies ω_{nk} can still be calculated employing Eq. (6), but now η is restricted to n discrete values[11]

$$\omega_{nk}=\omega_1\left[1+\frac{2F_1}{\omega_1^2}\cos\eta\right]^{1/2},\quad \eta=\frac{\pi k}{n+1}, \tag{9}$$

where $k=1,2,\ldots,n$.

The form of the corresponding normal modes and their associated relative infrared absorbances can be found by calculating the linear transformation $\underline{U}$ relating the intermolecular normal coordinates of the cluster (Q_k) to the intramolecular normal coordinates (q_l), through

$$q_l=\sum_{k=1}^{n}U_{lk}Q_k,\quad l=1,2,\ldots,n. \tag{10}$$

That transformation brings the Lagrangian for the cluster

$$L_n=\frac{1}{2}\sum_{l=1}^{n}\dot{q}_{l}^{2}-\frac{1}{2}\omega_1^2\sum_{l=1}^{n}q_l^2-\sum_{l=1}^{n-1}F_1q_lq_{l+1} \tag{11}$$

into the diagonal form

$$L_n=\frac{1}{2}\sum_{k=1}^{n}\dot{Q}_{k}^{2}-\frac{1}{2}\sum_{k=1}^{n}\omega_{nk}^2Q_k^2. \tag{12}$$

In the "*GF* formalism,"[12] this is equivalent to find a matrix $\underline{U}$ such that

$$\underline{U}^{-1}\underline{G}\,\underline{F}\,\underline{U}=\underline{\Lambda} \tag{13a}$$

and

$$\underline{U}\,\underline{U}^{T}=\underline{G}, \tag{13b}$$

where the inverse kinetic energy matrix $\underline{G}$ and the force-constants matrix $\underline{F}$ are defined in terms of the Lagrangian (11), and the elements of the diagonal matrix $\underline{\Lambda}$ are coincident with the squared eigenfrequencies given by Eq. (9). From Eq. (11), it results that $\underline{G}$ is the unit matrix and thus $\underline{U}$ is an orthogonal matrix [Eq. (13b)], while $\underline{F}$ is an $n\times n$ tridiagonal matrix of the form

$$\underline{F}=\begin{bmatrix}\omega_1^2 & F_1 & 0 & 0 & \cdots & 0 & 0\\ F_1 & \omega_1^2 & F_1 & 0 & \cdots & 0 & 0\\ 0 & F_1 & \omega_1^2 & F_1 & \cdots & 0 & 0\\ \vdots & \vdots & \vdots & \vdots & & \vdots & \vdots\\ 0 & 0 & 0 & 0 & \cdots & F_1 & \omega_1^2\end{bmatrix}. \tag{14}$$

Thus far we have dealt with the NO and FeN stretching normal modes of the whole $[Fe(CN)_5NO]^{2-}$ complex. These modes can be described approximately on the basis of a simpler linear three-bodies model FeNO, with force constants f_{11} and f_{22} associated with the NO and FeN bonds, respectively, and f_{12} corresponding to the interaction between the two bonds. These force constants can be adjusted to account for the experimental values of the NO and FeN stretching frequencies observed by ir spectroscopy. To this purpose, we solve the normal mode problem associated with the three-bodies model using as internal coordinates the NO (S_1) and FeN (S_2) stretchings in the "*GF* formalism." The inverse kinetic energy matrix $\underline{G}$ is given by

$$\underline{G}=\begin{bmatrix}\mu_1+\mu_2 & -\mu_1\\ -\mu_1 & \mu_1+\mu_3\end{bmatrix}, \tag{15}$$

where μ_1, μ_2, and μ_3 are the inverses of the mass values of the nitrogen, oxygen, and iron atoms, respectively.

The $\underline{F}$ matrix for the force constants is

$$\underline{F}=\begin{bmatrix}f_{11} & f_{12}\\ f_{12} & f_{22}\end{bmatrix}. \tag{16}$$

The $\underline{G}\,\underline{F}$ matrix is diagonalized to the squared eigenfrequencies matrix $\underline{\Lambda}$,

$$\underline{L}^{-1}\underline{G}\,\underline{F}\,\underline{L}=\underline{\Lambda}\ , \tag{17}$$

by the linear transformation $\underline{L}$ that relates the normal coordinates (q_1 and q_2) to the internal ones (S_1 and S_2),

$$S_\alpha=\sum_{k=1}^{2} L_{\alpha k}q_k,\quad \alpha=1,2\ , \tag{18}$$

and which satisfies the normalization condition

$$\underline{L}\,\underline{L}^T=\underline{G}\ . \tag{19}$$

In the limit of vanishingly small FeN force constant f_{22} (and consequently $f_{12}=0$), the matrix element L_{11} becomes $\mu^{-1/2}$ (μ is the reduced mass of the NO group), and the dispersion relation (6) reduces to the form

$$\omega(k)=\frac{1}{\mu^{1/2}}(f_{11}+2f_1\cos\eta)^{1/2}\ . \tag{20}$$

Equation (20) corresponds to a linear chain of unbonded nitrosyl groups with first neighbors interaction.[1] The corresponding coupling force constant is given by

$$f_1=\mu F_1\ . \tag{21}$$

Combining Eq. (10) with Eq. (18), we can calculate the relative stretchings of the NO and FeN bonds for clusters of any order vibrating in a given normal mode k:

$$S_{l1}^{(k)}=L_{11}U_{lk}\quad \text{(NO stretching)}\ , \tag{22a}$$

$$S_{l2}^{(k)}=L_{12}U_{lk}\quad \text{(FeN stretching)}\ , \tag{22b}$$

where $l=1,2,\ldots,n$; $k=1,2,\ldots,n$.

The infrared absorption by the kth mode of a cluster consisting of n anions is proportional to $(\partial m_T/\partial Q_k)_0^2$, where the total electric dipole moment m_T can be expressed (see Fig. 1) as

$$m_T=\sum_{l=1}^{n}(-1)^l m_l(q_l)\ . \tag{23}$$

From Eq. (23),

$$\left[\frac{\partial m_T}{\partial Q_k}\right]_0=\sum_{l=1}^{n}(-1)^l\left[\frac{\partial m_l}{\partial q_l}\right]_0\left[\frac{\partial q_l}{\partial Q_k}\right]_0, \tag{24}$$

which, after taking into account Eq. (10), becomes

$$\left[\frac{\partial m_T}{\partial Q_k}\right]_0^2=\left[\frac{\partial m}{\partial q}\right]_0^2\left[\sum_{l=1}^{n}(-1)^l U_{lk}\right]^2\ . \tag{25}$$

Following Decius,[6] if p is the fraction of isotopic anions of one kind randomly distributed in the crystal, then the number $g_n(p)$ of clusters integrated by n members of this kind is

$$g_n(p)=Np^n(1-p)^2\ , \tag{26}$$

where N is the total number of anions of both isotopic species. The infrared absorbance of the kth mode of clusters with n oscillators is then proportional to

$$I_{kn}(p)=Np^n(1-p)^2\left[\frac{\partial m}{\partial q}\right]_0^2\left[\sum_{l=1}^{n}(-1)^l U_{lk}\right]^2\ . \tag{27}$$

IV. RESULTS AND DISCUSSION

The elements f_{11}, f_{22}, and f_{12} of the force constants matrix $\underline{F}$ associated with isolated FeNO molecular fragments [Eq. (16)] were adjusted by least-squares fitting to account for the NO and FeN observed stretching frequencies of uncoupled nitroprusside in the infrared spectra of $Sr[Fe(CN)_5N(^{16}O,^{18}O]\cdot 4H_2O$ and $Ba[Fe(CN)_5N(^{16}O,^{18}O)]\cdot 3H_2O$ isotopic mixtures. The numerical values that gave the best fit were (in millidynes per angstrom) $f_{11}=15.91$, $f_{22}=5.26$, and $f_{12}=0.78$.

To compute the eigenfrequencies for isotopically normal clusters, the constant

$$\epsilon=\frac{F_1}{\omega_1^2} \tag{28}$$

in Eq. (9) was determined such that the limit form of Eq. (7) reproduces the frequency $^{16}\omega_\infty$ of the isotopic pure crystal. The corresponding constant ϵ' associated with the frequencies of ^{18}O-containing clusters, can be estimated on the basis of the coupling mechanism of Eq. (3) and employing Eq. (18) by the relation

$$\begin{aligned}\epsilon'=\frac{F_1'}{(\omega_1')^2}&=\left[\frac{\omega_1}{\omega_1'}\right]^2\frac{(\partial m/\partial q_1')_0^2}{(\partial m/\partial q_1)_0^2}\epsilon\\ &=\left[\frac{\omega_1}{\omega_1'}\right]^2\left[\frac{L_{11}'}{L_{11}}\right]^2\frac{(\partial m/\partial S_1')_0^2}{(\partial m/\partial S_1)_0^2}\epsilon\\ &\cong\left[\frac{\omega_1}{\omega_1'}\right]^2\left[\frac{L_{11}'}{L_{11}}\right]^2\epsilon\ .\end{aligned} \tag{29}$$

In Eq. (29) the primed symbols belong to the $FeN^{18}O$ species, and there it has been assumed that the dipole-moment derivative $(\partial m/\partial S_1)_0$ (taken at $q_2=0$) is an approximate isotopic invariant.[13]

The results of these calculations are summarized in Table I together with the experimental values for the NO stretching wave numbers of isolated normal and ^{18}O-labeled nitroprusside ions as well as with the limit wave numbers of isotopically pure crystals. The relative stretchings of the NO bonds for the first few clusters of nitroprusside ions vibrating in the different extended (intermolecular) normal modes [calculated by means of Eq. (22a)] are schematically drawn in Fig. 2.

The stretching mode of highest wave number of an aggregate with n adjacent isotopically alike neighbors is the most active infrared mode in the set of n normal vibrations of the cluster (see Fig. 2). The other modes are either infrared inactive (e.g., the modes of frequencies ω_{21} and ω_{32})[14] or very weak (e.g., ω_{31}). The wave numbers $\bar{\nu}_{nn}=\omega_{nn}/2\pi c$ for the most intense mode of clusters with up to ten members [calculated on the basis of Eq. (9)], and their associated intensities $I_{nn}(p)$ [computed using Eq. (27) and expressed in relative units] are presented in Fig. 3 for the strontium salt. For the sake of comparison, in the same figure are included the observed infrared spectra of $Sr[Fe(CN)_5N(^{16}O,^{18}O)]\cdot 4H_2O$ isotopic mixtures and the isotopically normal substance in the NO stretching region. The results corresponding to ^{18}O-enriched samples of barium nitroprusside trihydrate are included in Fig. 4.

TABLE I. Experimental wave number (in cm^{-1}) of isolated normal and ^{18}O-containing nitroprusside ions and of isotopically pure $Sr[Fe(CN)_5NO]\cdot 4H_2O$ and $Ba[Fe(CN)_5NO]\cdot 3H_2O$ at nitrogen boiling temperature. The ϵ and ϵ' constants, defined by Eqs. (28) and (29), respectively, were calculated using Eq. (7).

Isotopic mixture	$^{16}\omega_1$	$^{18}\omega_1$	$^{16}\omega_\infty$	ϵ	ϵ'
$Sr[Fe(CN)_5N(^{16}O,^{18}O)]\cdot 4H_2O$	1947	1904	1970	−0.0119	−0.0117
$Ba[Fe(CN)_5N(^{16}O,^{18}O)]\cdot 3H_2O$	1947	1904	1968	−0.0108	−0.0107

V. CONCLUSIONS

From Eq. (28) and the values of ϵ in Table I, there results the coupling constants $F_1 = -1.60\times 10^{27}$ $esu^2/g\,cm^3$ for $Sr[Fe(CN)_5NO]\cdot 4H_2O$, and $F_1 = -1.46\times 10^{27}$ $esu^2/g\,cm^3$ for $Ba[Fe(CN)_5NO]\cdot 3H_2O$. In the approximation of nonbonded nitrosyl groups, the corresponding force constant f_1 values calculated using Eq. (21) are −0.198 and −0.181 mdyn/Å for the strontium and barium salts, respectively. The values found for the coupling force constants are, in turn, entirely consistent with the hypothesis that transition dipole-transition dipole forces dominate the vibrational interaction between neighboring nitrosyl groups in the crystals as described by Eq. (3a).[1]

The similarity between corresponding features of the NO stretching bands in the infrared spectra of $N^{18}O$-containing $Sr[Fe(CN)_5NO]\cdot 4H_2O$ [space group $C2/m$ (C_{2h}^3)] and $Ba[Fe(CN)_5NO]\cdot 3H_2O$ [space group $Pca2_1$ (C_{2v}^5)] as shown by Figs. 3 and 4, can clearly be attributed to the similar packing exhibited by the nitrosyl groups along the chains in both crystals.[3,4]

The fairly close agreement between spectroscopic data and theoretical results (see Figs. 3 and 4) affords a conclusive proof about the basic correctness of the assumption made in these first-order calculations. An improved vibrational model should include second-order effects such as interaction beyond first neighbors of ions in clusters with more than two members and coupling between neighboring clusters of one isotopic kind on the same or different chains. To this degree of approximation, however, some other perturbations such as coupling of single ions and of clusters including two, three, etc. members with neighboring ions of the other species located at both sides, dielectric shielding due to crystal-lattice polarization effects, etc. should also be considered.

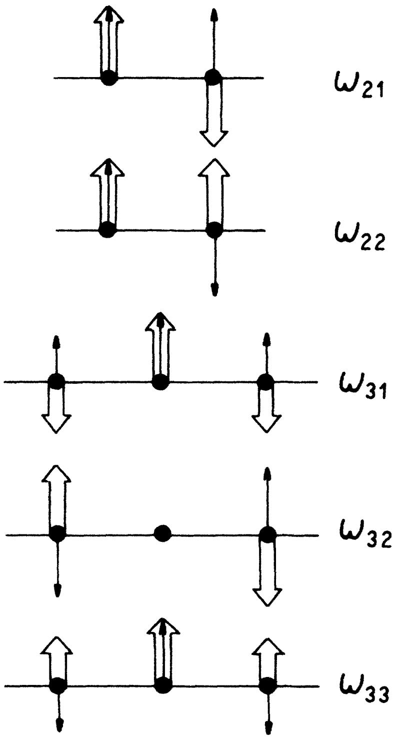

FIG. 2. Normal modes for clusters of two and three isotopically alike molecules. Upward (downward) thick arrows indicate the relative amplitudes for stretching (compressions) S_{l1} of the N—O bonds. For the sake of clarity, the associated FeN stretchings S_{l2} (which are approximately −0.61 times S_{l1}) are not represented in the drawing. The dipole moments (conventionally oriented) generated by the vibrations are schematically shown by double arrows.

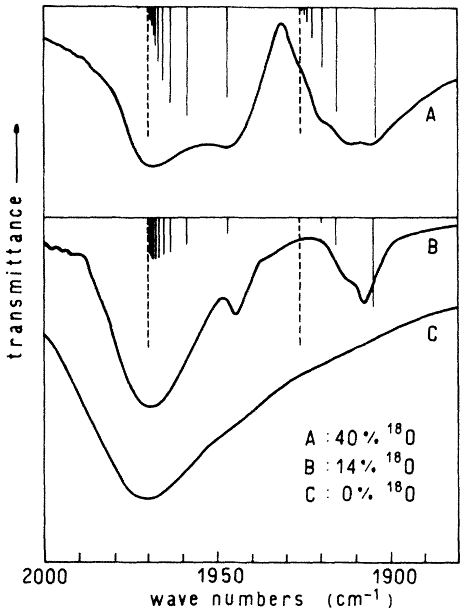

FIG. 3. Infrared absorption spectra of $Sr[Fe(CN)_5N(^{16}O,^{18}O)]\cdot 4H_2O$ isotopic mixtures containing 40% and 14% of $N^{18}O$ and of the normal compound at nitrogen boiling temperature. (Data taken from Ref. 1.) The solid vertical lines indicate theoretical wave numbers and relative intensities. Dotted lines indicate wave numbers for isotopically pure crystals.

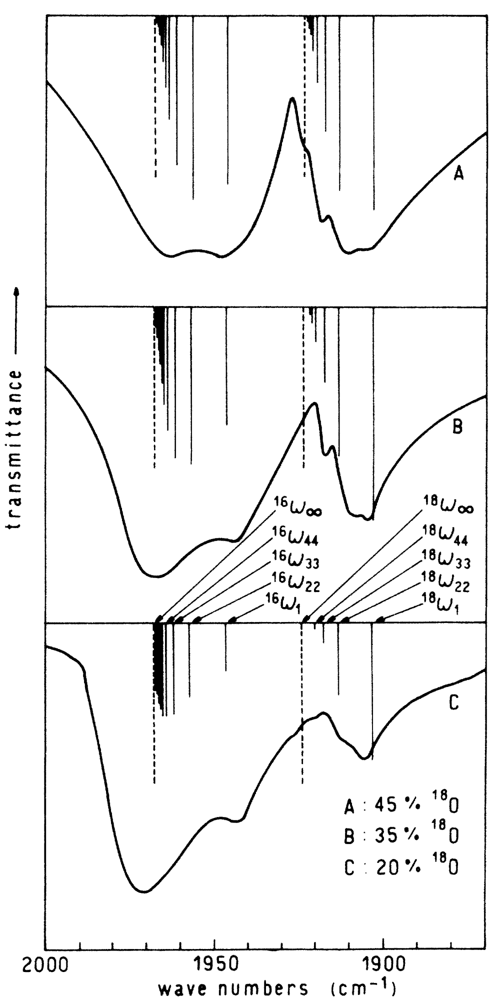

FIG. 4. Low-temperature ir absorption spectra of $Ba[Fe(CN)_5N(^{16}O,^{18}O)]\cdot 3H_2O$ isotopic mixtures containing 45%, 35%, and 20% of $N^{18}O$. Vertical lines indicate theoretical spectra.

In sharp contrast with the rich structure exhibited by the infrared absorption band of the strongly polar NO stretching vibrations of the ^{18}O-enriched strontium and barium salts, no fine structure is observed in the FeN stretching band of the infrared spectra of these compounds. As advanced in Sec. III, this fact can be traced to the very small dynamical dipole-dipole coupling between the weakly polar FeN stretching vibrations of neighboring nitroprusside groups in the lattices.

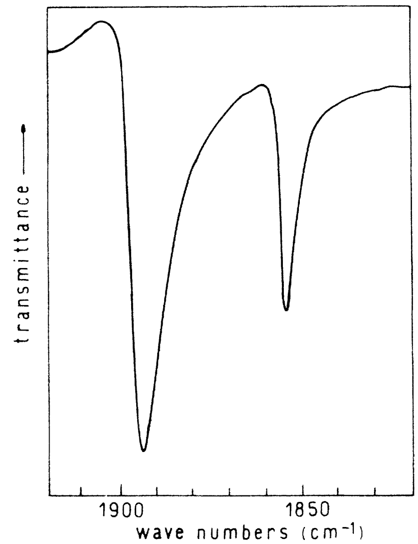

FIG. 5. Low-temperature ir absorption spectra in the NO stretching region of $[Fe(o\text{-phen})_3][Fe(CN)_5NO]\cdot 2H_2O$ containing 30% of $N^{18}O$.

Finally, it is also worth noting the absence of fine details in the NO stretching band of the infrared absorption spectrum of $[Fe(o\text{-phen})_3][Fe(CN)_5N(^{16}O,^{18}O)]\cdot 2H_2O$ isotopic mixtures (see Fig. 5). This fact is not surprising as the bulky complex cations $[Fe(o\text{-phen})_3]^{2+}$ keep the nitroprusside ions far apart from each other in the crystal[7] [giving rise to a large value for r_1 in Eq. (3a)], thereby rendering the transition dipole-transition dipole interaction between nitrosyl groups negligibly small.

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[10] In Ref. 1, for simplicity, the NO groups were considered nonbonded to the metal and arranged in a parallel fashion along the chains in the crystals. This leads to the value $k=0$ for the wave vector of the infrared active optic mode strongly polarized approximately along the crystal **a** axis. In the present work we are considering the actual antiparallel piling up that the FeNO molecular fragments exhibit in both compounds. Thus, there will be a shift of π radians (which corresponds to $k=\pm 1/2d$) in the phase of oscillations of neighboring NO stretching vibrations of the above-mentioned optic mode and a consequent change in the sign of the coupling force constant f_1 with respect to the situation described in Ref. 1.

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[13] The estimate for ϵ' is practically coincident (within one-half percent) with the value deduced assuming nonbonded nitrosyl groups, $\epsilon'=(\omega_1/\omega_1')^2(\mu/\mu')\epsilon$.

[14] In $Ba[Fe(CN)_5N(^{16}O,^{18}O)]\cdot 3H_2O$ isotopic mixtures, some of these modes (such as, e.g., ω_{12}) are very weakly polarized along the crystal **b** axis because the small angle existing between neighboring nitrosyl groups (see Fig. 1).