PHYSICAL REVIEW B VOLUME 31, NUMBER 2 15 JANUARY 1985

Transition dipole-dipole coupling between the antisymmetric stretching mode of azido ligands in $K_3[Co(CN)_5N_3]\cdot 2H_2O$

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(Received 4 January 1984; revised manuscript received 6 August 1984)

The nature and magnitude of intermolecular forces that couple the strongly polar N_3 antisymmetric stretching vibration of the $[Co(CN)_5N_3]^{3-}$ ions in $K_3[CO(CN)_5N_3]\cdot 2H_2O$ have been studied on the basis of previously reported results dealing with the crystal-structure determination and infrared and Raman spectra of this compound. The observed difference of 25 cm^{-1} between the measured wave numbers for the frequencies of the ir- and Raman-active optical fundamental vibrations associated with the N_3 antisymmetric stretching mode can be interpreted in terms of a linear-chain model of $[Co(CN)_5N_3]^{3-}$ oscillators coupled through their N_3 ligands via harmonic transition dipole-dipole forces operating between nearest neighbors on a chain. With this model, we obtain $|(\partial\mu/\partial Q_3)_0| = 263$ esu/$g^{1/2}$ for the dipole-moment derivative of the N_3 antisymmetric stretch, a value which can be compared with the corresponding value derived from integrated ir-absorption intensity measurements of $N_3{}^-$ ions isolated in alkali-halide lattices. A value $f_3 = +0.071$ mdyn/Å is calculated for the force constant of the interaction that couples such N_3 vibrations of neighbor azide ions in $K_3[Co(CN)_5N_3]\cdot 2H_2O$. The potentiality of combined ir and Raman spectroscopic techniques for the study of intermolecular vibrational coupling in solids is here emphasized.

I. INTRODUCTION

Crystallographic and spectroscopic studies on alkaline and alkaline-earth pentacyanometallates, including $Sr[Fe(CN)_5NO]\cdot 4H_2O$, $Ba[Fe(CN)_5NO]\cdot 2H_2O$, and $K_3[Co(CN)_5N_3]\cdot 2H_2O$, have suggested the possibility for strong intermolecular coupling between the polar vibrational modes of the sixth (noncyanide) ligands in the complexes.[1–6] Recently, the existence of measurable effects of such phenomena operating on the NO stretching vibrations of $[Fe(CN)_5NO]^{2-}$ ions in the former two crystals has been demonstrated by infrared spectroscopic techniques.[7]

In the present work we study the origin, magnitude, and sign of the interaction forces that couple the antisymmetric stretching mode of the azido (N_3) groups in potassium azidopentacyanocobaltate (III) dihydrate, $K_3[Co(CN)_5N_3]\cdot 2H_2O$ (space group $P\bar{1}$, $Z=2$). To this purpose, we will base our interpretation on previously reported results dealing with the crystal-structure determination[3] and the ir and Raman spectra[6] of this compound.

The perspective PLUTO projection[8] of $K_3[Co(CN)_5N_3]\cdot 2H_2O$ shown in Fig. 1 suggests that the proximity of the N_3 ligands in the crystal may cause an appreciable intermolecular coupling to be present between the polar vibrations of neighboring azido groups. Because of the presence of two symmetry-related molecules per unit cell in the crystal, each normal mode of $[Co(CN)_5N_3]^{3-}$ ion gives rise to one odd-parity (ir-active) and one even-parity (Raman-active) lattice vibration of $K_3[Co(CN)_5N_3]\cdot 2H_2O$. The wave number for the odd-parity optic fundamental vibration associated with the N-N-N antisymmetric stretching mode measured by infrared spectroscopy is 25 cm^{-1} higher than the corresponding value obtained for the even-parity lattice vibration using a Raman spectrophotometer (estimated experimental error[6] of ±2 cm^{-1}). This correlation (Davydov) splitting can be interpreted qualitatively in terms of vibrational electric dipole-dipole coupling operating between neighbor azido groups in the crystal (see Fig. 2).

A linear, noninteracting chain system of harmonic oscillators, coupled through transition dipole-dipole forces operating between first neighbors, provides a quantitative model for the calculation of the dispersion relation $\omega(k)$ associated with the N_3 stretching optical modes of $K_3[Co(CN)_5N_3]\cdot 2H_2O$. Combining these model calculations with the infrared and Raman spectroscopic results,[6] we obtain the value $|(\partial\mu/\partial Q_3)_0| = 263$ esu/$g^{1/2}$ for the dipole-moment derivative corresponding to the strongly polar N-N-N asymmetric stretching mode of the $[Co(CN)_5N_3]^{3-}$ ion, and the value $f_3 = +0.071$ mdyn/Å for the force constant that couples such vibrations of nearest-neighbor azido ligands in the solid.

TABLE I. ir and Raman spectra of the azido stretching vibrations in $K_3[Co(CN)_5N_3]\cdot 2H_2O$. (Data taken from Ref. 6.)

N_3 stretchings Assignments	ν(N-N-N)[a] Infrared	Raman
Σ_u^+(ir)$-A''$(antisym)	2060 (vvs)	2035 (vvw)
Σ_g^+(R)$-A'$(symm)	1296 (s)	1297 (vvw)

[a] Spectra run at room temperature on polycrystalline samples. ir, infrared-active bands; R, Raman-active bands; vvw, very very weak; s, strong; vvs, very very strong bands.

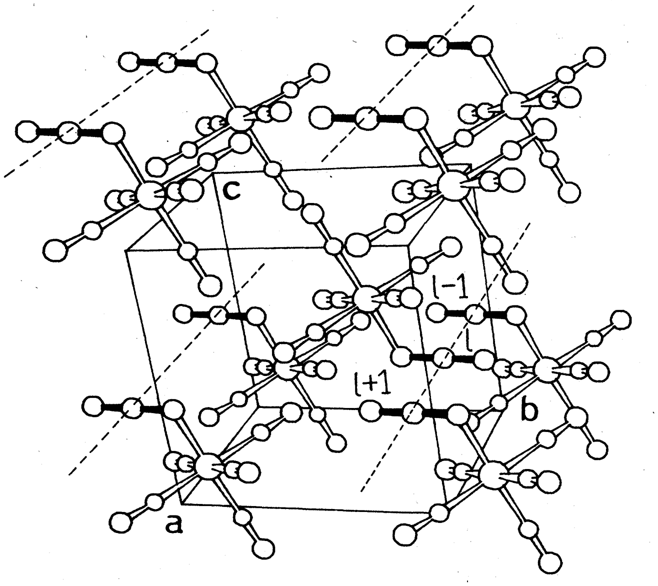

FIG. 1. Perspective view down reciprocal unit $\vec{a}^*$ vector displaying the arrangement of the complex ions in $K_3[Co(CN)_5N_3]\cdot 2H_2O$. Azido ligands are emphasized by darkened N—N bonds. Chains of complexes along the crystal $\vec{a}$ axis are indicated by dashed lines. Adjacent $[Co(CN)_5N_3]^{3-}$ ions on a chain are related through crystallographic inversion centers located at the middle points between nearest-neighbor N_3 groups.

II. EXPERIMENTAL BACKGROUND

The crystal- and molecular-structure determination of $K_3[Co(CN)_5N_3]\cdot 2H_2O$ is reported in Ref. 3. The complex ions are packed in the crystal with their azido groups piled up in an eclipsed antiparallel fashion, forming stacks along the basic $\vec{a}$ vector at intervals[3] of approximately $a/2=4.25$ Å (see Fig. 1). The infrared and Raman spectra of the compound are detailed in Ref. 6 and the results relevant to the present work are reproduced in Table I.

III. THEORETICAL MODEL

Let us consider the contribution of the N_3 stretching modes of the complex ions to the vibrational behavior of $K_3[Co(CN)_5N_3]\cdot 2H_2O$ in the region 1200—2100 cm^{-1}. For this purpose we shall regard such contribution as due to the collective harmonic oscillations of the complexes coupled through their azido ligands. These groups are considered evenly spaced (at a distance $d=a/2=4.25$ Å) along noninteracting chains (separated in distances greater than 8.5 Å between chain axes) parallel to the crystal $\vec{a}$ axis (see Fig. 1). We shall assume that harmonic transition dipole-dipole forces operate between nearest-neighbor azido groups on the chains.

The electrostatic dipole-dipole interaction between a pair of neighbor azido groups is given by

$$V_{l,l+1}=-\frac{\mu_l\mu_{l+1}}{d_{l,l+1}^3}(2\cos\theta_l\cos\theta_{l+1} - \sin\theta_l\sin\theta_{l+1}\cos\chi_{l,l+1})\ , \tag{1}$$

where μ_l and μ_{l+1} are the magnitudes of the two dipoles, $d_{l,l+1}$ is the distance between the centers of the N_3 groups, θ_l and θ_{l+1} are the angles that μ_l and μ_{l+1}, respectively, subtend from the line joining the centers, and $\chi_{l,l+1}$ is the angle between the projections of the dipoles onto a plane perpendicular to the line between centers. In the spectral region of interest, we can consider μ_l as a function of the molecular normal coordinates (Q_{1l},Q_{3l}) of the complex ion which are largely associated with the N-N-N symmetric and antisymmetric stretching mode, respectively, of the azido at the lattice site l.

Expanding μ_l in powers of the normal coordinates and neglecting terms in dipole derivatives higher than the first order, the electric dipole moment becomes

$$\mu_l(Q_{1l},Q_{3l})=\mu_l(0,0)+\left[\frac{\partial\mu_l}{\partial Q_{1l}}\right]_0 Q_{1l}+\left[\frac{\partial\mu_l}{\partial Q_{3l}}\right]_0 Q_{3l}\ . \tag{2}$$

Introducing Eq. (2) into Eq. (1) and considering the crystallographic data that apply to $K_3[Co(CN)_5N_3]\cdot 2H_2O$ $[\theta_l=\theta_{l+1}=\pi/2,\ \chi_{l,l+1}=0$ (Ref. 3)], we obtain for the quadratic contribution to the interaction energy

$$V_{l,l+1}=\frac{1}{d^3}\left[\left[\frac{\partial\mu}{\partial Q_1}\right]_0^2 Q_{1l}Q_{1l+1}+\left[\frac{\partial\mu}{\partial Q_3}\right]_0^2 Q_{3l}Q_{3l+1}+\left[\frac{\partial\mu}{\partial Q_1}\right]_0\left[\frac{\partial\mu}{\partial Q_3}\right]_0(Q_{1l}Q_{3l+1}+Q_{1l+1}Q_{3l})\right]\ . \tag{3}$$

From integrated ir-absorption intensities measurements of the N_3 stretching bands in polycrystalline $K_3[Co(CN)_5N_3]\cdot 2H_2O$, we can estimate that the $(\partial\mu/\partial Q_1)_0^2$ value associated with the weak symmetric stretching band is only about 3% of the squared dipole derivative corresponding to the strongly polar N-N-N antisymmetric stretching mode.[9] Thus the first term in Eq. (3) for the coupling of the symmetric azido vibration is very small compared with the interaction energy associated with the antisymmetric stretching mode. The third contribution to Eq. (3) is also small because it is proportional to $(\partial\mu/\partial Q_1)_0$, and it couples normal vibrations of neighbor azido groups of very different resonant frequencies.

The Lagrangian for the system of coupled linear harmonic oscillators in the spectral region of interest can be expressed by

$$L=\sum_l\left[\tfrac{1}{2}\dot{Q}_{1l}^2-\tfrac{1}{2}\omega_1^2Q_{1l}^2-\frac{1}{d^3}\left[\frac{\partial\mu}{\partial Q_1}\right]_0^2 Q_{1l}Q_{1l+1}\right]+\sum_l\left[\tfrac{1}{2}\dot{Q}_{3l}^2-\tfrac{1}{2}\omega_3^2Q_{3l}^2-\frac{1}{d^3}\left[\frac{\partial\mu}{\partial Q_3}\right]_0^2 Q_{3l}Q_{3l+1}\right]\ , \tag{4}$$

where the influence of the third term in the potential energy (3) together with the effects of nonresonant crystal-lattice polarization and short-range repulsive forces has been included approximately in the definition of the effective normal-mode frequencies ω_1 and ω_3. The first and second terms of both sums in Eq. (4) correspond to N_3 groups dynamically uncoupled, while the third terms take into account the vibrational dipole-dipole interaction between nearest-neighbor azido groups.

The Lagrange equations

$$\frac{d}{dt}\left[\frac{\partial L}{\partial \dot{Q}_{\alpha l}}\right]=\frac{\partial L}{\partial Q_{\alpha l}},\quad \alpha=1,3 \tag{5}$$

lead to the equations of motion

$$\ddot{Q}_{\alpha l}+\omega_\alpha^2 Q_{\alpha l}+\frac{1}{d^3}\left[\frac{\partial \mu}{\partial Q_\alpha}\right]_0^2 (Q_{\alpha l+1}+Q_{\alpha l-1})=0,\quad \alpha=1,3 \tag{6}$$

for the coupled N_3 stretching oscillations. Differential equation (6) can be solved with the following functions consisting of traveling waves which satisfy the Born—von Kármán cyclic boundary conditions[10]

$$Q_{\alpha l}=Q_{\alpha 0}e^{i(\omega_\alpha t-kld)},\quad \alpha=1,3 \tag{7}$$

where ω_α is the angular frequency of the optical vibrations, d is the distance between nearest-neighbor azido groups, and k takes values within the first Brillouin zone, $-\pi/d<k\leq\pi/d$. The dispersion relations $\omega_\alpha(k)$ expressed, for simplicity, in the "extended-zone scheme" are then obtained:[11]

$$\omega_\alpha^2(k)=\omega_\alpha^2+\frac{2}{d^3}\left[\frac{\partial \mu}{\partial Q_\alpha}\right]_0^2 \cos(kd),\quad \alpha=1,3\ . \tag{8}$$

So far we have been considering the N_3 stretching normal modes of the whole $[Co(CN)_5N_3]^{3-}$ complex in $K_3[Co(CN)_5N_3]\cdot 2H_2O$. To estimate the force constant f_3 that couples the strongly polar N_3 antisymmetric stretching vibrations in the crystal, we shall simplify the model by considering a linear-chain system of nonbonded azide ions (linear-symmetric N_3^- molecules). This further assumption is justified because of the relative weakness of the Co—N link compared with the N—N bonds.[3,12] The contribution of the N_3^- antisymmetric stretching vibrations to the Lagrangian of an infinite array of azide ions coupled through harmonic dipole-dipole interaction can be expressed by

$$L=\sum_l\left[\tfrac{3}{4}m\dot{q}_l^2-\tfrac{9}{4}(f-f_{13})q_l^2-\frac{1}{d^3}\left[\frac{\partial \mu}{\partial q}\right]_0^2 q_l q_{l+1}\right], \tag{9}$$

where m is the mass of the nitrogen atom, f is the force constant for both N-N bonds in the azide ion, f_{13} is the force constant that gives the interaction of the two bonds, and $q_l=x_{1l}+x_{3l}$ (sum of the displacements for the terminal nitrogens along the N_3^- axis) is the symmetry coordinate (not normalized) for the antisymmetric stretching vibration of the azide ion[13] at the lattice site l. The corresponding equations of motion are

$$\tfrac{3}{2}m\ddot{q}_l+\tfrac{9}{2}(f-f_{13})q_l+\frac{1}{d^3}\left[\frac{\partial \mu}{\partial q}\right]_0^2 (q_{l+1}+q_{l-1})=0\ . \tag{10}$$

Similar to the case of Eqs. (6), let us now look for solutions of Eq. (10) in the form of traveling waves:

$$q_l=q_0e^{i(\omega t-kld)}\ . \tag{11}$$

Substituting Eq. (11) into the differential equations (10),

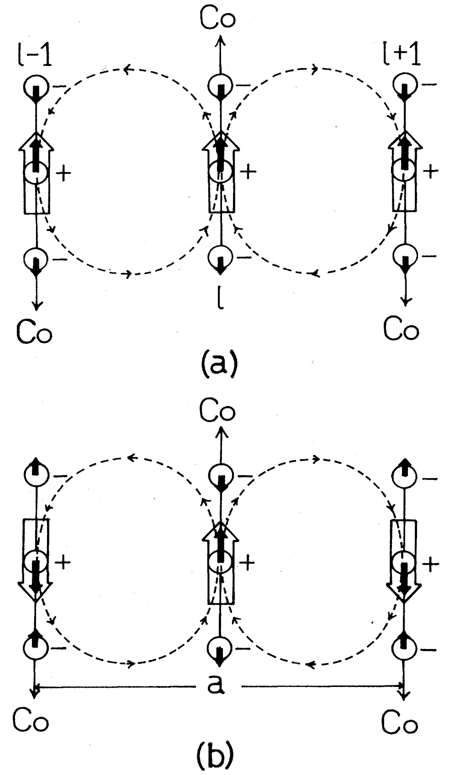

FIG. 2. Schematic illustration showing the electrostatic origin for the difference between the frequencies of the infrared- and Raman-active N-N-N antisymmetric stretching fundamental vibrations in $K_3[Co(CN)_5N_3]\cdot 2H_2O$. The polarity of the net charges on the azido nitrogens are indicated by plus and minus signs. The instantaneous displacements of the nitrogen atoms in the N_3 antisymmetric stretching mode are shown by thick arrows. The azido dipole moment generated by such vibration is displayed by double arrows, and the lines of force for the electric dipole field corresponding to the central N_3 group are denoted by dashed curves. (a) ir-active lattice vibration. Dipole-dipole interaction energy between neighboring azido groups varies during oscillation in the same sense as the molecular potential energy, thus formally increasing the N-N stretching force constant. Consequently, the N_3 lattice vibration frequency ω_3 (ir) is higher than the frequency ω_3 for uncoupled vibrators. (b) Raman-active N_3 lattice vibration. Dipole-dipole interaction energy between nearest N_3 ligands varies in opposition to molecular potential energy changes during vibration, thus formally reducing the N-N stretching force constant. Therefore, $\omega_3(\text{Raman})<\omega_3<\omega_3(\text{ir})$.

we obtain for the dispersion relation $\omega(k)$ associated with the N_3 antisymmetric stretching vibration of the linear triatomic chain

$$\omega^2(k)=\frac{3}{m}\left[(f-f_{13})+\frac{4}{9}\frac{1}{d^3}\left[\frac{\partial\mu}{\partial q}\right]_0^2\cos(kd)\right] . \tag{12}$$

Equation (12) provides us with a simple interpretation for the effects of the intermolecular coupling between neighbor oscillators: The vibrational dipole-dipole interaction modifies slightly the stretching force constant of individual azide ions to an effective value,

$$f_{\text{eff}}=f+\frac{4}{9}\frac{1}{d^3}\left[\frac{\partial\mu}{\partial q}\right]_0^2\cos(kd) , \tag{13}$$

giving rise to an apparent strengthening of the N—N bonds in the infrared-active optical mode [Eq. (13) with $k=0$],

$$f_{\text{eff}}(\text{ir})=f+2f_3 \tag{14a}$$

and a corresponding effective weakening of the N-N-N binding in the Raman-active optical mode [Eq. (13) with $k=\pm\pi/d$],

$$f_{\text{eff}}(\text{Raman})=f-2f_3 , \tag{14b}$$

where

$$f_3=\frac{2}{9}\frac{1}{d^3}\left[\frac{\partial\mu}{\partial q}\right]_0^2 \tag{15}$$

is the positive force constant that couples the strongly polar stretching modes of a pair of nearest N_3 neighbors (see Fig. 2). Comparing Eq. (12) with the equivalent Eq. (8) and taking into account that $\omega_3=[3(f-f_{13})/m]^{1/2}$ is the frequency for the N_3 antisymmetric stretching vibration of uncoupled azides, we obtain the following expression for the coupling force constant:

$$f_3=\frac{1}{3}\frac{m}{d^3}\left[\frac{\partial\mu}{\partial Q_3}\right]_0^2 . \tag{16}$$

IV. RESULTS AND DISCUSSION

The frequency of the lattice modes of $K_3[Co(CN)_5N_3]\cdot 2H_2O$ associated with the N-N-N stretchings which are ir active (antisymmetric in $P\bar{1}$) can be calculated from Eq. (8) with $k=0$:

$$\omega_\alpha^2(\text{ir})=\omega_\alpha^2+\frac{2}{d^3}\left[\frac{\partial\mu}{\partial Q_\alpha}\right]_0^2, \quad \alpha=1,3 \tag{17}$$

while the frequency corresponding to the collective N_3 stretching modes that are Raman active (symmetric in $P\bar{1}$) can be obtained from the dispersion relation (8) by setting the value $k=\pm\pi/d$:[14]

$$\omega_\alpha^2(\text{Raman})=\omega_\alpha^2-\frac{2}{d^3}\left[\frac{\partial\mu}{\partial Q_\alpha}\right]_0^2, \quad \alpha=1,3 . \tag{18}$$

Subtracting Eq. (18) from Eq. (17), there results

$$\omega_\alpha^2(\text{ir})-\omega_\alpha^2(\text{Raman})=\frac{4}{d^3}\left[\frac{\partial\mu}{\partial Q_\alpha}\right]_0^2, \quad \alpha=1,3 . \tag{19}$$

Introducing into relation (19) the experimental frequencies of Table I and the crystallographic parameter $d=4.25$ Å,[3] we can calculate the dipole-moment derivative of the strongly polar N-N-N antisymmetric stretching mode:

$$\left|\left[\frac{\partial\mu}{\partial Q_3}\right]_0\right|=263\ \text{esu/g}^{1/2} .$$

This value is 18% higher than the highest value derived from absolute infrared intensity measurements of the N_3^- antisymmetric stretching band for azide ions as an impurity in some alkali-halide lattices (corresponding to the IK host lattice).[15] In this connection, we must note that $|(\partial\mu/\partial Q_3)_0|$ of $N_3{}^-$ in these matrices displays a wide variation from one host lattice to another [$|(\partial\mu/\partial Q_3)_0|$ for $N_3{}^-$ hosted in KI is 29% higher than the corresponding dipole-moment derivative for the KCl host matrix[15]]. These values together with the value for $|(\partial\mu/\partial Q_3)_0|$ of $K_3[Co(CN)_5N_3]\cdot 2H_2O$ reported in this work probably reflect the sensitivity of this molecular parameter upon the type and degree of bonding of $N_3{}^-$ ions to the crystal lattices.

The force constant that couples the N_3 antisymmetric stretching vibrations in $K_3[Co(CN)_5N_3]\cdot 2H_2O$ can now be calculated from Eq. (16):

$$f_3=+0.071\ \text{mdyn/Å} .$$

Employing Eq. (19) we can estimate the expected difference $\Delta\omega_1$ in the wave numbers for the ir- and Raman-active lattice vibrations associated with the weakly polar N_3 symmetric stretching mode. To this purpose, we rewrite Eq. (19) as

$$\bar{\omega}_1\Delta\omega_1=\frac{(\partial\mu/\partial Q_1)_0^2}{(\partial\mu/\partial Q_3)_0^2}\bar{\omega}_3\Delta\omega_3 , \tag{20}$$

where the overbars indicate average values

$$\bar{\omega}_\alpha=\tfrac{1}{2}[\omega_\alpha(\text{ir})+\omega_\alpha(\text{Raman})], \quad \alpha=1,3 . \tag{21}$$

From the relationship

$$\frac{(\partial\mu/\partial Q_1)_0^2}{(\partial\mu/\partial Q_3)_0^2}=\frac{A_1}{A_3} , \tag{22}$$

where A_α ($\alpha=1,3$) is the ir absorbance integrated over the corresponding stretching bands ($A_1/A_3\cong 0.03$ for $K_3[Co(CN)_5N_3]\cdot 2H_2O$ (Ref. 9)) we obtain $\Delta\omega_1=1.2\ \text{cm}^{-1}$ through Eq. (20). This value is consistent with the observed agreement (within experimental accuracy) between the frequencies for the fundamental of both optical vibrations measured by ir and Raman spectrophotometers (see Table I).

Adding Eqs. (17) and (18), we obtain the relation

$$\omega_3^2=\tfrac{1}{2}[\omega_3^2(\text{ir})+\omega_3^2(\text{Raman})] , \tag{23}$$

useful for estimating the antisymmetric stretching frequency of uncoupled azido groups.

V. SUMMARY AND CONCLUSIONS

In Sec. III we calculated the dispersion relation $\omega(k)$ for the lattice vibrations of $K_3[Co(CN)_5N_3]\cdot 2H_2O$ associated with the strongly polar N_3 antisymmetric stretching mode [Eq. (8) with $\alpha=3$]. In Sec. IV this result was used to estimate the frequencies of the infrared- and Raman-active fundamental of these optical modes [Eqs. (17) and (18)]. The relationship of Eq. (19) combines infrared and Raman spectroscopic data (frequencies) and crystallographic information (distances and angles) with dipole-moment derivative of the N_3 ligand in $K_3[Co(CN)_5N_3]\cdot 2H_2O$. This molecular parameter, in turn, depends on the type and degree of bonding of the N_3 group in the crystal lattice. Equation (19) thus provides a method for the evaluation of this latter parameter as an alternative to the one based on absolute ir-absorption intensity measurements, a procedure which is often subjected to large experimental errors.

It can be shown that the inclusion of interaction between all oscillators in the three-atom chain model considered in this work modifies slightly the result expressed by Eq. (19) for first neighbors coupling into

$$\omega_\alpha^2(\text{ir})-\omega_\alpha^2(\text{Raman})=\frac{4}{d^3}\left[\frac{\partial\mu}{\partial Q_\alpha}\right]_0^2\sum_{n=1}^{\infty}\frac{1}{(2n-1)^3}\,, \qquad (24)$$

where the summation is equal to 1.0518. To this degree of approximation, however, complete three-dimensional dipolar sums including the dielectric shielding owing to the crystal-lattice polarization, particle size, and shape effects due to the microcrystalline domains have to be considered.[16]

The positive value for the force constant ($f_3=+0.071$ mdyn/Å) that couples the N_3 antisymmetric stretching vibrations of $K_3[Co(CN)_5N_3]\cdot 2H_2O$ is both consistent with the observed differences in the wave numbers for this mode measured by ir and Raman spectroscopy [$\omega(\text{ir})>\omega(\text{Raman})$],[6] and with the value derived from the electrostatic dipole-dipole energy given in Eq. (1). A positive value for the theoretical coupling force constant arises from the value taken by the angular factor in the expression (1) for the geometric arrangement of the azido ligands in the crystal.[3] In this regard, it can be noted that in strontium nitroprusside tetrahydrate, $Sr[Fe(CN)_5NO]\cdot 4H_2O$, and barium nitroprusside dihydrate, $Ba[Fe(CN)_5NO]\cdot 2H_2O$, the NO ligands are similarly arranged as the N_3 groups in $K_3[Co(CN)_5N_3]\cdot 2H_2O$, i.e., piled up in an alternating antiparallel quasi-eclipsed fashion, forming linear chains along a crystal axis. The NO groups are approximately perpendicular to the chains and at distances of about 4 Å from each other.[1,2] Consequently, it is expected on theoretical grounds that a positive force constant describes the coupling between the strongly polar NO stretching vibration in both crystals. This expectancy is substantiated by ir spectroscopic evidence.[7] In contrast, negative force constants are found for the coupling of the out-of-plane bending mode of NO_3^- ions in KNO_3 (Ref. 17), of CO_3^{2-} in $BaCO_3$ (Refs. 17 and 18), $CaCO_3$, and $SrCO_3$ (Ref. 18) (crystals of aragonite type), and CO_3^{2-} in Ag_2CO_3 (Ref. 19) (space group[20] $P2_1/m$). In all these compounds, the planar molecular ions are packed in a coaxial fashion, parallel to and at close distances from each other, forming linear stacks in the crystals. Therefore, the transition dipole moment of the out-of-plane bending mode of the NO_3^- or CO_3^{2-} ions are oriented along the coupling direction, a geometrical arrangement for which the angular factor in the electrostatic dipole-dipole energy (1) leads to a negative interaction constant.[17]

ACKNOWLEDGMENTS

I thank Dr. P. J. Aymonino for critical reading of the manuscript. I am indebted to Dr. K. Nakamoto for his interest in this work. Thanks are extended to S. R. González, H. R. Viturro, and P. Alzari for their help during the preparation of the manuscript. Financial support from the Consejo Nacional de Investigaciones Científicas y Técnicas, Subsecretaría de Ciencia y Técnica, and Comisión de Investigaciones Científicas de la Provincia de Buenos Aires, República Argentina, is gratefully acknowledged.

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[11] Actually, the real translational symmetry of the linear-chain system is of period $2d$ with two vibrators per cell. Therefore, there must be two optical branches associated with each collective N_3 stretching mode. The corresponding pair of dispersion relations

$$\omega_\alpha\pm(k)=\left[\omega_\alpha^2\pm\frac{2}{d^3}\left[\frac{\partial\mu}{\partial Q_\alpha}\right]_0^2\cos(kd)\right]^{1/2}$$

can be obtained from the dispersion curve (8) by translating through $\pm\pi/d$ (i.e., by reciprocal-lattice vectors of our double cell) the portions of the curve associated with k values outside the halved Brillouin zone into a "reduced-zone scheme" comprising wave vectors within the interval $(-\pi/2d,\pi/2d)$.

[12] From the spectroscopic data for $K_3[Co(CN)_5N_3]\cdot 2H_2O$ reported in Ref. 6, the values of the valence force constants $f_{\text{Co-N}}$ and $f_{\text{N-N}}$ associated with the Co-N and N-N bonds, respectively, have been estimated (Ref. 9). An estimate value of about 1.7 mdyn/Å obtained for $f_{\text{Co-N}}$ should be compared with the value 12.7 mdyn/Å obtained for $f=f_{\text{N-N}}$ [or with the value 11.5 mdyn/Å estimated for the force constant $f-f_{13}$ of Eq. (9) in the text].

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