PHYSICAL REVIEW B VOLUME 23, NUMBER 7 1 APRIL 1981

Cooperative stretching vibration absorption in alkali cyanides

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(Received 12 September 1980)

In all four alkali cyanides (NaCN, KCN, RbCN, CsCN), a weak satellite absorption band at ν_c is found to accompany the second-harmonic CN^- stretching absorption ν_2 (in the 4100-cm^{-1} range). This satellite band (of width equal to that of the ν_2 band) shifts with temperature through the phases of various molecular order exactly parallel to $\nu_2(T)$, shares the stress-alignment dichroism of the ν_2 band, and is unaffected by variations in the crystal purity. These properties exclude a perturbed CN^- molecule as a possible origin of this band. The position of the satellite band at twice the fundamental frequency suggests strongly that it is caused by excitation of two vibrational excitons by a single photon. We believe this to be an example of a two-stage process in which the radiation field excites (virtually) a second-harmonic ($n=2$) vibration at one site, followed by a transition to a state of two vibrational excitons by virtue of a vibration-vibration interaction of two CN^- molecules. An example of a mechanism for the latter step is the electric dipole-dipole interaction. Indeed, the relative strength of the ν_c band varies strongly among the cyanides with CN^- spacing in a manner consistent with CN^--CN^- dipole-dipole coupling. Moreover, an experiment with ^{13}C-enriched KCN provides a critical test of the validity of our assignment. A theoretical model is presented which is able to account for the overall features of the observations, though the use of the bare electric dipole-dipole coupling Hamiltonian leads to a predicted intensity lower than observed by ~ 6.8. We suggest that vibration-vibration modulation of the Born-Mayer repulsive interaction may be responsible for the difference. The experiments, and our preliminary theoretical analysis, give us confidence in the claim that this is the first conclusive experimental observation of a cooperative vibrational absorption effect.

I. INTRODUCTION

The phenomenon of *cooperative optical absorption*, the absorption of a single photon by a *pair* of excitons, has been the subject of theoretical interest.[1–4] It is based on the fact that the two-particle coupling between atoms can cause the energy of a photon to be shared between two excitons by virtue of an excitation process at both atoms. Experimentally, the creation of two exciton states by a single photon in solids has been clearly demonstrated for electronic excitations.[5(a)] Multiphonon—one-photon absorption has been identified,[5(b)] arising from the linear coupling between the phonon and photon fields, in conjunction with repeated phonon-phonon anharmonic interactions. Two-phonon structure is well known from Raman scattering experiments, where of course two photons are involved.[5(c)] Our study concerns two vibrational exciton—one-photon absorption. Because this process proceeds by virtue of the linear vibration-photon interaction, supplemented by two-site couplings (e.g., the electric dipole-dipole interaction), we refer to it as cooperative *vibrational* absorption in analogy with the electronic case.[5(a)] Conclusive experimental evidence for the existence of cooperative vibrational absorption, however, has been missing so far. The only possible observation of such an effect, as far as we are aware, has been reported in a short note by Ron and Hornig,[6] who attributed an unexplained peak in the first overtone spectrum of crystalline HCl to an excitation of a pair of HCl molecules. Its large intensity relative to the second harmonic band, and the absence of any further systematic variations or tests, make this assignment rather tentative.

In the course of an extended study of the CN^- stretching excitation in alkali cyanides with ir and Raman techniques,[7] we have discovered and studied an absorption effect, which, in our opinion, gives conclusive evidence for excitation of two vibrational excitons for the first time. Alkali cyanides—NaCN, KCN, RbCN, and CsCN—at room temperature are pseudo cubic and "alkali-halide-like," because of reorientational averaging of all CN^- molecular anisotropies. The high-purity and transparent single crystals undergo towards low-temperature disorder-order phase transitions, in which the molecules align parallel in terms of their elastic and/or electric dipole moments, producing a light-scattering multidomain structure of lower symmetry.[8] The high concentration of CN^- molecules in these systems allows for study of the CN^- stretching response not only in its fundamental (ν_1), but also in its second (ν_2) and third (ν_3) harmonic excitations. Infrared and Raman measurements of these excitations through the various crystal phases, and their treatment within an anharmonic oscillator model, give detailed insight into the molecular dynamics and order processes. This extended work will be published elsewhere.[7] We concentrate here on material related to two vibrational exciton absorption, which developed as a sideline to this larger work.

II. EXPERIMENTAL RESULTS

Figure 1 displays the infrared spectra in the range of the second-harmonic stretching absorption for the four investigated alkali cyanides, measured in the low-temperature phase of parallel molecular order. The position of the second-harmonic stretching band (ν_2) is found to shift systematically with increasing alkali-ion size towards lower energies. A corresponding shift (one-half in size) is observed for the fundamental stretching frequencies ν_1 of these systems, which are not shown here but tabulated (together with the ν_2 values) in Table I. In spite of the considerable variation of ν_1 and ν_2 with the substance, the difference between $2\nu_1$ and ν_2 remains nearly exactly constant, being $2\nu_1 - \nu_2 = 22.5 \pm 1.5\ \text{cm}^{-1}$. This shows that the anharmonicity (which gives rise to the second-harmonic ν_2 absorption) is determined by the intramolecular C—N binding, and is essentially unaffected by the crystal environment. The shift of ν_1 and ν_2 with substance variation is therefore *not* due to changing anharmonicity but due to a changing force constant of the CN^- oscillator. In agreement with this observation, the relative strength of the

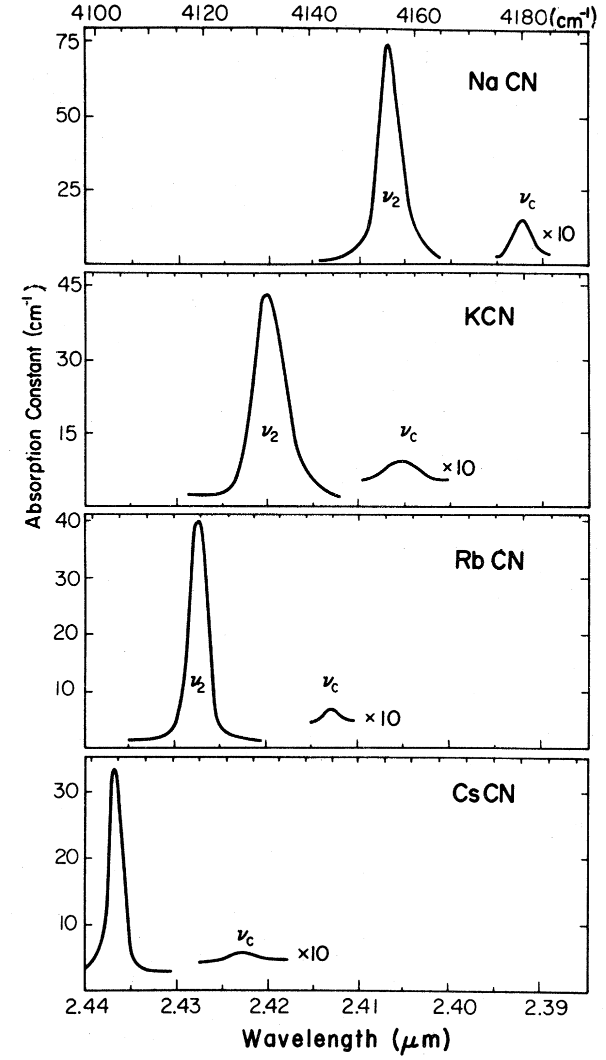

FIG. 1. Low-temperature absorption spectra of the four alkali cyanides in the first overtone spectral range, showing the second-harmonic CN^- stretching absorption (ν_2) and the accompanying ν_c band (the latter expanded by a factor of 10).

TABLE I. Relevant quantities for the stretching absorption of the four alkali cyanides (a = lattice parameter, ν_1 and ν_2 = first- and second-harmonic frequency. ν_c = cooperative absorption frequency. $\nu_2^{\text{isot.}} = {}^{13}C^{14}N$ second-harmonic frequency. [ ] = integrated absorption strength.)

	NaCN	KCN	RbCN	CsCN
a (Å) (cubic phase)	5.58	6.51	6.81	4.29
ν_1 (cm^{-1})	2090	2077	2071	2063
ν_2 (cm^{-1})	4156	4131	4121	4103
$2\nu_1 - \nu_2$ (cm^{-1})	24	23	21	23
$[\nu_1]:[\nu_2]$	113	120	106	122
$2\nu_1$ (cm^{-1})	4180	4154	4142	4126
ν_c (cm^{-1})	4181	4156	4145	4127
$[\nu_c]:[\nu_2^{\text{isot.}}]$	1.30	0.58	0.43	0.62

first- and second-harmonic absorption has been found to be rather constant (see Table I) among the four cyanides.

In all four materials, a weak satellite absorption band is observed on the high-energy side of the ν_2 band, as displayed—in 10 × extended scale—in Fig. 1. The width of this band, which we will call the ν_c band, is approximately twice that of the ν_1 band to within experimental accuracy. An extremely weak sideband like the ν_c absorption in a vibrational spectrum can arise from two possible "trivial" effects: (a) A small amount of CN^- ions in a "perturbed surrounding," which causes a shift of the stretching eigenfrequency; and (b) a combination of stretching excitation and some other (rotational or translational) excitation of the system. To exclude these two "trivial" explanations of the ν_c bands, several variations and experiments were conducted.

(i) Variation in the crystal purity (reagent-grade, highly-zone-refined and impurity-doped material) produced no measurable change in the relative strength and peak position of the ν_c bands. This excludes the possibility that these bands could be caused by a small number of CN^- molecules which are attached to chemical impurities, and therefore display a shifted stretching absorption. This conclusion is further supported by the fact that no indication for the existence of a perturbed ν_1 excitation was found in any crystal in the spectral range of the fundamental ν_1 absorption.

(ii) Figure 2 shows—for the cases of KCN and NaCN—the measured peak position of the ν_2 and ν_c band as a function of temperature. The two phase transitions of the system show up clearly as abrupt changes in the vibrational frequency: At T_{c1} a first-order phase transition produces ferroelastic order of the molecular system, while below T_{c2} a second-order phase transition produces electric dipole ordering of the molecules. The frequency shifts caused by these ordering processes, observed in the fundamental vibrational absorption ν_1, are found to be quantitatively reflected in the weak ν_c band (Fig. 2). This "replica behavior" suggests strongly that we are dealing in the ν_c band with a pure stretching excitation of CN^- molecules, which participate fully in the ordering processes of the molecular system.

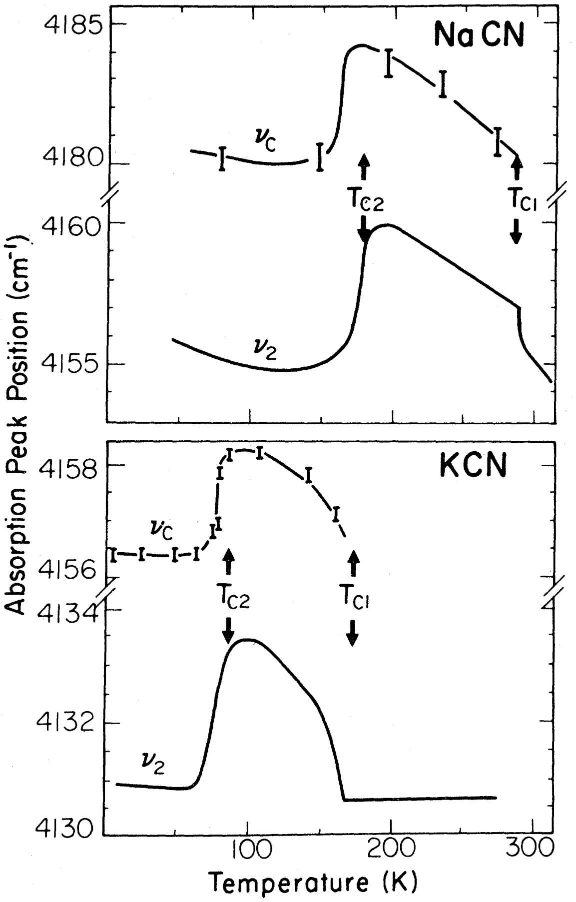

FIG. 2. Peak position of the ν_2 and ν_c bands of NaCN and KCN as a function of temperature. The critical temperatures of the two order-disorder phase transitions are indicated by T_{c1} and T_{c2} for both materials.

(iii) In the ordered phase below T_{c1}, the CN^- ions are arranged parallel in domains, which have their axes close to the six ⟨110⟩ orientation of the originally cubic crystal. Application of uniaxial stress can produce alignment of these domains, leading to the appearance of dichroism in the optical absorption.[9] The inserts of Fig. 3 illustrate for two stress geometries ($S_{[100]}$ and $S_{[110]}$) the expected alignment effect of the domain axes, and shows how a light beam propagating perpendicular to S can monitor the alignment by measuring the optical dichroism. The curves in Fig. 3 show the corresponding measured spectra in the range of the second-harmonic absorption. For the $S_{[100]}$ case [Fig. 3(a)], the absorption difference for light polarized ∥ and ⊥ to the stress measures directly the achieved alignment ratio. In the $S_{[110]}$ geometry [Fig. 3(b)], the molecules become aligned in the direction of light propagation, so that the stretching absorption (for unpolarized light) decreases compared to the unaligned case. As can be seen from the dichroism of the ν_2 band, an alignment ratio of better than 10:1 is achieved in both cases. The important result for our consideration is the fact that the small ν_c band shows the same dichroism as the ν_2 band. This proves beyond doubt that the ν_c *excitation is polarized parallel to the* CN^- *molecular axis,* like a normal stretching excitation. In particular, this experiment excludes the possibility that the ν_c band could be produced by a *combination of stretching and rotational excitation* of the CN^- molecule. Sideband spectra due to such a combination effect are indeed observed at larger splittings from the stretch band (40–200 cm^{-1} in KCN),[10] and show a different dichroism under stress alignment, compatible with an excitation polarized perpendicular to the molecular axis.[11]

Because of the large width of the stretching absorption in the high-temperature cubic phase, the ν_c band can be separated and detected only in the low-temperature phases (Fig. 2). *Domain walls* are always present in these phases, and one could suspect that CN^- molecules in the perturbed region of domain walls could have a shifted stretching frequency and might give rise to the ν_c band. The full participation of the ν_c band in the stress-alignment dichroism excludes this possibility.

If, in fact, the ν_c band would originate from a second-harmonic excitation of perturbed CN^- molecules with shifted eigenfrequencies, it is evident that a very much stronger first harmonic of this band would be expected on the high-energy side of the CN^- stretching fundamental ν_1. No band of this type is observed, i.e., the ν_c band has no first harmonic counterpart in the fundamental absorption spectrum.

A final conclusive experiment was performed on a crystal grown from KCN material, in which the natural abundance of ^{13}C isotopes (1.1 at. %) was enriched to a level of 33 at. %. Figure 4 shows the infrared absorption spectrum of this crystal at 70 K in the overtone region of the stretching absorption. The most prominent bands are, as expected, the absorptions due to the second-harmonic stretching motion of $^{12}C^{14}N$ and $^{13}C^{14}N$ molecules, located at 4131 and 4147 cm^{-1}, respectively. Their relative integrated strengths α were found to be $\alpha[^{13}C^{14}N]:[^{12}C^{14}N] = 0.48 \pm 0.03$, in agreement with the expected 33 at. % isotope enrichment of this material. A much

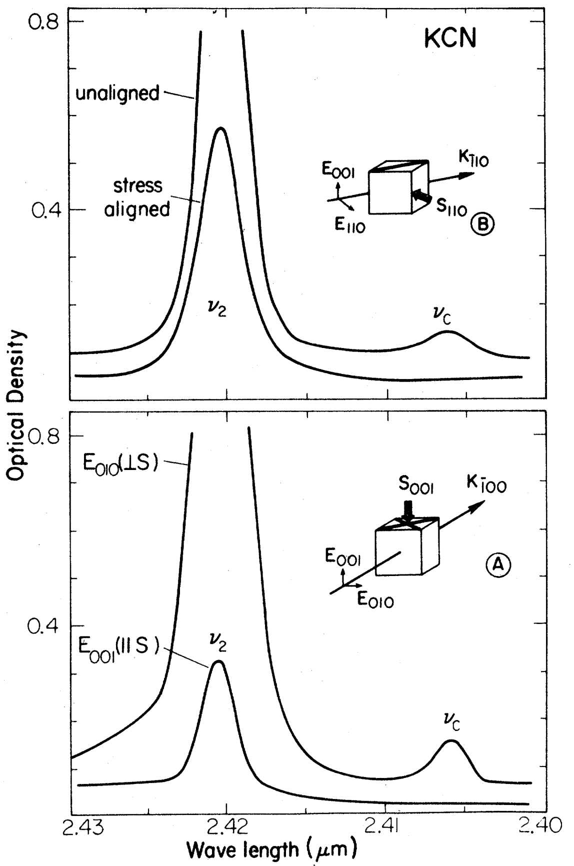

FIG. 3. Absorption spectra and dichroism in the region of the ν_2 and ν_c absorption, after stress alignment of the domains in the ferroelastic phase. The inserts illustrate the geometry of stress S, light propagation K, and light polarization E, and indicate the domain-axis orientations, which are accumulated by the stress alignment.

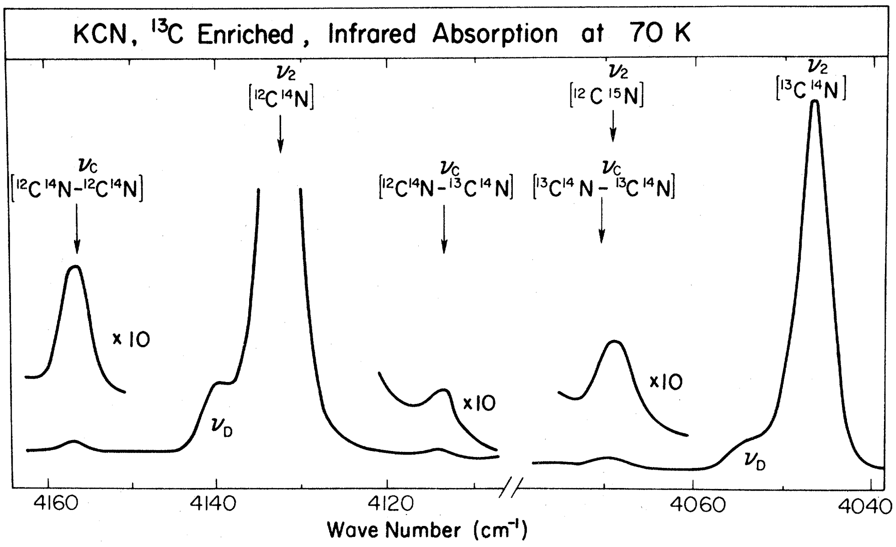

FIG. 4. Infrared absorption in the overtone region of the CN^- stretching, measured at 70 K in a KCN crystal grown from material with ~30% ^{13}C enrichment.

smaller second-harmonic absorption band, due to the 0.3 at.% naturally present $^{12}C^{15}N$ molecules, appears as expected at 4068 cm^{-1}. Aside from these three second-harmonic absorption bands from molecules with the three types of isotopes, we observe two small satellite absorptions: The ν_c band at 4156 cm^{-1} seen already before (Fig. 1) in the KCN crystals with natural isotope abundance, and a new ν_c band at 4113 cm^{-1}, which is not present in the nonisotope-enriched material. The analysis of position and relative strengths of these isotope-induced ν_c bands, performed in the next section, supplies the most conclusive proof for the nature of the ν_c absorption process.

It should be mentioned that the ν_c band could *not* be observed with Raman techniques. This is not surprising, because in Raman measurements the whole second-harmonic CN^- stretching response is extremely weak compared to the fundamental. While in infrared measurements the $[\nu_1]$:$[\nu_2]$ strength ratio is of the order of 10^2 (Table I), the same ratio in Raman is of the order of 10^4, so that the main second-harmonic ν_2 band is barely detectable above the noise. Evidently a ν_c excitation, which should be at least two more magnitudes smaller than ν_2, is undetectable in Raman scattering.

III. DISCUSSION

The experiments in Sec. II show definitely that the ν_c band, observed in four alkali cyanide crystals, is an intrinsic excitation of the unperturbed pure CN^- system, with a transition dipole moment polarized parallel to the CN^- molecular axis. We postulate that the *ν_c band is caused by excitation of two vibrational excitons of equal and opposite wave vector, from absorption of a single photon.*

For a simple theoretical description of this process, consider a pair of CN^- molecules in the crystal at sites i and j. In the *absence of any coupling* between the two molecules, the vibrational eigenstates of each molecule will be that of single-particle anharmonic oscillators in the $n=0,1,2,\ldots,$ vibrational state. The uncoupled eigenstates of the system are denoted by $|n_i,n_j\rangle$ with energy $E(n_i,n_j)$, where n_i,n_j labels the vibrational quantum number of the CN^- molecule at sites i,j, respectively. The oscillator strength f for absorption transitions (first-, second-, $\ldots$, harmonic transition $\nu_1,\nu_2,\ldots,\nu_n$) between these states depend on the relevant matrix element for each individual cyanide molecule. The anharmonicity of the molecular oscillator determines both oscillator strength of the second-harmonic transition ($f_{0,0\rightarrow0,2}$) and the downward shift Δ_0 of the second-harmonic state $|0_i,2_j\rangle$ compared to the double fundamental frequency. The $|1_i,1_j\rangle$ state, in which both molecules i and j are in the first excited state, cannot be reached by the absorption of a single photon, but only by two individual photon absorption processes at each molecule.

When the two site interaction energy is taken into account, a double vibrational excitations to the $|1_i,1_j\rangle$ final state can be reached because of the following t matrix (which will dominate for the systems we are considering):

$$t_{0,0\rightarrow1,1}=\frac{H_{\text{int}}|\text{intermediate}\rangle\langle\text{intermediate}|H_{\text{rad}}}{E_0-E_{\text{intermediate}}}\ , \quad (1)$$

where the sum over intermediate states is understood. H_{rad} is the interaction between the CN^- vibrational electric dipole and the external radiation field, H_{int} a two site (e.g., electric dipole-dipole) interaction, E_0 the initial system energy, and $E_{\text{intermediate}}$ the intermediate state energy. This process has been treated in extensive detail by Jortner and Rice.[4] The matrix element of the t matrix takes the form

$$\langle\ \text{final}\ |t_{0,0\rightarrow1,1}|\ \text{initial}\ \rangle$$

$$=\sum_{i<j}\frac{\langle1_i,1_j|H_{\text{int}}|0_i,2_j\rangle\langle0_i,2_j|H_{\text{rad}}|0_i,0_j\rangle}{\hbar\Omega_{\vec{q}}-[E(0_i,2_j)-E(0_i,0_j)]}\ , \quad (2)$$

where $\hbar\Omega_{\vec{q}}$ is the energy of the incident photon. On the energy shell, $\hbar\Omega_{\vec{q}}=E(1_i,1_j)$ so that the energy denominator in Eq. (2) becomes $\Delta\equiv E(1_i,1_j)-[E(0_i,2_j)-E(0_i,0_j)]$. This is small for the systems we investigate here, equal to 25 cm^{-1} for $(^{12}C^{14}N)^-$ pairs. The absorption intensity relative to that for direct second-harmonic excitation, W_c/W_2, apart from numerical factors arising from multiple-site contributions, is

$$\frac{W_c}{W_2}\propto\left(\frac{\langle\text{final}|t_{0_i,0_j\rightarrow1_i,1_j}|\text{initial}\rangle}{\langle0_i,2_j|H_{\text{rad}}|0_i,0_j\rangle}\right)^2$$

$$=\left(\frac{\langle1_i,1_j|H_{\text{int}}|0_i,2_j\rangle}{\Delta}\right)^2\ . \quad (3)$$

For neighboring CN^- molecules along a [110] direction in NaCN, for example, the numerator is approximately 0.5 cm^{-1}, while from above $\Delta=25$ cm^{-1}. This means that $W_c/W_2\simeq4\times10^{-4}$. We shall show below that this estimate is about an order of magnitude too low when numerical factors are included (e.g., summing over neighboring sites). Nevertheless, Eq. (3) is a useful expression for getting a feel of the strength of the effect.

To obtain the fully correct result for the intensity of this process is to recognize the two vibrational exciton character of the final states. Following the notation of Jortner and Rice,[4] this can be written as

$$|\Psi_{\vec{K},\vec{K}'}\rangle=\frac{1}{[N(N-1)]^{1/2}}$$

$$\times\sum_{i,j}\exp[i(\vec{K}\cdot\vec{R}_i+\vec{K}'\cdot\vec{R}_j)]|1_i,1_j\rangle\Delta_{i,j}\ , \quad (4)$$

where $\Delta_{i,j} = 1 - \delta_{i,j}$ and

$$|1_i, 1_j\rangle = |0_1, 0_2, \ldots, 1_i, 0_{i+1}, \ldots, 1_j, 0_{j+1}, \ldots, \rangle \;.$$

The intermediate state is

$$|\Psi_{\vec{q}}\rangle = \left(\frac{1}{N}\right)^{1/2} \sum_i [\exp(i\vec{q}\cdot\vec{R}_i)]|2_i\rangle \;, \qquad (5)$$

where

$$|2_i\rangle = |0_1, 0_2, \ldots, 2_i, 0_{i+1}, \ldots, \rangle$$

and $\vec{q}$ is the photon wave vector. We write

$$H_{\text{rad}} = \sum_i H_{\text{rad}}(i) \;,$$

$$H_{\text{int}} = \sum_{i<j} H_{\text{int}}(i,j) \;,$$

so that the full t matrix becomes

$$t_{0,0\to1,1} = \sum_{i'<j',i} \frac{H_{\text{int}}(i',j')|\Psi_{\vec{q}}\rangle\langle\Psi_{\vec{q}}|H_{\text{rad}}(i)}{\hbar\Omega_{\vec{q}} - (E_q - E_0)} \;. \qquad (6)$$

The absorption intensity is found from the golden rule expression for the transition probability per unit time. We shall ignore final state interactions associated with possible changes in $CN^- - CN^-$ interactions when interacting molecules are both in their $n=1$ vibrational state, as compared to one being in the $n=0$, the other in the $n=1$, vibrational states. These are known to be important, for example, in the two-magnon spectra of antiferromagnets.[12] We find,

$$W_c = (2\pi/\hbar) \sum_{\vec{K},\vec{K}'} |\langle\Psi_{\vec{K},\vec{K}'}|t_{0,0\to1,1}|\Psi_0\rangle|^2 \delta(\hbar\Omega_{\vec{q}} - E_{\vec{K}} - E_{\vec{K}'}) \;. \qquad (7)$$

After considerable algebra, choosing i' as the origin, and letting $j' = i' + \delta$, the transition probability per unit time for absorption of a photon of energy $\hbar\Omega_{\vec{q}} = E_{\vec{K}} + E_{-\vec{K}}$ [the state (4) has energy $E_{\vec{K}} + E_{\vec{K}'}$, and we have used the summation over sites to require $\vec{K} + \vec{K}' - \vec{q} = 0$, and then neglected the photon wave vector $\vec{q}$] is proportional to

$$W_c = (\tfrac{1}{2}N) \sum_{\vec{K}} \left[2 \sum_\delta \langle 1_0, 1_\delta|H_{\text{int}}(0,\delta)|2_0, 0_\delta\rangle \frac{\langle 2_0, 0_\delta|H_{\text{rad}}(0)|0_0, 0_\delta\rangle \exp(i\vec{K}\cdot\delta)}{E_{\vec{K}} + E_{-\vec{K}} - E(0,2)} \right]^2 \;, \qquad (8)$$

where $\vec{\delta}$ is the position vector from the origin to the site labeled by δ, and we have ignored terms in $\vec{q}\cdot\vec{\delta}$. The form of Eq. (8) allows for an immediate simplification in the limit of small exciton bandwidth. We are allowed to pass to this limit by virtue of the rough equality in linewidth of the ν_c band as compared to twice the ν_1 band linewidth. Under such a condition, the absolute square in Eq. (8) leaves only terms of the form

$$W_c = 2 \sum_\delta \left[\langle 1_0, 1_\delta|H_{\text{int}}(0,\delta)|2_0, 0_\delta\rangle \frac{\langle 2_0, 0_\delta|H_{\text{rad}}(0)|0_0, 0_\delta\rangle}{2E(0,1) - E(0,2)} \right]^2 \;, \qquad (9)$$

where use has been made of the relation $\sum_{\vec{K}} \exp(i\vec{K}\cdot\vec{r}_{ij})\delta_{\vec{r}_{ij},0}$. Thus, the intensity of photon absorption for two vibrational excitons is simply a sum of absorption intensities over sites δ connected by H_{int} with the origin. This would certainly not be the case if the exciton bandwidth were appreciable (greater than twice the width of the ν_1 transition) because of the dependence of the denominator in Eq. (8) on exciton wave vector $\vec{K}$. In such a case, the sum of cross terms in Eq. (8) would not vanish and one would need to evaluate the exciton Green's function explicitly, as done in Ref. 12.

The more interesting quantity, because it is directly measurable, is the ratio of Eq. (9) to the second-harmonic absorption intensity W_2. One finds

$$\frac{W_c}{W_2} = \frac{2}{\Delta^2} \sum_\delta |\langle 1_0, 1_\delta|H_{\text{int}}(0,\delta)|2_0, 0_\delta\rangle|^2 \;, \qquad (10)$$

where as before

$$\Delta = E(1_0, 1_\delta) - [E(0_0, 2_\delta) - E(0_0, 0_\delta)] \;.$$

We can now proceed to analyze our results using Eq. (10) to obtain a quantitative comparison with experiment.

A. Energy position of ν_c bands

In Table I we summarize and compare various experimental quantities which are relevant for our discussion. The given fundamental (ν_1) and second-harmonic (ν_2) frequencies are averaged values from infrared and Raman measurements. As these values have an absolute accuracy of about ±1 cm^{-1} they give values for the double fundamental frequency ($2\nu_1$) with an error of about ±2 cm^{-1}. The absolute accuracy for the ν_c band position is ±1 cm^{-1}.

As can be seen, the measured ν_c values in all four alkali cyanides lie extremely close to the double fundamental frequency $2\nu_1$. The deviation $\nu_c - 2\nu_1 = +2 \pm 1$ cm^{-1} lies within the experimental errors mentioned above, though the consistent small positive value of this deviation appears to be a real effect. We believe this could result from exciton dispersion, leading to photon absorption at $2E_{\vec{K}} > 2\nu_1$. As will be shown below, the absorption intensity for the ν_c band will result in a requirement that $\langle H_{\text{int}} \rangle \simeq 1$ cm^{-1}. Because $\langle H_{\text{int}} \rangle$ is also of the order of the exciton bandwidth, it is conceivable that this deviation is a manifestation of exciton dispersion.

We remark in passing that Jortner and Rice[4] attribute a shift in the two vibrational exciton absorption to a repulsion between the $|1,1\rangle$ and a symmetrized $|2,0\rangle$ state localized on neighboring CN$^-$ molecules. This is incorrect in principle because the final state to which optical transition is made is that of spatially separated excitons of equal and opposite wave vectors. Indeed, the difference in interaction energy at the site of two-exciton excitation will have an effect on the optical absorption spectrum, but this will arise from an alteration of the intensities of the relative contributions of the various $\vec{K}$, rather than their frequencies. In other words, the double excitation density of states for the vibrational excitons will be modulated by a $\vec{K}$ dependent weighting factor. In the case of two magnon absorption[12] this can lead to an absorption peak within the two magnon excitation band, with a shape quite different from the bare double excitation density of states. The narrow bandwidth of the alkali-cyanides makes such a calculation unnecessary. However, for HCl, where $\langle H_{\text{int}} \rangle$ will be shown to be ~ 8 cm^{-1}, one must include these "final state interactions" in the calculation of the optical absorption spectrum. We intend to report the results of such a calculation in the future.

For the case of the alkali cyanides, the small absorption intensity at ν_c, leading to small exciton dispersion, is consistent with our conclusion that *the energy position of the cooperative* $|1,1\rangle$ *should coincide with the double fundamental energy value within experimental accuracy, as it is observed.*

The most crucial test for the validity of the cooperative absorption comes from the experiment with ^{13}C enriched material. Here one should observe a ν_c band not only due to excitation of $[^{12}\text{C}^{14}\text{N}]_2$ pairs, but additionally due to $[^{12}\text{C}^{14}\text{N} - {}^{13}\text{C}^{14}\text{N}]$ and $[^{13}\text{C}^{14}\text{N}]_2$ pairs. As the fundamental stretching frequency of ^{13}C^{14}N molecules is shifted from that of ^{12}C^{14}N molecules downwards by 41 cm^{-1} to a value of 2036 cm^{-1}, we expect to see the additional combination effects:

$$\nu_c[^{13}\text{C}^{14}\text{N} - {}^{12}\text{C}^{14}\text{N}] = 2077 + 2036 = 4113 \text{ cm}^{-1} ,$$

$$\nu_c[^{13}\text{C}^{14}\text{N} - {}^{13}\text{C}^{14}\text{N}] = 2036 + 2036 = 4072 \text{ cm}^{-1} .$$

These two predicted positions are indicated in Fig. 4. At 4113 cm^{-1}, we indeed observe a small band, which is *not* present in material with natural isotope abundance. This clear observation of a new band with the exact combination frequency of the two different CN$^-$ isotopes, is possibly *the* most convincing proof for the validity of the cooperative absorption picture. Unfortunately the predicted position for the $[^{13}\text{C}^{14}\text{N}]_2$ pairs coincides nearly exactly with the second-harmonic absorption of the (0.37% naturally abundant) ^{12}C^{15}N molecules (Fig. 4), so that the observation of this (extremely small) band is obscured.

B. Relative variation of ν_c-band intensity with host material

Our simple model predicts that the intensity of the ν_c band, relatively to that of the second-harmonic absorption, should vary with $[\langle 1_i, 1_{i+\delta} | H_{\text{int}} | 0_i, 2_{i+\delta} \rangle / \Delta]^2$, Eq. (3). In the four investigated cyanide materials, the splitting energy Δ (or, in other words, the anharmonicity of the stretching motion) is essentially constant ($\Delta = 22.5 \pm 1.5$ cm^{-1}; see Table I). Therefore the relative intensity variation of the ν_c absorptions should basically reflect the variation of the interaction matrix element.

In Fig. 5 we plot the relative intensity of the ν_c band observed in four alkali cyanides in a double logarithmic scale against the distance between neighboring CN$^-$ molecules. The most accurate measurement of the ν_c band is obtained experimentally by compar-

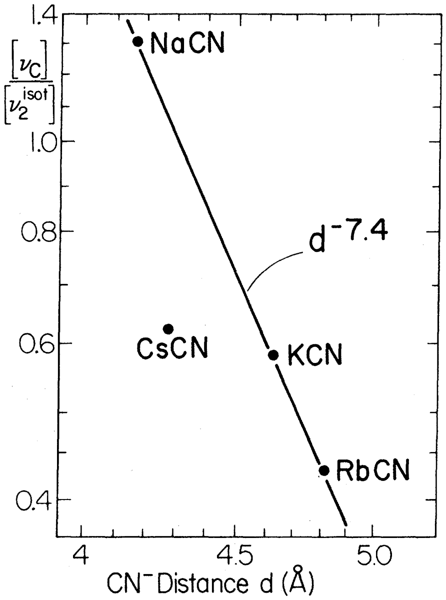

FIG. 5. Strength of the ν_c absorption band relative to the strength of the second-harmonic stretching band of ^{13}C^{14}N isotopes, plotted in double logarithmic scale for the four alkali cyanides.

ing it directly to the second-harmonic absorption band of the $^{13}C^{14}N$ isotopes. As both these bands are of about equal strength, they can be measured with high accuracy in the same sample and in the same scale of the spectrometer. For the three alkali cyanides with NaCl structure (NaCN, KCN, RbCN), we observe a monotonic variation of the normalized ν_c band intensity with the nearest-neighbor CN^- distance. (The CN^- distance d used in Fig. 5 is that in the high-temperature cubic phase of the material, which constitutes an average value for the actual nearest-neighbor distances in the low-temperature orthorhombic phase.) The monotonic variation of the ν_c band intensity in Fig. 5 can be fitted with a power law $\propto d^{-7.4}$, which should reflect the relative $[\langle H_{\mathrm{int}}\rangle/\Delta]^2$ dependence. This leads to a $\langle H_{\mathrm{int}}\rangle \propto d^{-3.7}$ relation, which is close to the d^{-3} dependence expected for the dipole-dipole interaction energy.

While in the cubic NaCl structure, a CN^- ion has 12 nearest and 6 next nearest CN^- neighbors, there are 6 nearest and 12 next nearest neighbors in the CsCl structure. Therefore it is not surprising that CsCN, the only material with a body centered CsCl structure, shows a ν_c band strength (or interaction energy V), which lies below the trend shown for the three cyanides with NaCl structure. [In fact, a summation over the squared interaction energies A/d^3 of all nearest and next nearest neighbors in both structures yields $\langle H_{\mathrm{int}}\rangle^2 \simeq 13(A/d^3)^2$ for the NaCl and $\langle H_{\mathrm{int}}\rangle \simeq 7.5(A/d^3)$ for the CsCl structure. The squared ratio of $\langle H_{\mathrm{int}}\rangle^2$ between both structures would be 1.8, which is close to the ratio between cyanides with NaCl and CsCl structure in Fig. 5.]

These very simple considerations neglect the angular dependence of the dipolar interaction, which surely is present too (we will return to this point under Sec. III D). Unquestionably, however, the pronounced dependence of the relative ν_c band intensity on CN^- distance and lattice structure is in qualitative agreement with the trends expected within the most simple dipole-dipole interaction model.

C. Variation of ν_c-band intensity with isotope exchange

While the variation of host materials allows one to test the ν_c-band dependence on a variation in $\langle H_{\mathrm{int}}\rangle$, isotope enrichment tests the predicted dependence of the ν_c band intensity on Δ. Figure 6 shows the levels of the second-harmonic excited states of $^{13}C^{14}N$ and $^{12}C^{14}N$ molecules in an energy diagram, as well as the levels of the three cooperative excited states which can be formed by pairing these molecules. Evidently, the two observed ν_c band cases (from $[^{12}C^{14}N]_2$ and $[^{12}C^{14}N-{}^{13}C^{14}N]$ pairs) involve very different Δ values which are effective for the mixing of the $|1,1|\rangle$ and $|2,0\rangle$ states. From Fig. 6 we see that the ν_c band intensity $[\propto (\langle H_{\mathrm{int}}\rangle/\Delta)^2]$ for the two isotope pairs should be

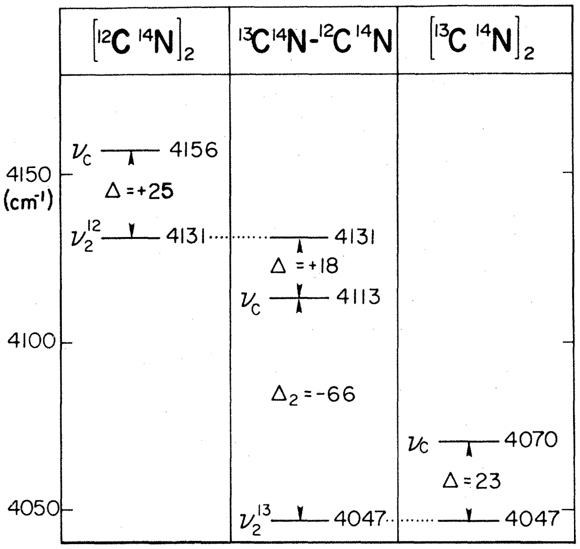

FIG. 6. Energy diagram (in units of cm^{-1}) of the excited state levels which are responsible for the second harmonic (ν_2) and the cooperative (ν_c) absorption, for a pair of $^{12}C^{14}N$ molecules, a mixed $^{12}C^{14}N-{}^{13}C^{14}N$ pair, and a $^{13}C^{14}N$ pair.

$$[^{12}C^{14}N]_2 \propto (2/25)^2\ ,$$

$$[^{12}C^{14}N-{}^{13}C^{14}N] \propto \left(\tfrac{1}{18}-\tfrac{1}{66}\right)^2\ ,$$

which yields a predicted ratio of intensities of 3.9. The ^{13}C enriched crystal possesses $\frac{1}{3}[^{13}C^{14}N]$ and $\frac{2}{3}[^{12}C^{14}N]$ molecules, so we expect

$$\begin{aligned}(\tfrac{2}{3})^2 &= \tfrac{4}{9}[^{12}C^{14}N]_2 \text{ pairs}\ ,\\ 2\cdot\tfrac{1}{3}\cdot\tfrac{1}{3} &= \tfrac{4}{9}[^{12}C^{14}N-{}^{13}C^{14}N] \text{ pairs}\ ,\\ (\tfrac{1}{3})^2 &= \tfrac{1}{9}[^{13}C^{14}N]_2 \text{ pairs}\ .\end{aligned} \qquad (11)$$

We have equal amounts of the first two pairs, so that the ν_c band intensity ratio should directly reflect the Δ variation, i.e., the above factor of 3.9. Experimentally, we observe in three different measurements ratios of 4.1, 3.9, and 2.9, which average to a value of 3.6 ± 0.4. This result coincides within the experimental accuracy to the expected value of 3.9, thus testing and confirming the Δ dependence of the cooperative absorption effect.

D. Absolute intensity of the cooperative absorption effect

Under Secs. III A–III C we have shown that the energy positions and the intensity variation with host lattice and isotope exchange of the ν_c bands exhibits a behavior in good agreement with the simple model for the cooperative absorption effect. The final remaining question is the *absolute strength of the cooperative effect.*

The coupling energy can be supplied by the electric and/or elastic interaction between the two molecular oscillators in the pair. The electric part of this energy per molecule is,

$$\langle H_{\text{int}} \rangle = 2\frac{\mu^2}{d^3} f(\theta) \tag{12}$$

with the dynamic electric dipole moment μ given by

$$\mu = \frac{\partial p}{\partial r} r_0 = \frac{\partial \mu}{\partial r}\left[\frac{\hbar}{2m\omega}\right]^{1/2} \tag{13}$$

(m being the reduced mass and ω the fundamental angular stretching frequency of the molecule). The factor of 2 in Eq. (12) arrives from the proper normalization of wave functions and matrix elements involved in the process. The transition dipole μ can be derived from the measured integrated absorption of the CN$^-$ fundamental stretch band. As the absorption band due to the abundant ^{12}C^{14}N isotopes is too intense to be quantitatively measured and integrated, we used the absorption strength of the less abundant ^{12}C^{15}N isotope assuming scaling of the relative absorption strength with the isotope abundance ratio. (This scaling was quantitatively checked and confirmed for the fundamental Raman stretching bands of the three CN$^-$ isotopes.) From the integrated absorption measured for N CN$^-$ molecules, the transition dipole moment μ can be derived[13] (taking properly into account that due to random dipole orientations effectively only one-third of the total CN$^-$ molecules contribute to the absorption of light for a given polarization direction). We obtain for the transition dipole moment

$$\mu \equiv \frac{\partial p}{\partial r} r_0 = 3.8 \times 10^{-2}\ \text{D} = 1 \times 10^{-2}\ e\ \text{Å} \ . \tag{14}$$

Using the appropriate values for m and ω, the vibrational amplitude r_0 of the CN$^-$ oscillator becomes $r_0 = 353 \times 10^{-2}$ Å, yielding for the dipole derivative (or effective charge) of the oscillator

$$\frac{\partial p}{\partial r} = 1.34\ \text{D/Å} = 0.28e \ . \tag{15}$$

The angular dependence $f(\theta)$ in Eq. (12) is determined by the angle θ between dipole axis and pair axis as

$$f(\theta) = 3\cos^2\theta - 1 \ . \tag{16}$$

For a "longitudinal" pair ($\theta = 0°$) of neighboring CN$^-$ molecules which have a distance of $d = 4.85$ Å in NaCN, we obtain $\langle H_{\text{int}} \rangle = 0.40$ cm^{-1}. As the strength of the ν_c band relative to the second-harmonic band [$W_c/W_2 = (\langle H_{\text{int}} \rangle/\Delta)^2$, Eq. (10)] is observed to equal 0.013, we would need (with $\Delta = 24$ cm^{-1}) an interaction energy of $\langle H_{\text{int}} \rangle = 2.7$ cm^{-1} to account for the strength of the observed effect. The energy estimated above on the basis of one pair of interacting electric dipoles is therefore too low by a factor of 6.7 and would produce an intensity lower by a factor $(6.7)^2 = 45$ compared to the observed one.

This large discrepancy is somewhat reduced, if one considers the fact that for a given molecule in the crystal (at site 0) not only one but many molecules at neighboring sites δ are available for the cooperative absorption process. Figure 7 illustrates the low-temperature orthorhombic structure of NaCN and KCN, and indicates the six different close pair configurations. In Table II we list, for the case of NaCN, the close pair distances d and the angles θ between dipole and pair axis. According to Eq. (10), the resulting total intensity for the cooperative absorption from all possible pair configurations compared to the single site second-harmonic absorption, W_c/W_2, will be given by a summation process over the squared interaction energies $\langle H_{\text{int}} \rangle$ for all ions on sites δ.

$$\begin{aligned} W_c/W_2 &= \frac{1}{\Delta^2}\sum_\delta \langle H_{\text{int}}(0,\theta) \rangle^2 \\ &= \frac{4\mu^4}{\Delta^2}\sum_\delta \left[\frac{3\cos^2\theta_\delta - 1}{d_\delta^3}\right]^2 \ . \end{aligned} \tag{17}$$

As can be seen from Table II, the two closest $\theta = 0°$ and $\theta = 90°$ neighbors account for the majority (77%) of the total effect. The eight neighboring dipoles on site 3 form an angle $\theta_\delta = 53°$, for which $3\cos^2\theta - 1 \simeq 0$ and therefore give no sizable contributions. Because of the strong (d_δ^{-6}) dependence, the neighbors

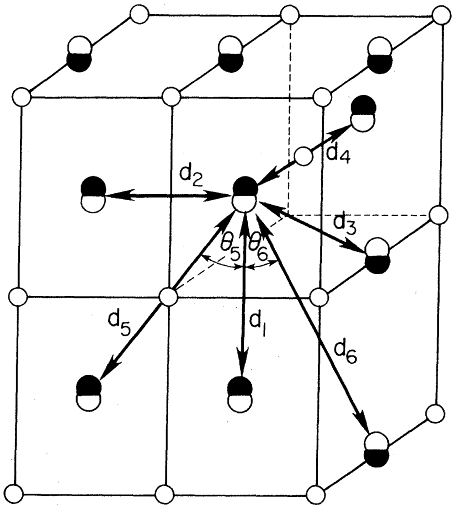

FIG. 7. Illustration of the low-temperature orthorhombic structure of NaCN and KCN, indicating the various close pair configurations of the CN$^-$ molecules with their pair distances d_δ and angle between dipole and pair axis θ_δ.

TABLE II. Relevant quantities for the summation of the squared dipole interaction energies between pairs of molecules at different sites δ (see Fig. 7), in NaCN. N_δ = number of equivalent pairs, d_δ = pair distance, θ_δ = angle between dipole and pair axis. Total: 1920×10^{-6} Å^{-6}.

Site	N_δ	d_δ (Å)	d_δ^{-3} (10^{-3} Å^{-3})	θ_δ	$3\cos^2\theta_\delta-1$	$N_\delta\left[\frac{3\cos\theta_\delta^2-1}{d_\delta^3}\right]^2$ (10^{-6} Å^{-6})
1	2	4.85	8.7	0°	+2.0	605.6
2	2	3.63	20.9	90°	−1.0	873.6
3	8	4.07	14.8	53.2°	+0.08	11.2
4	2	5.45	6.2	90°	−1.0	76.8
5	4	6.05	4.5	37°	+0.91	67.0
6	8	7.98	2.0	24.5°	1.5	72.0
7	4	6.55	3.5	90°	−1.0	49.0
8	2	7.26	2.6	90°	−1.0	13.5
9	2	9.90	1.0	0°	+2.0	8.0
10	8	8.14	1.8	53.2°	+0.08	0.1
Remainder of lattice						143.2

with large distance give only minor contributions and the sum in Eq. (17) converges rapidly, as shown in Table II. Compared to the case discussed above of a *single* ($\theta=0°$) pair at site 1, the summation over all pair configurations yields an increase a factor of 6.6 for the predicted relative strength of the cooperative absorption. This reduces the discrepancy between the observed and calculated intensity from a factor of 45 to a factor of $6.8=(2.6)^2$.

Doing a similar calculation as in Table II with the d_δ and θ_δ values for KCN yields a value for f_c which is lower by a factor 2.07 than the calculated value for NaCN. The observed ratio of the ν_c band intensity is $1.3/0.59=2.2$ (see Table I and Fig. 5). The relative variation with host lattice change is accounted for in our model.

It is difficult to see what could enhance the electric dipole-dipole interaction by a factor of 2.6 over its bare value to account for the experimentally observed relative absorption intensity W_c/W_2. Most dielectric effects tend to diminish the interaction strength [because they are proportional to $(\epsilon+2)/3\epsilon$, where ϵ is the dielectric constant], whereas an enhancement is necessary.

We suggest that the missing ν_c band strength is due to the complete neglect of elastic interaction effects in our calculation. It is well known from measurements of CN^- molecules diluted in an alkali-halide crystal that the *static* interaction due to the *elastic* dipole properties of the CN^- ions[14] is large compared to the rather weak *electric* dipole interaction. This general behavior remains valid under increase of the CN^- concentration as seen by the fact that the pure alkali cyanides exhibit a first-order ferroelastic ordering process at high temperatures, while electric dipole ordering occurs (if at all) only at low temperatures in a gradual way. It is reasonable to assume that the modulation of these static interaction energies by the stretching motion of the CN^- molecules produces a dynamic interaction effect, which has again a stronger elastic and weaker electric component.

Jortner and Rice[4] have analyzed an absorption found by Ron and Hornig[6] in the overtone spectrum of HCl in a similar way. Compared to our CN^- case, HCl has about a value of $\partial p/dr$ higher by a factor of 1.5, a reduced mass a factor of 6.6 smaller, an eigenfrequency higher by a factor of 1.33, and a distance between neighboring molecules of 4 Å. Compared to a longitudinal ($\theta=0°$) pair of molecules in NaCN ($d=4.85$ Å), the calculated electric dipole interaction energy for a ($\theta=0°$) pair of HCl should therefore be higher by a factor of $(1.5)^2\,6.6\,(1.33)^{-1}(4.85/4)^3\simeq20$, which would yield an interaction energy $\langle H_{\mathrm{int}}\rangle=(20)0.4\simeq8\ \mathrm{cm}^{-1}$.

Apparently, a numerical error in their calculation led to a value higher by nearly one order of magnitude, namely, 60 cm^{-1}. This large value was discussed in terms of its implications for "strong coupling" between the $|0,2\rangle$ and $|1,1\rangle$ states in HCl (though see our discussion in Sec. III A of this paper). With $\Delta = 90\ \mathrm{cm}^{-1}$ for this molecule, the large value of $\langle H_{\mathrm{int}}\rangle/\Delta = \frac{60}{90} = \frac{2}{3}$ would have produced the strong transfer of absorption intensity as required to interpret the observed band as a cooperative effect. (The measured overtone band, attributed to the ν_c absorption,[6] is stronger by a factor ~ 3 in integrated intensity compared to the band attributed to the second-harmonic absorption.) With the correct calculated value of $\langle H_{\mathrm{int}}\rangle = 8\ \mathrm{cm}^{-1}$, however, the relative intensity ratio for a pair would be predicted to be only $W_c/W_2 = (\frac{8}{90})^2 = 0.008$ (which would be slightly increased, like in our case, by summation over various pair sites in the crystal). This large discrepancy in relative intensity, and the fact that the Davydov splitting of the HCl fundamental has been completely neglected in the interpretation of the overtone spectrum, make it highly questionable that the observed strong HCl band is due to a cooperative absorption effect.

IV. SUMMARY

We have observed a weak satellite absorption band in four alkali cyanides at an energy double that of the fundamental absorption energy. We have assigned this band to an excitation of two vibrational excitons by a single photon. We have calculated the relative intensity of this absorption to the second-harmonic absorption. Measurements on ^{13}C isotopes give the predicted change in absorption intensity, verifying the form of the perturbation theory. We find that the bare electric dipole interaction gives an absorption amplitude too small by a factor of 2.6. However, the relative variation of the relative intensity between different alkali cyanides scales within experimental accuracy with the dipolar range dependence. These measurements, and their interpretation, give a convincing case for the observation of the cooperative vibrational absorption effect.

ACKNOWLEDGMENTS

The authors wish to acknowledge helpful correspondence with Professor S. A. Rice and Professor J. Jortner. Useful conversations with Mr. Hamid Hajiseyedjavadi are acknowledged. This research was supported by the U.S. National Science Foundation, the work at the University of Utah under Grant No. DMR 77-12675, the work at the University of California, Los Angeles, under Grant No. DMR 78-10312. One of the authors (L.C.S.C.) acknowledges personal support from PUC (Catholic University in Rio de Janiero, Brazil), and from the Conselho Nacional de Desenvolvimento Cientîfico e Tecnológico, Brazil.

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[1] D. L. Dexter, Phys. Rev. 126, 1962 (1962).

[2] L. N. Ovander, Sov. Phys. Solid State 4, 212 (1962).

[3] T. Miyakawa, J. Phys. Soc. Jpn. 17, 1898 (1962).

[4] J. Jortner and S. A. Rice, J. Chem. Phys. 44, 3364 (1965).

[5] (a) F. Varsanyi and G. H. Dieke, Phys. Rev. Lett. 7, 442 (1961); (b) M. Sparks and L. J. Sham, Phys. Rev. B 8, 3037 (1973); (c) J. R. Hardy and A. M. Karo, *Lattice Dynamics and Statics of Alkali Halides* (Plenum, New York, 1979), gives a good review and bibliography of the vast literature surrounding two phonon absorption and emission in Raman scattering experiments.

[6] A. Ron and D. F. Hornig, J. Chem. Phys. 39, 1129 (1963).

[7] L. C. Scavarda do Carmo, D. Durand, and F. Lüty (unpublished).

[8] Y. Kondo, D. Schoemaker, and F. Lüty, Phys. Rev. 19, 4210 (1979).

[9] L. C. Scavarda do Carmo and F. Lüty, International Conference on Defects in Insulating Crystals, Gatlinburg, Tennessee, October 1977 (available from the National Technical Information Service, U.S. Department of Commerce, 5285 Port Royal Road, Springfield, Virginia 22161), CONF771002, p. 379.

[10] L. C. Scavarda do Carmo and F. Lüty, Phys. Status Solidi B 89, K149 (1978).

[11] D. Durand, L. C. Scavarda do Carmo, A. Anderson, and F. Lüty, Phys. Rev. (in press).

[12] R. J. Elliott and M. F. Thorpe, J. Phys. C 2, 1630 (1969).

[13] G. Herzberg, *Molecular Spectra and Molecular Structure, I* (Van Nostrand, New York, 1950), p. 201.

[14] F. Lüty, Phys. Rev. 10, 3677 (1974).