Vibrational fluorescence from CN^- defects in 12 alkali halide hosts, pumped intracavity with F_B color-center laser

Klaus P. Koch,* Yihong Yang,[†] and Fritz Luty Physics Department, University of Utah, Salt Lake City, Utah 84112 (Received 14 November 1983)

Vibrational emission (around 4.8 μ m) of CN⁻ defects was detected and studied at 80 K in 12 different alkali halide hosts. By pumping the weak CN⁻ overtone absorption (at ~2.4 μ m) intracavity in a tunable $F_B(II)$ center laser, excitation spectra, relative intensities, and lifetime values of the vibrational emission were measured in all hosts. Variation in the CN⁻ defect concentration showed the existence of strong nonradiative luminescence quenching processes at CN⁻ concentrations above ~0.5%. This is interpreted to be due to intermolecular transfer and migration of the excitation energy to a "sink" with an efficient nonradiative decay channel. The pronounced observed effect of host material variation on the luminescence lifetime and intensity are discussed in terms of multiphonon or rotational models for relaxation processes, competing with the vibrational luminescence.

I. INTRODUCTION

Studies of the vibrational and rotational modes of simple molecules, embedded in dilute form—"matrix isolated"—in a solid-state environment, have been performed in primarily two types of hosts.

(a) Crystals of rare-gas atoms or molecules (such as N_2) in which the constituents are linked by weak and short-range bonds of the van der Waals type.

(b) Ionic crystals—most commonly used are the cubic alkali halides—in which the constituents are linked by a strong and long-range electrostatic interaction.

In both types of hosts, the guest molecule will be isolated on a substitutional site, if its dimension is roughly compatible with the dimensions of the constituents of the matrix lattice. For a large number of molecules, the intramolecular modes and the effect (normally rather small) of the solid environment on these modes have been studied in both van der Waal and ionic hosts. Owing to the change of mass and coupling constant by the substituted guest molecules, localized or resonance modes (with large vibrational amplitudes restricted to the vicinity of the molecular defect) can also be introduced into the crystal. These modes may or may not involve center-of-mass motion of the defect molecule.

Besides these translational modes, the rotational degrees of freedom of the molecular defect give rise to strongly localized rotational or librational modes. The height of the rotational barrier due to the interaction of the guest molecule with the surrounding host will decisively determine these types of localized modes. If the barrier is small or comparable to the free rotational energy of the molecules, almost free rotation will occur. With increasing barrier heights, the energy separation of the rotational levels increase, and hindered rotation and libration with decreasing angular amplitudes and increasing frequency will occur. The evolution of rotational-librational energies with the strength of a cubic potential has been studied theoretically by Devonshire¹ and Beyeler.²

In the weakly-coupled rare-gas matrices, nearly free rotation of the guest molecules is the rule, and libration is the exception. In the ionic crystals, on the other hand, higher rotational barriers producing strong angular localization and high-frequency—small-amplitude librational modes are the rule for most molecules, while weakly hindered rotation is the exception. CN^- molecules—the subject of this paper—substituted in certain hosts, belong to this exception.

A question of fundamental interest for all the systems of matrix-isolated molecules described is the following: If an intramolecular mode of the guest molecule, is excited, which has a high frequency compared to the phonons of the host, what is the mechanism of relaxation for this high-frequency localized mode? This question has, in recent years, been extensively studied in the rare-gas and in solid-N₂ matrices with weak van der Waals coupling.³ Four different decay channels (which may occur in any combination) must in principle be considered for the mode of an isolated molecule:

(a) Decay into multiphonon processes (which may involve also localized or resonance modes).

(b) Decay into lower-energy intramolecular modes (in the case of polyatomic molecules).

(c) Decay into rotational or librational modes.

(d) Decay by emission of a photon.

All these possible channels have been studied experimentally and theoretically in the van der Waals solids.³ We will focus on the question of their relative importance in Sec. IV. Owing to the large reduced mass m^* of a molecule compared to an electron and the infrared position of the vibrational frequency ω , the e^2/m and ω^3 factor in the expression for the radiative decay process (d) predicts transition rates for vibrational emission of 6–8 orders of magnitude smaller compared to allowed electronic emission in the visible range. This small transition rate makes

29 5840

it evident that nonradiative decay channels [(a)-(c)] of higher rates can easily quench the radiative transition, so that strong vibrational emission has been rarely observed in solids. One of the few examples is CO molecules isolated in rare-gas matrices, for which vibrational fluorescence with lifetimes in the millisecond range has been observed.⁴

In contrast to the rather well-studied van der Waal solid matrices, investigations into the vibrational relaxation kinetics of molecules in ionic solids have been very rare. Rebane and co-workers⁵ have investigated the vibrational (and rotational) relaxation effects of NO_2^- defects in alkalihalide hosts. By exciting the electronic transition (with vibrational-rotational substructure) and observation of hot luminescence, they could estimate vibrational relaxation times of NO_2^- molecules in the excited electronic state. Similar types of studies are currently under way on O_2^- defects in alkali halides.^{6,7} Moerner and co-workers⁸ have made extensive vibrational relaxation studies on the tetrahedral ReO₄⁻ molecule in alkali halides, which can be resonantly excited in its highest energy vibrational mode by CO₂ laser radiation. In all these studies very rapid $(10^{-11}-10^{-9} \text{ sec})$ relaxation processes have been found, discouraging any sizeable vibrational emission effect. For the ReO_4^- molecule it was shown⁸ that the rapid relaxation channel is due to decay of the excited mode into a combination of lower-energy vibrational modes of the tetrahedral molecule [channel (b)].

A simpler situation is presented for the case of diatomic molecules (such as OH^- , CN^- , ...), which have only one internal stretching mode, so that the decay channel (b) is not available. Moreover, the rotational behavior and modes of these dipole molecules have been extensively studied and clarified for many host materials. We have started a project of research into the vibrational relaxation kinetics of these simple model defects, with particular emphasis on the question of whether or not vibrational fluorescence [channel (d)] can be observed. As a first result, we have shown recently that CN⁻ defects in KCl can indeed emit vibrational fluorescence at the wavelength $(\sim 4.8 \ \mu m)$ of their stretching oscillation.⁹ In this work we used a very interesting but indirect excitation method for the molecular defect. After association of F centers to the CN⁻ defects, the stretching motion of the latter could be excited by optical pumping of the F centers. The perturbation effect of the neighboring F center on the CN⁻ molecule and its vibrational fluorescence, as well as the nature of the coupling or energy-transfer process between both entities, is not yet fully understood. In order to simplify this problem of the coupled defects and to study first the unperturbed vibrational fluorescence of isolated CN⁻ defects, we apply in this work as an alternative method direct internal excitation of isolated CN⁻ defects by pumping their vibrational overtone absorptions. The weak anharmonicity of the molecular potential determining the CN⁻ stretching motion produces, besides the strong fundamental v_1 (around 4.8 μ m), an overtone absorption v_2 around 2.4 μ m, about 2 orders of magnitude weaker in strength than the fundamental v_1 transition and shifted to low energies by $\sim 23 \text{ cm}^{-1}$ from $2v_1$. By pumping this weak overtone absorption with a tunable color-center laser, we have studied the vibrational emission of CN^- defects in 12 different alkali halide hosts. Together with variations in the concentration of the $CN^$ molecules, this broad survey establishes for the first time the conditions and important parameters for vibrational fluorescence in ionic solids.

II. EXPERIMENTAL APPARATUS AND TECHNIQUES

Single crystals from 12 different alkali halide hosts, doped with 1 mol % alkali cyanide in the melt, were grown in the Utah Crystal Growth Laboratory. For the KCl hosts, six crystals with different doping levels $(2 \times 10^{-4}, 4 \times 10^{-3}, 1 \times 10^{-2}, 2 \times 10^{-2}, 5 \times 10^{-2}, \text{ and}$ 10×10^{-2} CN⁻ in the melt) were also grown. The actual CN⁻ concentration in the crystal is about one-half of the nominal melt-doping concentration.

Tunable laser radiation covering the CN⁻ overtone absorption in all alkali halide hosts (2.38–2.47 μ m) can be conveniently supplied by an $F_B(II)$ -center laser.¹⁰. In preliminary experiments, an attempt was made to detect vibrational emission by pumping the CN^- overtone absorption of a KCl + 1% mole density CN^{-1} crystal with the tuned output beam of such a laser. Owing to the extremely weak absorption (optical density ~ 0.01), this attempt was unsuccessful. By applying evaporated gold layers on parallel faces of the sample and directing the laser beam in multiple reflection through this "cavity," the vibrational emission became detectable, though barely above the noise level.¹¹ The natural consequence of these preliminary tests was the decision to use the multiple-pass and power-increase properties of the laser cavity itself¹² for more effective pumping, and to insert the CN⁻-doped crystal intracavity for the final experiments.

Figure 1 shows the experimental setup used. The crystal intended as the active medium for laser emission (KCl + 3 mol % NaCl, additively colored with ~5×10¹⁶-cm⁻³ F centers) was attached to the cold finger of a cryostat, which forms the center of a folded (astigmatically corrected) laser cavity.¹³ Exposure of the crystal for 1 h at 230 K with 1 W of Ar⁺-ion (514 nm) laser light converts the F into F_B centers. This allows one to start the F_B -center laser at 80 K, pumped with either an Ar⁺or Kr⁺-ion laser in multiline operation. Using a 98.5% reflecting grating and a Burleigh system as an end mirror and tuning device, a small fraction of the tuned ir laser light could be coupled out and monitored by a PbS detector. Figure 2 shows in the upper trace a typical spectral tuning curve of this F_B -center laser arrangement. Continuous tuning between ~ 2.3 and 2.7 μ m with typical peak power of 80 mW (intracavity) was achieved. Absorption lines of water vapor, appearing in the low-energy spectral range, supply convenient means for wavelength calibration.

Test samples of the CN⁻-doped crystals (~3 mm thickness) were cut and polished, and attached as a sandwich to the F_B -center laser crystal, such that the visible and ir laser light passed through both crystals under Brewster's angle. The vibrational emission emerging from the CN⁻-doped test crystal was measured with a cooled InSb detector.



FIG. 1. Schematic illustration of the experimental setup for tunable intracavity pumping of vibrational emission.

III. EXPERIMENTAL RESULTS

The five lower curves in Fig. 2 display measured examples of F_B -center laser-tuning curves in the presence of various CN⁻-doped test crystals in the cavity. The weak CN⁻ overtone absorption-a single- or double-peak structure, shifting systematically with the lattice parameter of the host-shows up as pronounced dips in the laser-tuning curves. The nonlinearity of this intracavity absorption spectroscopy is evident. In spite of the extremely weak CN^{-} overtone absorptions (~0.01 optical density), these absorptions appear as pronounced power reductions of 10-25% in the tuning curves of the color-center laser. With this arrangement, vibrational emission could be detected in all crystals investigated. An increase of about 2 orders of magnitude in the vibrational emission is observed in this arrangement compared with external pumping using the ir laser output, dramatically demonstrating the advantage of increased power and multipass operation inside the cavity.

By tuning the F_B -center laser and recording the integrated vibrational emission strength using the setup in Fig. 1, excitation spectra of the CN⁻ vibrational emission were taken for all 12 CN⁻-doped host materials. (For quantitative analysis, the curves must be corrected for the strong wavelength dependence of the laser power.) Figure 3 shows examples of excitation spectra for four different hosts, selecting for illustration one example of each of the Na⁺, K⁺, Rb⁺, and Cs⁺ hosts. In all cases treated, the spectral shape of the excitation spectra (Fig. 3) and lossdip spectra (Fig. 2) coincide essentially, as expected.

The detection technique employed (chopped light and phase-sensitive lock-in amplification) allowed easy measurement of the vibrational emission lifetime τ . For all crystals investigated, the chopping frequency ν was varied (between ~5 and 1000 Hz) and the intensity $I(\nu)$ of the vibrational emission as well as the phase shift $\Delta\phi(\nu)$ between exciting and emitted light was recorded. Figure 4 shows, as examples for seven different hosts, measurements of these $\Delta\phi(\nu)$ and $I(\nu)$ variations. In all cases, an increase of $\Delta\phi$ and a decrease of I is observed with increasing chopping frequency ν . For a single exponential decay time τ of the luminescence we expect the wellknown¹⁴ dependence on the chopping frequency ν :

$$\tan\phi(\nu) = 2\pi\nu\tau , \qquad (1)$$

$$I(\nu) = \frac{I(0)}{\left[1 + (2\pi\nu\tau)^2\right]^{1/2}} .$$
⁽²⁾

As shown in Fig. 4, this predicted behavior (solid lines) can be fitted well to the experimental behavior. This fitting process of $\Delta \phi(\nu)$ and $I(\nu)$ yields values of the lifetime τ of the vibrational emission at the temperature of laser operation ($T \approx 80$ K). The $I(\nu)$ curves, extrapolated to low chopping frequency ν , yield for each crystal the static ($\nu \approx 0$) limit of the luminescence intensity I(0).

 CN^{-} -concentration variation was performed for the KCl host only, using crystals of six different dopings be-



FIG. 2. Spectral tuning curves of KCl: Na⁺ F_B -center laser with and without CN⁻-doped test crystals of different hosts sandwiched to laser crystal.

tween 10^{-4} and $5\!\times\!10^{-2}$ mole fractions. In Fig. 5 we display the measured phase shift $\Delta \phi$ as a function of the chopping frequency v for these six crystals. For CN⁻ concentrations up to 1 mol %, the $\Delta \phi(\nu)$ behavior is nearly independent of the CN⁻ concentration, indicating a rather constant lifetime τ . For higher CN⁻ concentrations, strong shifts of the $\Delta \phi(v)$ curves to higher frequencies occur. Parallel to these $\Delta \phi(v)$ measurements, the intensity of the vibrational emission was measured, and both results are summarized in Fig. 6 as a function of CN⁻ concentration in a double-logarithmic plot. As can be seen in this figure, the vibrational emission intensity increases roughly linearly with the CN⁻ concentration and has about constant lifetime up to $\sim 6 \times 10^{-3}$ mole fractions CN⁻, demonstrating that it is produced by independent additive contributions from noninteracting CN⁻ defects. Under further increase of the CN⁻ content by 1 order of magnitude, however, a drastic decrease (by ~ 2 or-



FIG. 3. Examples of excitation spectra of the CN⁻ vibrational emission in four different host crystals, obtained intracavity by tuning the F_B -center laser.



FIG. 4. Phase angle $\Delta \phi$ between exciting light and (a) vibrational fluorescence and (b) vibrational emission intensity *I*, measured at 80 K as a function of light-chopping frequency ν for CN⁻ defects in seven different hosts.



FIG. 5. Phase angle $\Delta \phi$ between exciting light and vibrational fluorescence, measured at 80 K as a function of lightchopping frequency ν for KCl:CN⁻ crystals of six different CN⁻ concentrations.

ders of magnitude) of the emission intensity occurs, accompanied by a parallel decrease of the lifetime τ . Both these effects together demonstrate clearly that nonradiative fluorescence-quenching processes become prominent in this concentration range, obviously based on CN^- interaction effects.

The results from Fig. 6, yielding a maximum efficiency of the vibrational emission around $[CN^{-}] \approx 5 \times 10^{-3}$ mole fractions, justify the constant use of this particular concentration for the second parameter variation, the host material environment of the CN⁻. Table I summarizes the data on relative emission intensity *I* and lifetime τ for 12 hosts, all obtained at 80 K. In order to eliminate the effects of the lifetime τ on the intensity of the chopped



FIG. 6. Relative intensity I and lifetime τ of CN⁻ vibrational emission at 80 K in KCl as a function of CN⁻ doping.

emission signal, the data in Table I were taken at (or extrapolated to) the "static limit" of very low chopping frequency $2\pi\nu < \tau_{\rm fluor}^{-1}$, where the signal becomes independent of ν . [See Fig. 4(b).] For comparison of emission strengths it must be noted that the CN⁻ overtone absorption shifts with host material variation relative to the F_B -center laser-tuning curve (Fig. 2), thus producing a variation in pump power when changing the hosts.

IV. DISCUSSION

We first summarize briefly the main concepts and results, obtained experimentally and theoretically in the much more extensively studied van der Waals systems. This will supply the framework for the discussion of the new results, obtained for the first time in ionic solids.

We focus on diatomic molecules, thus eliminating the

TABLE I. Relevant data for CN⁻ vibrational emission in 12 alkali halide hosts: (CN⁻) orientation, librational frequencies v_{libr} , emission lifetime τ_{fluor} , and relative intensity I_{fluor} (with the value for KBr chosen to be 1.0).

Host	CN ⁻ orientation	$\frac{\text{CN}^{-}}{\nu_{\text{libr}}} (\text{cm}^{-1})$	Vibrational $ au_{ m fluor}$ (msec)	Fluorescence I _{fluor}
NaBr	(100)	36 ^a	0.10	0.05
NaI	〈100〉	31ª	0.15	0.09
KCl	(111)	12,°15 ^b	5	2.3
KBr	(111)	12,°13 ^b	2	1.0
KI	(111)	11°	20	0.3
RbCl	(111)	19 ^c	8	5.2
RbBr	(111)	d	8	5.2
RbI	(111)	d	5	2.3
CsC1	d	d	9	4.5
CsBr	d	d	9	0.3
CsI	d	d	12	0.5

^air sideband of stretching mode (this work).

^bRaman, Ref. 23.

^cir sideband of stretching mode, Ref. 18.

^dQuestionable values.

effective relaxation channel (b) into lower energy intramolecular modes available for polyatomic molecules.⁸ We further restrict ourselves, initially, to very dilute molecular systems, thus excluding vibration-vibration energytransfer processes between molecules. The remaining nonradiative relaxation channels then are multiphonon processes (a) and decay into rotational or librational modes (c).

Various theoretical treatments of the multiphonon decay process have been done,^{15–17} based on coupling between molecule and medium linear in the intramolecular displacements and governed by short-range repulsive forces. Under simplified assumptions, this leads at low temperatures to an "energy-gap law," which in its simplest form predicts an exponential dependence of the relaxation rate τ^{-1} (phon) on the number N of the phonons (of energy ν_{phon}) necessary to relax the molecular mode ν_{mol} :

$$\tau^{-1}(\text{phon}) \propto \exp(-AN), \text{ with } N = \frac{\nu_{\text{mol}}}{\nu_{\text{phon}}}.$$
 (3)

For relaxation of the intramolecular mode into rotational modes one can show similarly that the relaxation rate $\tau^{-1}(\text{rot})$ should depend exponentially on the minimum number of rotational levels, matching the vibrational transition.¹⁸

Vibrational relaxation measurements on a variety of molecules in solid rare-gas and N₂ matrices³ did not display consistent agreement with the energy-gap law for multiphonon processes. They showed, however, for 13 different systems of molecules and hosts a rough exponential trend of the relaxation rate with the number of rotational levels matching the molecular mode.³ Crucial tests were supplied by isotope variations $H \rightarrow D$ in molecules such as NH and HCl, for which multiphonon and rotational relaxation models predict opposite effects on the relaxation rates. In all cases, it was found that $H \rightarrow D$ substitution decreases the relaxation rate, in agreement with the rotational and in opposition to the multiphonon relaxation model. Subsequent theoretical treatments could verify and explain the predominance of rotational over translational relaxation processes.¹⁸

Only for molecules with small splitting of the rotational levels is the nonradiative relaxation rate sufficiently low that radiative decay processes [channel (d)] can occur with reasonable efficiency. One of the few observed and thoroughly investigated cases is CO molecules in Ne and Ar, for which vibrational fluorescence with lifetimes in the $(10^{-2}-10^{-1})$ -sec range have been observed and studied.⁴ Our results on the vibrational fluorescence of CN⁻ in 12 alkali halide hosts represent the first quantitative experimental material which allows the application and testing of these concepts and results from van der Waal's solids to a molecule in an ionic crystal environment.

Vibrational relaxation rates are supplied in our experiments by the measured lifetime of the vibrational fluoresence $\tau_{\rm fluor}$. If no radiationless-decay processes are present, $\tau_{\rm fluor}$ would be equal to the radiative lifetime $\tau_{\rm rad}$, which can be calculated from the measured integrated vibrational absorption of a calibrated number of CN⁻ defects. For KCl hosts (the only carefully calibrated case) a value of $(4-5) \times 10^{-2}$ sec is expected.⁹ We assume—in the absence of accurate experimental data—that the matrix element for the CN⁻ vibrational absorption and emission is rather independent of the ionic host, so that $\tau_{rad} \approx 4-5 \times 10^{-2}$ sec is a representative value for all hosts.

In our experiments we find fluorescence lifetime values which span a wide range: from $\tau_{\rm fluor}=2\times10^{-2}$ sec in KI (close to the estimated $\tau_{\rm rad}$ value) down to $\sim10^{-5}$ sec in NaCl. Obviously, the fluorescence lifetime is shortened (from its maximum possible value $\tau_{\rm rad}$) by the presence of nonradiative processes of rate $\tau_{\rm nonrad}^{-1}$ according to

$$\tau_{\rm fluor}^{-1} = \tau_{\rm rad}^{-1} + \tau_{\rm nonrad}^{-1} \tag{4}$$

with the nonradiative rate varying strongly with host material. Since $\tau_{nonrad}^{-1} \gg \tau_{rad}^{-1}$ for basically all cases (except KI), the observed host variation of τ_{fluor} essentially reflects the host variation of τ_{nonrad} , so that $\tau_{fluor} \approx \tau_{nonrad}$.

In Fig. 7 we use the observed variation of the CN⁻ fluorescence lifetime with host materials to test possible correlations to the behavior expected for either multiphonon or rotational relaxation models. As the CN⁻ stretching frequency in the hosts treated varies by less than 2.5%, we can consider it as constant. In Fig. 7(a) we plot the logarithm of the measured fluorescence lifetime as a function of the number N of phonons, which are needed to match the molecular vibrational energy. This, however, can only be done by replacing the complex phonon spectrum of each host by some averaged effective phonon frequency, for which we take (as is done in most frequency theoretical treatments) the Debye [N=v(molecule)/v(Debye)]. As can be seen in Fig. 7(a), a reasonably good straight-line dependence is obtained, yielding the empirical relation



FIG. 7. Logarithmic plot of the measured lifetime τ_{fluor} of the vibrational emission vs the number N of the Debye frequencies matching the CN⁻-frequency (a), and vs the CN⁻ librational frequency (b) for various hosts.

 $\tau_{\text{fluor}} \approx \tau_{\text{nonrad}} = \tau_0 \exp(AN)$,

with
$$\tau_0 = 10^{-7}$$
 sec, $A = 0.54$. (5)

Before testing in Fig. 7(b) possible correlations to a rotational relaxation model, let us briefly review the rotational properties of CN⁻ defects. It was found, first by Seward and Narayanamurti,¹⁹ that the rotation of the CN⁻ molecule in potassium and rubidium halides is hindered by a rather weak crystal potential. This potential was shown—by elasto-optical 20,21 and Kerr-effect 22 measurements-to have minima in the (111) crystallographic direction. High-resolution ir (Refs. 20 and 21) and Raman²³ measurements revealed directly the groundstate splitting due to rotational tunneling. Owing to the weak crystal potential, the CN⁻ stretching absorption in these hosts at higher temperatures consists of an unresolved vibrational-rotation spectrum caused by the closely spaced hindered-rotor levels.¹⁹ This produces in our measurements at 80 K the broad absorptions (Fig. 3), which for KCl even shows a double structure, in close resemblence of the P- and R-branch absorptions of a free rotor.¹⁹ Nothing quantitative is known about the rotational properties and the potential minima for CN⁻ in the cesium halide hosts, but qualitatively all experimental indications point to a weak hindering potential similar to that in the potassium and rubidium halides. In contrast to all these hosts, CN⁻ in the sodium halides is localized in its orientation by a rather strong crystal potential,¹⁹ which has minima along the six $\langle 100 \rangle$ crystal directions²² and high rotational barriers.

Correlated to the different strengths of the rotational potential, the lowest librational excitation $v_{\rm libr}$ of the CN⁻ varies considerably with hosts, as expected from the Devonshire diagram.¹ Values of $v_{\rm libr}$ [as determined from stretching side bands measured with ir (Ref. 19) and Raman^{23,24} techniques] lie for the hosts with weak hindering potentials below 20 cm⁻¹, and for the hosts with strong potentials (the sodium halides) between 30 and 54 cm⁻¹. For NaBr and NaI hosts, we determined $v_{\rm libr}$ for the first time in this work by measurements of the librational combination band with the stretching absorption. The $v_{\rm libr}$ values, as far as they have been measured, are summarized in Table I.

It is difficult, however, to use these librational frequencies to test an energy-gap law, asking for the minimum number of libration-rotation levels J_m matching the molecular vibrational energy gap. In the rare-gas matrices with very weakly hindered rotation, a free-rotor model was used,³ yielding

$$J_m = (v_{\rm mol}/B)^{1/2} \tag{6}$$

(*B* being a rotational constant). In our case of the ionic crystal, the strength of the rotational potential varies strongly, producing a large variation in the values of librational energies. For an extremely strong rotational potential, the librational energies will approach the level structure of a torsional oscillator, producing approximately equal spacing. For this case, the minimum number of levels matching $v_{\rm mol}$ would be

$$J_m = v_{\rm mol} / v_{\rm libr} . \tag{7}$$

Our systems lie and vary between these extremes of a free rotor [Eq. (6)] and highly localized torsional oscillator [Eq. (7)]. Theoretical treatments of this intermediate case have not yet been made.

We therefore do not plot in Fig. 7(b) the measured τ logarithmically against a minimum number J_m of rotational-librational levels, but more plainly against the experimentally measured librational frequency. Again, similar to Fig. 7(a), a reasonable straight-line dependence results.

The data currently available therefore do not allow us to make a clear case for either multiphonon or rotational relaxation to supply the main nonradiative deexcitation channel competing with the vibrational emission. Moreover, it is not yet clear how an energy-gap law can be formulated for the case of strongly varying rotational potentials and librational energies. Theoretical work about this question is definitely needed. We can note, however, the empirical correlation in Fig. 7(b): Crystal potentials of increasing strength (indicated by increasing librational frequencies) are correlated to nonradiative decay processes of increasing rate, competing with the vibrational fluorescence and decreasing its efficiency and lifetime. It is interesting to note that for disappearing strength of the crystal potential [i.e., for $v_{\text{libr}} \rightarrow 0$, or more accurately, $v_{\text{libr}} \rightarrow v(\text{free rotation}) = 1.5 \text{ cm}^{-1}$], the line in Fig. 7(b) approaches $\tau_{\rm fluor} \approx 0.05$ sec. The latter is our estimated value of τ_{rad} , which obviously is reached only for extrapolation to the "free-rotor case."

It is evident that in our model of a constant τ_{rad}^{-1} and a stronger competing τ_{nonrad}^{-1} process, the intensity of the emission should vary among the hosts similar to the variation of τ_{fluour} in Fig. 7. Experimentally, however, the intensity measurement is much more sensitive to accidental and unavoidable parameter variations between different runs, such as performance of the color-center laser, optimum adjustment of the optical setup, crystal thickness, strength of the CN⁻ absorption and its spectral position on the tuning curve (Fig. 2), etc. (The measurement of $\Delta\phi$ determining τ_{fluor} is totally independent of all these parameters.) Therefore, the relative intensity values in Table I show much more scattering, but reflect at least the general trend from rather high intensities for K, Rb, and Cs halides to low intensities for Na halides.

The second important parameter variation in this work is the concentration of the active molecules in a given host, which we studied for the case of KCl. The results in Figs. 5 and 6 show that up to $\sim 0.5 \text{ mol }\% \text{ CN}^-$ the efficiency and lifetime of the vibrational fluorescence is essentially constant; for higher concentrations, however, a very effective nonradiative decay process takes over quickly, quenching the fluorescence intensity and reducing the lifetime. The simplest explanation is the assumption that with decreasing distance between CN⁻ defects, the excitation does not remain localized at a given CN site, but can be transferred to a neighboring CN⁻, thus producing energy migration through the system of interacting molecules. Transport of the excitation energy to a "sink," a site where the energy can be trapped and effciently lost in a nonradiative decay process, produces the fluorescence quenching. The existence of vibrationvibration energy-transfer processes has been convincingly observed for CO in rare-gas matrices,²⁵ occurring at similar molecular concentrations as in our case. Moreover, it has been shown that particular molecular impurities can work as effective sinks for the relaxation of the excitation energy.

In our case the nature of the sink for nonradiative decay of the excitation energy is not yet known. Doping of the crystals with CN⁻ leads inadvertently to incorporation of a smaller amount of CNO⁻ into the crystal. Owing to the large number of modes and combination modes²⁶ with $\nu \le 2000$ cm⁻¹, these CNO⁻ molecules could be prime candidates for being effective energy sinks. As a second possibility, it could well be, too, that the CN⁻ system itself supplies the sinks. At higher doping levels there is an increasing statistical chance that pairs of CN^- molecules on (110) neighboring sites are formed. (Since there are 12 $\langle 110 \rangle$ sites, for 2 mol % of CN⁻, 2 $mol\% \times 12 = 24 mol\%$ of the molecules should already be present in pairs.) Owing to the strong elastic dipole interaction between the neighboring molecules, their rotational potential can become severely changed from the case of the isolated defect. It can be expected (and there are experimental indications²⁷) that in the case of pairs the CN⁻ defects become more strongly localized in their orientation, thus shifting their librations to higher frequencies. This could, according to the arguments discussed above and summarized in Fig. 7(b), produce the strong nonradiative decay. It is evident that this important question of intrinsic (CN⁻) versus extrinsic (CNO⁻) sinks for the excitation energy can be decided by experiments with crystals of systematically varied CNO- doping. If CNO⁻ is found to be the predominant sink, purification of crystals may allow the scaling up of the vibrational fluorescence to higher CN⁻ densities.

Beyond this exploration and clarification of the energy-transfer and trapping processes, which are under way, some of the evident questions and necessary experiments resulting from this work are the following. (a) Instead of the sandwiching to the laser crystal (Fig. 1), the CN^- -doped crystal should be placed in a separate intracavity cryostat, allowing independent temperature variation. Fluorescence efficiency and lifetime data over the whole temperature range will be obtained this way.

(b) Spectral analysis of the vibrational fluorescence, instead of the spectrally integrated detection used so far, should be performed. As we excite the weak $0\rightarrow 2$ overtone absorption of 2.4 μ m in our experiments, the observed 4.8 μ m fluorescence should consist of two components ($2\rightarrow 1$ and $1\rightarrow 0$) with a frequency shift of $\Delta \nu \approx 22$ cm⁻¹ due to the anharmonicity of the CN⁻ oscillator.

(c) Pulsed excitation of the 4.8- μ m fundamental absorption (instead of the ~ 100 times weaker 2.4- μ m overtone), realized by a frequency-doubled CO₂ laser, will drastically increase the pump rate. This will allow us (as was done in the CO-rare-gas matrix work)²⁵ to follow the time evolution of the occupation of the various excited states by temporal and spectral monitoring of the vibrational emission.

All these experiments are either under intense preparation or already under way. Besides the scientific interest in these first vibrational emission effects in ionic solids, the application interest and potential is very high. Effective pumping of higher excited vibrational states, producing population inversion, will definitely lead to laser operation of the CN^- vibrational fluorescence. Host material and CN^- isotope variation can supply continuous spectral tuning of the emission over the (4.8–5.03)- μ m range. Experiments directed towards the realization of this potential for laser applications are under way.

ACKNOWLEDGMENT

This work was supported by National Science Foundation Grant No. DMR 81-05332.

- *Present address: Carl Zeiss Forschungslabor, Oberkochen, West Germany.
- [†]On leave from Northwest University, Xian, People's Republic of China.
- ¹A. F. Devonshire, Proc. R. Soc. London Ser. A <u>153</u>, 601 (1936).
- ²H. U. Beyeler, Phys. Status Solidi B <u>52</u>, 419 (1972).
- ³For a review on vibrational relaxation in van der Waal matrices, see F. Legay, in *Chemical and Biochemical Applications* of Lasers, edited by C. B. Moore (Academic, New York, 1977), Vol. II.
- ⁴H. Dubost, L. Abouaf-Marguin, and F. Legay, Phys. Rev. Lett. <u>29</u>, 145 (1972).
- ⁵K. K. Rebane, P. M. Saari, and T. H. Mauring, in *Lumines-cence of Crystals, Molecules and Solutions*, edited by F. Williams (Plenum, New York, 1973).
- ⁶R. Florian, L. O. Schwan, and D. Schmid, Phys. Rev. A <u>29</u>, (1984).
- ⁷W. H. Knox, Ph.D. thesis, University of Rochester, 1983.

- ⁸W. E. Moerner, A. J. Sievers, and A. R. Chraplyvy, Phys. Rev. Lett. <u>47</u>, 1082 (1981).
- ⁹Y. Yang and F. Luty, Phys. Rev. Lett. <u>51</u>, 419 (1983).
- ¹⁰G. Litfin, R. Beigang, and H. Welling, Appl. Phys. Lett. <u>31</u>, 381 (1977).
- ¹¹We are thankful to W. Gellermann for active help and advice in these preliminary experiments, which were reported for the first time in Bull. Am. Phys. Soc. <u>28</u>, 452 (1983).
- ¹²T. D. Harris in *Ultrasensitive Laser Spectroscopy*, edited by D.
 S. Kliger (Academic, New York, 1983), Chap. 6.
- ¹³H. W. Kogelnik, E. P. Ippen, A. Dienes, and C. B. Shank, I. E. E. E. J. Quantum Electron. QE- <u>8</u>, 373 (1972).
- ¹⁴W. Demtröder, Laser Spectroscopy (Springer, New York, 1981), Chap. 11.
- ¹⁵H. Y. Sun and S. A. Rice, J. Chem. Phys. <u>42</u>, 3826 (1965).
- ¹⁶A. Nitzan, Sh. Mukamel, and J. Jortner, J. Chem. Phys. <u>63</u>, 200 (1975).
- ¹⁷S. H. Lin, J. Chem. Phys. <u>61</u>, 3810 (1974).

- ¹⁸M. Berkowitz and R. B. Gerber, J. Chem. Phys. <u>37</u>, 369 (1979).
- ¹⁹W. D. Seward and V. Narayanamurti, Phys. Rev. <u>148</u>, 463 (1966).
- ²⁰F. Luty, Phys. Rev. B <u>10</u>, 3677 (1974).
- ²¹H. U. Beyeler, Phys. Rev. B <u>11</u>, 3078 (1975).
- ²²A. Diaz-Gongora and F. Luty, Phys. Status Solidi B 86, 127

(1978).

- ²³D. Durand and F. Luty, Phys. Status Solidi B <u>81</u>, 443 (1977).
- ²⁴R. Callender and P. S. Pershan, Phys. Rev. A <u>2</u>, 672 (1970).
- ²⁵H. Dubost and R. Charneau, Chem. Phys. <u>12</u>, 407 (1976).
- ²⁶A. Maki and J. C. Decius, J. Chem. Phys. <u>28</u>, 1003 (1958), <u>31</u>, 772 (1959).
- ²⁷D. Durand and F. Luty, Ferroelectrics <u>16</u>, 205 (1977).