

Vibrational Fluorescence of CN^- Defects in KCl Excited by Coupling to Optically Pumped F Centers

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Vibrational emission from molecular defects in ionic crystals has been observed for the first time, realized by dilute CN^- defects in KCl which emit a long-lifetime fluorescence at $4.8 \mu\text{m}$. After association of F centers to the CN^- defects, the emission can be pumped efficiently by optical F -center excitation through electronic-vibrational coupling. This coupling is confirmed through Raman experiments. Relative intensity, emission spectra, and lifetime data as a function of crystal temperature are reported for the $4.8\text{-}\mu\text{m}$ emission.

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In this Letter we address two fundamental open questions: (a) Can substitutional molecular defects in ionic crystals, when excited in their internal vibrational mode, undergo radiative deexcitation processes and emit *vibrational fluorescence*? (b) Can electronic defects, like color centers, when optically pumped into excited states, transfer energy into the excitation of vibrational modes of molecular defects? Both of these open questions are answered affirmatively by the experiments reported here, resulting in the first realization of (long-lifetime) vibrational fluorescence in ionic solids, which can be conveniently pumped by visible light irradiation.¹

For our experiments, KCl single crystals doped with substitutional CN^- defects (typical concentrations 0.2–1.0 mol%) have been used. CN^- molecules in KCl are known to reorient rapidly ($\tau_{\text{reor}}^{-1} > 10^9 \text{ sec}^{-1}$ even at 2 K) in a very shallow orientational potential² with minima in the eight $\langle 111 \rangle$ directions.³ Therefore the ground state shows tunneling splitting into a manifold of four levels with 1.2-cm^{-1} separation, with a low-lying hindered rotor state manifold at $\sim 12 \text{ cm}^{-1}$ above and extending to higher energies. The absorption due to the CN^- stretching vibration (at 2089 cm^{-1} or $\sim 4.8 \mu\text{m}$) is sharp and reflects the tunneling splitting at low temperature.^{3,4} Towards high temperatures it develops into a broad vibrational-rotational spectrum with double band structure corresponding closely to the P and R branches of a free rotor.²

F centers (concentration $\sim 3 \times 10^{16} \text{ cm}^{-3}$) introduced by additive coloration into these KCl: CN^- crystals show after quenching (i.e., in statistical distribution) optical properties like in pure KCl, essentially unaffected by the small number of CN^- defects. Optical excitation (by Xe lamp or Ar^+ -ion laser) of the broad F -band absorption in

the visible leads, as a result of the strong electron-phonon coupling, to the broad Stokes-shifted F -emission band at $\sim 1.2 \mu\text{m}$, which is known to have full quantum efficiency and a lifetime of $\tau = 0.8 \times 10^{-6} \text{ sec}$ around 80 K. In KCl crystals doped with CN^- defects (Fig. 1, stage I) we find in addition to this unchanged electronic emission a very weak emission around $4.8 \mu\text{m}$, coinciding closely with the CN^- stretching-vibration absorption. Evidently this new ir emission must originate from CN^- defects which are excited through coupling to the optically pumped F centers.

We assume that this coupling is effective only

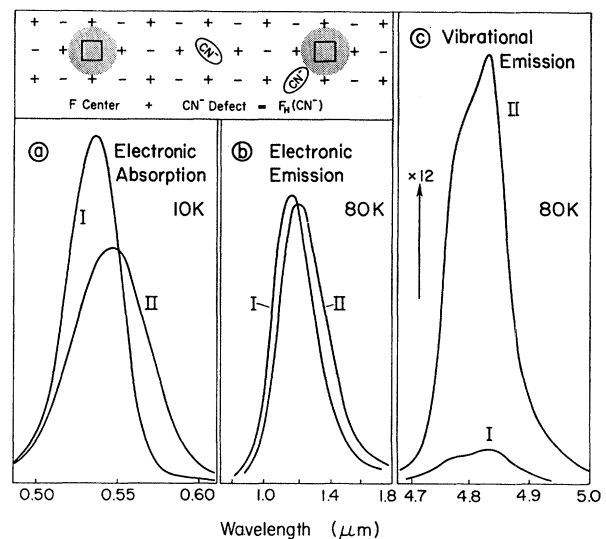


FIG. 1. Electronic (a) absorption and (b) emission, and (c) vibrational emission of KCl+0.8-mol%-KCN crystal, additively colored with $3 \times 10^{16} \text{ cm}^{-3}$ F centers. (Emission excitation with 568-nm Kr^+ -ion laser light.) (I) Quenched crystal. (II) After optical aggregation of F centers to CN^- defects (see inset).

for F -center/ CN^- pairs on the closest possible $\langle 110 \rangle$ next nearest neighbor—sites. For statistical distribution of the defects as used in Fig. 1, stage I (8×10^{-3} and $\sim 10^{-5}$ mol parts CN^- and F centers, respectively), we expect that initially only $(8 \times 10^{-3}) \times 12 = 9\%$ of the F centers will have a CN^- defect in their next-nearest-neighbor shell of 12 anions. An increase of the vibrational emission by a factor of 11 is therefore expected if all F centers could be associated to CN^- defects. It is well known that by optical ionization and thermally activated vacancy migration above 240 K, F centers can be associated to a variety of other defects (like Li^+ , H^- , anion vacancies, or other F centers) forming the various primary F -aggregate centers (F_A , F_H , F_2^+ , $F_2 \dots$). Application of this optical aggregation process to the F centers in our CN^- doped crystals leads to three distinct effects (Fig. 1, stage II): (a) a change of the original F absorption into a broadened band (half-width $0.16 - 0.23$ eV), shifted by ~ 0.04 eV to lower energies, (b) a shift of the original F -emission band by ~ 0.04 eV to lower energies, (c) a strong increase—by a factor of ~ 11 —of the vibrational emission. We conclude that the light irradiation at 240 K has produced migration and essentially full association of F centers to CN^- defects on $\langle 110 \rangle$ next-nearest-neighbor sites. The resulting defect pair [$F_H(CN^-)$ center] is characterized in terms of its electronic absorption and emission and its vibrational emission properties by the spectral features in Fig. 1 (II). The presence of the CN^- defect near the F center evidently causes two effects on the optical F -center transitions: a redshift (most likely due to a small local lattice expansion) and a broadening of the absorption (most likely due to an unresolved splitting of the threefold degenerate $1s - 2p$ transition). As the most important effect, coupling between CN^- and F center leads to transfer of electronic excitation energy into stretching motion of the CN^- defect, producing the $4.8\text{-}\mu\text{m}$ vibrational fluorescence. The quantum efficiency of the latter can be estimated from measurements of its integrated intensity relative to that of the F -center emission, yielding a value of about 3–4%. Similar results were obtained using KBr instead of KCl as host material.

The lifetime τ of the vibrational emission could be easily detected with chopped light excitation and phase-sensitive detection by measuring the phase angle ϕ between excitation and emission light for various values of the chopping frequency ν . The measured $\phi(\nu)$ dependences [Fig. 2(a)]

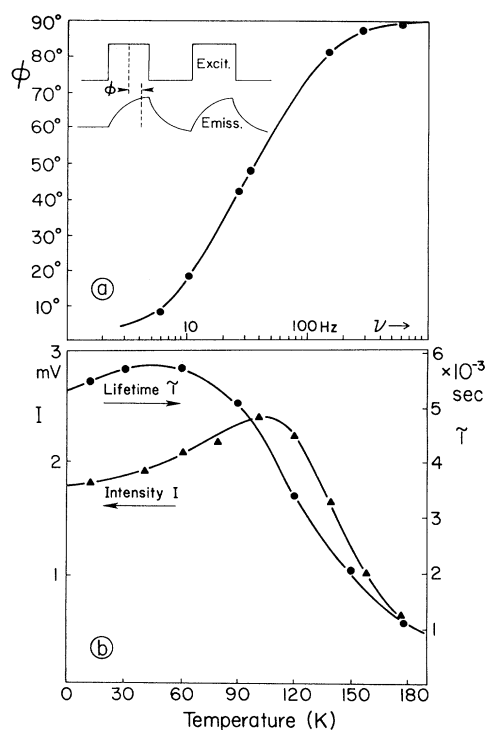


FIG. 2. (a) Phase angle ϕ between laser excitation and vibrational emission as a function of chopping frequency ν . (b) Lifetime τ and intensity I of vibrational emission as a function of temperature.

gives one example] follow accurately the relation $\tan\phi = 2\pi\nu\tau$ expected for a single relaxation time τ . The resulting $\tau(T)$ values show a rather constant behavior ($\tau \approx 6$ msec) up to ~ 70 K, before decreasing at higher temperatures [Fig. 2(b)]. Parallel to this decrease of τ , the intensity of the vibrational emission decays too. Both of these decreases give evidence for the growing effect of multiphonon (nonradiative) deexcitation processes towards higher temperatures.

The long radiation lifetime is expected for a molecular vibration. For a diatomic molecule of dipole moment p , equilibrium distance r_0 , reduced mass m^* , effective charge $e^* = (dp/dr)_{r=r_0}$, and eigenfrequency ω , we expect that the spontaneous emission transition will have a lifetime τ , the inverse of which is

$$\tau^{-1} = (2e^* \omega^2 / m^* c^3) \times (2m^* \omega / 3\hbar) \langle \vec{r} \rangle^2 \quad (1)$$

with the second factor in the product—the oscillator strength defined as usual—being ≈ 1 for the quasiharmonic oscillator.

From the integrated vibrational absorption at $4.8 \mu\text{m}$ an effective charge of $e^* \approx 0.3e$ is estimated for isolated CN^- defects; this would yield from Eq. (1) a radiative lifetime of $\tau_r = 46$ msec.

The presence of a neighboring F center could easily change the dipole moment p and its derivative $e^* = (dp/dr)_{r=r_0}$ of the CN^- defect. (For $e^* \approx e$ the expected radiative lifetime would coincide with our observed low-temperature value of $\tau \approx 6$ msec.) Of course the presence of nonradiative competing deexcitation processes of rates τ_{nr}^{-1} reduces the measured emission lifetime τ according to $\tau^{-1} = \tau_r^{-1} + \tau_{nr}^{-1}$.

The most unknown—and interesting—phenomenon in the processes described is the *nature of the coupling or energy transfer between optically excited F centers and CN^- defects*, which must occur at some stage(s) of the optical excitation cycle. Qualitatively, the following physical processes can be considered:

(a) The change in the F -center electronic wave function in the optical transition or during the relaxation process can cause by *electric polarization* a change in the CN^- dipole moment. This will produce a change in the equilibrium distance of the C and N in the molecule and therefore excite the stretching mode.

(b) After the optical transitions, the CN^- defect will participate—together with the other ions neighboring the F center—in large-amplitude center-of-mass vibrations during the process of lattice relaxation. This *mechanical motion* could couple energy into the internal molecular mode.

(c) Electronic excitation energy (~ 1 eV) stored in the relaxed excited state of the F center for $\sim 10^{-6}$ sec could by an *energy-transfer process* excite the CN^- stretching mode.

For a first attempt towards clarifying the nature of the F -center/ CN^- defect coupling, we have performed preliminary Raman experiments in the CN^- -stretch regime (Fig. 3). An uncolored $KCl:CN^-$ crystal shows—both in optical absorption and in Raman scattering⁵—only the peak (A) at 2088 cm^{-1} due to the stretch motion of isolated CN^- defects. The same crystal after coloration and F -center aggregation to CN^- defects displays additionally 3 peaks, shifted from peak A to lower energies by 3, 7, and 12 cm^{-1} . Obviously these are due to CN^- defects perturbed by and coupled to neighboring F centers. In spite of the fact that less than 1% of the total CN^- defects are attached to F centers, their combined Raman signal (B, C, D) is more intense than that of the isolated CN^- defects (A). This reflects the strong coupling of the attached CN^- defects to the electronic transition of the resonantly excited F centers. We attribute tentatively the observed splitting into three components (B, C, D) to the three

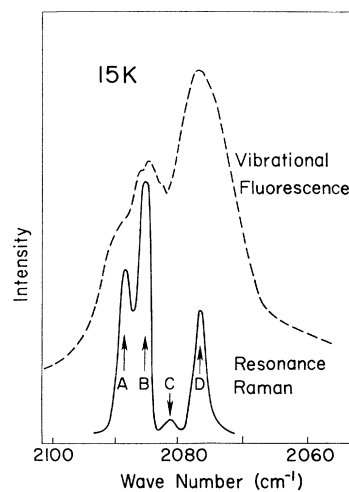


FIG. 3. Low-temperature vibrational emission and resonance Raman spectrum of $F_H(CN^-)$ defects in KCl.

inequivalent CN^- orientations relative to the $\langle 110 \rangle$ neighboring F center. This situation is very similar to the one of F centers attached to $\langle 110 \rangle$ neighboring H^- defects [$F_H(H^-)$ center], which exhibit in their resonance Raman spectra the H^- local mode split by the reduced symmetry into three components.⁶ Similarly, as discussed in the work for H^- , the shift to lower energies of the CN^- stretch mode can be explained qualitatively by the higher polarizability of the neighboring F center compared to the Cl^- ion which it replaces.

Comparison of the Raman spectrum to the vibrational emission spectrum of the same crystal at low temperatures (dashed curve in Fig. 3) confirms our interpretation. Though much more broadened out, the low-temperature CN^- emission spectrum matches in position the Raman spectrum, displaying the splitting into the strong (B and D) components of the F -center-perturbed CN^- defect. After its excitation through F -center pumping, it is possible that during the long lifetime (~ 6 msec) this “vibrational exciton” could migrate (spatially and spectrally) into the much more abundant isolated CN^- defect system, so that emission from the A component could occur as well. This interesting question of possible energy transfer and migration within the CN^- system is under current study.

In summary we have observed—for the first time in ionic solids—vibrational fluorescence, realized by dilute CN^- defects in KCl and KBr. To our knowledge, the only previously observed vibrational emission in any solid has been obtained at very low temperatures for CO molecules

isolated in solid rare-gas matrices.⁷ Additionally, we have found a new mechanism for energy transfer by attachment and coupling of the CN⁻ defects to *F* centers, which can be used effectively to pump the vibrational emission with visible light. Application possibilities of these systems for infrared lasers are under active study. Experiments with alternative excitation schemes of the vibrational emission—pumping it directly into the overtone absorption with a tunable color-center laser—have been successful, too, and will be reported in a separate publication.⁸

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²V. Narayanamurti and R. O. Pohl, Rev. Mod. Phys. 42, 201 (1970).

³F. Luty, Phys. Rev. B 10, 3677 (1974).

⁴H. U. Beyeler, Phys. Rev. 11, 3078 (1975).

⁵D. Durand and F. Luty, Phys. Status Solidi (b) 81, 443 (1977).

⁶D. Pan and F. Luty, Phys. Rev. B 18, 1868 (1978).

⁷H. Dubost, L. Abouaf-Marguin, and F. Legay, Phys. Rev. Lett. 29, 145 (1972).

⁸K. Koch, Y. Yang, and F. Luty, to be published.