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HIGHLY EXCITED CN⁻ MOLECULAR DEFECTS AND STEPWISE RADIATIVE RELAXATION IN CsCl

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Abstract: Optical excitation of a new F center/CN⁻ defect complex in CsCl produces --instead of any electronic emission--a highly efficient 5 band vibrational emission around -4.8 μm (~0.25 eV), involving the 5 lowest states of the CN⁻ anharmonic oscillator. Pulsed laser excitation shows that the energy transfer from the excited F electron occurs mainly at 1 eV into the 4th CN⁻ level producing a sequence of Δn=1 population inversions and emissions with great potential for laser application.

The simplest O₉ symmetry electronic defect in ionic crystals--the F center--has been associated to a great variety of cationic, anionic or vacancy point (or pair) defects. These F aggregate centers of reduced local symmetry, changed wave functions and electron-lattice coupling share with F centers one common feature: Highly efficient, spectrally broad and Stokes-shifted electronic emission bands. Several of these systems (like F₁, F₂, F₂⁻, F₂⁻ centers) have gained significance as solid state systems capable of tunable near IR laser emission.

A new optical property can be introduced by associating F centers to substitutional diatomic molecular defects. This attempt was originally motivated by trying to answer 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, when optically pumped into excited states, transfer energy into the excitation of vibrational modes of molecular defects? Both of these open questions have been answered and demonstrated affirmatively by our first realization of FH(CN⁻) center, i.e., an F center/CN⁻ defect pair on (nnn)<110> positions, in KCl.

As we know, CN⁻ molecules as substitutional defects in most alkali halides are found to reorient rapidly (τ<sub>reorient</sub> > 10⁻¹ sec⁻¹ even at 2K in KCl) in a very shallow orientational potential with minima in either one of the various possible directions such as <111>,<110> and <100>. Therefore the absorption due to the CN⁻ stretching vibration ( at ~ 2080 cm⁻¹ or ~ 4.8 μm) shows a small splitting due to the tunneling among the shallow wells at low temperature. 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.
The new developed configuration, i.e., the association of an F center with the CN⁻ defect in KCl shows an electronic absorption and emission band of similar strength and only slight spectral broadening and redshift compared to the F center (Fig.1). As a new effect, however, it displays a very weak energy transfer from the excited F electron to the CN⁻ internal stretching mode (\(E_{\text{vibr}} = 0.25\) eV), leading to \(n = 0 \rightarrow 1\) excitation and subsequent \(n = 1 \rightarrow 0\) radiative relaxation of this CN⁻ mode². Though this produced the first discovery of molecular vibrational fluorescence in ionic solids, the weak coupling of the CN⁻ to the optical F center excitation (at \(E_a = 2.3\) eV) allowed only low quantum efficiency (\(\eta = 0.04\)) and an energy conversion of rate \(\eta = \eta \cdot E_{\text{vibr}}/E_{\text{abs}} = 4 \times 10^{-6}\) from visible pumping into infrared emission light.

We report here -- after systematic search -- a new \(F_H(CN^-)\) center in CsCl with dramatic increase in the F electron/CN⁻ vibrational coupling and great application potential. Unlike the NaCl structure of KCl, the body-centered cesium halide structure should produce for a \((n.n.n.)\) F/CN⁻ pair a \(<100>\) oriented complex as illustrated in Fig. 2. As for \(F_A\) centers in KCl, one can expect that the excited F center \(2p\) state could split into two spectrally separate absorption transitions \((F_H(1))\) and \(F_H(2))\), polarized \(\perp\) to the pair axis.

Our first experiments confirm this (Fig. 3a): CsCl crystals, containing low (6 \(\times\) 10⁻⁶ to 6 \(\times\) 10⁻³) mole ratios of CN⁻ defects, when additively colored, quenched and cooled show essentially only the well known F absorption band (with its characteristic spin orbit splitting spectral structure). Irradiation into the F band around 170K leads to conversion into two absorption bands (0.27 eV separation), which we attribute to migration and association of the F centers with CN⁻ defects, forming the \(F_H(CN^-)\) center as illustrated in Fig.3. The strong interaction existing among an F center and the neighboring CN⁻ molecule in both directions leads us to observe that the association or aggregation gives rise to an extra, although small, IR absorption band due to the perturbed CN⁻, which is about 10 cm⁻¹ downshifted from the non-perturbed or isolated CN⁻ absorption band (Fig. 4). The perturbed fraction of CN⁻ defects obtained in the full aggregated stage is basically determined by the available F center concentration, which is usually two or three orders of magnitude lower than CN⁻ concentration. The most dramatic effect of this \(F \rightarrow F_H(CN^-)\) conversion occurs in optical emission, as shown by excitation spectra in both stages (Fig. 3b). The normal F emission at 1.25 eV, observed in the quenched state, becomes totally suppressed by \(F \rightarrow F_H\) conversion, and replaced by a much stronger emission around 4.8 \(\mu\)m (excited in both \(F_H\) absorption bands). In both stages the emissions were measured with broad bandpass filters.
isolated \( \text{CN}^- \) defect (Fig. 5a). As the band separation \( \Delta v \approx 25 \text{ cm}^{-1} \) corresponds to the anharmonicity shift among the \( \text{CN}^- \) oscillator states, we interpret the five emission bands as the \( \Delta n=1 \) transitions among the six lowest energy \( \text{CN}^- \) vibrational states of the \( \text{F}_\text{H}(\text{CN}^-) \) center. In fact, this can be understood if we assume that the \( \text{CN}^- \) molecular potential energy curve has the form of the Morse potential

\[
V(R) = D_e \left[ 1 - \exp\left(-a(R-R_e)\right) \right]^2
\]

where \( D_e \) is the depth of the potential minimum, \( a = (k/2D_e)^{1/2} \) with the spring constant \( k = (d^2V/dr^2)_{R=R_e} \), \( R \) and \( R_e \) are separations between two nuclei of \( \text{CN}^- \) for the general and equilibrium cases, respectively. The Schrödinger equation can be solved exactly for this potential, the eigenvalues being

\[
E_n = (n + 1/2)\hbar \omega - (n + 1/2)^2 \hbar^2 \omega x
\]

with \( x = \hbar a^2/2 \mu \omega \). The energy separation between two consecutive transitions will be yielded by

\[
\Delta E = (E_{n+1} - E_n) - (E_{n+2} - E_{n+1}) = 2\hbar \omega x
\]

which is exactly independent of the quantum number \( n \), in agreement with the observed equal spacing in the \( \text{CN}^- \) emission spectrum. By the way, the dissociation energy is \((D_e-E_0) = 0 \) with zero-point energy \( E_0 = \hbar \omega/2 - \hbar \omega x/4 \). The five band structure remains resolved at higher temperatures (at least to \( T = 120 \text{K} \)) and the emission strength decreases only gradually over this temperature range, in contrast to the rapid temperature decrease of the normal \( F \) emission in \( \text{CsCl}^3 \).

For the high \( \text{CN}^- \) concentration case (Fig. 5c and d), the \( 15 \text{ K} \) emission spectrum looks similar, but contains an added extra band at the spectral position of the isolated \( \text{CN}^- \) defect emission. Modest temperature increase (to \( 36 \text{ K} \) in Fig. 5d) produces strong decrease of the \( \text{F}_\text{H} \) center emission bands (particularly for the low \( n \) value transitions), combined with the increase of the isolated \( \text{CN}^- \) defect \( n=1 \rightarrow 0 \) emission band. Note that the isolated \( \text{CN}^- \) defect has \( 10 \text{ cm}^{-1} \) higher \( n=1 \rightarrow 0 \) emission than the perturbed peaking around 1.0 and 4.8 \( \mu \text{m} \) and with InSb detector. From these conditions and the observed relative emission strength we estimate that the \( \text{F}_\text{H} \) luminescence quantum efficiency \( \eta \) must be considerably higher (4-6 times) than \( \eta \) value of the \( F \) luminescence.

Fig. 5 shows the \( \text{F}_\text{H}(\text{CN}^-) \) emission spectra in \( \text{CsCl} \) containing \( 6 \times 10^{-5} \) and \( 6 \times 10^{-4} \) mole ratio \( \text{CN}^- \), both measured at two temperatures. For the low \( \text{CN}^- \) concentration case we obtain five almost equally separated emission bands, all shifted to lower energies compared to the indicated position of the \( n=1 \rightarrow 0 \) emission of the

\[
\text{CN}^- \text{ Stretching Absorption}
\]

\[
\text{CsCl} + 5 \times 10^{-4} \text{CN}^-, T = 23 \text{K}
\]

(a) Before Aggregation

(b) After Aggregation

Fig. 4

\[
\text{Optical Density (arb. units)}
\]

\[
\text{Wave Number (cm}^{-1})
\]

\[
2090 \hspace{1cm} 2070 \hspace{1cm} 2050
\]
CN" does, as implied by the absorption measurement in Fig. 4. Obviously for high CN" defect densities the excitation of the CN" in the FH(CN") complex can efficiently transfer with the help of thermal activation energy its energy into the abundant isolated CN" defect system. Migrating by resonance energy transfer through this system, the CN" excitation can be transported to some trap with a radiationless de-excitation channel (e.g. a CN" defect pair 5), resulting in a quick decay and disappearance of the FH(CN") emission with increasing temperature. Evidently, the dilute case of non-interacting FH(CN") and isolated CN" defects has a much more simple, powerful and temperature independent behavior compared to the concentrated CN" interactive case.

The symmetry of the FH(CN") complex was determined by polarized emission measurements (Fig. 6), performed in CsCl:CN" crystal oriented with X-ray analysis to a <100> orientation. [100] polarized excitation in the FH(1) band produces nearly completely parallel [100] polarization of the CN" emission, preserved essentially under increase of temperature to 70K. The same [100] excitation of the FH(2) absorption leads to strong perpendicular [010] polarization of the CN" emission. These two polarized measurements confirm the model illustrated in Fig. 2:

(a) <100> orientation of the F/CN" complex, with FH(1) and FH(2) absorptions polarized \( \parallel \) and \( \perp \) to the <100> axis respectively.

(b) The CN" molecule (a weakly hindered rotor in the isolated defect case) is aligned along the <100> pair axis by strong interaction with the neighboring F center even up to high temperatures.

In Fig. 7a we summarize the measured time dependence of five FH(CN") emission bands after excitation with a 40 nsec excimer-laser pumped dye laser pulse. The high level emissions (\( n = 5/4 \) and 4/3) start immediately and decay rapidly. The emissions from the lower levels occur with small initial value, but mostly in delayed build-up (by transitions from the higher levels) and subsequent slow emission decay. In Fig. 7b we plot the relative size of the \( t = 0 \) initial emission with bars for all excited states, illustrating their direct pump probability through coupling to the electronic excitation. Obviously, pumping occurs with a distribution with strong peak at the 4th state (4 \( \cdot \) \( E_{vibr} = 1.0 \) eV), indicating a very high quantum efficiency of 1 vibrational emission (\( \eta = 4 \)) and energy conversion efficiency (\( \eta = \eta^* \cdot E_{vibr}/E_{abs} = 0.5 \)).

In the presented emission measurements (Figs. 5, 6, 7), the pump light intensity used was low enough to excite FH(CN") centers only with their CN" in the vibrational ground state. Under considerably increased pump light intensity (focused cw laser), however, repeated FH excitation can occur prior to the
slow CN⁻ relaxation in the F/CN⁻ complex. This leads to partial pumping of 'vibrationally excited FH centers' into higher CN⁻ levels, as we could observe by a relative increase of the 5 + 4 emission and an appearance of a higher 6 + 5 emission band in spectral measurements of the type in Fig. 5.

Figure 7 illustrates directly the population inversion among the CN⁻ levels achieved under pulsed pumping (strongest between n=4 and 3), indicated by the rapid initial decay of the 4 + 3 emission which is most likely by stimulated transitions. Some questions will be certainly raised if one recalls that the transition probability among the various levels of CN⁻ is proportional to the matrix elements like

$$|\langle n-1, n-1 | \mu | E_n, n \rangle|^2 = n^2 (\omega^2/2m_\mu) \left( \frac{d\mu}{dR} \right)_{R=Re}^2 (4)$$

with \( \mu \) = the dipole moment of CN⁻. This transition rate is characterized by the linear dependence of the quantum number n. The discrepancy between this general feature and what we observed implies that the actual dynamical process occurring among the various levels of CN⁻ is much more involved than it looks like.

Experiments with this system for powerful 4.8 \( \mu \)m laser applications are actively under way. They possibly allow laser light tuning by the above described shift of the inversion into higher CN⁻ levels under strong pump light intensity. Efforts to fully understand this highly efficient and novel energy transfer process between F and CN⁻ are also under way--both theoretically and by further experiments. Resonance Raman measurements on the \( F_{\mu}(CN^-) \) defects will clearly decide, if the FH electron/CN⁻ vibrational coupling occurs in the absorption process itself, or during and/or after excited state relaxation. If the latter is the case, the electronic energy of the normal F emission (\( E = 1.25 \) eV) fits closely to the 4th CN⁻ vibrational level excitation energy, suggesting a direct and highly efficient transfer process between both. Experiments on FH centers in CsBr and CsI are already under way.

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References