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F-Center Excitation Energy Transfer to CN^- Vibrational Levels in CsCl

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ABSTRACT

The rapid quenching dynamics of the F-center excitation by CN^- defects in CsCl crystals were investigated by monitoring the ground state bleach recovery kinetics of F-centers, using a picosecond streak camera absorption spectrometer. The F-centers in CN^- doped quenched samples show two bleach recovery components. Optical aggregation converts the slow component to the fast component. The slow one is due to the normal relaxation of the F^*-centers as found in CN^- free crystals. The fast one is due to the energy transfer of the F-center electronic excitation to the vibrational energy levels of CN^- molecualr defects. The energy transfer occurs only in the F-center-CN^- defect pairs, $F_H(CN^-)$-centers.

INTRODUCTION

A great deal of the basic properties in alkali halides are well investigated and understood.[1-3] One commonm feature of the F-centers in alkali halides is a highly efficient, spectrally broad, long-lived, and largely Stokes-shifted electronic fluorescence. However, the F-center emission can be quenched by the presecnce of molecular defects such as OH^- and CN^-.[4-7] Recent studies[4-14] of the interaction of substitutional diatomic molecular defects with F-centers in alkali halides have revealed very interesting phenomena. As diatomic molecualr defects have additional vibrational and rotational degrees of freedom and a large electric dipole, they have very interesting perturbational effects on the luminescence properties of the F-centers. The presence of OH^- molecular defects in alkali halides drastically reduces the electronic fluorescence and thermalionization of the relaxed excited state of the F-centers (F^*-centers).[4,5] The quenching is due to the energy transfer to the vibrational energy levels of OH^- defects.

The optical excitation of F-

center-CN^- defect pairs, $F_H(CN^-)$-centers, in KCl leads to the excitation of the CN^- internal stretching mode, and consequently to the vibrational emission from the CN^- stretching oscillators.[6] In CsCl, the optical excitation of $F_H(CN^-)$ centers produces a highly efficient five band vibrational emission, involving the five lowest states of the CN^- anharmonic stretching oscillators.[7] By using this coupling, the laser action in near IR region was obtained between CN^- vibrational energy levels while pumping the F-center in the visible.[16-18] The previous studies[6-8,15-18] show direct evidences that the electronic excitation energy of F-centers transfers to the vibrational energy levels of CN^- defects in alkali halides. However, due to the temporal resolution of the previous measurements, the rate of the energy transfer could not be determined. As the result, the nature of the electronic coupling between F-center and OH^- defect has to be determined.

The main purpose of this work is study the quenching processes of F-center excitation by CN^- in CsCl by measuring the ground-state bleach recovery kinetics of the F-centers as a function of CN^- concentration, aggregation and temperature, using a picosecond streak camera absorption spectrometer.[19] In this paper we will show the experimental results to elucidate the nature of the coupling between F-centers and CN^- defects in CsCl crystals.

EXPERIMENTAL SECTION

The samples of CsCl single crystals with different CN^- dopings were grown in the Utah Crystal Growth Laboratory. A typical concentration of the additively colored F-centers for the present experiment is $5x10^{-6}$ in mole fraction which is smaller than the concentration of CN^- at least by 2 orders of magnitude. The actual CN^- contents in the samples were determined by the IR or UV measurement of the vibrational or electronic CN^- absorption.[20,21] The sample surfaces were polished for optical experiment since the crystals did not give a good cleavage. All the samples used for the experiments were freshly quenched from 470-500 K and immediately cooled without light exposure to low temperature. The samples were mounted on the cold finger of a Air Products Liquid Transfer Heli-Tran LT-3-110. For optical aggregation, the quenched samples were illuminated at 180 K with a light longer than 530 nm from a 100-W Hg arc lamp with controlled exposure

times.

The experimental setup of bleach recovery kinetics measurements was described previously.[19,22] Ground-state population recovery kinetics were obtained on the basis of a single laser shot with a picosecond transient absorption spectrometer utilizing dye emission and a streak camera. The fluorescence from a laser dye, excited by the second harmonic pulse (532 nm, 30 ps) of a passively/actively mode-locked Quantel 471 Nd:YAG laser, was used for the probe light. Samples were excited by the Stokes-shifted stimulated Raman lines of the second harmonic pulse generated using a high pressure Raman cell filled with CH_4 or SF_6 gas. The wavelength of the probe light is selected by the use of a Jarrell Ash 0.25-m monochromator with a 590-groove/mm grating or a 10-nm band filter. A Hamamatsu C979 streak camera with a 10-ps temporal resolution, coupled to a Princeton Applied Research intensified 1420 reticon, is used as a detector. This is interfaced to a Digital LSI 11/23 computer. A ground-state bleach in the sample alters dye emission kinetics seen by the streak camera. The comparison of these dye emission kinetics without and with excitation yields ground state bleach recovery kinetics.

Bleach recovery times were extracted by fitting the computer simulated recovery curve convoluted with the instrument response function to the measured kinetics. The rate is defined as the inverse of the bleach recovery constant.

RESULTS AND DISCUSSION

Figure 1. shows typical bleach recovery kinetics of F-center absorption at 40 K in optically heavily aggregated crystals. The signal-to-noise ratios of the kinetics are rather not good, compared to those in KCl samples,[22] because of the scattering from the polished opaque crystal surface and the improper excitation wavelength from the stimulated Raman-shifted second harmonic pulse of a Nd:YAG laser. Quenched CN^- doped CsCl crystals show two bleach recovery components. However, CN^- free CsCl crystals show a single recovery component which is too slow to determine the recovery time at low temperature (for example, at 40 K) with the current experimental method. The amplitude of the fast component in CN^- doped samples increases as the concentration of CN^- increases. However, the amplitude of the fast component is small compared to that of

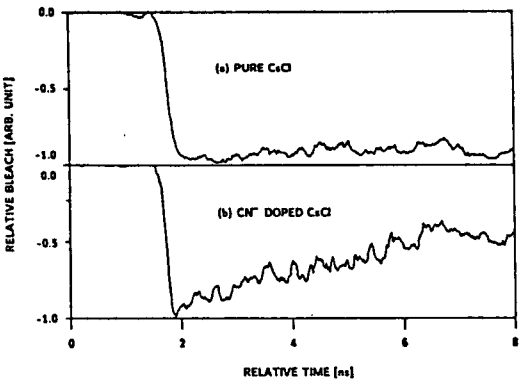

Figure 1. Typical bleach recovery kinetics of F-center absorption at 40 K in optically heavily aggregated (for 30 min) (a) pure and (b) CN^- ($7x10^{-4}$ in mole fraction) doped CsCl crystals. The samples were excited at 630 nm and probed at 595 nm. The deconvoluted recovery times were estimated as 90 and 8 ns for (a) and (b) recovery kinetics, respectivey.

the slow component for quenched samples where F-centers and CN^- defects are believed to be randomly distributed.

To change the concentation effect, we also measured the bleach recovery kinetics as a function of optical aggregation time. The aggregation brings F-centers to CN^- defects closer, finally producing F-center-CN^- defect pairs, $F_H(CN^-)$-centers. Optical aggregation increases the amplitude of the fast component. Heavy optical aggregation converts the slow component almost entirely to the fast component. We measured the ratio of bleach amplitude-to-static absorbance with aggregation time to check if a superfast bleach recovery component, which is too fast to observe with the current temporal resolution, forms by aggregation. The ratio, within our experimental errors, does not change with aggregation. This indicates that the energy transfer to the nearest neighbor, probably energy transfer in $F_H(CN^-)$-centers, is measurable with our current method. Although the amplitude of the fast component increases with aggregation, the recovery time of the fast component does not change with optical aggregation within our experimental errors. These indicate that heavy optical aggregation brings almost entire F-centers to CN^- defects, forming $F_H(CN^-)$-centers. If the formation of $F_H(CN^-)$-center is favorable, heavy optical aggregation would transform almost entire F-centers into $F_H(CN^-)$-centers since CN^- concentration is larger than the concentration of F-centers at least by two orders of magnitude. This is supported by the previous observation that electronic F-center emission is totaly transformed into CN^- vibrational emission in CsCl by optical aggregation.[9] For CN^- free

samples, optical aggregation does not change the amplitude and a single recovery component but heavy aggregation reduces the recovery time. This reduction of recovery time is probably due to the association of an F-center with another F-center, F_2-center.

It was reported[7] that body-centered cesium halide structure produces a <100> oriented complex for a next nearest neighbor F-CN^- pair and the excited F-center 2p state splits into two spectrally separate absorption transitions [$F_H(1)$ and $F_H(2)$], polarized parallel and perpendicular to the pair axis. We measured the wavelength dependence of the bleach recovery kinetics, especially to compare the bleach recovery kinetics between $F_H(1)$ and $F_H(2)$ absorption bands. For the quenched samples of 10^{-3} CN^- concentration, no significant wavelength dependence of the kinetics was observable in aspects of relative amplitude and recovery time. For same laser intensity, optical aggregation decreases bleach amplitude at 580 nm (about maximum absorption wavelength of quenched F and $F_H(2)$ bands[7]) and increases the amplitude at 670 nm (about maximum absorption wavelength of $F_H(1)$ band[7]). The relative amplitude of the fast component increases with aggregation and finally the fast component only is observable after heavy aggregation. At 670 nm, bleach recovery kinetics were not measurable for quenched samples and only the fast component forms with aggregation. After heavy aggregation, the bleach recovery time, excited at 630 nm and probed at 595 nm, was identical to that excited at 630 nm and probed at 670 nm, with the current instrument resolution. This indicates that the bleach recovery times, measured above 10 K are the same for both $F_H(1)$ and $F_H(2)$ absorption bands. For CN^- free samples, the bleach amplitude decreases at 580 nm and increases at 630 nm slowly with optical aggregation. The recovery time at 630 nm in aggregated samples is faster than that at 580 nm in quenched samples. The increased bleach at 630 nm is probably due to the formation of F_2-centers by aggregation.

Figure 2 shows the temperature dependence of F-center bleach recovery rate in heavily aggregated CN^- doped CsCl crystals. As described earlier, heavy aggregation converts almost entire F-centers into $F_H(CN^-)$-centers. Thus the shown bleach recovery recovery rate would be the energy transfer rate of F-center electronic excitation to CN^- vibrational levels in $F_H(CN^-)$-centers. The energy

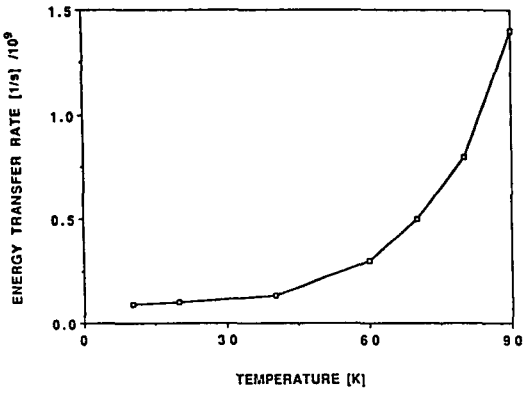

Figure 2. Temperature dependence of the F-center excitation quenching rate by CN^- defects in CsCl crystals. The samples with $7x10^{-4}$ CN^- defect concentration were optically heavily aggregated for 30 min, excited at 630 nm and probed at 595 nm.

transfer rate increases linearly with temperature below 50 K and increases exponentially with temperature above 50 K as temperature increases. The observed activation energy from Arrhenius plot using datum points above 50 K is 190 cm^{-1}. The linear dependence indicates that the enegy transfer is assisted by one phonon process below 50 K and the exponential dependence suggests that the energy transfer is assisted by two phonon processes above 50 K.[23] The activation energy from Arrhenius plot might correspond to the energy difference between the donor and the acceptor. In one-phonon assisted process, energy transfer rate is independent of the energy difference between donor and acceptor.[23]

The important observations can be summarized as follows. In CN^- doped CsCl crystals, the electronic excitation energy of F-center transfers to CN^- vibrational energy levels for only $F_H(CN^-)$-centers. The energy transfer rates are the same for both $F_H(1)$ and $F_H(2)$ excitation. The energy transfer is assisted by one phonon process below 50 K and assisted by two phonon process above 50 K.

Energy transfer in CN^- doped samples must be quite different from that in OH^- doped samples. In OH^- doped samples, the energy transfer rate is much faster[12,22] than in CN^- doped samples and the energy transfer occurs in distant F---OH^- pairs as well as in $F_H(OH^-)$-centers[22] while that in CN^- doped samples occurs only in $F_H(CN^-)$-centers. These differences would not be surprising if we consider that the larger vibrational and librational energy quanta and the larger dipole moment of OH^- would increase the excitation energy dissipation and interaction of F-center. The same energy transfer rate between $F_H(1)$ and $F_H(2)$ band excitations indicates that the interconversion rate between two excited states or the dephasing rate

of the splited F absorption is faster than the energy transfer rate at the temperatures we studied.

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