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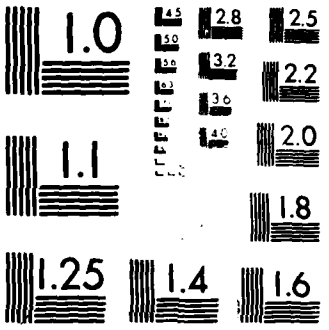

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The nature of the electronic and phonon coupling between the excited state F-centers and OH^- in KCl is investigated with picosecond streak-camera bleach recovery studies.

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Determination of the Rapid Quenching Rates of Excited State F-Centers by OH^- Defects in KCl

by

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DETERMINATION OF THE RAPID QUENCHING RATES OF EXCITED STATE F-CENTERS BY OH^- DEFECTS IN KCl

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1. Introduction

Recently, active studies of the interaction and association of substitutional diatomic molecular defects with F-centers in alkali halides have been carried out [1-3]. It was shown [1] that the electronic luminescence and photoionization of the relaxed excited state of F-centers (F^*-centers) in KCl reduce drastically with increasing the concentration of OH^- molecular defects, suggesting a strong coupling between F^*-centers and OH^- defects. The main purpose of this work is to measure the rates of this quenching using picosecond techniques to determine the type of the electronic coupling (i.e., multipolar vs electron exchange) as well as the phonon assistance in the process. The rates of the quenching are determined by the measurement of the ground state bleach recovery of the F-centers as a function of OH^- concentration and temperature using a picosecond streak camera absorption spectrometer [4].

2. Experimental

Single wavelength ground state bleach recovery kinetics were obtained on the basis of a single laser shot with a picosecond transient absorption

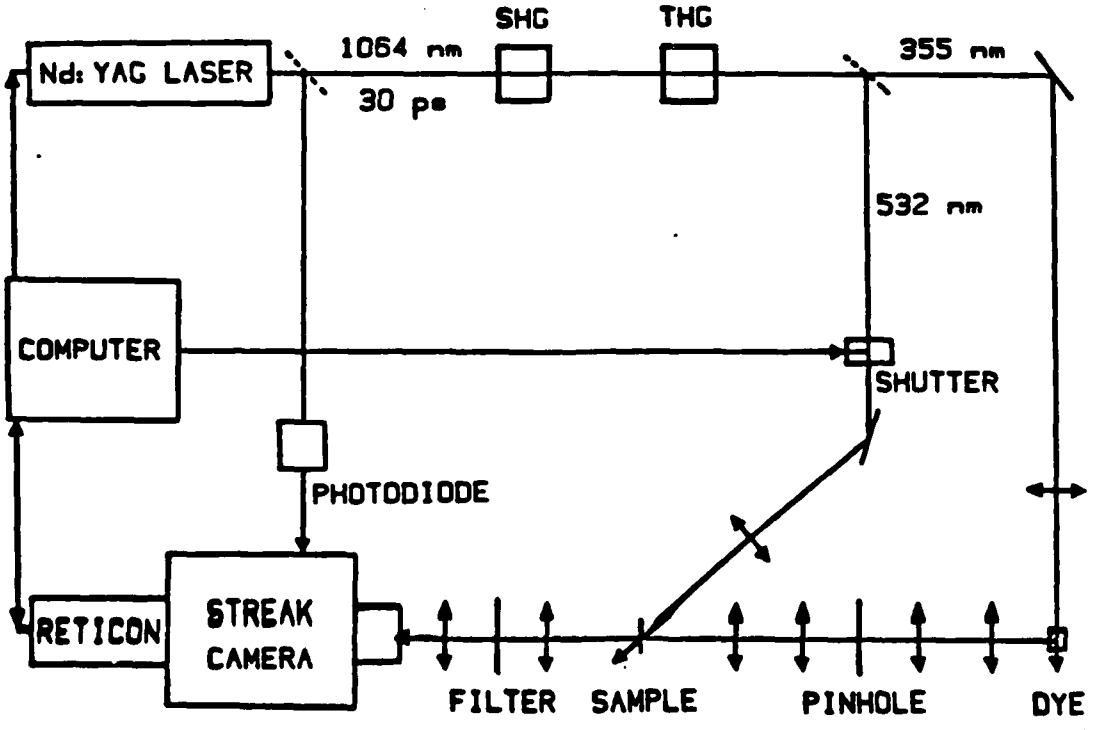

Fig. 1: Schematic diagram of the experimental apparatus. SHG/THG = second/third harmonic generator. Double headed arrow = convex lens.

spectrometer utilizing dye emission and a streak camera [4]. The optical setup of the transient absorption spectrometer is shown schematically in Fig. 1. The fluorescence from an organic dye, excited by the third harmonic pulse of a passively/actively mode-locked Quantel 471 Nd:YAG laser, is used for the probe light. The wavelength of the probe light is selected by passing a 5-nm band filter. A Hamamatsu C979 streak camera with a 10-ps time resolution, coupled to a P.A.R. intensified 1420 Reticon with a P.A.R. 1218 multichannel controller, is used as a detector. This is interfaced to a digital LSI 11/23 computer. A ground state bleach in the sample alters the apparent kinetics of the dye emission seen by the streak

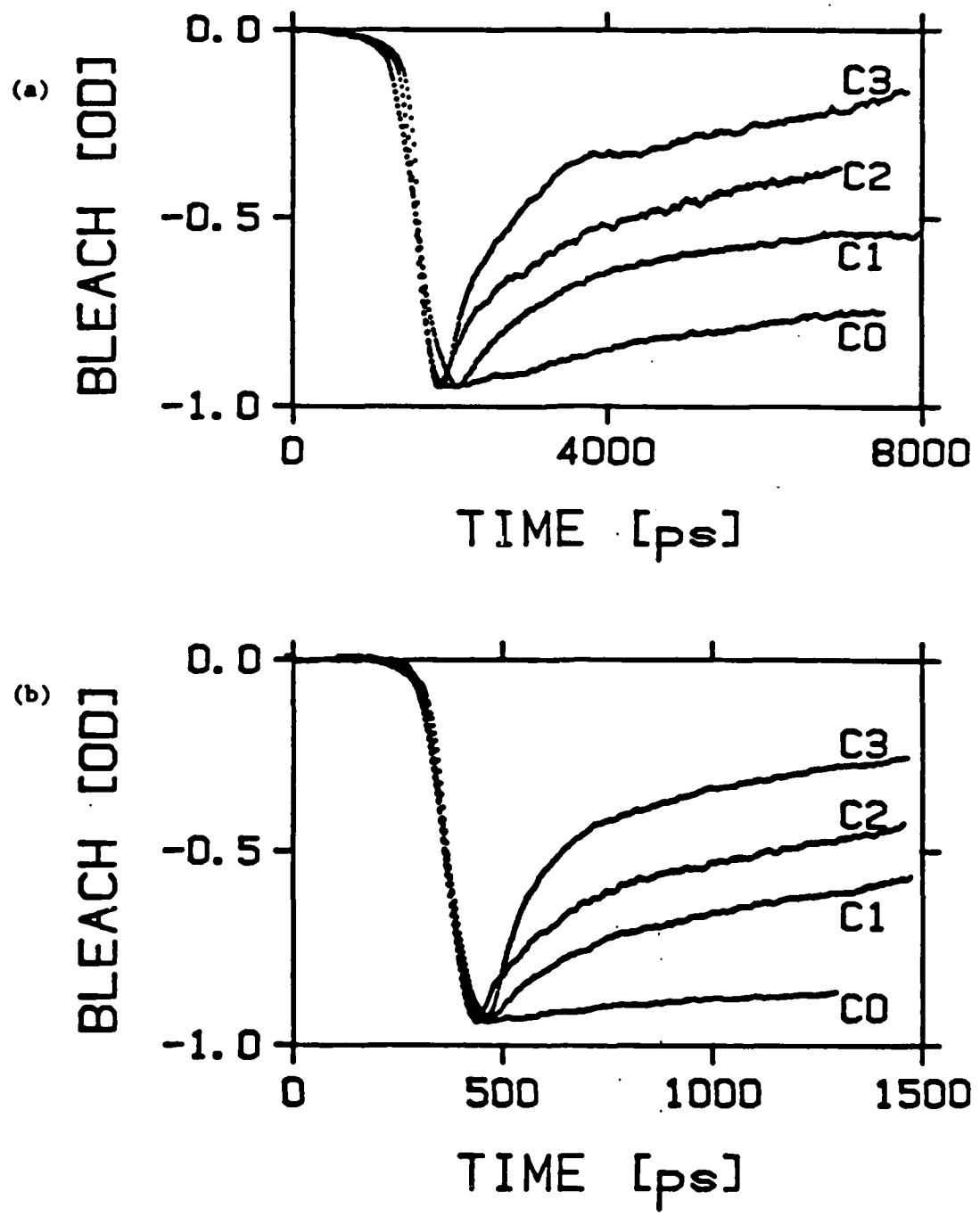

Fig. 2: Typical bleach recovery kinetics of the F-centers in KCl with various OH^- concentrations measured at 120K, using relatively long (a) and short (b) time windows. The samples are excited at 532 nm and probed at 550±5 nm and the OH^- concentrations in mole fractions are 0, 6.1×10^{-4}, 9.4×10^{-4}, and 2.3×10^{-3} for (C0), (C1), (C2), and (C3), respectively.

camera. Comparison of the dye emission kinetics without and with the sample excitation by the second harmonic pulse of the laser yields very accurate bleach recovery kinetics. The single crystals of different OH^- and OD^- dopings were additively colored and quenched. The samples were mounted on the cold finger of a Air Products Liquid Transfer Heli-Tran LT-3-110.

3. Results and Discussion

A. Temporal and Concentration Dependence

Figure 2 shows typical bleach recovery kinetics obtained at different OH^- concentrations (about 2 orders of magnitude higher than the F concentration). The kinetics of the OH^- doped crystals show two distinguishable relaxation processes. The fast process is due to energy transfer from the excited electronic state of the F-centers to the vibrational states of the OH^- stretching mode. The fitting of the observed temporal dependence to the equations derived from multipolar and exchange mechanisms are carried out [5]. The results suggest an exchange type at short times. At long time, all the mechanisms fit the observed results. The slow relaxation process is slightly faster than that observed in the absence of OH^-.

B. Temperature Dependence

The temperature dependence of OH^- quenched fast relaxation process presented in Figs. 3 and 4 shows that the transfer rate increases linearly with temperature below 90K. Above this temperature, it increases exponentially with temperature. Below 90K, the energy transfer is assisted by a one phonon process [6]. Above 90K, activation energies (ΔE_a) of 390 cm^{-1} for OH^- and 270 cm^{-1} for OD^- sample are obtained from the Arrhenius plots shown in Fig. 4. These correspond to the librational energies of OH^- and OD^- respectively in KCl [7,8]. The temperature dependence of the slow relaxation is similar to that of OH^- free samples. The slow relaxation rate is almost independent of temperature below ~100K. Above this

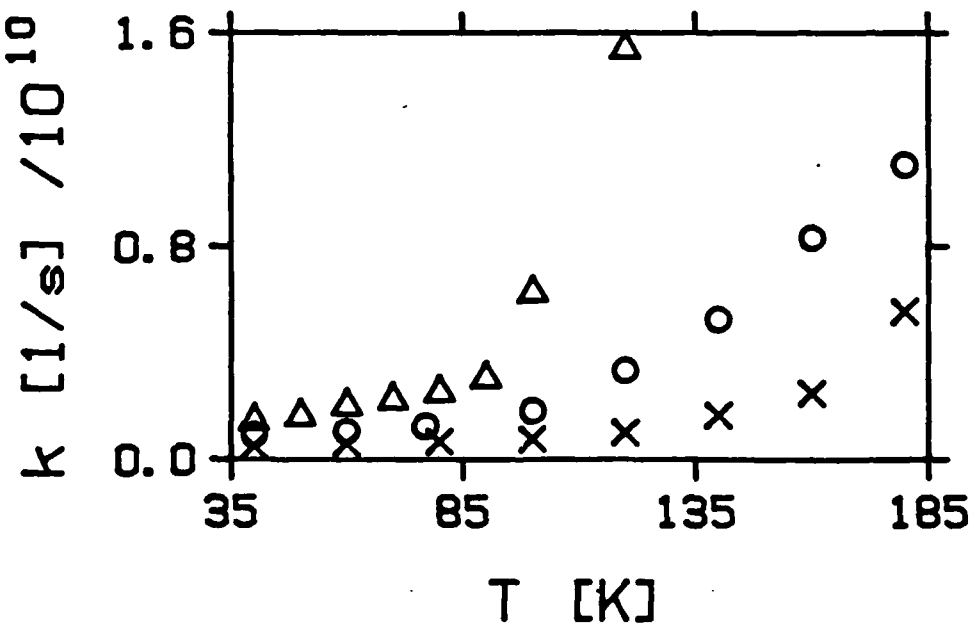

Fig. 3: Temperature dependence of the fast relaxation rate of the F-centers in OH^- doped KCl. The concentrations in mole fraction are 2.3×10^{-3} OH^- for (Δ), 1.8×10^{-3} OD^- for (o), and 9.4×10^{-4} OH^- for (×) respectively.

temperature, the rate increases exponentially with a corresponding ΔE_a of 660 cm^{-1}. This corresponds to the energy difference between the relaxed excited state of the F-center and the conduction band [9]. This suggests that the mechanism of the slow relaxation process involves the thermal activation of F^* electron to the conduction band followed by rapid trapping leading to bleach recovery as found in pure KCl [9]. One thing to note, however, is that our lifetimes of the slow relaxation below ~100K seen in the time window of ~10 ns are shorter by a factor of ~10 for both pure and OH^- doped samples than the lifetime of F^*-centers previously reported for pure KCl [9]. The lifetimes observed in our experiments decrease as the sample excitation intensity increases. The F^*-F^* annihilation interaction could produce in our experiment an additional quenching mechanism due to the large population of the F^* generated by the high power used in our picosecond experiment.

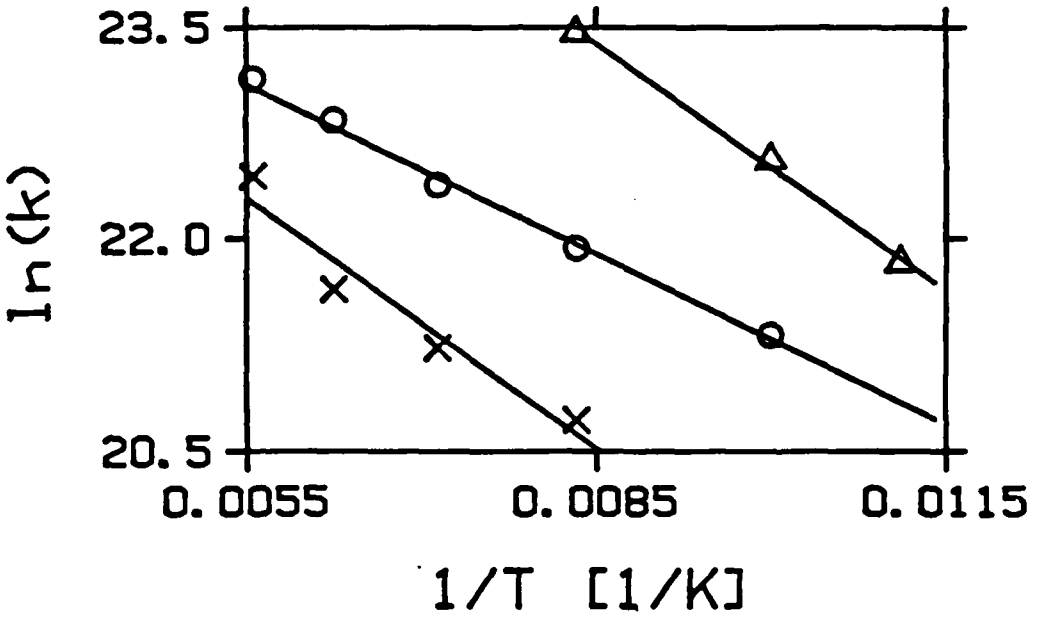

Fig. 4: Arrhenius plots of fast relaxation rates using data taken above 90K. The OH^-/OD^- concentrations are shown in Fig. 3 caption. The activation energies are determined to be 390 cm^{-1} for (Δ) and (×) OH^- samples and 270 cm^{-1} for (O) OD^- sample.

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