

Excited-state spectroscopy and picosecond relaxation at F centers

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A picosecond absorption spectrometer using tunable parametric light sources has been used for direct measurements of the relaxation times in excited states of F centers in a KBr crystal. An absorption band, which corresponds to transitions beginning from the bottom of the relaxed excited state, has been observed. The kinetics of the binding of a free electron at an F center is studied.

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1. Vibrational relaxation in an excited electronic state of F centers has been observed experimentally for the first time. In the experiments, in which we used a picosecond absorption spectrometer with multifrequency excitation and probing, we observed an absorption band beginning from an excited electronic state. We measured the vibrational relaxation times in the excited electronic states.

2. The development of lasers using color centers in alkali halide crystals has stimulated corresponding spectroscopic measurements. Some new opportunities are presented here by laser spectroscopic methods. Mollenauer¹ has used a modulation spectroscopic technique to observe absorption bands beginning from a relaxed excited state of F_2^+ centers in KF and NaCl crystals. In the present experiments we observed absorption from a relaxed excited state in a simple electronic defect of an alkali halide crystal: an F center. Using tunable picosecond-pulse lasers, we were able to measure the relaxation time of an F center in a relaxed excited state both from higher-lying electronic terms and within the first excited state.

3. The experiments were carried out by a probing method with preliminary excitation in a picosecond absorption spectrometer.² We measured the change (ΔD) in the optical density of the crystal caused by a change in the populations of F centers induced by the exciting light.

The method used in these measurements involved the production of a nonuniform population of excited states of F centers by short pump pulses (the pulse length was 15–20 ps) in the absorption band and the observation of the relaxation of this “excess” population to an equilibrium state. We studied the dependence of the change in the absorption of the probe pulse, with tunable wavelength λ_p , on the wavelength of the exciting pulse λ_e , and on Δ , the time delay between the exciting pulse and the probe pulse.

The exciting pulses were produced by a picosecond parametric light source using KDP crystals, which was pumped by the harmonics of a YAG:Nd³⁺ laser oscillator with passive-mode locking. The probe beam was the beam from a second picosecond parametric light source, using an LiNbO₃ crystal, with thermal tuning of the output wavelength. The length of the exciting and probe pulses was $\tau_{\text{pulse}} = 15\text{--}20$ ps; the spectral width of these pulses was $\Delta\nu = 5 \text{ cm}^{-1}$.

In a first series of experiments we studied the spectra of the change in the absorption of the probe wave for various delays between the exciting and probe pulses. In a second series of experiments (Fig. 1a) we studied the time dependence of the absorption of the probe wave at several fixed points in the induced absorption band, with excitation in the fundamental absorption band of the F center. In a third series of experiments (Fig. 1b) we excited the crystal with ultraviolet light, which put the F centers in higher-lying electronic states. In the fourth and final series, we observed the kinetics of ΔD in the case in which the exciting and probe pulses were in the fundamental absorption band and were tuned over it.

4. Figure 2 shows the spectrum of the change in the optical density of KBr with F centers (the density of F centers was $N_F = 10^{17} \text{ cm}^{-3}$; these measurements were carried out at room temperature) for excitation at the wavelength $\lambda_e = 580 \text{ nm}$. We

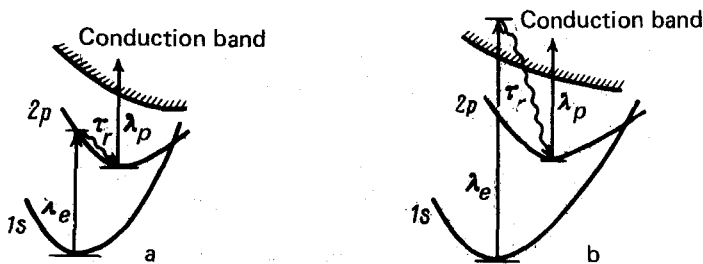


FIG. 1. Schematic diagram of the energy structure of F centers and of the present experiments, carried out to measure the relaxation time τ_p for relaxation to a relaxed, excited state. a—The frequency of the exciting light is in the absorption band of the $1s\text{--}2p$ transition; b—the exciting light puts the F centers in high-lying electronic states in the conduction band of the crystal.

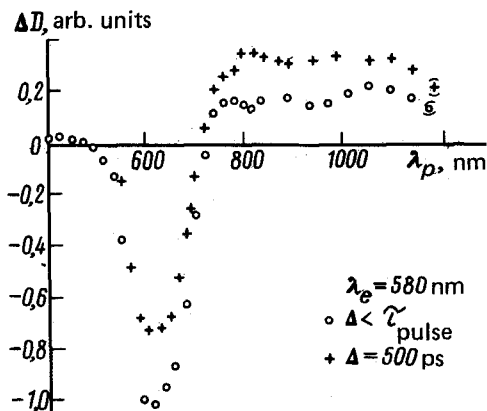


FIG. 2. Spectrum of the change (ΔD) in the optical density of a KBr crystal containing F centers upon excitation by light with a wavelength $\lambda_e = 580$ nm. Circles—The delay time is $\Delta < \tau_{\text{pulse}}$; crosses— $\Delta = 500$ ps. $\Delta D = \log(W_0/W_1)$, where W_0 and W_1 are the energies of the probe pulses transmitted through the sample with and without the exciting light, respectively.

observed a decrease in the absorption of the probe beam ($\Delta D < 0$) over the spectral interval of the absorption band (500–700 nm); this decrease resulted from a decrease in the population of ground-state F centers under the influence of the exciting light. In other words, the decrease was caused by a “brightening” of the fundamental band. We attribute the appearance of a new absorption band in the spectral interval 700–1200 nm ($\Delta D > 0$) to a pump-induced absorption band beginning from an excited electronic state (Fig. 1a). In the absence of a pump, this spectral interval was transparent to the probe beam. Figure 2 shows experimental results for measurements with a short delay between the exciting and probe pulses ($\Delta < \tau_{\text{pulse}}$) and for long delays ($\Delta = 500$ ps). There is a decrease in the brightening of the F absorption band with increasing Δ , and the absorption from the relaxed, excited state increases (there is an increase in the population at the bottom of the excited electronic state).

A detailed study of the Δ dependence of the absorption from the relaxed, excited state was carried out for various exciting and probe wavelengths. Figure 3a shows the results of experiments corresponding to the diagrams in Figs. 1a and 1b. In the first case (points 1 in Fig. 3a; $\lambda_e = 580$ nm, $\lambda_p = 800$ nm), the exciting light is in the fundamental absorption band of F centers in KBr. The solid curve here shows the results calculated for $\Delta D(\Delta)$ on the basis of a three-level model with allowance for a short delay due to relaxation within the excited electronic state of the F center (Fig. 1a) with $\tau_r = 10$ ps. Taking the experimental error into account, we may conclude that the relaxation time within the first excited electronic state is 10 ± 2.5 ps (for this particular exciting wavelength).

In the second case (curve 2 in Fig. 3a; $\lambda_e = 355$ nm, $\lambda_p = 800$ nm) the exciting light puts the F centers in the conduction band. The first point of note is the very fact that there is absorption from a relaxed excited state upon excitation of an F center to higher-lying states. This absorption means that there is a relaxation channel

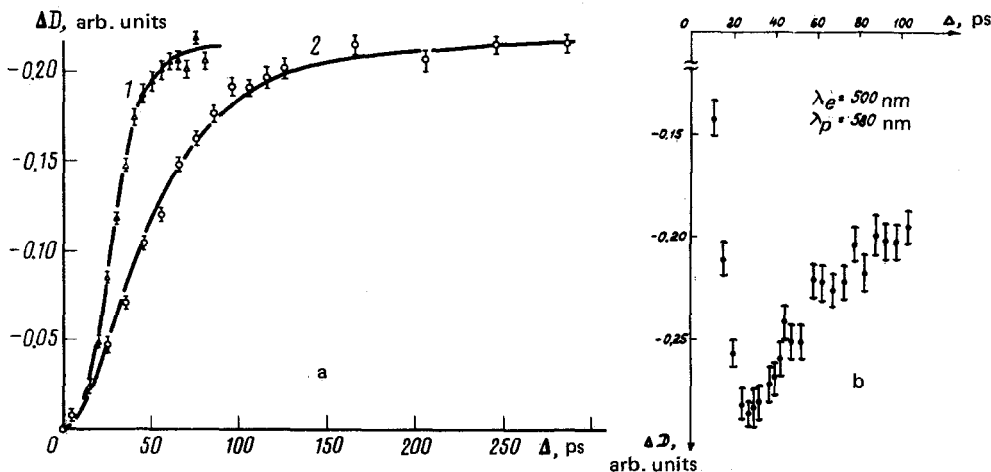


FIG. 3. Kinetics of the change in the absorption of the probe light, $\lambda_p = 800$ nm. a—Dependence of the absorption from the relaxed, excited state on Δ , for $\lambda_e = 580$ nm (curve 1) and $\lambda_e = 355$ nm (curve 2); b—dependence of the brightening of the $1s$ - $2p$ transition on Δ ($\lambda_e = 500$ nm, $\lambda_p = 580$ nm).

from high-lying states to the first excited state (Fig. 1b). The characteristic time for this relaxation is found to be 45 ± 5 ps on the basis of the three-level approximation.

In the final series of experiments we made a detailed study of the dependence of the brightening of the fundamental absorption band on the delay time Δ . We varied the wavelengths of the exciting and probe beams over the range 500–700 nm. Figure 3b shows the kinetics of $\Delta D(\Delta)$ for $\lambda_e = 500$ nm and $\lambda_p = 580$ nm. The leading edge ($0 < \Delta < 30$ ps) of the $\Delta D(\Delta)$ dependence results from a decrease in the population in the ground state of the F center and an increase in the population in the excited states. Over the interval $30 < \Delta < 100$ ps, we observe a decrease in the brightening, which we attribute to vibrational relaxation to a relaxed, excited state. After this time, the change $\Delta D(\Delta)$ lies on a plateau (corresponding to nanosecond relaxation from the relaxed excited state to the electronic ground state).

5. In summary, these experiments have revealed absorption from a relaxed, excited state in F centers in KBr for the first time. We have observed a relaxation from high-lying, excited states in the conduction band of the alkali-halide crystal to the first excited state. We have estimated the scale time for vibrational relaxation in the excited electronic state.

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