

Femtosecond Cascade-Excitation Spectroscopy for Nonradiative Deexcitation and Lattice Relaxation of the Self-Trapped Exciton in NaCl

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Optical-absorption change following photoexcitation of the lowest triplet self-trapped exciton (STE) in NaCl has been measured in the femtosecond time regime. It is found that a short-lived intermediate state is generated within 1 ps and decays accompanied by restoration of the lowest STE. An oscillation in the population of the lowest STE and the intermediate state with a period of 1.1 ps was observed. Formation of Frenkel pairs has been found to occur not at the initial stage of relaxation but as a result of the relaxation leading to the lowest STE.

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In many nonmetallic solids, strong local lattice rearrangement is induced by excitation of either bulk or defect electronic states [1,2]. In order to understand the microscopic processes of the phenomena, which arise from strong coupling of the electronic system with particular modes of the lattice vibration, it is important to trace the dynamics of the relaxation following electronic excitation on the time scale of lattice vibrations, using a sub-picosecond pulse technique [3].

The self-trapping of excitons and the formation of vacancy (*F* center), interstitial (*H* center) pairs, accompanied by self-trapping of excitons, are the best-studied examples of local lattice rearrangement induced by bulk electronic excitation [4–6]. The dynamic studies of the formation of the self-trapped excitons (STEs) and of defect pairs utilizing nanosecond and picosecond bulk excitation carried out so far [7–11] have not revealed the dynamic relaxation processes on the real-time scale. In these experiments, the duration of the excitation pulse was not short enough, and, furthermore, several consecutive processes are involved after electron-hole pair generation until the STEs and defects are produced. Since formation of the STEs and defects is considered to be governed by the relaxation at either the lowest [6] or the next excited state [12], measurements of the real-time relaxation processes after the lowest STEs are excited to one of the low-lying excited states are considered to yield the most direct information on electronic vibrational relaxation.

This Letter reports for the first time the observation of the lattice relaxation, in the femtosecond time regime, on the lowest adiabatic potential-energy surfaces (APES) of the STE. Relaxation in a potential well with two minima representing two relaxed states of the STE and the accompanying defect formation were observed clearly.

Specimens of NaCl with a thickness of 5 mm were irradiated consecutively with a KrCl (222-nm) excimer laser pulse and a femtosecond 605-nm laser pulse, separated by 5 μ s, at 5 K. The former populates the lowest triplet STEs by two-photon absorption, and the latter excites STEs. The femtosecond laser pulses were generated

by a laser system consisting of a mode-locked Ar⁺-ion laser, a synchronously pumped, cavity-dumped dye laser with Rhodamin 6G, a pulse compressor, and a three-stage amplifier with a XeCl excimer laser. The 605-nm laser pulses generated by this system have a time duration of 120 fs, and an energy of 50 μ J. They were divided by a dichroic mirror into two beams; one was used for exciting the lowest triplet STEs, and the other for generating a white-light beam by passing through a D₂O cell. The white-light beam, the spectral distribution of which was measured by polychromators, was used for determining the optical-absorption changes induced by the femtosecond light pulses.

In Fig. 1(a), curve *a* shows the optical-absorption spectrum induced by the KrCl laser pulses only and represents the optical-absorption spectrum due to the electron transition from the lowest 1s-like level to the excited 2p-like levels [13] of the STEs. Curve *b* is the optical-absorption spectrum induced by the consecutive excitation, obtained 700 fs after excitation of the STEs by 605-nm laser pulses. We show the difference between the two spectra by curve *c* in Fig. 1(b), in which curve *d* is the STE absorption curve fitted to curve *c* in the range 1.7 to 1.9 eV. It is clear that curve *c* is a superposition of an optical-absorption band growing around 500 nm (curve *e*) and the reduced STE absorption band (curve *d*), indicating that the lowest triplet STEs are depopulated and new centers (hereafter called the *X* center) are generated by the electron excitation of the STEs.

The time evolution of the change of the STE and *X* absorption bands was examined by measuring the absorption spectra at delays from –2.0 to 10 ps with respect to the time of incidence of the 605-nm laser pulse. The spectrum at each time delay was analyzed similarly to that of Fig. 1(b) to obtain the heights of the bleached STE band and the *X* band produced. As shown in Fig. 2, damped oscillations are observed in the change of the two quantities. Clearly the maxima of the time evolution of the *X*-band height and the minima of the STE-band height occur at the same time delay; the concentration of the lowest STEs and that of the *X* centers are anticorrelated.

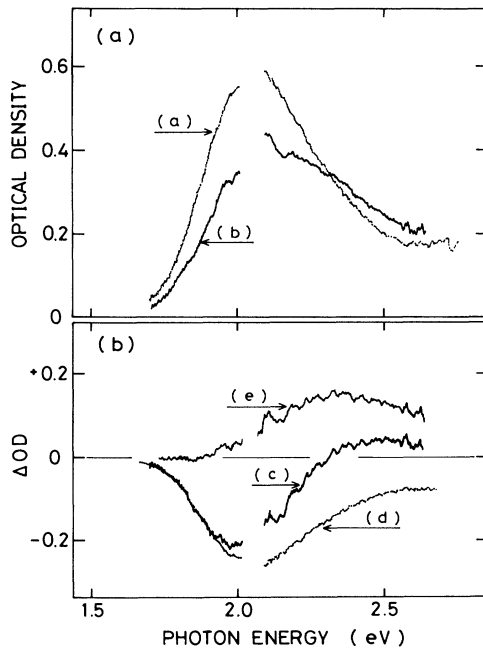


FIG. 1. (a) Optical-absorption spectra after two-photon excitation by a KrCl laser pulse, measured without additional excitation (curve *a*), and at 700 fs after additional excitation with a 605-nm light pulse (curve *b*) in NaCl at 5 K. (b) The change in the optical-absorption spectrum induced by excitation of the STEs by a 605-nm light pulse [curve *c*, the difference between curves *a* and *b* of (a)]. The spectrum is decomposed into a reduced part (curve *d*), due to bleaching of the STEs, and an increasing part (curve *e*).

lated with respect to the time delay. We obtained the period of oscillation to be 1.1 ps. Besides the oscillation, we note that the STE band is initially bleached in about 200 fs, recovers partially within 500 fs, and then shows an oscillatory gradual reduction until it reaches a constant value (90% of the initial optical-absorption strength) at 7 ps. On the other hand, the *X* band grows first, reaching a maximum at 900 fs after the excitation, and then decays showing oscillation within 7 ps. We evaluated the overall decay time constant to be 3 ps.

The time-resolved spectra near the *X*-band maximum are shown in Fig. 3. It is clear that, from the onset of formation of the *X* centers, the peak energy of the *X* band moves to the lower-energy side, and the width becomes narrower. This feature is characteristic of the optical band shapes of absorption (or emission) during relaxation in a strongly coupled electron-lattice system, as has been observed for large molecules in solutions [14]. Furthermore, both the shift of the peak and the change of the bandwidth terminate almost at 3 ps, which is nearly the same as the time by which the oscillatory behavior of the concentrations of the STEs and the *X* centers disappear. We note further in Fig. 3 that the absorption band due to the *F* center has become appreciable at 3 ps after excita-

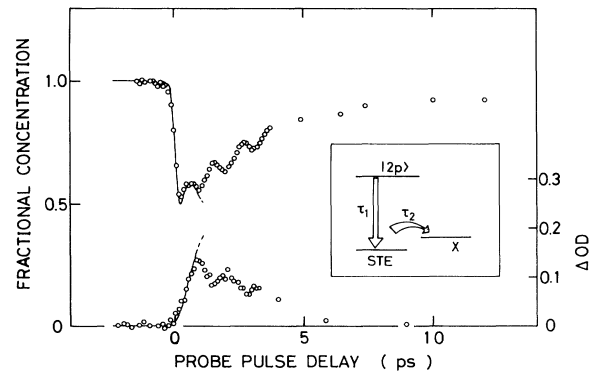


FIG. 2. The fractional change in the optical density measured at the STE-band maximum and at 500 nm for NaCl at 5 K, as a function of delay after excitation of the STEs by a 605-nm light pulse. The optical density is normalized with respect to the height of the STE band at 500 nm at the time of incidence of the light pulse. The solid curves show the concentration change analyzed using the level diagram shown in the inset.

tion: only at the late stage of the damped oscillation and not before the formation of the *X* centers.

The *X* and STE bands are clearly resolved after 3 ps. Furthermore, the *X* band is located at the high-energy side when it is generated, opposite to the STE band.

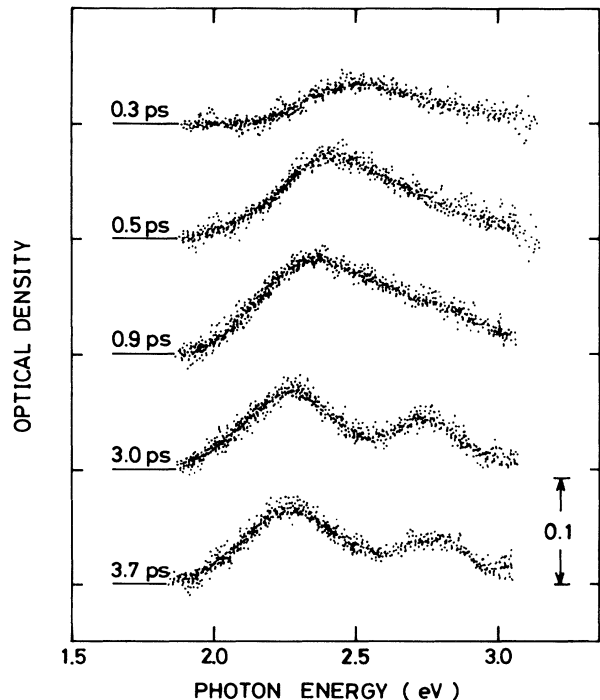


FIG. 3. Optical-absorption spectra produced in NaCl at 5 K at the indicated delays after excitation of the lowest STEs by a 605-nm light pulse. The contribution of the reduction of the STE concentration due to photoexcitation has been subtracted using the method shown in Fig. 1(b).

Thus, evidently these two bands are due to two separate optical transitions. The area of the X band, in curve e of Fig. 1, is roughly the same as the area of the STE band bleached. Since the concentration of the X centers generated is not larger than that of the STE depopulated, the oscillator strengths of these two transitions are nearly the same. Furthermore, the peak energy of the X absorption band is located between the peaks of the STE and F bands. Since the excited state of the F centers is known to be close to the continuum [15], it is unlikely that the X band is the transition from the APES for the electron-excited state. We conclude that the lowest STE and X center lie on the same APES; there are two minima in the lowest APES.

It has been established that the STEs in alkali halides consist of a hole localized as a halogen molecular ion (Cl_2^- molecular ion) and an electron [5]. Recent investigation by Kan'no, Tanaka, and Hayashi [16] of the Stokes shift of the STE luminescence and Tanimura and Itoh [17] of the Mollwo-Ivey relation for the absorption bands from the lowest APES show that the STEs in alkali halides can take three configurations (type I, II, and III). According to these classifications, the STE in NaCl, the lowest minimum of the lowest APES, is type II. The peak energy 2.5 eV of the X band, which is the same as that observed by picosecond spectroscopic studies at higher temperature by Williams, Craig, and Faust [7], lies on the Mollwo-Ivey plot of the type-III STE. Thus it is likely that the X center and the STEs in NaCl are type-II and -III STEs, respectively.

From Fig. 2, it is clear that the STE is restored first within 1 ps after excitation, followed by the oscillatory change. The first restoration of the STE and generation of the X center was analyzed using a rate equation model shown in the inset of Fig. 2. The rate equations were solved numerically by taking into account the finite pulsewidths of the exciting and probing light pulses. The calculated curves for the temporal change are shown by solid curves in Fig. 2, and the rate constants characterizing each step shown in Fig. 2 are obtained to be $\tau_1 = 430$ fs and $\tau_2 = 440$ fs, respectively. We did not try to obtain the best fit; nevertheless, the results of our simulation are satisfactory, as seen in Fig. 2. It follows that the lowest STE is restored within 430 fs, indicating that the nonradiative transition from the excited state to the lowest APES occurs as fast as 430 fs, corresponding to a few periods of the highest-frequency mode of LO phonons, the period of which is 135 fs. This may indicate that the transition from the excited state to the lowest APES is dynamic in nature; the nonradiative electronic transition is related to the lattice vibration in a coherent way [18].

The period of oscillation between the STE and the X center is much longer than that of the LO phonons. Since both are on the lowest APES, apparently the oscillation is governed by an APES having two potential minima. In order to substantiate our interpretation of the oscillation, we tried to construct an APES which can ac-

count for the low-frequency oscillation, using the available knowledge on the STEs. Although the atomic structures of the three types of STEs are still controversial [5], it is most likely at the present stage that they arise from relaxed configurations in which the halogen molecular ion is located differently. Assuming that the APES is a composite of two parabolas, the minima of which are separated by 2.0 Å, which is about half of the halogen-halogen distance in NaCl, we carried out a calculation of the oscillation frequency using classical mechanics, which has been shown to account for the general features of the dynamical motion of the wave packet on the APES [19]. We obtained the APES as shown in Fig. 4, for which the obtained vibrational period is 1.1 ps. The value of the period of oscillation in each parabola is 920 fs, close to the period of 610 fs of the translational vibration of the halogen molecular ion occupying two halogen sites (the V_k center), obtained by simulation of the translational vibration of the halogen molecular ion [20]. The energy separation of the two minima was taken rather arbitrarily to be 130 meV. This energy satisfies the requirement that the X luminescence is not seen under continuous irradiation below the temperature, 100 K, at which the STE luminescence is quenched. Thus the slow local oscillation observed in the present study can be explained in terms of a wave packet coherently propagating in a double-minimum potential well at the natural oscillation

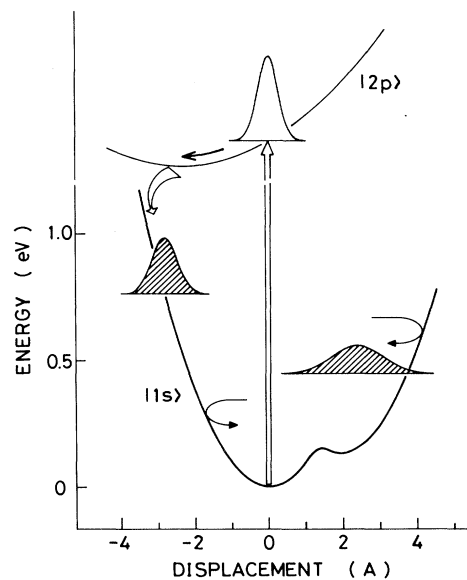


FIG. 4. An adiabatic potential-energy surface for the lowest and electronically excited STEs, describing the deexcitation and F - H pair-formation processes. The transition from the higher branch to the lower branch occurs in 430 fs. The oscillation frequency in the lowest APES agrees with the experimental value of 1.1 ps. The vibration deexcitation leads to the annihilation of the X center and the recovery of the STE. Transformation to the distant F - H pair is induced during the relaxation process in the lowest APES.

frequency. The potential well reflects the complex local structure for the self-trapped excitons in alkali halides. We note that the vibrational relaxation in a double-well potential as shown in Fig. 4 leads to the decay of the X band and the recovery of the STE band.

The present experimental results show clearly that the F centers, probably together with the H centers, are formed as a result of the dynamic relaxation in the lowest APES. Williams, Craig, and Faust have shown that the F centers are produced by thermal activation on the lowest APES of NaCl at higher temperatures [7]. We showed here that dynamic lattice relaxation on the lowest APES is also responsible for F -center formation at low temperatures, where the thermally activated process is prohibited.

By applying cascade-excitation spectroscopy in the femtosecond time regime to the STE in NaCl, we have observed the dynamics of a low-frequency coherent vibration and vibrational relaxation in the lowest APES after a nonradiative transition from the electron excited states. The presence of a short-lived intermediate state on the lowest APES has been found. Thus the oscillation is the first demonstration of coherent vibration in a double-well APES and vibrational relaxation. It has been shown also that the mechanism of dynamic formation of Frenkel pairs in alkali halides at low temperatures originates from the vibrational relaxation in the lowest APES.

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