One-Center Small Polarons as Short-Lived Precursors in Self-Trapping Processes of Holes and Electron-Hole Pairs in Alkali Iodides

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Initial processes of self-trapping of holes and electron-hole pairs in KI and RbI crystals have been investigated by means of a femtosecond pump-probe spectroscopy. We have found that a new short-lived intermediate is formed as a precursor of the self-trapped hole in the form of the halogen molecular ion with a D_{2h} symmetry. This state is identified to be a one-center type self-trapped hole on the basis of the quantum mechanical cluster calculations. A one-center self-trapped state is also created as a precursor for self-trapped excitons.

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The small polaron has been a long-lasting subject of extensive studies in solid state physics since the original suggestion by Landau in 1932 [1–4]. It is characterized as a carrier which is localized by self-induced potentials formed by strong electron-phonon interaction. From the first experimental observation of the self-trapped hole (STH) in the form of X_2^- (where X denotes a halogen atom) in alkali halides by Känzig [5], atomic structures, transport properties, and related phenomena of small polarons in many nonmetals with different properties have been studied experimentally and theoretically [6–8]. However, the initial process of the small-polaron formation, i.e., the dynamics of lattice relaxation leading to the small-polaron state, is far from being well understood. In particular, the lack of precise knowledge of the initial process has left several fundamental questions unresolved; a formation time, barriers for self-trapping, and relative roles of phonon modes in triggering and/or stabilizing the self-trapping states.

The recent development of a femtosecond pulse technique sets a new stage for experimental studies of the dynamical processes in the condensed phase after electronic excitations [9–12]. By means of the femtosecond pump and probe method, we reported previously the observation of the transient absorption before forming the STH in KBr [12]. However, the nature of the state giving rise to the transient absorption and its properties are not clarified at all. Therefore, more extensive studies of the process are highly desired. In this Letter, we study the lattice-relaxation process of holes and electron-hole pairs in alkali iodide crystals in the femtosecond time regime both experimentally and theoretically. A new short-lived intermediate, which is identified to be a one-center type self-trapped hole (one-center STH) on the basis of quantum mechanical cluster calculations, is found as a precursor of the self-trapped hole in the form of X_2^-. Such a one-center self-trapped state also plays a crucial role in the formation of self-trapped excitons (STE's) consisting of a halogen molecular ion and a trapped electron ($X_2^- + e$).

The specimens of alkali halides were excited with the two-photon absorption by the uv laser pulses with wavelength of 302.5 nm and pulse duration of ~200 fs. To investigate the self-trapping of a free hole, we used NO_2^- doped KI crystals [13]. The concentration of NO_2^- in the doped crystal was about 10^{17} cm^{-3}, and the electron-hole pair density generated by the two-photon absorption (~10^{16} cm^{-3}) was much lower than the electron trap concentration. We used pure crystals of KI and RbI to investigate formation processes of STE. The thickness of specimens was about 3 mm. The details of the experimental setup for the pump and probe spectroscopy can be found in Ref. [12].

Figure 1 shows time-resolved absorption spectra of NO_2^- doped KI measured for various delay times (τ_d) at 80 K. In the top frame in which the spectrum at 10 ps is shown, the solid curve illustrates a spectrum measured at 7 μs after irradiation of an electron pulse at 80 K. The spectrum is characterized by absorption bands peaked at 1.55, ~2.2, and 3.10 eV. These bands are due to the hole transitions of the V_K center: They are ascribed to the transitions from the lowest Σ_u orbital to the Π_g,Π_u, and Σ_g orbitals, respectively, of the halogen molecular ion [14]. An interesting finding from transient spectra is that several distinct absorption bands appear before the V_K bands are formed. In the absorption spectrum delayed at 0.3 ps after the femtosecond pulse excitation, an absorption band, peaked at ~2.1 eV, and a tail about

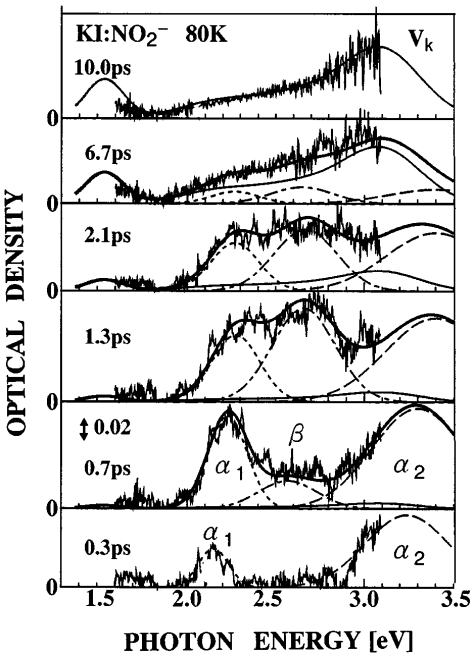

FIG. 1. Time resolved absorption spectra of KI:NO_2^- measured for various delay times at 80 K by the two-photon excitation above the band gap. Fitted curves represent α_1 band (dotted line), β band (dash-dotted line), α_2 band (dashed line), and V_K center band (solid line). The thick solid line shows the spectrum consisting of these bands.

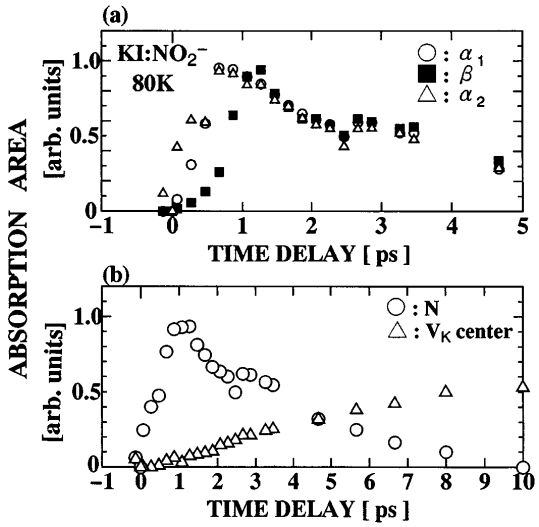

FIG. 2. (a) The time evolution of the absorption area of the three bands obtained by the spectral fitting. Open circles, triangles, and closed squares show the α_1, α_2, and β bands, respectively. (b) Time evolution of the N band (open circles) and the V_K center band (open triangles).

3 eV are observed. The two bands continue to grow until $\tau_d = 0.7$ ps. In the delay times from 0.7 to 1.3 ps, it appears that another band peaked at $\simeq$2.7 eV starts to grow, and at a late time delay the V_K band is finally formed. We refer to the transient bands observed for $\tau_d \sim 0.3$–2 ps as α_1, β, and α_2 from the lower energy side and, further, refer to them as N band as a whole. To investigate in more detail the time evolution of these bands, we tentatively decomposed the observed spectrum into α_1, α_2, β, and V_K bands. We assumed that the corresponding states interact with the surrounding lattice strongly enough to give the Gaussian absorption band. Fitted spectra are illustrated by dotted (α_1), dash-dotted (β), and dashed (α_2) curves, respectively, in Fig. 1. The illustrated spectrum could reproduce most likely the spectrum observed at each delay time. Figure 2(a) shows the time evolution of the absorption area of the band, which was deduced from the integration of the fitted spectrum in Fig. 1. The α_1 and α_2 bands exhibit the same time evolution, while the β band appears to be delayed by about 500 fs. This temporal behavior suggests that the α_1 and α_2 bands originate from the same state, but the origin of the β band is different from this state. After 2 ps, however, no distinct behavior is noticed among these bands. Figure 2(b) shows the time variation of the V_K band and that of the total area of the α_1, α_2, and β bands, i.e., the N band. The decay of the N band corresponds to the rise of the V_K band, which means that the intermediate state giving the N band is directly converted into the V_K center. Therefore, the intermediate state is a precursor state for the V_K center.

In order to obtain deeper insight into the transient absorption before the formation of the V_K center, we performed quantum mechanical *ab initio* calculations for some self-trapped states of holes: They are a one-center STH (small polaron) and a two-center STH (V_K center). An embedded molecular cluster technique was used within *ab initio* (ICECAP) and semiempirical (CLUSTER) molecular orbital–linear combination of atomic orbitals calculation techniques which take into account the polarization of the lattice by the hole in a self-consistent way, as described in Refs. [15,16]. The ICECAP method was used for the calculation of relaxed configurations of the hole states. The size of the quantum cluster in the ICECAP method did not exceed two anions and ten nearest-neighbor cations. The CLUSTER code was employed to calculate the spectra of electron excitations of the hole states. In this technique, the quantum cluster included 24 I and 24 K ions. In Fig. 3, pictorial representations of lattice configurations for the one-center STH and two-center STH are shown, viewed in the (001) plane. For the one-center STH, the displacements of nearest-neighbor K^+ ions and the next nearest I^- ions surrounding an I^- ion on which a hole is localized are calculated to be $0.1a_0$ along the $\langle 100 \rangle$ direction and $0.02a_0$ along the $\langle 110 \rangle$ direction, respectively, where a_0 is the lattice constant. On the other hand, the displacements of I^- ions for the two-center STH are $0.14a_0$. The one-center STH occupies one of the p orbitals of a halogen atom and has a C_{4v} symmetry due to the Jahn-Teller distortion of the lattice. Hole transition energies for these self-trapped hole states

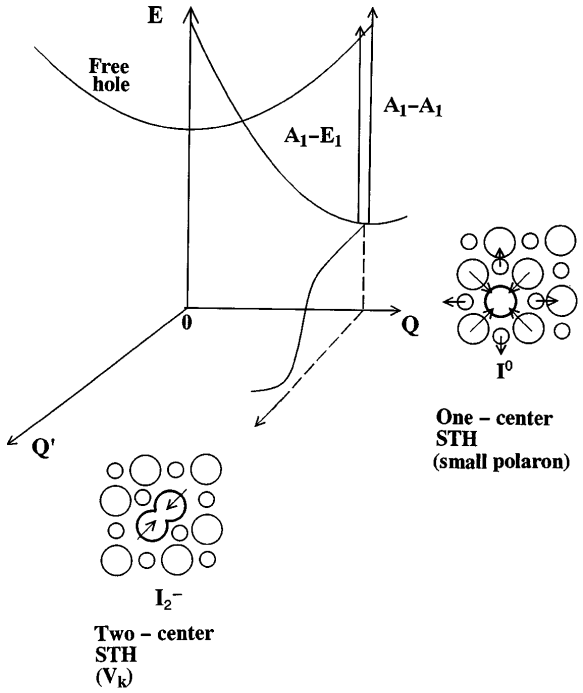

FIG. 3. Schematic illustration of the relaxation pathways of *e-h* pairs with local lattice distortion on the two-dimensional adiabatic potential surfaces. In the figure, pictorial representations of lattice configurations for the one-center STH and two-center STH are shown, viewed in the (001) plane.

in KI are summarized in Table I. Calculated energies for the two-center STH agree well with the experimental values of the V_K center, and this agreement demonstrates that our calculations are adequate to evaluate transition energies of self-trapped states [17]. Allowed optical transitions from the lowest state of the one-center STH to a resonant quasilocalized state in the valence band are A_1-E_1 and A_1-A_1 transitions. The calculated energies of these transitions are 2.4 and 3.3 eV, which are in good agreement with the peak energies of the 1 and 2 bands. Therefore, it is concluded that one of the short-lived intermediates is the one-center STH. The peak energy of the β band, however, does not correspond to any transition energy of the one-center STH. A possible explanation for this band is a three-center STH, although other configurations are also possible as an intermediate state which is less stable than the V_K center.

The formation processes of the V_K centers are illustrated schematically in Fig. 3 by the configurational coordinate model. Two allowed transitions of the one-center STH are indicated by arrows. As shown in the two-dimensional adiabatic potential surface of the figure, there should be two distinct modes which have different symmetries in the relaxation process: One (Q) induces the one-center configuration, and the other (Q') forms the two-center configuration which is the so-called V_K mode. The Q' mode is induced after the one-center configuration is realized. Therefore the mode that induces the one-center configuration can be regarded as a triggering mode and the V_K mode as a stabilizing one.

In what follows, we investigate relaxation processes of electron-hole pairs, leading to formation of the STE [18,19]. Shown in Fig. 4 are transient absorption spectra of a pure KI crystal at 80 K. The dashed curve in the frame of $\tau_d = 101$ ps in Fig. 4 indicates an absorption spectrum of the STE [19]. During 1 ps after the pulse excitation, an absorption band similar to the N band of KI:NO_2^- appears, and a broad band emerges simultaneously in the energy region of the electron transition of STE. The broad band was not observed in KI:NO_2^-. After 10 ps the spectrum in the 1–2 eV region is converted into the typical spectrum of the electron transition of STE. When we compare this spectrum with the STE band observed under the long pulse excitation as shown by the dashed line in the frame of $\tau_d = 101$ ps, we notice a disagreement in the energy region higher than 2.5 eV. This is due to the inclusion of the π emission from STE peaked at 3.31 eV to the absorption detection system. In fact, the absorption spectra in RbI in which the π luminescence of STE is not emitted in this region show more clearly the presence of short-lived bands. The top frame of Fig. 4 shows the transient absorption spectrum of RbI at 0.3 ps. Short-lived bands at 2.1 and 3.0 eV are more clearly observed. Considering the experimental situation in KI, the short-lived absorption band above 2 eV is quite similar to the N band of KI:NO_2^-, and the time evolution in the early stage coincides very well with that of the one-center self-trapped hole. We note that the V_K center band which is illustrated by the dotted curve

TABLE I. Hole transition energies for the one- and two-center type STH in KI (in eV). Both calculated and experimental values are shown. Experimental values for the one-center type indicate the results of this study.

	Two-center STH (V_K center)			One-center STH (small polaron)	
Transition	Theory (eV)	Expt. (eV)	Transition	Theory (eV)	Expt. (eV)
$\Sigma_u \rightarrow \Pi_g$	1.62	1.55	$A_1 \rightarrow E_1$	2.4	2.1
$\Sigma_u \rightarrow \Pi_u$	2.28	2.03	$A_1 \rightarrow A_1$	3.3	~3.2
$\Sigma_u \rightarrow \Sigma_g$	3.12	3.10			

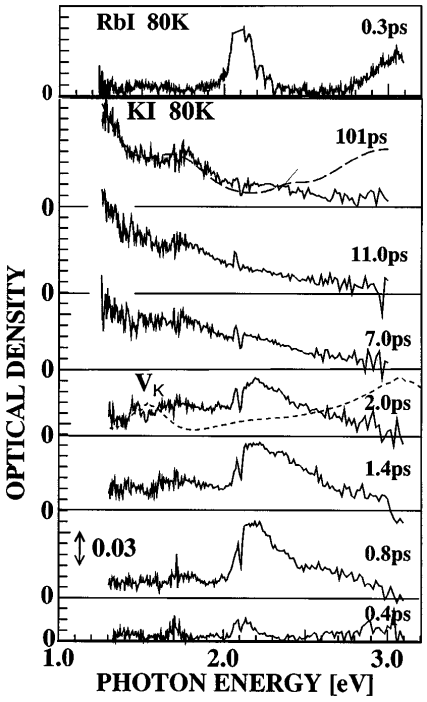

FIG. 4. Time resolved absorption spectra of KI measured for various delay times at 80 K. Dashed curve in the frame of $\tau_d = 101$ ps shows the STE band. The V_K band is illustrated in the frame of $\tau_d = 2.0$ ps by the dotted curve. The top frame shows the transient absorption spectrum measured for RbI at 0.3 ps after the excitations.

in the frame of $\tau_d = 2.0$ ps cannot be seen in any time region, and thus the V_K center is not formed before the formation of STE. From the experimental results for pure KI and RbI, we found that the one-center self-trapped state is formed as a precursor for the STE in the short time region in pure alkali iodides. This is in contrast to the model that a free hole is initially self-trapped into the configuration of X_2^- in the ultrashort time region such as 100 fs, and subsequently the X_2^- molecular ion captures an electron [20,21].

In summary, the one-center type self-trapped state has been found as a precursor for the V_K centers in the initial stage of the lattice relaxation process of holes. This state also plays an important role in the formation of STE's consisting of $X_2^- + e$. Our finding reveals that different modes of phonons trigger and stabilize the self-trapped states. The triggering mode forms the one-center configuration with the C_{4v} symmetry, and the stabilizing one forms the largely distorted configuration of X_2^- molecular ion in the [110] direction.

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