

Transient Absorption Due to the Self-Trapped Exciton Localized at an Iodine Dimer in KCl:I

S. Hirota, K. Edamatsu, and M. Hirai

Department of Applied Physics, Faculty of Engineering, Tohoku University, Sendai 980, Japan
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The transient absorption spectrum of the self-trapped exciton (STE) localized at an iodine dimer (I_2^{--*}) in an iodine-doped KCl crystal (KCl:I) has been investigated at 80 K. The absorption band due to the electronic transition was found around 0.36 eV, and the bands due to the hole transitions around 1.5 and 3.0 eV. The electronic transition band occurred in an extremely lower-energy region than that of the STE in KI or RbI crystals, suggesting the "on-center" configuration of the STE (I_2^{--*}) in KCl:I.

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Since the proposal of the "off-center" self-trapped-exciton (STE) model [1], the relaxed state of the excitons in alkali halide crystals has been discussed from a new point of view [2-4]. It has been suggested that the STE relaxes into various types, depending on crystals. The first typical model for the STE is the "on-center" type, which consists of a halogen molecule ion (X_2^-) occupying two adjacent anion sites in the $\langle 110 \rangle$ direction and an electron trapped by it. The second is the off-center type, in which an X_2^- ion and an electron occupy separately two adjacent anion sites. The third is an "intermediate" case between the above two types. This new idea for the STE is expected to provide answers for the problems which the on-center model has not resolved. One of the examples is the transient absorption due to the electronic transition in the STE. Various calculations based on the on-center model predicted absorption bands in the infrared region (0.1-1.1 eV) [4-8], while bands were observed experimentally around 2 eV [9,10]. Recently, however, this discrepancy was explained by the off-center model [1-4]. On the other hand, an absorption band due to the electronic transition in the on-center-type STE has never been reported. The search for such bands is very interesting and important for the study of the STE relaxation.

It seems easy to form the on-center-type STE in the crystals with large halogen ions relative to the lattice constants, but to form the off-center-type STE in the crystal with small halogen ions [2]. The introduction of halogen ions of different size into the host crystals makes it possible to form the STE with a different size X_2^- from that in the host, and thus we can extend the systematic study of the STE. The STE localized at an iodine dimer (I_2^{--*}) in an iodine-doped KCl crystal (KCl:I) is expected to be the on-center type because of its large halogen size relative to the host lattice constant, in spite of the off-center-type STE (Cl_2^{--*}) in the host (KCl) crystal. In this paper we present the transient absorption spectrum of the I_2^{--*} in KCl:I, including the first observation of the infrared absorption, possibly due to the electronic transition in the on-center-type STE.

A single crystal of KCl doped with about 1 mol% of KI was grown in an argon atmosphere by the Czochralski

method. The sample was excited by an ArF excimer laser ($h\nu=6.42$ eV, pulse duration of 17 ns), the photon energy of which fell in the excitation band for the so-called UV luminescence originating from I_2^{--*} [11,12]. The transient absorption spectrum after the excitation was measured by a conventional optical system using a Xe flash lamp with a pulse duration of 6 μ s. The probe light for the absorption measurement was detected by a photomultiplier tube in the visible region ($2.0 \leq h\nu \leq 4.0$ eV), by a Ge photodiode in the near-infrared region ($0.7 \leq h\nu \leq 2.5$ eV), or by an InSb detector in the infrared region ($0.23 \leq h\nu \leq 1.1$ eV).

Figure 1 shows the transient absorption spectrum immediately after the excitation at 80 K. The absorption decayed with a single component of $\tau=0.25$ μ s, which coincided with the decay time of the UV luminescence [13]. This coincidence indicates the same initial state for the transient absorption as that for the UV luminescence.

The transient absorption spectrum of Fig. 1 exhibits three distinct bands around 0.36, 1.5, and 3.0 eV. The absorption band around 0.36 eV is attributed to the electronic transition ($1s \rightarrow 2p$) in I_2^{--*} as described below. In the D_{2h} symmetry, the $2p$ state splits into three levels,

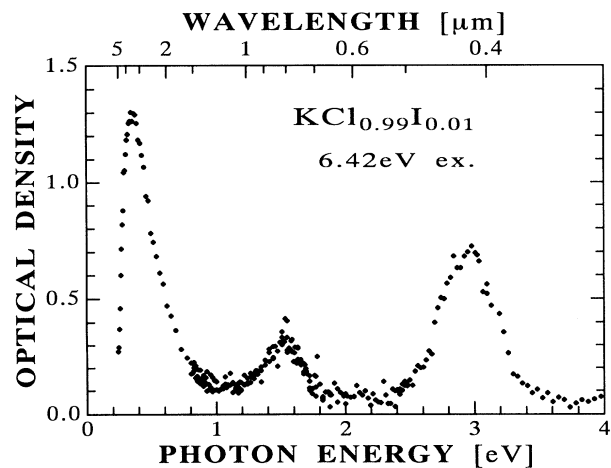


FIG. 1. Transient absorption spectrum of the $KCl_{0.99}I_{0.01}$ crystal excited by an ArF excimer laser at 80 K.

TABLE I. Peak positions of the transient absorption bands due to electronic transitions in the STE of alkali iodides and KCl:I.

Crystal	Peak position (eV)
NaI ^a	≪ 1.2
KI ^a	1.1
RbI ^a	1.2
KCl:I	0.36

^aFrom Ref. [9].

i.e., b_{1u} , b_{2u} , and b_{3u} . The calculations based on the on-center model [5–8] predict that the b_{3u} state is the lowest and that the others stand at somewhat higher energy. Thus the 0.36-eV band is tentatively attributed to the $a_{1g} \rightarrow b_{3u}$ transition. Although the other two bands are not clear at present, a tail at the higher-energy side of the 0.36-eV band and a part of the band around 1.5 eV might be attributed to them. The peak energy of the 0.36-eV band is extremely low compared to those attributed to the electronic transitions in the STE in other alkali halide crystals [9]. For instance, bands in KI or RbI appear above 1 eV, as listed in Table I. This difference possibly originates from the difference of their STE type, i.e., the on-center type in KCl:I, while the off-center and the intermediate type in KI and RbI. Suggestive evidence for such origin is the discrepancy between the experiments [9,10] and the calculations based on the on-center model [4–8] for the electronic transition energy of the STE in alkali chlorides, as described earlier. Although this discrepancy has been a puzzle for many years, the recent discussion [1–4] based on the off-center model is likely to give an answer for it. According to the calculation [4], if the STE is the on-center type, the absorption band due to the electronic transition is expected in the low-energy region. This hypothesis seems to be true for the localized STE (I_2^{--*}) in KCl:I showing the 0.36-eV band. It is also interesting to explore the lower-energy absorption band in other crystals such as NaI and NaBr, in which the on-center-type STE is expected. From this point of view, the tail observed below 1 eV in the transient absorption spectrum of the STE in NaBr [9] might be due to the electronic transition.

TABLE II. Peak positions of the V_k bands in alkali iodides and the transient absorption bands of KCl:I.

Crystal	$\pi_g 5p \leftarrow \sigma_u 5p$ (eV)	$\sigma_g 5p \leftarrow \sigma_u 5p$ (eV)
NaI ^a	1.41	2.87
KI ^b	1.55	3.10
RbI ^a	1.56	3.06
KCl:I	1.53	2.95

^aFrom Ref. [16].

^bFrom Ref. [17].

TABLE III. Transient absorption bands due to hole transitions in the STE of alkali iodides and KCl:I.

Crystal	Peak position (eV)	Half-width (eV)
NaI ^a	3.0	0.5
KI ^a	3.2	0.8
RbI ^a	2.9, 3.5 ^b	...
KCl:I	2.95	0.55

^aFrom Ref. [9].

^bThe reason for the double peaks in RbI is not clear at present. It might be attributed to the coexistence of different types of STE's.

The two bands around 1.5 and 3.0 eV are attributed to the hole transitions ($\pi_g 5p \leftarrow \sigma_u 5p$ and $\sigma_g 5p \leftarrow \sigma_u 5p$, respectively) in I_2^{--*} because of their peak positions which almost coincide with those for the V_k (I_2^-) centers in pure alkali iodide crystals (Table II). Since the V_k centers are the on-center type in the configuration of the halogen molecule (X_2^-), coincidence of the peak positions suggests the on-center-type STE (I_2^{--*}) in KCl:I. It is also interesting to compare the hole transition band around 3.0 eV with those due to the STE in pure alkali iodide crystals (Table III). The 3.0-eV band due to I_2^{--*} in KCl:I is very similar to that in NaI, but not to those in KI or RbI. This result indicates the close similarity of the configuration between the STE's (I_2^{--*}) in KCl:I and NaI. This similarity is also reflected by the luminescence spectra. The UV luminescence of KCl:I and the π luminescence of NaI are close to each other in the spectra [11,12] and also in the decay times [14,15]. Meanwhile, the hole transition bands around 3.0 eV of the STE's in KI and RbI shift to the higher-energy side compared with those in KCl:I and NaI. The blueshift is probably due to the shortening of the interatomic distance between two iodines caused by the off-center configuration of the STE in KI and RbI.

In conclusion, the transient absorption spectrum of KCl:I suggests the on-center configuration for the exciton localized at the iodine dimer. We note that the transient absorption spectrum, especially the electronic transition band, sensitively reflects the configuration of the relaxed exciton, and is able to be a useful tool to investigate the relaxation form of the excitons.

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