Resonance Raman Scattering of the Self-Trapped Exciton in Alkali Halides

K. Tanimura, T. Suzuki, and N. Itoh
Department of Physics, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-01, Japan

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We have studied resonance Raman scattering of the self-trapped exciton (STE) in NaCl tuned to the $\sigma_g \rightarrow \sigma_u$ hole transition and to the $1s \rightarrow 2p$ electron transition. The former spectrum is characterized by a sharp line at 366 cm^{-1}, which coincides with the stretching-vibration frequency of the *H* center, while the latter is characterized by broad bands, similar to that of the *F* center, situated below the LO phonon frequency. The result provides evidence that the STE is essentially an interacting *F-H* pair.

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Self-trapping of excitons is a typical example of phenomena arising from strong interaction between electronic and lattice systems in solids [1,2]. It has been observed in many solids with different crystal structures and bond strengths, and can be regarded as an initial step of several defect processes induced by electronic excitation [2–4]. The alkali halide is the material for which most extensive studies on the self-trapped exciton (STE) have been carried out; nevertheless the relaxed configuration of the exciton in this material is still controversial. The problem to be clarified is concerned with the fact that the STE is essentially a two-particle system consisting of a localized electron and a localized hole, interacting with each other and with the lattice [4,5].

It is now clear that the STE in alkali halides consists of a X_2^- (X denotes a halogen atom) molecular ion on which a hole is localized and an electron is bound by the Coulomb potential [4,6]. Evidently the hole couples most strongly with the Q_1 mode, primarily the stretching mode of the X_2^-. It has been pointed out theoretically that the cooperative electron-phonon and hole-phonon coupling induces the off-center instability of the X_2^- along a $\langle 110 \rangle$ direction [4,5,7] by coupling with the Q_2 mode, the symmetry-breaking mode. Although several features of the experimental results can be explained [4,8,9], the atomic structure of the STE predicted theoretically depends strongly on the methods used in the calculation [4,7,10,11]. Experimental studies to reveal the phonon modes which are incorporated in the STE are highly desired.

Resonance Raman scattering (RRS) spectroscopy is one of the most useful methods to reveal the phonon modes which couple to an electronic system [12–16]. The method is particularly valuable for clarifying the phonon modes incorporated in the STE configuration, since it has a capability of separating the modes coupling to the electron and hole in the STE. In this Letter, we present for the first time the results of RRS for the STE in alkali halides. The results show clearly that the STE in NaCl is essentially an interacting pair consisting of a localized electron at an anion vacancy (the *F* center) and a X_2^- molecular ion at a nearest-neighboring anion site (the *H* center).

Specimens of pure NaCl were obtained from a crystal block purchased from Harshaw Chemical Co. Specimens doped with NO_2^-, grown by the Kyropoulos method in a dry Ar atmosphere, were also used. A specimen with a size of $8 \times 10 \times 4$ mm^3 was attached to a cold finger of a cryostat capable to be cooled to 5 K. For measuring RRS spectra of stable color centers, specimens (pure NaCl for the *F* and *H* centers and NaCl doped with NO_2^- for the V_K centers) were irradiated first by electron pulses generated by a Febetron accelerator (HP-43710A) and then the RRS spectra were measured. For measuring RRS spectra due to the STEs, a spot of the specimen was irradiated coaxially with two synchronized pulsed laser beams. One at 266 nm was generated with a *Q*-switched Nd-doped yttrium-aluminum-garnet laser (Continuum, 461-B), and used to produce electron-hole pairs to form the lowest triplet STEs; the second was generated with an excimer-laser-pumped dye laser (Lambda Physik EMG-201 MSC and FL3002), and probed the Raman scattering. The dye-laser pulse was delayed from the 266-nm pulse with a delay generator to accomplish time-resolved Raman spectroscopy [17]. The scattered light was focused onto the entrance slit of a triple monochromator (Spex Triplemate), and was detected by a gated multichannel detector (Prinston D/SIDA 700).

In Fig. 1, we show the absorption spectrum of the lowest triplet STE in NaCl measured at 9 K. The band at 2.0 eV has been assigned to the electron transitions from the lowest to the symmetry-split 2*p*-like triplet levels [18]. It has been decomposed, based on dichroic absorption measurements [19], as shown by the thin solid curves; the three subbands are labeled here as I, II, and III in order of increasing peak energies [20]. The band at 3.8 eV is due to the hole transition from bonding to antibonding states of the X_2^- molecular ion [18]. During the RRS measurements, the wavelength λ_p of the probe light pulses was tuned to the resonance excitation of either the electron or hole transitions.

In Fig. 2, we show the spectra of scattered light measured at 65 K for $\lambda_p = 337$ nm (3.68 eV) which falls in resonance with the hole transition. The four spectra are obtained for different delay times (τ_p) of the probe pulse with respect to the 266-nm excitation pulse. A Raman line at 366 cm^{-1} with monotonically decreasing overtones is clearly seen. The intensities of these Raman lines

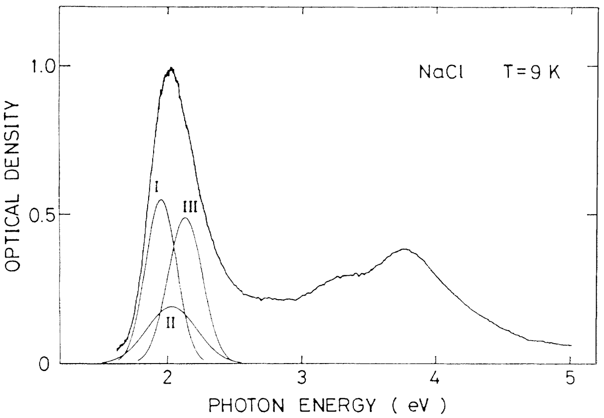

FIG. 1. Optical absorption spectrum of the STE in NaCl measured at 9 K. The band around 2 eV, due to the electron transition, is decomposed, as shown by thin solid curves, into three Gaussian bands I, II, and III (see Refs. [19] and [20]).

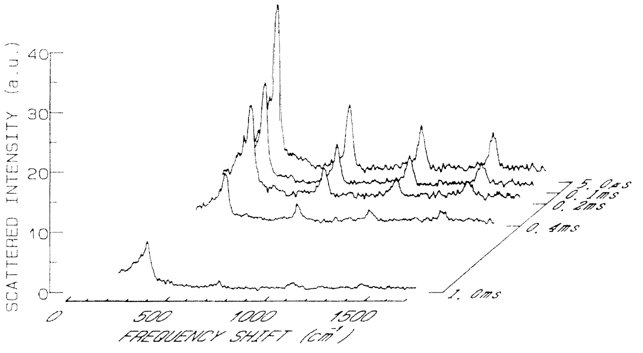

FIG. 2. Spectra of Raman scattering measured at 65 K probed at 337 nm (3.68 eV) in resonance with the $\sigma_g \rightarrow \sigma_u$ hole-transition band. Each curve was obtained for the probe pulses with different delays with respect to the 266-nm excitation pulse. The second-order bulk Raman line dominates in the 1.0-ms spectrum.

decrease with increasing τ_p with a time constant of 230 μs, which is the lifetime of the lowest triplet STE at this temperature [21]. Similar time-resolved measurements were made also at 78 K. We observed the same Raman spectra, but the intensities decayed with respect to τ_p with a time constant of 70 μs, the lifetime of the lowest triplet STE at 78 K [21]. Thus it is clear that the Raman spectrum shown in Fig. 2 is exclusively due to the lowest triplet STE in NaCl. The features of the Raman spectra were found to be the same when measured for several λ_p ranging from 330 to 345 nm, as expected for a center showing a homogeneously broadened optical absorption band.

The Raman line of 366 cm^{-1} should be assigned to the stretching vibration of the X_2^- molecular ion, and the frequency $\nu(Q_1)$ of this mode reflects the stiffness of the bond of the X_2^- molecular ion. In order to get more insight into the nature of the X_2^- molecular ion in the STE, we compare in Fig. 3 the RRS spectrum of the STE with that of the V_K center and the H center, both of which include the X_2^- molecular ions, but with different configurations [22,23]. The RRS spectra of the V_K and H centers were measured for the first time in the present study. The Raman spectrum for the V_K center consists of the two split lines and their overtones; the mean value of the two split lines, 243 cm^{-1}, agrees with the $\nu(Q_1)$ of the V_K centers in KCl and RbCl measured by Goovaerts and Schoemaker [24]. The splitting can be attributed most reasonably to the combined motions of the X_2^- and its two nearest-neighbor alkali ions [25]. The Raman spectrum for the H center is characterized by a sharp line at 366 cm^{-1} and its overtones, and it is evident that $\nu(Q_1)$ of the STE coincides with that of the H center.

The frequency of the 366-cm^{-1} Raman line for the Q_1 mode of the X_2^- molecular ion in the STE is far above the phonon cutoff frequency (264 cm^{-1}) of NaCl, indicating the local nature of the mode. The strong hardening in the Q_1 mode of the H center, compared to that of the V_K center, can be ascribed to the smaller internuclear separation R_e of the two halogen ions, on which a hole is localized, as has been demonstrated by an electron-spin-resonance study [23] and theoretical calculation [26]. Suzuki, Tanimura, and Itoh have measured $\nu(Q_1)$ of several Cl_2^- centers in alkali halides and found that it is

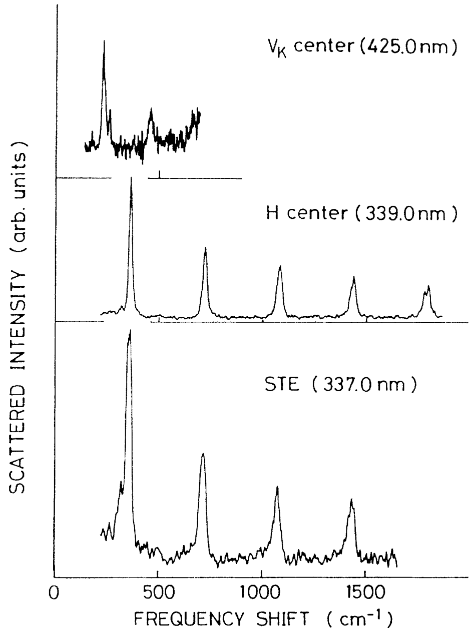

FIG. 3. Spectra of Raman scattering for resonance with $\sigma_g \rightarrow \sigma_u$ hole transition of the V_K center measured at 78 K, the H center measured at 5 K, and the STE measured at 65 K in NaCl. For the STE Raman spectrum the second-order bulk Raman line has been subtracted.

a monotonically decreasing function of R_e [25]. Based on their result, we conclude that the agreement of the magnitude of $\nu(Q_1)$ of the X_2^- in the STE with that of the H center is not accidental, but a clear indication that R_e of the X_2^- in the STE is the same as that of the X_2^- in the H center; this indicates that the X_2^- of the STE takes approximately the same configuration as the X_2^- in the H center. Although the magnitude of $\nu(Q_1)$ of the STE is the same as that of the H center, its line shape shows some differences; the width is much broader [27], and the main line is associated with a structure at the low-frequency region, as seen in Fig. 3. The difference indicates the presence of a perturbation on the H center composing an STE.

In Fig. 4, we show the RRS spectra obtained for λ_p of 580 nm (2.14 eV) and 633 nm (1.95 eV) measured at 78 K. The former falls in resonance with the electron transition at band III, while the latter with the transition at band I, although band II underlies both with almost equal absorption strength. The dependence of the intensities of these Raman spectra on τ_p was found to follow an exponential decay with the time constant of 70 μs, which is the same as the lifetime of the STE at 78 K [21]. Thus it is clear that the spectra shown in Fig. 4 are due to the lowest triplet STE. In contrast to the case of the hole transition, the Raman spectrum under resonance with the electron transition is featured by a broad spectrum below the LO phonon frequency. In the figure, the RRS spectrum of the F centers measured with the 488-nm line of an Ar$^+$-ion laser is shown for comparison. The spectrum is essentially the same as that reported previously [16]. It is noted that the spectral feature for $\lambda_p = 580$ nm is quite similar to that of the F-center spectrum. By tuning λ_p to band II and band III, the spectrum of scattered light exhibits significant changes in shape: the relative height of the broad bands at low and high wave-number regions and the structure and magnitudes of sharp peaks at the central region.

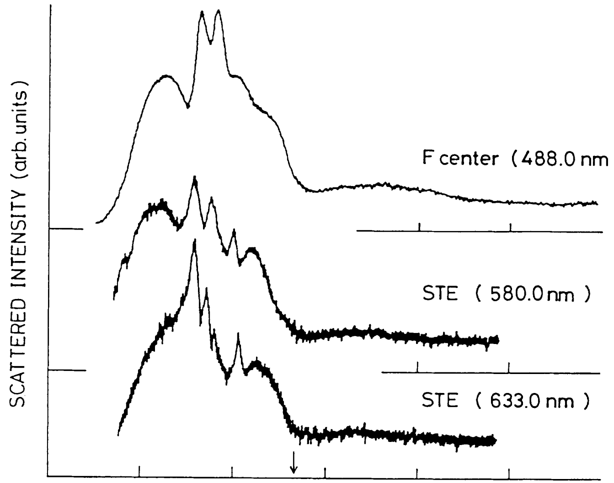

FIG. 4. Spectra of Raman scattering of the STE in NaCl measured at 78 K for resonance with the electron transition obtained with probe light of 633 and 580 nm. The spectrum of the resonance Raman scattering of the F center measured at 78 K probed by 488-nm Ar$^+$-ion-laser line is also shown for comparison. The LO frequency of NaCl is shown by an arrow.

The result that the RRS spectra tuned to the hole and electron transitions show totally different features from each other indicates first that the STE includes a localized electron and a localized hole, each of which is interacting with different phonon modes. Furthermore, comparison of the STE Raman spectra with those for F, V_K, and H centers shows that the localized electron and the hole have configurations similar to those of the F and the H center, respectively. Thus the STE in NaCl can be regarded, as a first approximation, as a pair consisting of an F center and an H center; there exists interaction between each other which induces significant deviations of Raman spectra from those of isolated centers. The Raman spectra in resonance with the electron transitions are influenced more strongly by the interaction as seen in Fig. 4. According to the previous studies of the Raman scattering of the F center in NaCl [16], the spectral features of the scattering light are determined mainly by the force-constant changes of alkali ions surrounding the vacancy. Theoretical calculations on the H center [26,28] have shown that the six alkali ions neighboring the site at which the X_2^- is located are displaced more strongly. Thus, the energy and the resonance Raman spectrum tuned to the transition, of which the dipole moment is directed to these distorted alkali ions, are presumed to deviate from those of the F center. Three F-H neighboring pair configurations are conceivable: the X_2^- molecular axis has an angle of 0°, 60°, or 90° with respect to the line connecting the F and H centers, although the theoretical studies on the STE configuration have been restricted only to the configuration of an angle of 0°. For each of these configurations, symmetry consideration based on the dichroic properties of the absorption bands due to the electron transition showed that the transition dipole moment of band III is not oriented to the distorted alkali ions, but that the dipole moments of bands I and II are oriented to these alkali ions. Furthermore, the Raman spectrum tuned to the transition closest to the F-absorption band in energy is the most F-center-like. These results are consistent with the conclusion that the STE in NaCl is an interacting nearest-neighbor pair of the F and H centers, although it is not yet possible to differentiate the three possible orientations of the H center.

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