

Resonance-Raman-scattering spectroscopy of the self-trapped excitons in alkali halides

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We have studied resonance Raman scattering tuned to the $\sigma_g \rightarrow \sigma_u$ hole transition of the self-trapped excitons (STE's) in alkali halides. The Raman spectrum is characterized by a sharp line of 137 cm^{-1} in NaBr, 361 cm^{-1} in NaCl, and 139 cm^{-1} in RbI. Each line has been assigned to the stretching vibration of the halogen molecular ion (X_2^-) composing the STE. Comparison of the Raman frequencies with those of V_K and H centers obtained by similar measurements indicates that the frequency of the STE in NaBr coincides with that of the V_K center, while those in NaCl and in RbI are almost identical to the frequencies of the H centers. These results provide evidence that the X_2^- of the STE in NaBr occupies two adjacent halogen sites and the X_2^- of the STE in NaCl and in RbI occupies a single halogen site.

I. INTRODUCTION

Exciton self-trapping, caused by strong electron-lattice interaction, is a phenomenon observed in many solids with different crystal structure and bonding nature.¹⁻⁴ One of the direct consequences of exciton self-trapping is the generation of emission bands with large Stokes shifts and broad width.¹ The luminescence due to the radiative decay of the self-trapped exciton (STE), the STE luminescence, has been studied extensively for many kinds of nonmetallic solids.^{2,3} Alkali halides are the materials for which the most extensive and systematic studies on the luminescence have been carried out both experimentally and theoretically. One of the interesting features of the STE luminescence in alkali halides is that more than one emission bands with different decay characteristics and Stokes shifts are observed under fundamental excitation, indicating the presence of more than one relaxed state with different electronic nature and/or configurations in a given solid. In spite of extensive research for more than two decades after the establishment of the concept of the STE,⁵ the model of the initial state of the luminescence in alkali halides remains controversial.

Studies of the luminescence induced by recombination of an electron with a V_K center^{5,6} and of optically detected magnetic resonance⁷⁻¹⁰ indicate clearly that an STE in alkali halides consists of an X_2^- (X denotes a halogen atom) molecular ion, or a hole localized on two neighboring halogen sites, and an electron bound by the Coulomb field around the hole. The radiative recombination of the STE's in alkali halides results in the emission of either σ - or π -polarized light with respect to the orientation of the molecular axis.^{5,11} The σ luminescence exhibits a short lifetime, of the order of a few nanoseconds, indicating the singlet character of the initial state, while the π luminescence exhibits a long lifetime ranging from microseconds to milliseconds, indicating the triplet nature of the initial state. The triplet nature of the π luminescent state has been demonstrated through optically detected magnetic resonance studies.⁷⁻¹⁰ In certain

alkali halides, only the π luminescence is observed, while in some others both π and σ luminescence are observed; the σ band is located 1-2 eV above the π band. In the special case of RbI, two different π -polarized luminescence bands are observed at 2.27 eV and at 3.07 eV;^{12,13} the former is known as the π band and the latter is often called the E_X band. In any case, the π luminescence band is the lowest in energy. Thus the π luminescent state has been assigned as the lowest triplet state of the STE.

It was suggested earlier that the X_2^- of the STE was placed at a D_{2h} crystal field, as in the case of a self-trapped hole.⁵⁻¹¹ We refer to the model of the STE having the D_{2h} symmetry as the on-center model. Some experimental results on the STE's presented after the initial suggestion, however, cannot be explained by the on-center model of the STE. For example, the result of electron-nuclear double resonance (ENDOR) experiments for the lowest triplet STE in KCl (Ref. 14) indicates two values of the quadrupole interaction parameter for the halogen nuclei in the STE, in conflict with the on-center model. Furthermore, all theoretical calculations based on the on-center model showed that, among optical absorption bands due to the transitions to the symmetry-split $2p$ orbitals, the one parallel to the molecular axis is the lowest, which is inconsistent with the experimental results.^{15,16}

Song *et al.*¹⁷⁻²⁰ have shown theoretically that the on-center configuration of the STE at the lowest triplet state is unstable, leading to spontaneous symmetry-breaking relaxation into an off-center configuration having a C_{2v} symmetry. The results of theoretical calculation based on this off-center model are consistent with those of ENDOR experiments and indicate that the transition energy parallel to the molecular axis is the highest.^{2,3} Thus the off-center instability of the STE is presumed to be a crucial factor in order to understand the several properties of STE's. Kan'no *et al.* have classified the STE luminescence bands in alkali halide crystals into three groups in terms of the Stokes shift.²¹ One group (referred to as

type I) is characterized by relatively small Stokes shifts of about $0.3E_{\text{ex}}$, where E_{ex} is the optical transition energy to form a free exciton. The σ bands in all NaCl-type alkali halides and the π bands in NaBr and NaI belong to this group. Another group (described as type III) is characterized by large Stokes shifts of $0.6E_{\text{ex}}$ or even larger. The emission bands of this group are π polarized and have long lifetimes. The rest (described as type II) are intermediate between type I and type III in terms of the Stokes shift. The π band in KI and the luminescence at 3.07 eV in RbI belong to this group. Almost the same grouping as that by the Stokes shift of the STE luminescence has been obtained in terms of the Mollow-Ivey relation for the electron-transition energy of the STEs;²² suggesting strongly that the classification of the three types comes from the difference in relaxed configurations of excitons. The relationship between the mechanism of the evolution of three types of luminescent states and the possible off-center instability of the STE has not yet been clarified, although several authors have discussed it.²³⁻²⁶

Resonance Raman scattering (RRS) spectroscopy is one of the most useful methods to reveal the phonon modes which couple to an electronic system. This spectroscopy is particularly valuable for clarifying the phonon modes incorporated in the STE configuration, because of its capability of separating the modes coupled with the electron and hole in the STE. Recent studies of the Raman scattering in resonance with the $\sigma_g \rightarrow \sigma_u$ transition of the X_2^- centers in alkali halides have revealed that the phonon mode involved is almost single mode, which is primarily the stretching vibration mode (Q_1 mode) of the X_2^- , and that the frequency of the mode is very sensitive to the crystalline position where the X_2^- is placed. Since the STE's of any type classified includes the X_2^- molecular ion as a hole component, the resonance Raman scattering spectroscopy for the STE is expected to give valuable information on the structure of the STE. In this paper, we report the results of the Raman scattering of the STE in NaBr, NaCl, and RbI. The STE's in these materials have been classified into distinctive types of STE's. It is shown that the X_2^- of the STE in NaBr occupies two adjacent halogen sites and the X_2^- of the STE in NaCl and RbI occupies a single halogen site.

II. EXPERIMENT

Pure specimens used in this study were obtained from blocks of single crystal of pure NaCl purchased from Harshaw Chemical Co. and of pure RbI and NaBr from the University of Utah. NaBr and NaCl crystals doped with NO_2^- grown by the Kyropoulos method in a dry Ar atmosphere were also used. Pure crystals were used for measuring the Raman scattering for the STE and H center, and the doped crystals were used for measuring that for the V_K centers.

In order to characterize the optical absorption bands due to the STE's, we measured the transient optical absorption change induced by irradiation with a 20-ns electron pulse generated by a Febetron accelerator (Hewlett-Packard model 43710A) or by a 266-nm laser pulse gen-

erated with a Q -switched Nd-doped yttrium aluminum-garnet (Nd:YAG) laser (Spectra-Physics GCR-170). The change in the optical absorption of the specimen at fixed wavelengths was measured with a probe beam and generated with a discharge lamp (Hamamatsu L2482). The detection system of the optical absorption comprises a monochromator (Jobin Yvon H-20VIS), a photomultiplier (EMI 6256B), and an oscilloscope (Iwatsu TS-8123). To obtain the transient optical absorption spectrum, we used a multichannel spectrometer consisting of a monochromator (Jobin Yvon UFS-200) and a multichannel optical detector (Princeton Instruments IRY-1024). The dichroism and annealing characteristics of the stable color centers in doped and pure specimens introduced by band-to-band excitation were investigated using a conventional spectrophotometer (Shimadzu UV-3100).

For measurements of RRS spectra, a specimen with a size of $8 \times 10 \times 4 \text{ mm}^3$ was attached to a cold finger of a cryostat capable of being cooled to 5 K. A spot of the specimen was irradiated coaxially with two synchronized pulsed laser beams, a 266-nm laser, and dye-laser beams. The former, generated with a Q -switched Nd:YAG laser, produces electron-hole pairs to form color centers and the lowest triplet STE's and the latter, generated with an excimer laser pumped dye laser (LambdaPhysik EMG-201 MSC and FL3002), probes the Raman scattering. The incidence of the dye-laser pulse was delayed from that of the 266-nm pulse with a delay generator to accomplish time-resolved Raman spectroscopy. The scattering light was focused onto an entrance slit of a triple monochromator (Spex Triplemate) and was detected by a gated multichannel detector (Princeton D/SIDA 700).

III. RESULTS

In order to identify unambiguously the Raman spectrum in resonance with the hole transition of the STE, it is first necessary to make clear the properties of the absorption bands due to the transition. Temporal behavior as well as thermal properties of the absorption due to STE's are particularly important, since electronic excitation produces the absorption bands due to different species, such as the V_K and/or the H center, in the wavelength region where the absorption due to the STE is generated. Since the information necessary for these investigations is not enough at the present stages, we carried out a detailed optical-absorption study for the centers generated by irradiation with a pulsed laser beam or a pulsed electron beam.

In Fig. 1(a), we show the absorption spectrum of NaBr measured 1 μs after pulsed electron irradiation at 5 K. The band decays entirely with a time constant of 100 μs , which is the lifetime of the lowest triplet STE in NaBr at this temperature. Therefore, it is concluded that these bands originate from the lowest triplet STE. No stable absorption bands can be detected. Similar results have been obtained by Williams and Kabler.²⁷ In Fig. 1(b) the dichroic absorption spectrum of the V_K center in NaBr: NO_2^- at 5 K is shown. In order to obtain the experimental data, a specimen was irradiated by an elec-

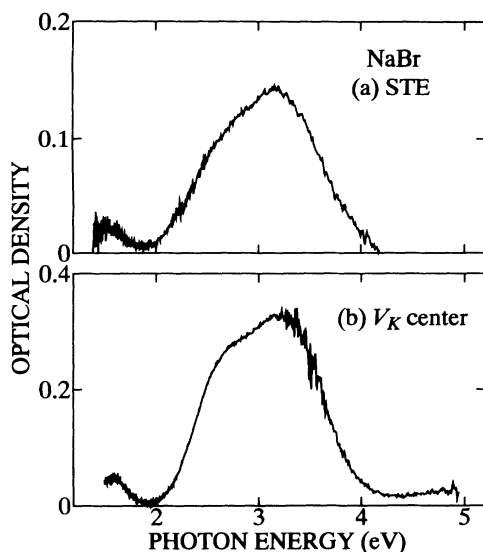


FIG. 1. Optical absorption spectra of the STE and V_K center in NaBr: (a) absorption spectrum measured 1 μ s after electron pulse irradiation at 5 K and (b) dichroic absorption spectrum in NaBr:NO₂⁻ obtained by bleaching with $\langle 110 \rangle$ -polarized 405-nm light for specimens irradiated by an electron pulse at 78 K.

tron pulse and the optical absorption spectra were measured by $[110]$ - and $[1\bar{1}0]$ -polarized light after bleaching the center by $[1\bar{1}0]$ -polarized 405-nm light. Curve (b) in Fig. 1 is the difference (dichroic absorption spectrum) between the two spectra measured with light polarized along $[110]$ and $[1\bar{1}0]$. The V_K -absorption band can be decomposed into two bands peaked at 3.22 eV and at 2.58 eV, both of which are highly σ polarized. It is clear from Fig. 1 that the spectrum of the STE is very similar to that of the V_K center.

In Fig. 2 the dichroic absorption spectrum of the V_K center (a) in NaCl:NO₂⁻ at 80 K and that of the H center (b) at 5 K is shown. In order to obtain the spectrum of the V_K band, $\langle 110 \rangle$ -polarized 365-nm light was used. On the other hand, as demonstrated in a previous paper,²⁸ the H band shows a $\langle 110 \rangle$ dichroism but no $\langle 100 \rangle$ dichroism, indicating that the H center is oriented along a $\langle 111 \rangle$ direction. The dichroic absorption spectrum of the H center shown in Fig. 2 was obtained by using $[110]$ -polarized 365-nm light after irradiation with an electron pulse at 5 K. Curve (c) in Fig. 2 is the transient absorption spectrum of the STE in NaCl at 5 K. Two peaks at 3.8 eV and 3.2 eV are observed. A dichroic absorption measurement by using $\langle 100 \rangle$ -polarized 308-nm laser pulse shows that dichroism is certainly induced for the two bands, indicating clearly that the X_2^- molecular ion in STE is oriented not along the $\langle 111 \rangle$ but along a $\langle 110 \rangle$ crystallographic axis, in contrast to the H center in NaCl. A similar dichroic experiment was done for RbI. Figure 3 shows (a) the dichroic absorption spectrum of the H center and (b) the absorption bands due to the STE measured at 10 K. Preferential bleaching for the H bands was done by using $\langle 100 \rangle$ -polarized light having a photon energy of 2.88 eV. The spectrum of the H center consists of two bands peaked at 2.8 eV and at 2.1 eV,

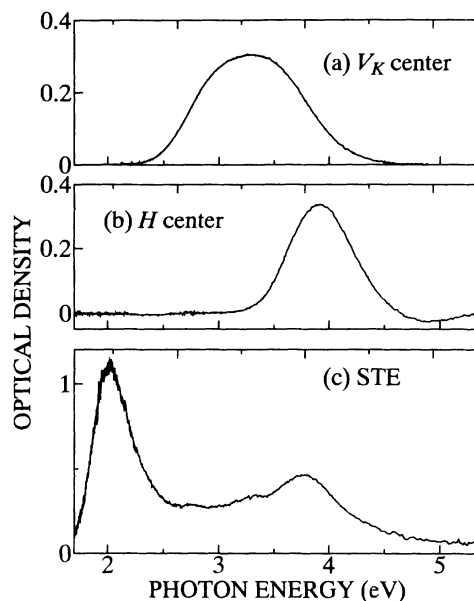


FIG. 2. Optical absorption spectra of (a) the V_K center, (b) the H center, and (c) the STE in NaCl. Curves in (a) and (b) show, respectively, dichroic absorption spectra in NaCl:NO₂⁻ at 78 K and in pure NaCl at 5 K after irradiation of an electron pulse and bleaching with $\langle 110 \rangle$ -polarized 365-nm light. Curve (c) shows absorption spectrum measured 10 μ s after electron-pulse irradiation at 10 K.

both of which are σ polarized. The spectrum of the STE in RbI consists of three peaks above 2 eV. Dichroic absorption measurement shows that all of the three bands are σ polarized with respect to the I₂⁻ molecular ion oriented along a $\langle 110 \rangle$ axis.

In Fig. 4, we show the time-resolved spectra of scattered light measured at 65 K for pure NaBr. The wavelength λ_p for probing Raman scattering is $\lambda_p = 488$ nm

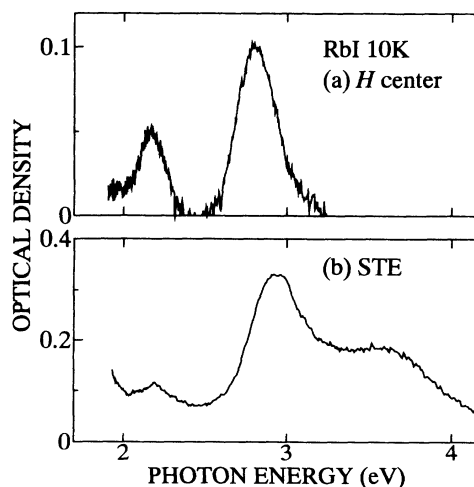


FIG. 3. Optical absorption spectra of (a) the H center and (b) the STE in RbI measured at 10 K. Curve (a) shows dichroic absorption spectrum obtained by bleaching with $\langle 100 \rangle$ -polarized 430-nm laser pulse after pulsed electron irradiation. Curve (b) shows absorption spectrum measured 5 μ s after electron-pulse irradiation.

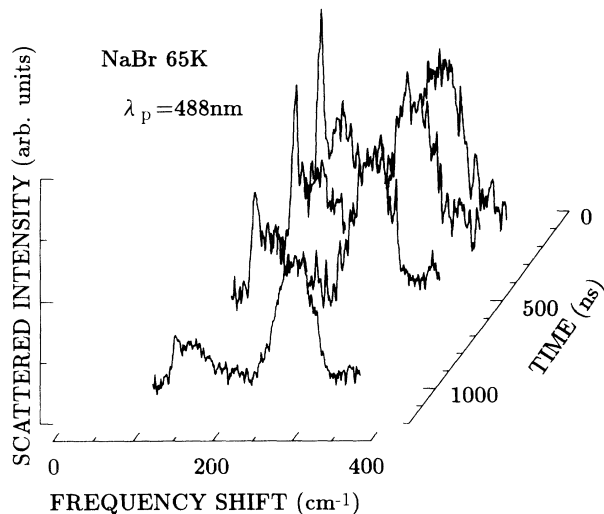


FIG. 4. Spectra of Raman scattering measured at 65 K. The spectra were probed by 488-nm (2.54 eV) light pulse which is in resonance with the $\sigma_g \rightarrow \sigma_u$ hole transition band. Each curve was obtained for the probe pulses with different delays with respect to the 266-nm excitation pulse.

(2.54 eV), which falls in resonance with the lower-energy band of the hole transition. The four spectra shown in Fig. 4 were obtained by using different delay τ_p of the probe pulse with respect to the incidence of the 266-nm laser pulse. The spectra exhibit the second order bulk Raman bands; the Raman band is in particular dominant in the 1.2- μ s spectrum. The spectra for smaller τ_p 's include a sharp line of 137 ± 2 cm^{-1} together with the bulk Raman bands. The height of the 137-cm^{-1} line decreases with increasing τ_p . Figure 5 shows the decay of the 137-cm^{-1} Raman line; the intensity is plotted as a function of τ_p . The solid curve in Fig. 5 is the decay curve of the optical absorption at 457.9 nm induced by a laser pulse; the decay time constant is 520 ns. It is evident that the decrease of the 137-cm^{-1} Raman line is in parallel to the decay of the lowest triplet STE. Thus it is concluded that the 137-cm^{-1} line is due to the STE in NaBr. Similar time-resolved measurements were made also for $\lambda_p = 390$ nm (3.18 eV), which falls in resonance with the hole transition of the high-energy band. The similar Raman spectra which include 137-cm^{-1} line and exhibit the same temporal behavior were observed.

In order to get more insight into the nature of the X_2^- molecular ion in the STE, we compared the resonance Raman scattering spectrum of the STE with those of the V_K and the H centers. In order to obtain the Raman spectrum for the V_K centers, we used NaBr doped with NO_2^- and the Raman spectrum was measured at 80 K. Since the NO_2^- exhibits a series of sharp absorption lines in the wavelength region shorter than 380 nm, λ_p was selected to be 400 nm and 488 nm. Curve (a) in Fig. 6 shows the Raman spectrum probed by 488-nm light for a pure specimen and curve (b) for a doped specimen, both of which are not irradiated with uv pulses. Curve (a) indicates the second order Raman bands of bulk NaBr. On the other hand, the spectrum of the $\text{NaBr}:\text{NO}_2^-$, curve (b),

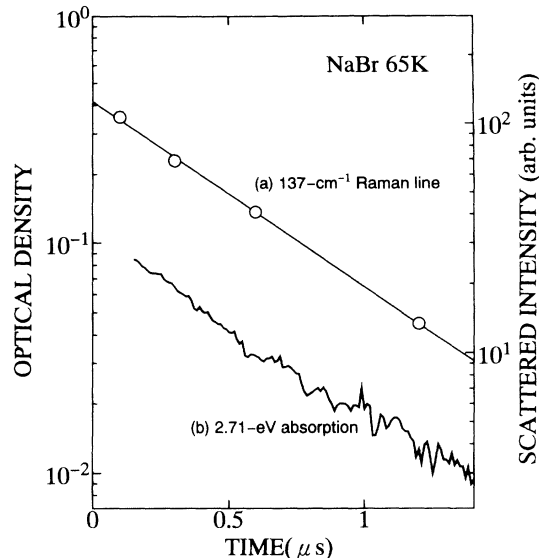


FIG. 5. Decays of (a) 137-cm^{-1} Raman line and (b) 2.71-eV optical absorption, induced by 266-nm laser pulse irradiation at 65 K in NaBr.

includes the 110-cm^{-1} Raman line together with the second order spectrum. The Raman line of 110 cm^{-1} is assigned to be due to the rotational vibration of the NO_2^- group.²⁹ Curve (c) in Fig. 6 shows the Raman spectrum for $\text{NaBr}:\text{NO}_2^-$, measured 100 ms after uv-laser excitation. It is evident that a line at 137 cm^{-1} is observed in this case. The line, although the frequency is the same, is different from that due to the STE which has a lifetime of 520 ns. Since it has been shown that only the V_K band is induced in the wavelength range between 300 nm and 800 nm by uv laser irradiation for $\text{NaBr}:\text{NO}_2^-$, it is con-

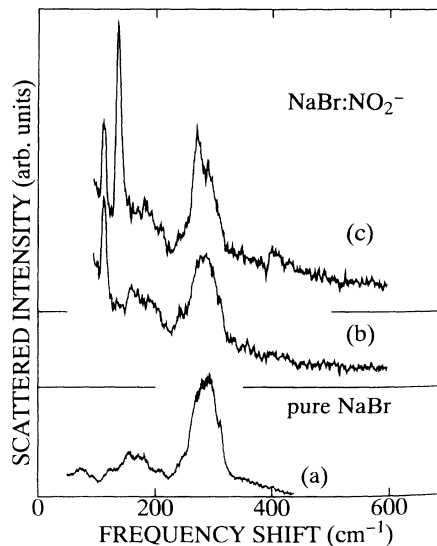


FIG. 6. Raman scattering spectra of NaBr crystals probed by 488-nm light at 78 K. Spectra shown by curves (a) and (b) were measured for pure NaBr and $\text{NaBr}:\text{NO}_2^-$ without 266-nm laser pulse irradiation, while the spectrum shown by curve (c) was measured for $\text{NaBr}:\text{NO}_2^-$ 100 ms after 266-nm laser pulse irradiation.

cluded that the 137 cm^{-1} originates from the V_K center. We measured Raman spectra also for the probe wavelength of 400 nm . The same Raman line of 137 cm^{-1} as that for $\lambda_p = 488\text{ nm}$ was observed for specimen irradiated by uv laser pulses. The Raman spectrum of the H center in NaBr was measured for the probe wavelength of 400 nm at 5 K after irradiation of a specimen by 266-nm laser pulses up to $\sim 10^4$ shots. We compare the Raman spectra of (a) the V_K center, (b) the H center, and (c) the STE in NaBr in Fig. 7, where the Raman spectrum of each specimen without uv laser irradiation is subtracted for convenience. The Raman spectrum for the H center consists of two split lines of which the frequencies are 225 cm^{-1} and 241 cm^{-1} and their overtones, while the spectrum for the V_K center or for STE is characterized by a single sharp line at 137 cm^{-1} .

Similar measurements of Raman spectra for the STE, the V_K center, and the H center in NaCl were also made at several temperatures. Since a description of the results has been given in a previous Letter,³⁰ we briefly describe here the essential results of the Raman spectrum for the STE in NaCl. In Fig. 8, curve (a) shows the Raman spectrum measured $5\text{ }\mu\text{s}$ after 266-nm laser excitation at 65 K with $\lambda_p = 337\text{ nm}$, which falls in resonance with the hole transition of the STE. Curve (b) portrays the Raman spectrum for the specimen without 266-nm laser excitation, which is the second order Raman spectra of bulk NaCl. It is evident in Fig. 8 that the 361-cm^{-1} line with monotonically decreasing overtones is induced by 266-nm excitation. Figure 9 presents the decay of the 361-cm^{-1} Raman peak in NaCl at 65 K and 78 K against the time delay with respect to the incident laser pulse. It is clear that the intensity of the Raman line de-

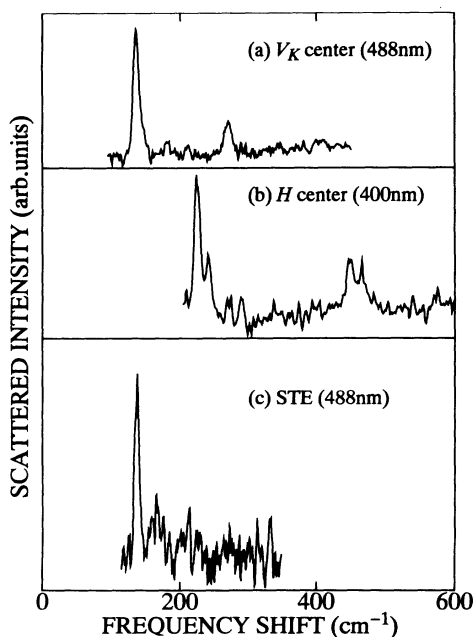


FIG. 7. Spectra of Raman scattering in resonance with $\sigma_g \rightarrow \sigma_u$ hole transition of (a) the V_K center measured at 78 K , (b) the H center measured at 5 K , and (c) the STE measured at 65 K in NaBr.

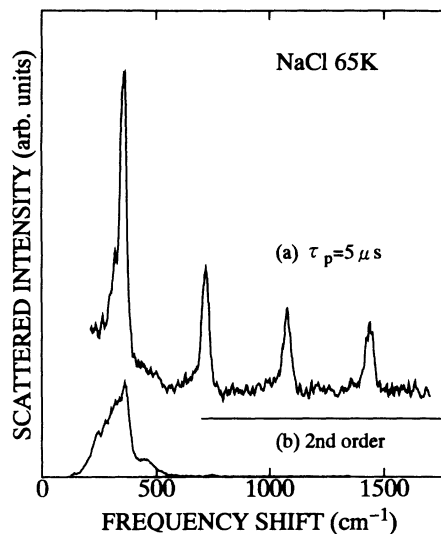


FIG. 8. Spectra of Raman scattering probed by 337-nm light, (a) measured $5\text{ }\mu\text{s}$ after 266-nm laser excitation and (b) without laser excitation in NaCl. Measurements were made at 65 K .

creases with increasing τ_p with a time constant of $230\text{ }\mu\text{s}$ at 65 K and of $70\text{ }\mu\text{s}$ at 78 K , both of which are exactly the lifetimes of the lowest triplet STE at respective temperatures. Thus it is clear that the 361-cm^{-1} Raman line in Fig. 8 is exclusively due to the lowest triplet STE in NaCl. A comparison of the Raman spectrum of the STE with those for the V_K center and the H center³⁰ has shown that the frequency of the Raman line of the STE in NaCl coincides with that of the H center. The Raman line of the V_K center shows a paired line structure; the average 243 cm^{-1} of the two frequencies is almost identical to that of the V_K center in KCl and RbCl (Ref. 31) and is lower than that of the H center. The Raman spectra for both the STE and the H center are characterized by a sharp line of 361 cm^{-1} .

In Fig. 10(a), we show the spectrum of scattered light in RbI measured at 5 K for $\lambda_p = 435\text{ nm}$ (2.85 eV), which

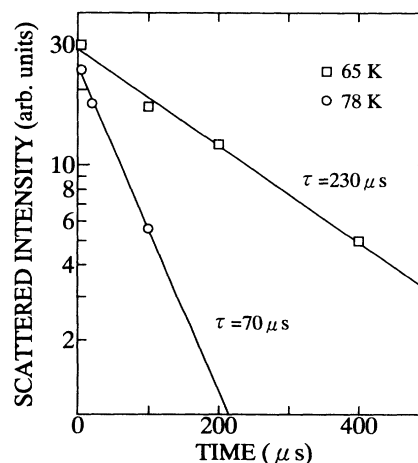


FIG. 9. Decays of the 361-cm^{-1} Raman line (a) at 65 K and (b) at 78 K in NaCl.

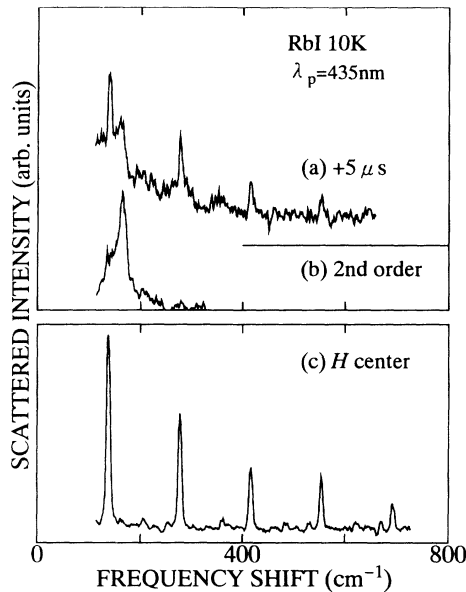


FIG. 10. Spectra of Raman scattering at (a) measured 5 μ s after 266-nm laser excitation and (b) without laser excitation in RbI. The wavelength of the probe light was 435 nm, and measurements were made at 5 K. Resonance Raman spectrum of the H center in RbI at 5 K is shown in (c).

falls in resonance with the hole transition. The spectrum is obtained for delay $\tau_p = 5 \mu$ s of the probe pulse with respect to the incident of the 266-nm laser pulse. The Raman spectrum includes the second order bulk Raman line shown by curve (b). The 5- μ s spectrum shows a sharp line of 139 cm^{-1} and its overtones together with the second order bulk Raman line. It is found that the line disappears within a lifetime of 15 μ s, which agrees with that of the lowest triplet STE at this temperature. Thus it is concluded that the Raman line of 139 cm^{-1} shown in Fig. 10(a) is due to the lowest triplet STE in RbI. In Fig. 10(c), we show also the Raman spectra for the H center in RbI (Ref. 28) measured at 5 K for $\lambda_p = 435$ nm. Comparison of the Raman spectrum of the STE with that for the H center indicates that the frequency of the Raman line in resonance with the hole transition of the STE is almost identical to that for the H center in RbI.

IV. DISCUSSION

A. Stretching-vibration frequency of X_2^- in the STE

From the data described in the preceding section, it is clear that we are observing transient Raman scattering spectra due to the STE's in NaBr, NaCl, and RbI. All Raman spectra were found to be characterized by a sharp Raman line and its overtones. Since Raman spectra have been measured under the resonance to the bonding-to-antibonding transition of the X_2^- of the STE, these Raman lines are assigned to be due to the stretching vibration (Q_1 mode) of the halogen molecular ions.

The frequency of the 361- cm^{-1} Raman line for the Q_1

mode of the X_2^- molecular ion in the STE in NaCl and that of the 139- cm^{-1} line in RbI is far above the phonon cutoff frequencies,³² indicating the strong local nature of the mode. The frequency of the 137- cm^{-1} line of Raman spectra of the STE in NaBr is just above the gap region,³³ ranging from 105 cm^{-1} to 126 cm^{-1} . The frequency of the 137- cm^{-1} Raman line almost coincides with the resonance Raman frequency of the F center in NaBr.³⁴ However, this agreement is accidental and the Raman spectrum in Fig. 4 is certainly due to the STE in NaBr for the following reasons. First, the intensity decreases with a time constant that is the same as the lifetime of the lowest triplet STE. Second, the Raman spectrum of the F center is a doublet (separation about 11 cm^{-1}), while that of the STE spectrum is a single line; no paired line is observed. Thus it is clear that the Raman spectrum shown in Fig. 4 is exclusively due to the lowest triplet STE in NaBr and the frequency of 137 cm^{-1} can be assigned to the stretching-vibration frequency $\nu(Q_1)$ of the Br_2^- molecular ion.

In Table I, we summarize the stretching-vibration frequencies of the X_2^- molecular ion for the STE, V_K , and H center in NaCl, NaBr, and RbI. From Table I it is evident that the value of the stretching-vibration frequency of the X_2^- of the STE in NaBr agrees with that of the V_K center and is smaller than that of the H center. On the other hand, those of the X_2^- molecular ions of the STE's in both NaCl and RbI agree with those of the H centers in responsible solids. Although no experimental results for the V_K center in RbI are available, it can be presumed that the frequency of the V_K center is about 90% of the experimental intraionic vibration frequency of $M^+X_2^-$ complexes (M^+ denotes an alkali ion) in an argon matrix,³⁵⁻³⁷ based on the results of the V_K centers in LiF, KCl, RbCl,³¹ NaCl, KBr,²⁸ and NaBr. From the experimental results for the $\text{Rb}^+I_2^-$ complexes in an argon matrix,³⁷ the value of the Raman frequency for the V_K center in RbI is estimated to be 110 cm^{-1} , which is very close to that calculated by Harding.³⁸ Thus the $\nu(Q_1)$ of the STE's in NaCl and RbI are much higher than those of the V_K center.

In a previous paper, we carried out an extensive study for the Raman scattering of the X_2^- molecular ion centers in several alkali halides.²⁸ The one essential point of the results is that the stretching-vibration frequency of the H center is higher by more than 30% than that of the V_K center in each salt. It has been also demonstrated that the frequency of the H center depends strongly on the lattice constant, whereas that of the V_K center is almost kept constant. Based on a systematic analysis of these results, we have shown that the hardening of the

TABLE I. The vibrational frequency $\nu(Q_1)$ for the STE, the V_K center, and the H center.

	STE	V_K	H
NaBr	137	137	225,241
NaCl	361	228,258	361
RbI	139		139

frequency for the H center originates from the bond tightening due to the Madelung potential at an anion site. On the other hand, the force constant of the Q_1 -mode vibration of the X_2^- in the V_K center configuration is softened somewhat by the crystalline potential at two anion sites. These results have revealed that the frequency of the stretching vibration of the X_2^- depends strongly on the location of the X_2^- in the lattice: whether the X_2^- molecular ion occupies two adjacent halogen sites such as a V_K center or a single halogen site such as an H center. This feature of the Raman spectra of the V_K and the H center has provided a solid basis to argue the configuration of the X_2^- molecular ion of the STE in view of resonance Raman scattering spectra of the X_2^- molecular ion.

From the experimental results summarized in Table I, we can conclude that the X_2^- of the STE in NaBr occupies two anion sites similar to the V_K center, while the X_2^- molecular ion of the STE in NaCl and in RbI is placed at a single anion site just as the H center. Based on the results, we discuss the structure of STE's in alkali halides in the next section.

B. Relaxed configuration of excitons

As described in the Introduction, STE's in alkali halides are classified into three groups, each of which has been proposed to have different structures. The type I STE emits the luminescence band with the smallest Stokes shift, whereas the type III STE emits the luminescence band with the largest Stokes shift. Type II is intermediate between the two. The STE in NaBr is a typical example of type I. Recent spectroscopic measurements²³ have shown that the peak of electron-transition energy of the STE in NaBr is as low as $0.2 \sim 0.3$ eV, which is much less than those of type II and type III STE's. This result indicates that the lattice relaxation which forms the potential well for the trapped electron is much less in type I STE than in types II and III STE. Based on this spectroscopic feature, together with characteristics of the luminescence band,²⁴ it has been proposed that the type I STE has a configuration very close to the V_K center on which an electron is bounded (the on-center model).^{23,25,26} The present result of the resonance Raman scattering for the STE and the V_K center in NaBr has provided direct evidence for the model that the STE in NaBr is essentially ($V_K + e$). The spectroscopic features of the absorption bands due to the hole transition, shown in Fig. 1, substantiate strongly the conclusion.

In contrast to the case of the STE in NaBr, the resonance Raman spectra of STE's in NaCl and RbI show characteristic frequencies which are identical to those of the H centers. The results indicate clearly that the X_2^- molecular ion in the STE in these materials is located nearly on a single halogen site; a direct consequence of the off-center shift of the X_2^- from the V_K -center position upon relaxation leading to the lowest triplet STE's.

It has been shown that in RbI there exist three distinctive relaxed configurations of the excitons, each of which is classified into different types. The type I STE, which

is responsible for the σ luminescence, has a lifetime of a few nanoseconds at 5 K. Therefore, this is not related to the state in which we studied RRS's. A characteristic feature of the relaxed excitons in RbI is that two configurations responsible for π (type III) and E_X (type II) luminescence bands are in thermal equilibrium;¹³ the population of the type II STE increases with increasing temperature. Since our measurements of RRS have been done at 5 K, where the type III STE dominates over the type II STE, the spectrum of RRS measured is presumed to be due to the type III STE. Thus we conclude that the type III STE in RbI is a pair of the I_2^- at an anion site and an electron localized at the vacancy site.

The classification of the STE in NaCl is somewhat on the border; properties of the STE in NaCl show complicated features. The Mollow-Ivey plot of the electron-transition energy²² suggests that the STE belongs to type II, whereas the Stokes shift is as much as $0.58E_{ex}$, which is almost the same as the typical value of the type III STE in other materials. Also, femtosecond spectroscopic study³⁹ has demonstrated the presence of the other relaxed-exciton state which can be classified into type III, although the state is metastable. Theoretically, it has been pointed out that adiabatic potential-energy surfaces (APES) of the lowest triplet state of the exciton has several minima which correspond to different configurations of the pair comprising the X_2^- and a vacancy trapping an electron.⁴⁰ The optical absorption peak due to the electron transition of the STE (Ref. 41) shows a significant blueshift with increasing temperature, suggesting the significant population of the intermediate state at higher temperature where Raman measurements were made. By taking into account all these features of the STE in NaCl, it is safe at this moment to conclude only that the APES of the lowest triplet STE in NaCl includes the state which is described as a pair of the X_2^- at an anion site and the electron localized at the primitive vacancy site formed by the off-center shift of the X_2^- .

For the STE configuration formed through the off-center shift of the X_2^- , the interaction between the localized electron and the X_2^- molecular ion is presumed to be substantial; nevertheless the frequency of the stretching vibration of the X_2^- in the STE is almost identical to that of the H center. In a previous paper,²⁸ we have shown that the $\nu(Q_1)$ of the X_2^- which is placed at an anion site is not affected significantly by both the distortion of surrounding ions and the orientation of the X_2^- . One of the basic results leading to the conclusion stated above is concerned with resonance Raman spectra of the $H_A(Li^+)$ and $H_A(Na^+)$ centers in KCl. The H_A center is a X_2^- molecular ion occupying a single halogen site next to a substitutional alkali ion having a smaller ionic radius. The electron paramagnetic resonance (EPR) studies have shown that replacing a neighboring alkali ion with a foreign alkali ion induces a significant change in the orientation of the X_2^- molecular ion. The $H_A(Na^+)$ center in KCl has an axis 5.7° off from a $\langle 110 \rangle$ direction,^{42,43} while the $H_A(Li^+)$ center has an axis intermediate between a $\langle 100 \rangle$ and a $\langle 111 \rangle$ direction.⁴⁴ Thermal and optical properties of the H_A centers are significantly different from those of the H centers, indicating strong changes of the

local lattice surrounding the X_2^- molecular ion. However, the $\nu(Q_1)$ of the H , $H_A(\text{Li}^+)$ and $H_A(\text{Na}^+)$ centers in KCl are almost identical to each other. This result indicates clearly that orientation of the X_2^- molecular ion, as well as the lattice configuration surrounding it, does not give rise to large changes in frequencies of the stretching vibration of the X_2^- .

In NaCl, it is shown that the H center is oriented along a $\langle 111 \rangle$ direction from an EPR study⁴⁵ and optical dichroism,²⁸ while the X_2^- molecular ion of the STE is oriented along a $\langle 110 \rangle$ direction. Because of this difference and/or of the possible perturbation on the X_2^- by the localized electron associated with it in the STE, the line shape of the Raman spectrum of the STE in NaCl shows some differences from that of the H center; the width is much broader and the main line is associated with a structure at the low-frequency region. However, it is not straightforward to draw any quantitative information about the effects of the localized electron to determine the structure of the STE from the change in the Raman spectrum at present.

Since the electronic wave function for the hole center is strongly localized on the anions, the frequency of the Q_1 mode can be quite insensitive to the perturbation. The Q_1 mode is primarily the stretching-vibration mode of the X_2^- at its electronic ground state. On the other hand, any perturbation to the X_2^- is presumed to become more pronounced for the excited states; the optical absorption spectra reflect the changes. In RbI, three distinctive peaks are observed above 2 eV (Fig. 3). A comparison of the spectrum with that of the H center shows clearly that the bands peaked at 2.8 eV and at 2.1 eV are almost the same as the peaks due to the H center. This result itself substantiates our conclusion that the I_2^- of the STE occupies an anion site. However, the spectrum of the STE has an additional band peaked

at 3.5 eV, which is completely absent in that of the H center. The absorption spectrum due to the hole transition of the STE in NaCl, shown in Fig. 2, is composed of two bands at 3.8 eV and 3.4 eV. The energy of the high-energy band is similar to that of the H center. However, the presence of the low-energy band is a characteristic feature of the Cl_2^- in the STE. These differences in the absorption spectra of the STE, compared with those of the H center in NaCl and RbI, may indicate the presence of significant perturbation to the excited states of the X_2^- composing an STE.

In summary, we conclude that the X_2^- of the STE in NaBr occupies two adjacent anion sites, while the X_2^- molecular ions of the STE's in NaCl and in RbI are located at a single anion site, although the details of the structure of the STE are left unsolved. In contrast to the Raman scattering in resonance with the hole transition of the X_2^- , Raman scattering in resonance with the electron transition is more sensitive to the local-lattice deformation as demonstrated for the STE in NaCl.³⁰ The more systematic study of the resonance Raman scattering for the STE tuned to the electron transition certainly will give more detailed information for the configuration of the STE. Such a study is now in progress.

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