Resonance-Raman-scattering spectroscopy for the halogen-molecular-ion centers in alkali halides

T. Suzuki, K. Tanimura, and N. Itoh

Department of Physics, Nagoya University, Furo-cho, Chikusa, Nagoya 464-01, Japan

(Received 20 May 1993)

We have measured the Raman scattering in resonance with the bonding-to-antibonding transitions of two types of dihalogen-molecular-ion centers in alkali halides, the V_K and H centers; the molecular ion occupies two adjacent halogen sites in the former and a single halogen site in the latter. It is found that the stretching-vibration frequency of the molecular ion is higher by more than 30% for the H center than for the V_K center. The hardening is ascribed to the bond tightening due to the Madelung potential. Although the Raman line due to the stretching vibration consists of a single line in most alkali halides, two closely lying lines are observed for the H centers in alkali halides with small alkali-metal to halogen radius ratio and also for the V_K center in NaCl. The paired-line structure is ascribed to the coupling of the stretching vibration of the halogen molecular ion with the lattice.

I. INTRODUCTION

The X_2^- molecular ion (a dihalogen molecular ion where X denotes a halogen atom) in alkali halides takes two distinct forms: a V_K center or a self-trapped hole and an H center or an interstitial halogen atom.[1,2] A free hole in alkali halides, which can be regarded as a Bloch state comprising a halogen atom located at the halogen lattice point, eventually forms a small polaron or an X_2^- molecular ion[3] because of the strong coupling of a hole with a lattice. The X_2^- molecular ion formed from a hole, the V_K center, occupies two adjacent halogen sites and its center is located at the center of the square formed by two halogen and alkali-metal sites.[3-5] It is known that the formation of excitons or electron-hole pairs leads to the formation of Frenkel pairs comprising an F center (an electron trapped by a halogen vacancy) and an H center (an interstitial halogen atom relaxed to an X_2^- molecular ion).[6,7] An H center occupies a halogen site and its center is located at the anion lattice point.[8]

Although the optical and paramagnetic properties of these X_2^- molecular ion centers in alkali halides are described essentially in terms of the molecular properties,[1,2,4] there are significant differences in the properties of the V_K and H centers in the same alkali halides. For example, the optical-absorption bands due to the bonding-to-antibonding $(\sigma_g \to \sigma_u)$ transition observed in the ultraviolet (UV) region and due to the bonding-to-nonbonding $(\pi_g \to \sigma_u)$ transition observed in the near infrared (IR) region for the V_K and H centers have different band shapes and even different peak energies.[1,2,9] The hyperfine spectra of the electron-paramagnetic-resonance (EPR) spectroscopy have demonstrated that both centers consist of an X_2^- molecular ion and that the wave function of the hole of the H center extends to the outer two halogen ions along the $\langle 110 \rangle$ molecular axis in some crystals.[3,8] It has been shown recently that the resonance Raman spectra of the V_K and H centers in NaCl exhibit a

remarkable difference in their stretching-vibration frequencies; the H-center vibration is much harder than the V_K-center vibration.[10] These differences of the properties of the V_K and H centers indicate that the interaction of the X_2^- molecular ion with the lattice is different for these two centers; the nature of the interaciton is not yet clear.

It is known that the motion of the X_2^- molecular ion plays a crucial role in the relaxation process of an exciton.[6,7] The hole component of a self-trapped exciton (STE) is known to form an X_2^- molecular ion. However, unlike a self-trapped hole which relaxes exclusively to the V_K center, self-trapping of an exciton leads to the formation of a variety of configurations,[7,11,12] in which the X_2^- molecular ion is displaced along the direction of the molecular axis, possibly accompanied with reorientation. Thus, understanding the configuration of the X_2^- molecular ion at the several relaxed configurations is of primary importance to clarify the process of the exciton relaxation. Recent measurements of resonance Raman scattering of self-trapped excitons in NaCl have revealed that the stretching-vibration frequencies of the X_2^- molecular ion in the self-trapped excitons is very close to that of the H centers.[10] In order to reveal the significance of the result and to understand the correlation between the properties of the X_2^- molecular ion and its location in the lattice, it is necessary to carry out a systematic study of the difference in properties of the H and V_K centers in several alkali halides.

The purpose of this paper is to investigate the resonance Raman scattering (RRS) for the X_2^- molecular-ion centers in several alkali halides and to reveal the rule that governs the stretching vibration of the X_2^- molecular ion of the V_K and H types in several alkali halides. It is shown that the stretching-vibration frequency of the H centers is larger than the V_K centers in the same alkali halide and the difference increases as the lattice constant increases. It is also found that some of the X_2^- molecular ions exhibit paired Raman-active modes in the frequency range of the stretching vibration.

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II. EXPERIMENT

Single crystals of pure NaCl, KCl, RbCl, KBr, and RbBr were purchased from Harshaw Chemical Co. and those of pure NaBr, KI, and RbI were obtained from the University of Utah. Single crystals doped with NO_2^-, Li^+, or Na^+, grown by the Kyropoulos method in a dry Ar atmosphere were also used. In order to characterize the color centers generated in these specimens, we measured the transient optical-absorption change induced by irradiation with a 20 ns electron pulse generated by a Febetron accelerator (HP-43710A) or by a 266 nm laser pulse generated with a Q-switched Nd-doped yttrium aluminum garnet (YAG) laser (Continuum, YG661-10). The optical-absorption changes at fixed wavelengths were obtained with an optical system comprised of a Xe lamp, a grating monochromator (Jobin Yvon H20-UV) and a photomultiplier (EMI 6256B). The output signals of the detector were recorded by a storage oscilloscope (Iwatsu TS-8123). Dichroism and thermal annealing behavior of the absorption bands due to stable color centers were also examined by a conventional spectrophotometer (Shimazu UV-3100).

For measuring RRS spectra, a specimen with a size of $8 \times 10 \times 4$ 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; one at 266 nm from the Nd-doped YAG laser was used to produce electron-hole pairs and to form color centers through two-photon absorption; the second from an excimer-laser-pumped dye laser (Lambda Physics EMG-201 MSC and FL3002) was used to probe the Raman scattering. The dye-laser pulse was delayed from the 266 nm pulse by using a delay generator to accomplish time-resolved Raman spectroscopy. 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). The Raman signals were accumulated for typical $10^2 - 10^3$ pulses to obtain reasonable signal-to-noise ratios.

III. EXPERIMENTAL RESULTS

A. Optical-absorption bands due to the X_2^- molecular ion in laser-irradiated pure and doped alkali halides

In order to identify unambiguously the Raman spectra of either the V_K or H centers in several alkali halides, it is necessary to prepare specimens which include exclusively one of the two types of X_2^- molecular-ion centers or to employ time-resolved spectroscopy to differentiate between centers having different decay times after generation by pulsed excitation beams. Since the information necessary for these investigations is not sufficient at the present stage, we carried out a detailed study for the optical-absorption spectra due to the X_2^- molecular-ion centers, including temporal behavior, dichroism, and thermal stability. Because of the ability of repeatable excitation up to 10 Hz, we employed pulsed laser excitation, which generates electron-hole pairs by two-photon absorption, to produce the X_2^- molecular-ion centers for

RRS. Since the temporal behavior of the X_2^- molecular-ion centers have been studied mainly by using pulsed electron beams, we compared the behavior of these centers produced by pulsed electron and laser beams.

It has been shown that the F and H centers produced by an electron pulse in KCl, KBr, and RbBr at 5 K annihilate mostly with decay times of less than 1×10^{-3} s; this rapid decay has been ascribed to the annihilation of the close F-H pairs.[13,14] We observed similar rapidly annihilating F and H centers produced by electron pulses in RbCl. The specimens after irradiation with an electron pulse have been shown to exhibit stable optical-absorption bands, the F band and a band in the UV region, whose origin is not necessarily clear.

We find that irradiation of KCl, RbCl, KBr, and RbBr with a 266 nm laser pulse produces transient F and H centers and STE's and also the stable optical-absorption bands. All the transient species have been found to decay completely within 50 ms after excitation, leaving the stable color centers. The yield of the stable F centers relative to that of the transient F centers is typically higher by a factor of about 2–3, depending on the laser intensity, to that induced by an electron pulse. For NaCl, KI, and RbI, for which the yields of the transient and stable F centers are much smaller, specimens were irradiated with laser pulses up to 10^2 shots in order to examine properties of the stable UV-absorption bands. For NaBr, a sufficient amount of the H centers could not be obtained even by laser irradiation up to 10^3 shots.

Measurements of thermal annealing show that the thermal stability of the UV-absorption band induced by UV-laser irradiation in pure specimens is nearly the same as the thermal stability of the H centers found in the literature,[1,2,15] although about 10–20 % of the initial height remains in KBr and KCl. The remainder in KCl and KBr are found to be the V_K bands from the band shapes and thermal stabilities. The molecular axes of the H centers in KCl, KBr (Ref. 8), and KI (Ref. 16) are known to be oriented along the $\langle 110 \rangle$ direction from studies of EPR and optical dichroism. We confirmed the orientation of the H centers in these materials, and also found that the H centers in RbCl, RbBr, and RbI had the same orientation. It has been shown from an EPR study that the H center in NaCl is oriented along a $\langle 111 \rangle$ direction,[17] similar to LiF.[18] We present the dichroic absorption spectra after dichroic bleaching of the H band in NaCl in Fig. 1; curve (b) by $\langle 110 \rangle$ polarized light and curve (c) by $\langle 100 \rangle$ polarized light. It is clear that no dichroism is induced by $\langle 100 \rangle$ polarized light, while it is induced by $\langle 110 \rangle$ polarized light. This result confirms the EPR observation that the H center in NaCl is oriented along a $\langle 111 \rangle$ crystallographic direction. The results described above show that the UV-absorption band of the pure specimens after pulse excitation of more than 100 ms is almost exclusively due to the H centers. Thus, we used pure alkali halides irradiated with 266 nm laser pulses at 5 K for the measurements of the RRS of the H centers.

In order to obtain RRS spectra for the V_K centers, we used alkali halides doped with NO_2^-, which are known to be an efficient electron trap.[19] The NO_2^- exhibits a series
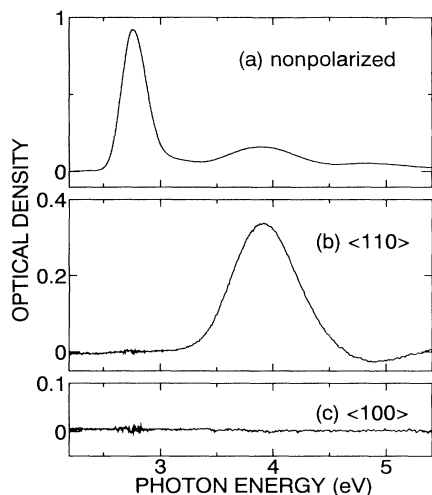
FIG. 1. The effects of dichroic bleaching of NaCl irradiated with 1 MeV electron pulses. (a) shows the optical-absorption spectrum after irradiation, (b) shows the $\langle 110 \rangle$ dichroic spectrum after bleaching with $\langle 110 \rangle$ polarized 340 nm light, and (c) is the similar dichroic spectrum for $\langle 100 \rangle$ polarized 340 nm light.

of sharp absorption lines around 300 nm, which can be easily differentiated from the broad V_K band. Irradiation of NO_2^--doped alkali halides with an electron pulse or with an UV-laser pulse at 80 K produces no transient optical absorption, but only stable absorption bands. The stable absorption bands induced in doped specimens are ascribed to the V_K bands by comparing the peak energies, half-widths, dichroism, and thermal stability with existing results.[5] Thus, we used NO_2^--doped alkali halides for the measurements of the RRS of the V_K centers.

We also measured the properties of the UV-absorption bands induced by UV-laser irradiation of KCl crystals doped with Li^+ or Na^+ alkali impurities, in order to obtain the optical-absorption bands due to the H_A centers, the H centers associated with a nearest neighboring alkali-impurity ion.[20–22] The UV absorption around 340 nm induced by a laser pulse, as well as by an electron pulse, of doped KCl at 80 K shows a decay component with a time constant of 10 ms and a stable component. The stable absorption bands in the UV region in $KCl:Li^+$ and in $KCl:Na^+$ are identical to the well-defined H_A absorption bands.[20–22] Thermal annealing experiments revealed that no V_K band is included. The transient component is ascribed to the H band on the basis of the time-resolved absorption spectrum. Thus, in these doped specimens, probing Raman scattering 100 ms after pulse excitation at 80 K will yield a RRS spectrum exclusively due to the H_A center.

B. Resonance Raman spectra of the X_2^- centers

In Fig. 2 are shown the Raman-scattering spectra in resonance with the $\sigma_g \rightarrow \sigma_u$ transition of the V_K center in KBr, (a), and in NaCl, (b). The spectrum for the V_K center in KBr consists of a single line at 144 cm^{-1} and its
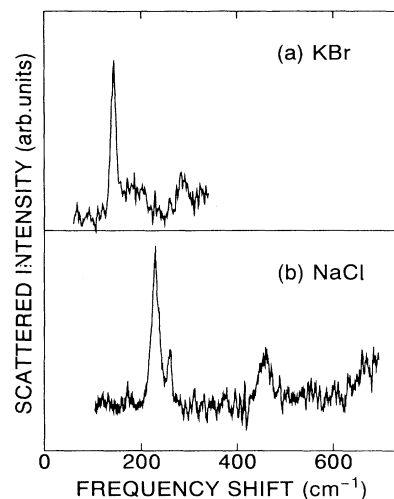

Fig. 2. Resonance Raman spectra of the V_K centers (a) in KBr and (b) in NaCl measured at 80 K. The wavelength of probe light pulses was 425 nm for both specimens.

overtone. The magnitude of the frequency is slightly lower than the Raman line for the Br_2^- molecular ion in an argon matrix.[23] On the other hand, the RRS spectrum of the V_K center in NaCl is characterized by the paired lines at 228 and 258 cm^{-1}. The overtone of the former is clearly observed, but that of the latter is not discernible because of the broadening of the lines. The Raman spectra of the V_K centers in KCl and RbCl obtained by Goovaerts and Schoemaker consist of a single line at 241 and 244 cm^{-1}, respectively.[24] Therefore, appearance of the paired lines is a characteristic feature of the V_K center in NaCl.

In Figs. 3–5, we show the Raman spectra in resonance with the $\sigma_g \rightarrow \sigma_u$ transition of the H centers in chlorides,
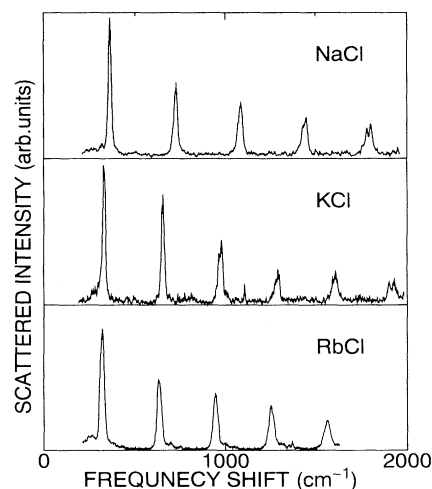

FIG. 3. Resonance Raman spectra of the H centers at 5 K, (a) in NaCl, (b) in KCl, and (c) in RbCl; the wavelengths of probe light pulses were 339 nm in NaCl, 340 nm in KCl, and 337 nm in RbCl.
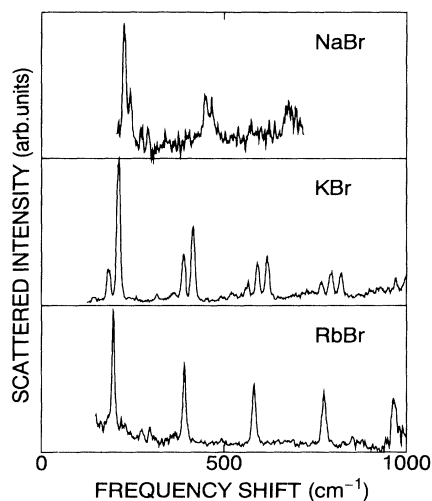
FIG. 4. Resonance Raman spectra of the H centers at 5 K, (a) in NaBr, (b) in KBr, and (c) in RbBr; the wavelengths of probe light pulses were 400 nm in NaBr, 396 nm in KBr, and 390 nm in RbBr.

Fig. 5. Resonance Raman spectra of the H centers at 5 K, (a) in KI and (b) in RbI; the wavelengths of probe light pulses were 430 nm in KI and 435 nm in RbI.

bromides, and iodides. In chlorides, the RRS spectrum of the H center consists of a sharp fundamental line and its overtones. Clear progression of the overtones with monotonically decreasing intensities is a characteristic feature of Raman scattering in a resonance condition.[25] The frequencies of the fundamentals are 361, 329, and 318 cm^{-1} in NaCl, KCl, and RbCl, respectively; the frequency decreases with increasing lattice constant. In bromide crystals, the RRS spectra in NaBr and KBr show paired lines at the fundamental Raman shift region, while that in RbBr consists of a single line as in the case of the H centers in the chlorides. In the spectrum for KBr, the combination tones of the two fundamental lines
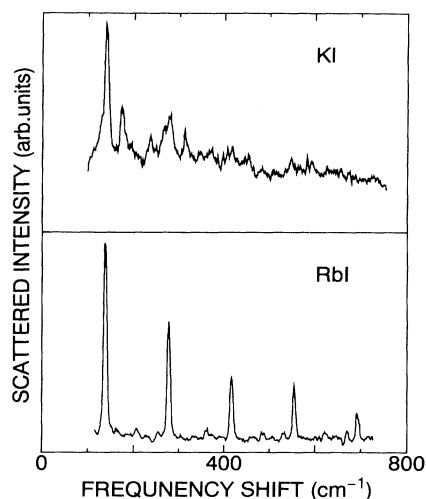
are clearly resolved. In KI, the RRS spectrum of the H center exhibits paired lines, whereas that in RbI exhibits a single line.

In order to elucidate the origin of the paired-line structure in the Raman spectra, detailed spectroscopic studies were made for the H center in KBr. First, we examined the spectra with a probe light of 395, 400, and 405 nm. It was found that the structure of the Raman lines was not dependent on the probe light wavelength. The difference in the photon energies of the probe light is within the energy difference between each of the paired lines. Therefore, this result rules out the possibility that one of the two lines is related to the hot luminescence induced as a result of real absorption;[26] both components of the paired

TABLE I. The vibrational frequency ω_H for the H center, ω_V for the V_K center, and the LO-phonon frequency ω_{LO} in alkali halides. Vibrational frequency ω_M for the $M^+ \rightarrow X_2^-$ complex in a solid argon matrix are included. The ratios of frequencies for the LO-phonon mode relative to those for the H and V_K centers are also listed.

	ω_H	ω_V	ω_{LO} [b]	ω_M [c] in solid Ar	ω_V calculated value[d]	ω_{LO}/ω_{HH}	ω_{LO}/ω_V
NaCl	361	228,258	260	225	238	0.72	1.07
KCl	329	241[a]	211	264	238	0.64	0.88
RbCl	318	244[a]	171	260	241	0.54	0.70
NaBr	225,241		201		142	0.86	
KBr	182,209	144	163	(162)	147	0.83	1.13
RbBr	195		129		148	0.66	
NaI			170	115	104		
KI	139,174		141	114	101	0.90	
RbI	138		106	116	112	0.77	

[a]Reference 24.
[b]Reference 33.
[c]References 27 and 28.
[d]Reference 30.

lines are certainly due to the intrinsic Raman process. Second, we carried out time-resolved Raman measurements to examine the possibility that the two Raman lines arose from the interaction of the H centers with the F centers located in the proximities. The Raman spectra were measured at 5 K by changing the time difference τ_p between the excitation to produce electron-hole pairs and the probing RRS from 10 μs to 200 ms, across the decay time (100 μs) the transient H center. The measurement for $\tau_p < 100$ μs probes the RRS for the transient H center predominantly, and that for $\tau_p > 100$ μs for the stable H center. Although a transient H center is considered to be accompanied with an F center in its proximity, the observed spectra are found to be the same, irrespective of τ_p. Measurements were also made at 80 K, where most of close F-H pairs were annihilated within 1 μs. Again, the paired-line structures are observed. Therefore, it can be concluded that the paired-line structures of the Raman spectra observed in KBr are the intrinsic properties of the isolated H centers.

The frequencies of the fundamental RRS lines for the H and V_K centers are summarized in Table I together with the LO-phonon frequency of each material studied in the present experiment. The frequencies of the X_2^- molecular ion matrix isolated[23,27,28] are also listed for comparison. It is clearly seen in Table I that the frequency of the H center is much higher than that of the V_K center.

In order to get some insight into these hardening effects, we also measured similar RRS spectra of the H_A (Li$^+$) and H_A (Na$^+$) centers at 80 K. On the basis of the decay curve analysis of the UV-absorption band, we used $\tau_p = 150$ ms, where unperturbed H centers were annihilated completely. The wavelength of the probe light was 345 nm for the H_A (Li$^+$) center and was 360 nm for the H_A (Na$^+$) center, which correspond to the peak energy

of each of the absorption bands. Figure 6 shows the RRS spectra of the H_A (Li$^+$) and H_A (Na$^+$) centers in KCl. For both centers, the spectra consist of a single fundamental line and its overtones. The frequency of the fundamental, 326 cm^{-1} for the H_A (Li$^+$) center and 322 cm^{-1} for the H_A (Na$^+$) center, is very close to that (329 cm^{-1}) of the H center. The results indicate clearly that replacement of a nearest neighboring alkali ion of an H center with a foreign alkali ion do not cause any significant effects on the fundamental RRS frequency.

IV. DISCUSSIONS

A. The stretching-vibration frequencies of the V_K and H centers

All the Raman spectra described in the previous section were measured under the resonance with the UV-absorption band of the V_K, H, and H_A centers. It is well known that the transition is essentially the bonding-to-antibonding transition of the X_2^- molecular ion.[11] Therefore, the transition couples strongly to the stretching vibration of the X_2^-. Thus, the Raman spectra can be interpreted primarily in terms of the stretching vibration of the X_2^- molecular ion placed on different lattice points in the alkali halide lattice.

One of the most striking features of the results described in the previous section is the strong hardening of the frequency ω_H of the stretching vibration of the H center, compared with ω_V of the V_K center in a given salt. To demonstrate this feature, we plot in Fig. 7 the stretching-vibration frequencies of the H and V_K centers in three chlorides as a function of the lattice constant $a/2$. It is clear that ω_H is higher by more than 30% than ω_V. It is also evident in Fig. 7 that ω_H depends strongly on a, whereas that of the V_K center is almost constant; the average of the two split lines for the V_K center in NaCl is identical to the vibrational frequency of the V_K
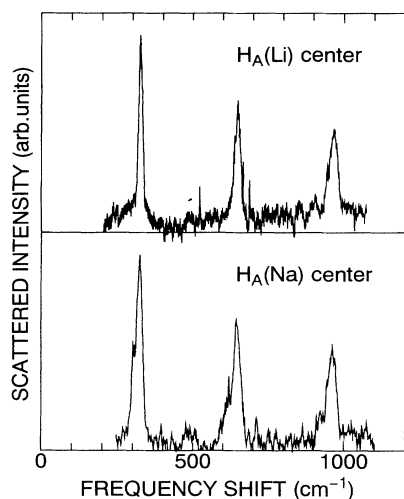
FIG. 6. Resonance Raman spectra of the H_A centers at 78 K, (a) in KCl doped with Li$^+$ and (b) in KCl doped with Na$^+$; the wavelength of probe light pulses was 360 nm for both specimens.
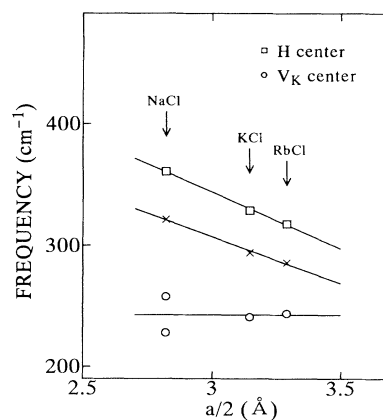
FIG. 7. Frequencies of the stretching vibration of the V_K centers (open circles) and of the H centers (open squares) in alkali chlorides as a function of the lattice parameter $a/2$. The crosses show the calculated vibrational frequencies of the H centers (see the text).

center in KCl and RbCl.

The H center in alkali halides is regarded as the X_2^- molecular ion occupying an anion site. In some crystals in which the molecular axis is oriented along a $\langle 110 \rangle$ direction, the configuration has often been described as X_4^{3-}.[1,2] On the other hand, as described in Sec. III, the X_2^- is oriented along a $\langle 111 \rangle$ direction in NaCl. We first discuss the effects of the orientation of the X_2^- molecular ion on the hardening of the stretching vibration.

The EPR studies have shown clearly that replacing a neighboring alkali ion with a foreign alkali ion having a smaller ionic radius induces a significant change in the orientation of the X_2^- molecular ion, and hence, in the atomic configuration of the H center. The H_A (Na^+) center has an axis 5.7° off from a $\langle 110 \rangle$ direction,[20,21] while the H_A (Li^+) center has an axis intermediate between a $\langle 100 \rangle$ and a $\langle 111 \rangle$ direction.[22] As a result, optical and thermal properties of these H centers associated with a foreign alkali ion differ significantly from those of the unperturbed H centers. However, as shown in Fig. 6, the frequency of the fundamental line in the RRS spectrum of the H, H_A (Li^+), and H_A (Na^+) centers in KCl is almost identical with each other, irrespective of the significant differences in the configuration of the X_2^- molecular ion and surrounding lattices. This result indicates clearly that orientation of the X_2^- molecular ion, as well as the lattice configuration surrounding it, is not a crucial factor that causes the hardening of the stretching vibration of the X_2^- molecular ion. The hardening of the stretching-vibration frequency of the H center in specific halides is scaled reasonably by the lattice constant, as plotted in Fig. 7, irrespective of the orientations of the X_2^- molecular ions.

We ascribe the hardening that can be scaled by the lattice constant to the Madelung force applied on the X_2^- molecular ion. In order to substantiate our interpretation, we first evaluated the force constant and hence, the frequency of the stretching vibration of the Cl_2^- center placed at an anion site, using a simple model in which the potential function for the Cl_2^- is a superposition of the Madelung potential function and the molecular potential-energy function of the free Cl_2^- molecular ion obtained by Tasker, Balint-Kurti, and Dixson.[29] The vibrational frequencies thus evaluated in NaCl, KCl, and RbCl are shown by crosses in Fig. 7. Although they are lower than those observed experimentally, they show significant hardening and the dependence on the lattice constant is parallel to the experimental results. A similar calculation for the V_k center shows that the Madelung potential reduces slightly the stretching-vibration frequency of the X_2^- molecular ion, although the effect is small. As seen in Table I, the frequency of the V_K center is about 90% of that observed in the argon matrix. We consider that the softening is due to the effect of crystal potential. The difference of the crystal potential in the force constants for the H and V_K centers arises from the location of the X_2^- molecular ion; a strong inward force acts on the molecular ions for the H centers but a weak outward force acts for the V_K center.

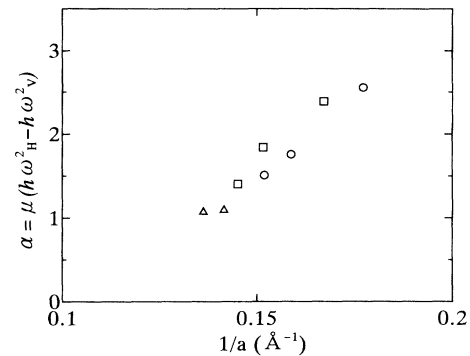Now, we generalize the scaling of the hardening to in-

FIG. 8. The hardening factor α, the difference between the force constant for the stretching vibration of the H center and the V_K center in alkali halides as a function of the inverse of the lattice constant.

clude H centers in bromides and iodides by introducing the following empirical quantity. We simply write the stretching-vibration frequency of the H center as

$$[\hbar\omega_H(Q_1)]^2 = \mu^{-1}k_H ,$$

where μ is the reduced mass for the stretching mode of the X_2^- molecular ion and k_H is the force constant of this mode in the H-center configuration. μ can be taken to be $\mu = (M_X/2)$. Similarly, the frequency ω_V of the V_K-center configuration is given by replacing k_H by k_V, the force constant in the V_K-center configuration. Therefore, the quantity α, which is defined as

$$\alpha = \mu[\hbar\omega_H(Q_1)^2 - \hbar\omega_V(Q_1)^2] ,$$

gives a measure of the hardening of the force constant in the H-center configuration with respect to that in the V_K-center configuration, irrespective of the kind of halogen.

Based on the results of the chlorides shown in Fig. 7, we assume that ω_V is not dependent on the lattice constant. For the bromides, we put $\hbar\omega_V = 144$ cm^{-1}, the experimental value of the V_K center in KBr. For iodides, since no experimental results for the V_K center are available, we take the value of 90% of the I_2^- molecular ion in the Ar matrix by taking into account the softening effect of the crystal potential. The estimated value of the V_K center in the iodides is very close to that calculated by Harding.[30] For the H centers which show paired fundamental lines, the frequency of the line showing the highest intensity is adopted.

In Fig. 8, we plot α's for the H centers obtained in the present study as a function of the inverse of the lattice constant. It is clear that α is uniquely scaled by $1/a$. The result shown in Fig. 8 further substantiates our interpretation that the main origin of the hardening of $\hbar\omega_H$ is the Madelung potential in a given lattice.

B. Origin of the paired Raman lines in the X_2^- centers

As seen in Figs. 2–5, RRS spectra for some X_2^- centers are characterized by the paired fundamental lines. This structure results either from the structures of Raman-

active modes or from the interaction of the Raman-active mode with other modes. A candidate for the latter may be the combination of the stretching vibration with the rotational modes as observed in free molecules.[31] In this case, the line with the higher frequency corresponds to the Raman process of exciting a vibrational and rotational quantum simultaneously. Since we do not have any quantitative information for the rotational mode of the V_K and H centers, the validity of this process cannot be judged simply from a quantitative viewpoint. However, for the case of the H center in KBr, the result that the high-frequency line is much more intense that the low-frequency one is not in favor of this interpretation. Furthermore, unanswered questions arise if we adopt the combination of the rotation modes with the mode of the stretching vibration as the origin of the paired lines; it is almost impossible to explain why the paired lines are observed only in specific alkali halides, although the thermal properties of the H centers in many alkali halides are similar. Below we examine the other option that causes the paired-line structure in the Raman spectra; i.e., the presence of two Raman-active modes which couple to the $\sigma_g \rightarrow \sigma_u$ hole transition.

In theoretical studies of the H center in KBr, it has been shown that the six alkali ions at nearest-neighbor sites of the X_2^- is distorted strongly.[32] This means that the distortions and vibrations of these alkali ions are closely related to the vibration of the X_2^- molecular ion. Therefore, it is presumed that the breathing-type vibration of these alkali ions is coupled to the stretching vibration of the X_2^- center. When we introduce the interaction between the stretching mode and the breathing modes, any of the combination modes can be coupled to the $\sigma_g \rightarrow \sigma_u$ hole transition; their Raman intensities depend on the magnitude of the cross term of the force constant for the stretching and breathing modes and also by the ratios of their frequencies.

In order to illustrate effects of the coupled oscillation, we show in Fig. 9 a schematic diagram indicating the coupling of a stretching-vibration mode which has a constant frequency ω_X and a breathing mode which has a variable frequency ω_A. The curves in Fig. 9(a) show the frequencies of the two normal modes in the presence of a cross term, while the curve in Fig. 9(b) represents the square of the amplitude of the breathing mode incorporated into the two normal modes of the coupled oscillation; for $\omega_A \ll \omega_H$ and $\omega_A \gg \omega_H$, the coupling of the stretching and breathing modes is negligible, whereas they are coupled strongly in the region where ω_A is close to ω_H. We take the bulk-phonon mode having the
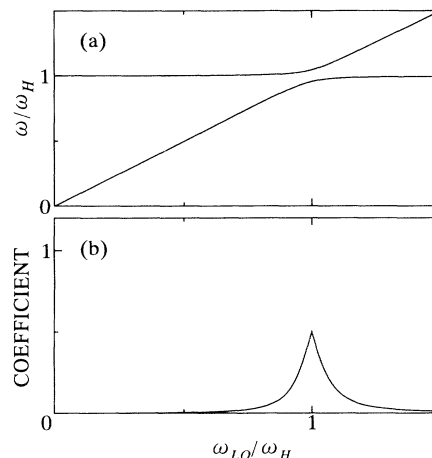

FIG. 9. Schematic diagram showing the effects of coupling between the stretching vibration of the X_2^- molecular ion and a breathing mode of surrounding ions. The curves in (a) show the frequencies of the two normal modes in the coupled oscillation, and the curve in (b) shows the square of the relative amplitude of the breathing vibration mode incorporated into the two normal modes of the coupled oscillation.

highest frequency, LO-phonon mode,[33] as a measure of the frequency of the breathing mode. For the eight materials studied here, we list the ratio ω_{LO}/ω_H in Table I, in which the average of two frequencies is taken for crystals showing paired lines. It is found that the system which shows a single Raman line for the H center has the ratio of ω_{LO}/ω_H smaller than 0.8, while the systems which show the paired-line structure have ratios larger than 0.8. Thus, we interpret that the paired-line structure is due to the strong coupled oscillation of the stretching vibration of the X_2^- molecular ion and the breathing vibrations of the alkali ions. Based on the above-mentioned argument, we interpret the paired lines of the RRS spectrum for the V_K center in NaCl to be caused by the same origin. In Table I, the ratio of ω_{LO}/ω_V is also listed; it is clear that the ratio is very close to unity only in NaCl.

ACKNOWLEDGMENTS

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