Dichroism of V Bands in Potassium and Rubidium Halides*

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Ultraviolet absorption bands which are homologous to the V_2, V_3, and V_4 bands in KBr have been studied in the potassium and rubidium chlorides, bromides, and iodides. They are generated by x irradiation above liquid-nitrogen temperature, and they are apparently intrinsic in the sense that no tendency to saturate has been observed as a function of radiation dose. The predominant V band which accompanies the F band depends on the conditions of irradiation. The effect of illumination in the bands with polarized uv light shows that the V_4 centers can be optically reoriented by $\langle 100 \rangle$-polarized light absorbed in the band at 100 K. The dichroism is washed out by warming the crystal from 100 to 200 K. The V_2 band can be preferentially bleached by $\langle 100 \rangle$ light absorbed in the band at 100 K. Again the dichroism is washed out upon warming to 200 K. The V_3 band is not affected at all by light absorbed at 100 K. Above room temperature, isotropic bleaching occurs. In addition, in KCl an irreversible thermal transformation of some of the V_4 centers into V_2 and also of some V_2 into V_3 occurs when the crystal is warmed above the temperature of irradiation. The peak wavelengths of these V bands lie between 200 and 360 nm, and are strongly dependent on the halide, but nearly independent of the alkali species. The close grouping of their peak wavelength positions, and the dependence on halogen species, indicate that they may all be X_3^- centers, in accordance with a suggestion of Hersh. The V_4 and V_2 centers show a $\langle 100 \rangle$ symmetry axis. The irreversible thermal conversions observed in KCl suggest that the three centers differ by ionic constituents and not merely by their state of ionization.

I. INTRODUCTION

THE F center produced by irradiation in the alkali halides is an intrinsic defect, in that no impurity atom is incorporated in its structure (even though the *rate* of F-center production may depend on impurity content of the crystal). The total concentration of F centers can build up to many times the impurity concentration. Since the F center is an electron trapped at an anion vacancy, there must also be complementary intrinsic centers which consist of holes trapped at interstitial anions and/or cation vacancies. Possibly these centers could also form aggregations, as do the F centers. It was suggested[1] that these complementary hole centers might be responsible for the V bands, optical-absorption bands which occur in the uv at shorter wavelengths than the F band.[2,3] The peak wavelengths of the bands indicate[4] that the hole centers are in fact halogen molecular ions, whose optical absorption is only slightly affected by their crystalline environment. A specific model[5] which is of particular interest here consists of an X_3^- molecular ion formed from two holes trapped at an anion in a cation vacancy.

So far, the only intrinsic complementary hole center whose structure has been established[6-8] is the H center, which is formed along with F centers at temperatures near 4 K. It is an X_2^- center which is chemically equivalent to an interstitial halogen atom. The H center

becomes unstable as the temperature increases. The intrinsic hole centers which accompany F-center production above 80 K are probably stabilized by migration of an ionic constituent—possibly a cation vacancy.[5,9] They are apparently two-hole centers, since no spin-resonance signal has even been associated with them.

Of the V centers numbered V_1 to V_7 by Dorendorf,[3] only the V_2, V_3, and V_4 bands presently appear to be intrinsic, in the sense that they can be generated in large numbers.[10,11] Which V band predominates depends on the temperature during irradiation,[2,3] and on whether the radiation is hard or soft.[2] Under our conditions, we find that the V_4 band dominates in crystals irradiated near 100 K, the V_2 near 200 K, and the V_3 near 300 K. The three bands are distinguished by their peak wavelength position, although they are not well resolved. They are more positively distinguished by the dichroism which is produced by bleaching with polarized uv light. In KCl a band at 255 nm was named V_4 by Dorendorf,[3] but this band does not appear to be intrinsic. Instead it is a band at about 240 nm, which appears to be the analog of the V_4 in KBr, based on its intrinsic character and bleaching behavior.[11,12] We shall call this 240-nm band in KCl the V_4, in disagreement with the usual nomenclature.

The close grouping of the V_2-, V_3-, and V_4-band wavelengths in a given salt suggests that these centers are related to each other.[4] This suggestion is reinforced by the observation[3] that V_2 centers can convert into

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V_3 and[13] V_4 into V_2, in KCl. (We have not observed this conversion in other salts.) When a KCl crystal containing V_2 centers and F centers is warmed up, two effects occur[3]: F centers and V_2 centers are destroyed, and V_3 centers are produced. On the other hand, when it is optically bleached with F-band light instead of warming, only the first effect occurs, with no V_3-center production.[2] More quantitatively,[14] thermal bleaching of V_2 centers between 200 and 300 K is approximately exponential with time, showing an activation energy of about 0.2 eV. The thermal conversion of V_2 centers to V_3 centers appears to be much more strongly temperature-dependent. Below 250 K the conversion is minute, whereas at higher temperatures the conversion is fast, indicating an activation energy which is probably greater than 0.7 eV. Since the conversion occurs thermally with a relatively large activation energy and is irreversible, it probably depends on ionic (or vacancy) motion, not merely on ionization of the centers. Thermal bleaching of the V_3 center in KCl occurs above room temperature. Near 450 K, both the F and the V_3 bands decay more or less exponentially, after an initial rapid drop,[15] with an activation energy of the order of 0.7 eV.

Because the V_2, V_3, and V_4 bands are thought to be related to each other, we have investigated their bleaching behavior in six potassium and rubidium halides. The dichroism we find agrees with that of the V_4 band already known in KCl[12] and KBr.[12,16]

II. EXPERIMENTAL

The potassium halide crystals were obtained from the Harshaw Chemical Co. A few measurements have also been made on KCl crystals obtained from other sources.[17] The rubidium halide crystals were obtained from various sources.[18] They were cleaved into absorption samples 1 or 2 mm thick. These were irradiated in a cryostat, with 50-keV x rays from a tungsten target filtered through about 1 mm of aluminum. The optical absorption was always measured at about 90 K without removing the samples from the cryostat after irradiation. This measurement was made in a Unicam SP700 recording spectrophotometer, in the wave-number range 4100–48 000 cm^{-1} (0.5–6.0 eV). The short-wavelength limit was determined by the cutoff of the polarizer used for the dichroism measurements. This was a calcite Glan prism with 12-mm aperture (Karl Lambrecht, Inc.). An identical prism was put in the reference beam

of the spectrophotmeter. The same prism was used to polarize the bleaching light. Monochromatic bleaching light was obtained from a Bausch and Lomb High Intensity Monochromator, with a deuterium or high-pressure mercury light source. The bleaching was carried out with the samples at about 90 K.

III. RESULTS

The peak wavelengths (measured at 90 K) for the V_2, V_3, and V_4 bands are listed in Table I. The terminology for KBr is that of Dorendorf.[3] As was mentioned above, the band listed as V_4 in KCl is not the one so named by Dorendorf. The three bands are illustrated in Fig. 1 for the case of KBr. The corresponding bands in the other salts are identified by their similar dichroic characteristics after bleaching with polarized uv light, as will be described below.

The peak wavelength of the V_3 band in KBr actually lies at about 230 nm, but the band is exceptionally asymmetrical, as seen in Fig. 1. This band can be resolved[19] into two approximately Gaussian peaks, one at 255 nm and a smaller one at 225 nm. Since the former peak is more than three times the area of the latter, it is listed first in Table I. The two peaks apparently correspond to two transitions of the V_3 center, rather than to two distinct centers, since they always grow and bleach together. The V_3 band in RbBr may also be composite, although we have not analyzed it in detail. The growth of the composite V_3 band in KBr is roughly proportional to the square root of the x-irradiation time,[19] as was previously found[9] in KCl. In fact, for heavy irradiations the F band also grows roughly as the square root of time,[19] so that the V_3-center concentration is apparently proportional to the F-center concentration.

The effect of illumination with polarized uv light on the V_2, V_3, and V_4 bands was investigated as follows: After illumination with monochromatic polarized light
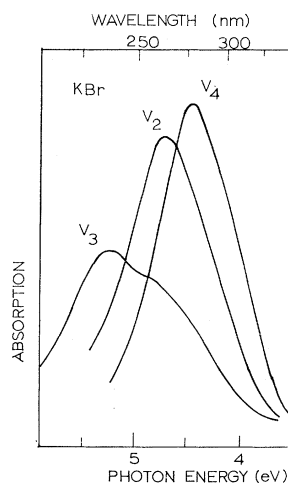

FIG. 1. Relatively pure V bands in KBr produced at different irradiation temperatures. Absorption measured at about 90 K.

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absorbed in the band, any resulting dichroism was tested by measuring the optical absorption of light polarized both parallel and perpendicular to the polarization directions of the bleaching light. Polarization directions along the ⟨100⟩ and ⟨110⟩ crystallographic axes were used. The ⟨110⟩ polarization direction introduced no dichroism.

No dichroic effects on the V_3 band, created by irradiation at 300 K, were observed as a result of bleaching with polarized uv light absorbed in the band. These bleaching experiments were done in the temperature range 100–400 K. At 100 K, the band was unaffected by the bleaching light, but above room temperature isotropic bleaching occurred. (That is, the band decreased by the same amount whether measured with light polarized parallel or perpendicular to the bleaching light.) This bleaching has been studied in detail[10] in KCl, and it appears to be qualitatively similar in the other salts. In KCl the high-temperature isotropic bleaching of the V_3 center showed a relatively large thermal activation energy of 0.6 eV, from which it was concluded that the bleaching process depends on an

TABLE I. Peak wavelengths (in nm) for intrinsic V bands. The irradiation temperature at which each band predominates is in parentheses.

	V_4 (100 K)	V_2 (200 K)	V_3 (300 K)
KCl	240	230	215
RbCl	235	230	205
KBr	275	260	255 (225)
RbBr	285	280	260
KI	355	325	310
RbI	360	355	345

ionic jump while the center is in an excited state following the absorption of a photon.

The V_2 band, created by x irradiation at 200 K, could be preferentially bleached by ⟨100⟩ light absorbed in the band at 100 K, whereas ⟨110⟩ light caused isotropic bleaching. This means that after a crystal is bleached with [100] light, it is dichroic, the absorption measured with [100] light being smaller, while the absorption measured with [010] light is nearly the same as before the bleaching. Results for a KBr crystal are shown in Fig. 2. The dichroism was washed out by warming the crystal from 100 to 200 K, in KCl and KBr. One may conclude that the V_2 center has a ⟨100⟩ symmetry axis, and that it can undergo thermal reorientation at 200 but not at 100 K. As mentioned above, when a KCl crystal containing V_2 centers is warmed above 250 K, in addition to thermal bleaching, some of the V_2 centers are converted to V_3.

The V_4 band, created by x irradiation at 100 K, could be optically reoriented by ⟨100⟩ light absorbed in the band at 100 K. This means that after a crystal is illuminated with [100] light it is dichroic, the absorption measured with [100] light being smaller while the
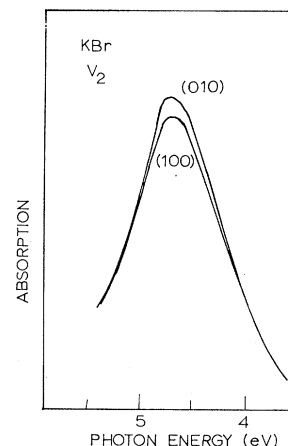

FIG. 2. Dichroism of V_2 band in KBr produced by [100] bleaching. Before bleaching, absorption coincided with upper curve for both polarization directions.

absorption measured with [010] light is correspondingly larger than before the illumination. Results for KBr are shown in Fig. 3. The dichroism was washed out (in KCl and KBr) by warming the crystal from 100 to 200 K. One therefore concludes that the V_4 center has a ⟨100⟩ symmetry axis, and can undergo thermal reorientation at 200 but not at 100 K. In addition, in KCl, a certain fraction of the V_4 centers is converted to V_2 on warming to 200 K. This conversion is evidenced by a slight shift in the peak position, as well as by the fact that subsequent illumination with ⟨100⟩ light at 100 K causes preferential bleaching instead of reorientation.

IV. DISCUSSION

The study of polarized bleaching of the V_2, V_3, and V_4 bands in six different alkali halides has shown that each of the three bands has its own characteristic dichroic behavior (or lack of dichroism in the case of V_3). This characteristic gives increased confidence that bands with the same name in different salts are actually homologous structures. It also shows that the three bands are structurally distinct from each other in a given salt,
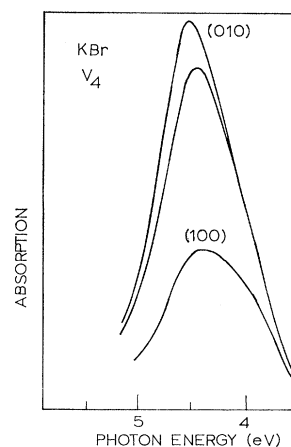

FIG. 3. Dichroism of V_4 band in KBr produced by [100] bleaching. Middle curve shows absorption before bleaching for both polarization directions.
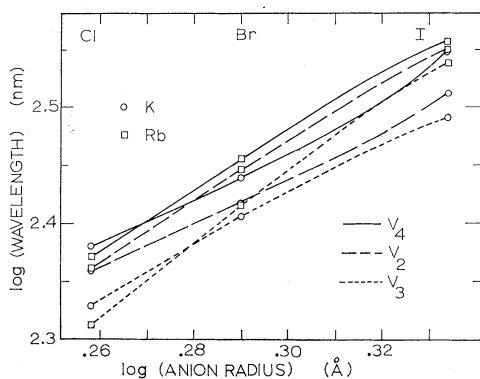
FIG. 4. Dependence of V-band peak wavelength positions on anion radius. (The base of the logarithms is 10.)

even though we believe that they are all some form of X_3^- molecular ion on the basis of their absorption wavelengths.[4] Because the bands are poorly resolved in a given salt, and because two of them may be simultaneously produced under certain conditions of irradiation, the experimental absorption curves can look like a single broad band whose peak wavelength shifts continuously with the irradiation temperature. It has been suggested[20] that the absorption in KCl peaking in the vicinity of 210–230 nm is simply the envelope of many narrower bands due to a distribution of different sizes of clusters of interstitial halogen atoms. We believe, however, that our observations of distinct dichroic behavior and crystallographic symmetry do not favor this interpretation.

The band positions in Table I are shown graphically in Fig. 4, where the peak wavelength is plotted versus anion radius. We have already noted that the V_2, V_3, and V_4 positions are close together in a given salt. Here we see that for a given band the peak position is even less dependent on the alkali ion species. Thus to a rough approximation the peak wavelengths are a function of the anion alone. This relation is in sharp contrast to the Mollwo-Ivey relation for F centers, where the peak position depends on lattice constant (i.e., the sum of anion plus cation radius). It is strong evidence that these centers are molecular halogen centers. Further confirmation of this assumption derives from observations of the V_3-band position in mixed crystals.[21] In KCl-RbCl mixed crystals, the V-band position shifted smoothly with composition (like the F band), but in KCl-KBr the one V band went down while the other rose up (unlike the F band). This behavior is consistent with a molecular halogen center absorption which is only slightly affected by the crystalline environment.

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Previous studies of the production[9] and destruction[10] of the V_3 center in KCl were consistent with a model, similar to Varley's,[5] in which a linear Cl_3^- molecular ion occupies one cation and two anion sites with a $\langle 100 \rangle$ axis. This model appears to be consistent with our results also, even though no $\langle 100 \rangle$ dichroism could be produced in the V_3 bands. If the excitation of the X_3^- occurred by a dissociation mechanism,[22] optically assisted reorientation of the center would be expected. If it occurs by a charge-transfer mechanism[23] it would not be expected, although preferential bleaching could occur provided that its temperature range extended below that where purely thermal reorientation would wash out any observable effect. It seems most likely to us that thermal reorientation of this center would be possible down to rather low temperatures. Because of the symmetry of the environment, thermal reorientation would not require any ionic motion, but merely a reformation of the covalent bonding of the central X^+ with other X^- neighbors. In fact, it might be preferable to regard this center as a resonance between the three possible orientations, which would be described as an X_7^{5-} configuration, although this is not known in solutions. If no dichroism of the center could be found in the vicinity of 4 K, this latter interpretation would definitely be favored.

We are left with the problem of inventing models for the V_2 and V_4 centers. The considerations which have been adduced require that they should be X_3^- molecular ions in an environment which has an ionically stabilized $\langle 100 \rangle$ axis, but without including impurity ions. We therefore conjecture that these are like the V_3 center, with two different vacancy configurations in near-neighbor positions. An admittedly speculative suggestion is that the V_4 center has one cation vacancy as a neighbor and that the V_2 has a cation-anion vacancy pair as a neighbor. These configurations preserve charge neutrality in the crystal during F-center production, and it seems at least plausible that the former should reorient more easily and the latter should bleach more easily.

It appears that considerations of anion radius are important in the production and stability of these centers. As the anion radius increases the rate of production goes down, especially in the case of the V_3 centers. On the other hand, the thermal stability of the V_4 and V_2 centers appears to go up.

ACKNOWLEDGMENTS

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