

EPR and Optical Absorption Study of BrCl^- and Associated Centers in Doped KCl Crystals. I*†

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Correlated optical and EPR studies show that after x - or γ -ray irradiation combined with proper thermal treatment, BrCl^- molecule ions aligned along the six $\langle 110 \rangle$ directions are present in crystals of KCl doped with a small amount of KBr. The BrCl^- molecule ions, which have a strong σ -polarized transition at 382 nm and a much weaker but still somewhat σ -polarized transition at 760 nm, are thermally more stable than the V_K centers (Cl_2^-) from which they are formed. The increased thermal stability of BrCl^- is believed to arise primarily because the electronegativity of chlorine is greater than that of bromine. A study of the reorientation kinetics at 88°K reveals that the reorientation of BrCl^- proceeds by 90° jumps as well as 60° jumps, and very probably also by 120° jumps, whereas many homonuclear molecule ions reorient only by 60° jumps.

I. INTRODUCTION

It has been shown in earlier studies that high concentrations of Cl_2^- ions can be produced in KCl crystals doped with Ag^+ , Tl^+ , or Pb^{++} by exposing them, at 77°K, to x rays or γ rays.¹ The added impurity ions Ag^+ , Tl^+ , and Pb^{++} act as very efficient electron traps and become Ag^0 ,² Tl^0 ,^{3,4} and Pb^+ , respectively. These impurities are not only good electron traps but also, under proper conditions, are very good hole traps. For example, when a KCl:AgCl crystal containing Cl_2^- and Ag^0 is warmed to 210°K, one observes the disappearance of all of the Cl_2^- and a small fraction of the Ag^0 , and also observes the formation of Ag^{++} .² These reactions are caused by the instability of Cl_2^- which diffuses through the lattice at temperatures above 160°K; if the Cl_2^- encounters an Ag^0 , annihilation of the electron and hole occurs, and if it encounters an Ag^+ , it is retrapped to form Ag^{++} . Corresponding reactions occur in KCl:TlCl and KCl:PbCl₂ crystals after irradiation and subsequent thermal treatment.^{3,5}

After these initial studies with cation impurities, it seemed reasonable that Br^- in KCl would also act as a hole trap since the electronegativity of Br is less than that of Cl. The fact that Br^- acts as a hole trap was established some time ago in this laboratory when the formation of BrCl^- was reported.⁶ The present paper reports a detailed study of the electron paramagnetic resonance (EPR) and optical properties of BrCl^- in KCl, the formation and destruction of this center as a result of optical or thermal excitation, and the mechanism of reorientation of the molecule in the lattice. The BrCl^- center has also been observed in LiCl, NaCl, and RbCl, but these results will not be reported in this paper.

II. EXPERIMENTAL PROCEDURE

The crystals used in these experiments were

grown in air by the Kyropoulos method, and were pulled from a melt of KCl containing 0.2 mole% KBr and 0.27 mole% PbCl_2 . Since Br^- does not segregate appreciably in KCl, the concentration of Br^- in the grown single crystal is almost the same as that in the melt, but the Pb^{++} concentration is reduced by approximately a factor of 10. Similar crystals were grown with Ag^+ , Tl^+ , and NO_2^- ions instead of Pb^{++} , all of which are good electron traps. The color centers were produced at 77°K either by x -ray irradiation from a 50-kV 50-mA Machlett tube with a tungsten target filtered by ~1-mm fused silica or with γ rays from a 2000-Ci ^{60}Co source. Before irradiation, the Pb^{++} -doped crystals were heated to about 520°K for a few minutes and then quenched to room temperature. This treatment apparently disperses agglomerated lead in the crystal, increasing the concentration of electron traps. As a result, it is found that the hole-center concentration is increased by about a factor of 3 with respect to the unquenched crystals. Details of the EPR measurements have been given before.⁷ Optical absorption spectra were obtained by using a Cary 14R recording spectrophotometer. Polarized light was produced by means of an Ahrens prism. Optical excitation of the crystals was accomplished by exposure to light from an HBO-500 high-pressure mercury arc lamp or a 750-W filament lamp in conjunction with appropriate interference and/or Corning glass filters. The correlation of the optical absorption and EPR measurements was done on different crystal specimens, cleaved from the same large single crystal, which were treated identically.

A TC 101 Cryogenic Research Co. temperature controller in conjunction with a platinum resistance thermometer was used to measure and control the temperature in the reorientation experiments. The resistance thermometer was embedded in a cold-finger-type copper block; the crystal was attached

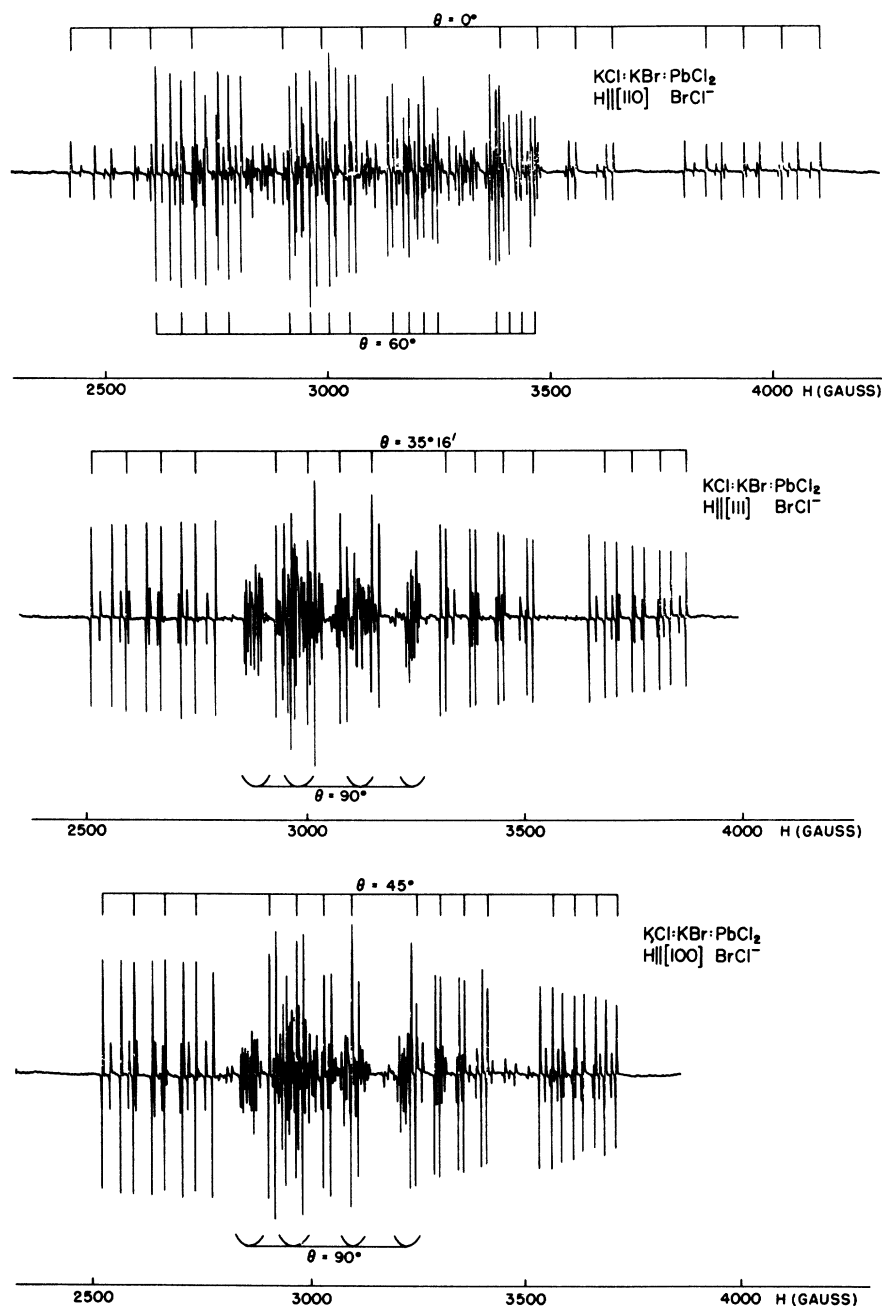


FIG. 1. EPR spectra at 77°K of BrCl^- in $\text{KCl}:\text{KBr}:\text{PbCl}_2$ for three special orientations of the magnetic field \vec{H} . Weakly allowed $\Delta M_I(\text{Br}) = \pm 1$ transitions are observable in the $\theta \neq 0^\circ$ spectra.

to the block by means of clamps. The temperature of the block was controlled to better than $\pm 0.01^\circ\text{K}$. It is estimated from experiments with sensors on the crystal that the temperature of the crystal was no greater than 0.1°K warmer than the copper block and that the crystal temperature was also controlled to about $\pm 0.01^\circ\text{K}$.

III. EPR AND OPTICAL ABSORPTION SPECTRA

A. Qualitative Analysis of the EPR Spectrum

Irradiating a Br^- - and Pb^{2+} -doped KCl crystal

with x or γ rays at 77°K produces a strong Cl_2^- and weak BrCl^- EPR spectrum. The Cl_2^- center is the well-known "self-trapped hole" or V_K center.⁸⁻¹⁰ Warming the crystal to about 210°K for a few minutes completely destroys the Cl_2^- centers and at the same time the concentration of BrCl^- centers is greatly enhanced. The BrCl^- EPR spectra, taken at 77°K, are shown in Fig. 1 for three special orientations of the static magnetic field \vec{H} with respect to the crystal axes. For the chosen Br^- concentration, this BrCl^- spectrum is the princi-

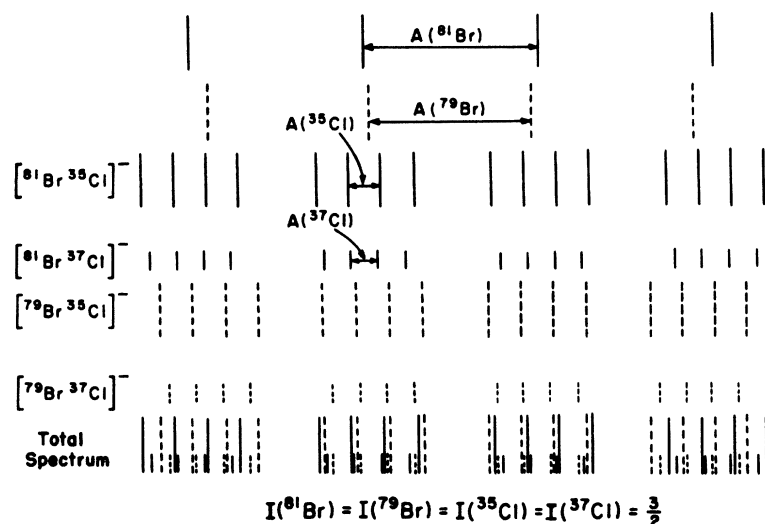


FIG. 2. Basic BrCl^- hyperfine pattern. The ratio of $A(\text{Br})$ to $A(\text{Cl})$ corresponds to that of the $\theta = 0^\circ$ spectrum in Fig. 1.

$$\begin{aligned} \mu(^{81}\text{Br}) &= 2.269 \quad 49.4\%, & \mu(^{35}\text{Cl}) &= 0.8210 \quad 75.4\% \\ \mu(^{79}\text{Br}) &= 2.106 \quad 50.6\%, & \mu(^{37}\text{Cl}) &= 0.6835 \quad 24.6\% \end{aligned}$$

pal resonance that can be detected at 77°K after the above treatment. A small concentration of Pb^{++} is also present, and an even lower concentration of $\langle 110 \rangle$ -oriented Br_2^- is observed. The basic BrCl^- pattern is constructed in Fig. 2. Both Cl and Br have two isotopes each, and all of these nuclei have spin $\frac{3}{2}$. Consequently, there are four BrCl^- ions possible, viz., $[\text{Cl}^{35}\text{Br}^{81}]^-$, $[\text{Cl}^{35}\text{Br}^{79}]^-$, $[\text{Cl}^{37}\text{Br}^{81}]^-$, and $[\text{Cl}^{37}\text{Br}^{79}]^-$ with each combination giving rise to $(2I_1 + 1)(2I_2 + 1) = 16$ lines. One expects, therefore, a total of 64 lines, which is indeed observed. Furthermore, from the isotopic abundance, one deduces that these four possible combinations of BrCl^- must have intensity ratios of about 3:3:1:1, which is also observed in Fig. 1. Finally, the ratio of the experimentally determined hyperfine interaction constants of the two

Br isotopes is accurately equal to the ratio of the nuclear moments; the same holds for the hyperfine constants of the two Cl isotopes. Thus, the fact that the spin-resonance spectrum arises from BrCl^- molecule ions is established.

An angular variation study of the strongly anisotropic BrCl^- spectrum shows that the symmetry axis z , which is identical with the g tensor axis and the two hyperfine tensor axes and which coincides with the molecular axis, is oriented exactly along a $\langle 110 \rangle$ direction. Though axial symmetry is a good approximation, a quantitative analysis indicates that BrCl^- reflects the orthorhombic symmetry of the surrounding lattice. A set of principal axes is $z \parallel [110]$, $x \parallel [001]$, and $y \parallel [\bar{1}10]$; there are six such sets of principal axes. Table I classifies the number and types of spectra that are observed in Fig. 1 for three special orientations of the static magnetic field \vec{H} .

B. Optical Absorption Spectrum of BrCl^-

Curve a of Fig. 3 shows the absorption introduced into a $\text{KCl}:\text{KBr}:\text{PbCl}_2$ crystal after exposure at 77°K to γ rays and subsequent exposure to light ($\lambda = 546 \text{ nm}$) for a short time to remove the F centers present in the crystal. After this treatment, the principal γ -ray-induced species present in the crystal are Cl_2^- and Pb^+ . Curve b of Fig. 3 was taken after the crystal had been warmed to 210°K for 5 min. This thermal treatment causes the Cl_2^- ions to migrate through the crystal¹⁻³; if they encounter Br^- ions, BrCl^- is formed, if they encounter Pb^{++} ions, Pb^{+++} is formed, or if they encounter Pb^+ ions, electron-hole recombination oc-

TABLE I. Classification of the number and types of BrCl^- (and Cl_2^- and Br_2^-) EPR spectra for three special orientations of the magnetic field \vec{H} . θ and φ are the polar angles measured from z and x , respectively.

Direction of \vec{H}	Angles ($\theta; \varphi$)	Degeneracy or relative intensity
$\langle 110 \rangle$	$(0^\circ; \varphi)$	1
	$(60^\circ; 35.3^\circ)$	4
	$(90^\circ; 90^\circ)$	1
$\langle 001 \rangle$	$(45^\circ; 90^\circ)$	4
	$(90^\circ; 0^\circ)$	2
	$(90^\circ; 54.7^\circ)$	3

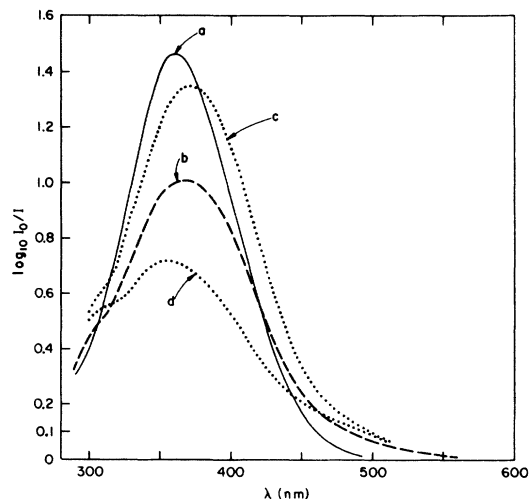


FIG. 3. Optical absorption spectra, measured at 77°K, of a KCl:KBr:PbCl₂ crystal after the following sequential treatments: The crystal was (i) exposed to γ rays at 77°K for 15 min and then excited with 546-nm light for 1 min; (ii) warmed to 210°K for 5 min and measured with unpolarized light and [011] and [011] polarized light; (iii) excited with [011] polarized light of λ > 650 nm and measured with [011] light, (iv) measured with [011] light.

curs and Pb²⁺ is reformed. Because the concentration of Br⁻ is much greater than either Pb²⁺ or Pb⁺, most of the Cl₂⁻ ions interact with Br⁻ ions to form BrCl⁻. However, the rise in absorption near 300 nm indicates the formation of a small amount of Pb³⁺. In addition to the absorption shown, if the measurements are continued to longer wavelengths and the ordinate expanded considerably, it is observed that a weak BrCl⁻ absorption is present, having a peak at about 760 nm.

From the work on the homonuclear molecule ions of Cl₂⁻ and Br₂⁻ it was concluded^{9,11} that the ground-state configuration of these ions is

$$\dots \sigma_g^2 \pi_u^4 \pi_g^4 \sigma_u^4, \quad (1)$$

which defines the $^2\Sigma_u^+$ ground state. The strong σ-polarized transition in the ultraviolet is to the excited state $\sigma_g \pi_u^4 \pi_g^4 \sigma_u^2 (^2\Sigma_g^+)$. The weak transition in the near infrared is to the excited state $\sigma_g^2 \pi_u^4 \pi_g^3 \sigma_u^2 (^2\Pi_g)$. The near-infrared transition of Br₂⁻ has an appreciable amount of σ character associated with it because of the admixture of σ_g into the π_g level as a result of spin-orbit coupling.¹¹ By analogy, it is expected that in the case of the heteronuclear molecule ion BrCl⁻ the ground state can be represented by

$$\dots \sigma_1^2 \pi_1^4 \pi_2^4 \sigma_2^2 (^2\Sigma_2). \quad (2)$$

Since BrCl⁻ has no inversion symmetry, the *u* and *g* classification does not apply; the subscripts 1 and 2 indicate the bonding and antibonding orbitals,

respectively. We propose that the strongly allowed σ-polarized transition in the ultraviolet arises from the $^2\Sigma_2 \rightarrow ^2\Sigma_1$ transition, and the weakly allowed σ-polarized transition in the near infrared is associated with the $^2\Sigma_2 \rightarrow ^2\Pi_2$ transition. Although the $^2\Sigma_2 \rightarrow ^2\Pi_1$ transition is not forbidden on symmetry grounds for BrCl⁻, it must be so weak that the tail of the $^2\Sigma_2 \rightarrow ^2\Sigma_1$ transition obscures it. The optical and EPR results in this paper are in qualitative accord with these proposals.

The anisotropic absorption of BrCl⁻ was determined in much the same manner as that for Cl₂⁻ and Br₂⁻.^{1,11} Since the method has been described before, only a brief summary of it will be given here. The face diagonals of the cube in Fig. 4 represent the six orientations of the molecular axes of BrCl⁻. After production of BrCl⁻ from thermally unstable Cl₂⁻, there is a random distribution of molecule ions among the six equivalent <110> directions. Although the two ends of BrCl⁻ are different, the experiments we performed do not distinguish between the two different orientations of BrCl⁻ along a given <110> direction; therefore, we consider only six possible orientations of BrCl⁻. As in the case of Cl₂⁻ and Br₂⁻, absorption of ultraviolet light polarized along either [011] or [010] can produce a difference in population among the <110> directions because of reorientation of the molecular axes of the molecule ions, and thus produce an anisotropy in the optical absorption. In the case of BrCl⁻, in addition to reorientation of the axes of the molecules by absorption of light, destruction to give Cl₂⁻ occurs with relatively high

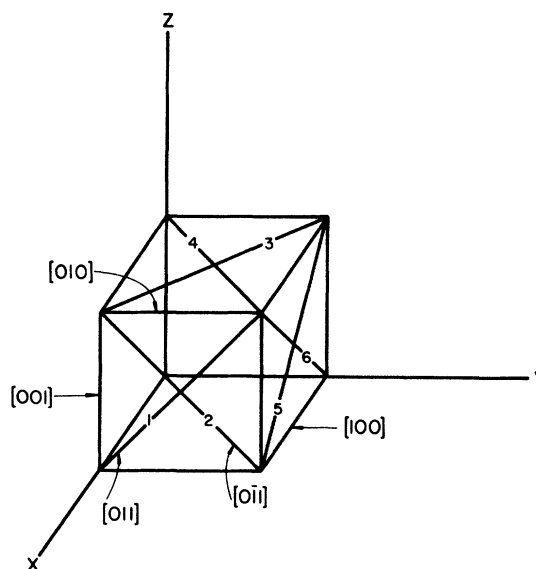


FIG. 4. Cube showing the various crystal directions relevant to the optical experiments and the numbering system used in the reorientation kinetics.

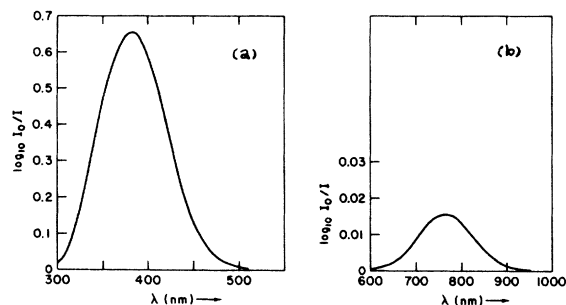


FIG. 5. Anisotropic optical absorption spectrum of BrCl^- obtained by subtracting curve d of Fig. 3 from curve c. The ordinate in B is expanded by a factor of 10 over that in A.

efficiency. Since the preferential orientation of Cl_2^- would interfere with the measurement of the ultraviolet anisotropic absorption of BrCl^- , the anisotropy was produced by excitation with polarized light absorbed in the near-infrared band which produces reorientation with very little destruction.

Curve b in Fig. 3 shows not only the absorption as measured with unpolarized¹² light but also with $[011]$ and $[0\bar{1}1]$ polarized light, since there is a random distribution of BrCl^- among the six $\langle 110 \rangle$ directions. Curves c and d of Fig. 3 show the $[011]$ and $[0\bar{1}1]$ absorptions, respectively, after exciting with $[0\bar{1}1]$ light ($\lambda > 650$ nm). It is seen that an anisotropy has been produced and also that a slight amount of Pb^{3+} again has been formed. Since no anisotropy has been produced in the Pb^{3+} and Pb^+ absorption bands, a subtraction of curve d from c gives the anisotropic spectrum of BrCl^- as shown in Fig. 5.¹³ The long-wavelength BrCl^- band is shown on an expanded scale. The data show that BrCl^- has absorption bands with peaks in the ultraviolet at 382 nm and in the near infrared at 760 nm. Correlated experiments have been performed using EPR techniques. Excitation with $[0\bar{1}1]$ light absorbed by the long-wavelength band causes an increase in the 0° spectrum with $\vec{H} \parallel [011]$; this EPR result proves that the infrared transition is σ polarized and, coupled with the anisotropic optical data, proves that the ultraviolet transition is σ polarized as well. The anisotropic spectrum of BrCl^- has also been obtained by using $[010]$ and $[001]$ polarized light. The normalized spectrum is the same as that shown in Fig. 5.

C. Quantitative Analysis of the EPR Spectra

The experimental EPR spectra of the BrCl^- center indicate that the axes of the hyperfine and g tensors coincide; therefore, the spin Hamiltonian used to analyze the BrCl^- EPR spectrum is taken as

$$\begin{aligned} \frac{\mathcal{H}}{g_0\beta} = & \frac{1}{g_0} (g_x H_x S_x + g_y H_y S_y) \\ & + \sum_{k=1}^2 (A_{x,k} S_x I_{x,k} + A_{y,k} S_y I_{y,k} + A_{z,k} S_z I_{z,k}) \\ & + \sum_{k=1}^2 P_k I_{x,k}^2, \end{aligned} \quad (3)$$

where the usual notation is used and $z \parallel [110]$, $x \parallel [001]$, and $y \parallel [1\bar{1}0]$. Spin Hamiltonian (3) was matched to the experimental BrCl^- spectrum using a second-order perturbation theory solution.⁷ Initially, all angles given in Table I were analyzed, and though a good over-all description of the spectra was obtained, small internal discrepancies, mostly for the g components, were found. These can be attributed to the perturbation solution whose accuracy decreases with increasing angle θ (though it improves again when $\theta \approx 90^\circ$). The spin-Hamiltonian parameters of Table II, which are more accurate than the earlier ones,¹⁴ were finally based upon the analysis of the following three spectra: (i) the nondegenerate $\theta = 0^\circ$ spectrum observable when $\vec{H} \parallel \langle 110 \rangle$; (ii) the triply degenerate $\theta = 35.3^\circ$, $\varphi = 90^\circ$ spectrum observable when $\vec{H} \parallel \langle 111 \rangle$; and (iii) the nondegenerate $\theta = 35.3^\circ$, $\varphi = 0^\circ$ spectrum observable when \vec{H} makes an angle of 35.3° with the $\langle 110 \rangle$ direction in the $\{100\}$ plane. Extrapolation of the g values of the latter two spectra to $\theta = 90^\circ$ yielded g_x and g_y , respectively. The sign and approximate magnitude of

$$A_y(\text{Br}) - A_x(\text{Br}) \approx +4 \text{ G}$$

were obtained from inspection of the $\theta = 90^\circ$ spectra observable when $\vec{H} \parallel \langle 111 \rangle$ and $\vec{H} \parallel \langle 100 \rangle$.

For comparison, Table II also includes the spin-Hamiltonian parameters of Cl_2^- and Br_2^- in $\text{KCl}:\text{KBr}$, ICl^- and I_2^- in $\text{KCl}:\text{KI}$, and IBr^- in $\text{KBr}:\text{KI}$. The reasons for giving all the hyperfine components a positive sign have been presented.⁷

The g shifts of the X_2^- centers, based on configuration (1), have been calculated¹⁵ and originate in the fact that the spin-orbit coupling mixes some $|\pi_u\rangle$, and only $|\pi_u\rangle$, into $|\sigma_u\rangle$. As a result, the orbital angular momentum makes a nonzero contribution to the g shift. It was found that the parallel g shift

$$\Delta g_\parallel(X_2^-) \equiv g_\parallel(X_2^-) - g_0$$

is completely second order and negative, in agreement with the experimental results. The perpendicular shift

$$\Delta g_\perp(X_2^-) \equiv g_\perp(X_2^-) - g_0$$

is predominately first order and positive. To this order of approximation it is given by

$$\Delta g_\perp(X_2^-) = 2\delta_u \lambda_u / E_u,$$

TABLE II. Spin-Hamiltonian parameters of the BrCl^- center in KCl. The results for Cl_2^- , Br_2^- , ICl^- , and I_2^- in KCl and IBr^- in KBr are included for comparison. The hyperfine and quadrupole parameters (expressed in gauss) correspond to the ^{35}Cl , ^{81}Br , and ^{127}I nuclei. ΔH is the linewidth (in G) between the extrema of the first derivative.

Center X_2^- or XY^-	g_z [110]	g_x [001]	g_y [110]	$A_z(X)$ [110]	$A_1(X)$	$A_z(Y)$ [110]	$A_1(Y)$	$P(X)$	$P(Y)$	ΔH
BrCl^-	1.9840 ± 0.0003	2.133 ± 0.001	2.135 ± 0.001	+484.0 ± 0.2	+113 ^a ± 2	+89.5 ± 0.1	+8 ± 1	+37 ^b	-5 ^b	1.9 ± 0.1
Br_2^-	1.9830 ± 0.0003	2.169 ± 0.001	2.164 ± 0.001	+450.6 ± 0.2	+80.9 ± 2			+28.6 ^c ± 1		2.8 ± 0.2
Cl_2^-	2.0014 ± 0.0001	2.0444 ± 0.0004	2.0423 ± 0.0005	+101.3 ± 0.1	+12.2 ± 0.5			-4.8 ^c ± 0.5		1.3 ± 0.1
ICl^- ^d	1.855 ± 0.007	2.326 ± 0.008	2.392 ± 0.007	+394.5 ± 1.5	+300 ^e ± 16	+61.2 ± 1.5	<4	-43 ± 3	...	3.5 ± 0.5
I_2^- ^f	1.9118 ± 0.0003	(2.27)		+397.9 ± 0.3	+147 ± 2			-34.9 ± 0.5		5.0 ± 0.5
IBr^- ^g	1.9041 ± 0.0003	+408.2 ± 0.5	+229 ± 5	+358.0 ± 0.5	+52 ± 5	3.5 ± 0.5

^aThe analysis suggests that $A_x < A_y$ with $A_y - A_x \approx 4$ G.

^bObtained from the second-order shifts of the allowed EPR lines. Experience indicates that these values may be too high by 10–20%.

^cDetermined from the weakly allowed $\Delta M_I = \pm 1$ transitions observed in the $\theta = 45^\circ$ spectrum.

^dFrom Ref. 28.

^e $A_x = 283 \pm 3$ G and $A_y = 316 \pm 3$ G.

^fFrom Ref. 26

^gFrom Refs. 26 and 27.

where δ_u and λ_u are the absolute values of, respectively, the orbital angular momentum and the spin-orbit coupling between $|\sigma_u\rangle$ and $|\pi_u\rangle$. E_u is the energy of the $\pi_u - \sigma_u$ excitation.

The g components of the heteronuclear XY^- halogen molecule ions have also been calculated⁷ using configuration (2). In this case, both π_1 and π_2 contribute to the g shifts. Again it is found that the parallel g shift is completely second order and negative, in agreement with the experimental result of Table II. The perpendicular g shift is predominantly first order and positive and given by

$$\Delta g_{\perp}(\text{BrCl}^-) = \Delta g_{\perp 1} + \Delta g_{\perp 2}$$

with $\Delta g_{\perp k} = 2\delta_k \lambda_k / E_k$, where δ_k and λ_k are the absolute values of, respectively, the orbital angular momentum and the spin-orbit coupling between $|\pi_k\rangle$ and $|\sigma_k\rangle$; E_k is the energy of the $\pi_k - \sigma_k$ excitation. For homonuclear molecules $\Delta g_{\perp 2} = 0$, but for heteronuclear molecules $\Delta g_{\perp 2}$ may be appreciable. The magnitude of $\Delta g_{\perp 2}$ for the BrCl^- center can be estimated by making the following approximations: $\delta_1 \approx \delta_u \approx 1$ and

$$\lambda_1 \approx \frac{1}{2}[\lambda(\text{Br}) + \lambda(\text{Cl})] \approx \frac{1}{2}[\lambda_u(\text{Br}_2^-) + \lambda_u(\text{Cl}_2^-)],$$

where $\lambda(\text{Br}) = +2456 \text{ cm}^{-1}$ and $\lambda(\text{Cl}) = +587 \text{ cm}^{-1}$ are the spin-orbit coupling constants of Br and Cl. Furthermore, the optical absorption bands of Cl_2^- , Br_2^- , and BrCl^- occur at comparable energies, and therefore the values of E_k are very likely comparable too. Thus one estimates that

$$\Delta g_{\perp 1} \approx \frac{1}{2}[\Delta g_{\perp}(\text{Br}_2^-) + \Delta g_{\perp}(\text{Cl}_2^-)] \approx +0.100.$$

Experimentally, $\Delta g_{\perp}(\text{BrCl}^-) = +0.134$, and therefore

$$\Delta g_{\perp 2} \approx +0.034,$$

which is appreciable indeed.

The magnitude of $\Delta g_{\perp 2}$ is completely dependent upon the heteronuclear character of the molecule. The value of λ_2 is given approximately⁷ by $\frac{1}{2}[\lambda(\text{Br}) - \lambda(\text{Cl})]$, which is appreciable since $\lambda(\text{Br})$ is much larger than $\lambda(\text{Cl})$. However, the value of δ_2 is relatively small and roughly equal to the ionicity of the molecule, i. e., the difference in hole density on the two sides of the molecule.⁷ The smallness of δ_2 is somewhat balanced by the fact that $E_2 < E_1$. E_2 is known experimentally since it corresponds to the $^2\Sigma_2^- \rightarrow ^2\Pi_2$ transition which is observed at 760 nm for BrCl^- .

A similar rough analysis for ICl^- (see Table II) shows that

$$\Delta g_{\perp 2} \gtrsim \Delta g_{\perp 1} \approx 0.15 \text{ to } 0.20.$$

This is not surprising in view of the larger ionicity of this molecule and the large value of $\lambda(\text{I}) = +5068 \text{ cm}^{-1}$. The results for IBr^- in Table II suggest that also for this molecule ion $\Delta g_{\perp}(\text{IBr}^-) > \Delta g_{\perp}(\text{I}_2^-)$ and $\Delta g_{\perp 2} \gtrsim \Delta g_{\perp 1}$.

Inspection of the hyperfine components in Table II shows that the hyperfine interaction with the Br nucleus is larger in BrCl^- than in Br_2^- , while the Cl hyperfine interaction is smaller in BrCl^- than in Cl_2^- . Since the magnitude of the hyperfine interaction with a nucleus gives an indication of the density of the hole at and around this nucleus, these

observations indicate that the hole density is larger on the Br side of the BrCl^- molecule ion than on the Cl side. Thus, the BrCl^- molecule ion exhibits an electric dipole moment corresponding to the chlorine having a slightly higher net negative charge than the bromine; this result is as expected, since Br has a lower electronegativity¹⁶ [$\chi(\text{Br}) = 8.2 \text{ eV}$] than Cl [$\chi(\text{Cl}) = 8.9 \text{ eV}$].

A more quantitative analysis of the hyperfine components, with the purpose of obtaining a precise idea of the hole distribution, is more involved. However, some of the qualitative features of this calculation will be discussed. Consider first the homonuclear X_2^- centers. The largest part of the hyperfine components is given by $\langle \sigma_u | \mathcal{H}_{\text{HF}} | \sigma_u \rangle$ in which \mathcal{H}_{HF} is the hyperfine Hamiltonian comprising the isotropic Fermi-interaction term and the traceless magnetic dipole-dipole interaction between the electron and nuclear spins. To this order of approximation, the term describing the interaction between the orbital angular momentum and the nuclear spin does not contribute. However, the spin-orbit interaction mixes appreciable amounts of $|\pi_u\rangle$ into $|\sigma_u\rangle$ as evidenced by the large g shifts. As a result of this mixing, both the orbit-nucleus and the electron spin-nuclear spin terms make sizable contributions to the HF components. These correction terms have been calculated to first order for the X_2^- center by Jette.¹⁷ Because only one excited state is involved, this first-order result can be conveniently expressed as a function of the perpendicular g shift Δg_{\perp} . Actually, for the heavier molecule ions (Br_2^- and I_2^-), the large parallel g shifts Δg_{\parallel} indicate that for an accurate analysis, these calculations should be carried out to second order.

A similar calculation can, in principle, be performed for the XY^- centers. As is the case for the g shifts, both $|\pi_1\rangle$ and $|\pi_2\rangle$ will contribute to the correction terms of the hyperfine components. The resulting expressions will not only contain more unknown parameters than in the case of the X_2^- centers, but because the contributions arise from two excited states it will not be convenient to express these correction terms as a function of Δg_{\perp} and Δg_{\parallel} . It is clear that, especially for ICl^- and IBr^- where the parallel g shifts Δg_{\parallel} are very large, such expressions must be calculated to a second-order accuracy.

The quadrupole terms P for Cl_2^- and Br_2^- (see Table II) were obtained from an analysis of the weakly allowed $\Delta M_I = \pm 1$ transitions which are readily observed, for example, in the $\theta = 45^\circ$ EPR spectra of these molecule ions. The Br_2^- and Cl_2^- values in Table II are somewhat lower, and probably more accurate, than the earlier values⁷ which were obtained from the second-order shifts of the allowed EPR lines. P_{Br} and the rough estimate for P_{Cl} of BrCl^- were obtained from the second-order

shifts and it is quite possible that they too are somewhat too high. Weakly allowed transitions of the type $\Delta M_I(\text{Br}) = \pm 1$ are observed experimentally for BrCl^- (see Fig. 1). A more accurate value for P_{Br} probably can be obtained from them; however, the correct assignment of these lines is rather tedious, and could be done more easily on a sample of very pure KCl doped with KBr highly enriched with ^{79}Br or ^{81}Br isotopes. The magnitude of the quadrupole interaction is determined primarily by the amount of p character of the ground state. The fact that $P_{\text{Br}}(\text{BrCl}^-) > P_{\text{Br}}(\text{Br}_2^-)$ indicates again, in agreement with the hyperfine results, that the hole density on Br is greater in BrCl^- than in Br_2^- . Similarly, it is observed that $P_I(\text{ICl}^-) > P_I(\text{I}_2^-)$ which is as expected since the electronegativity $\chi(\text{I}) = 7.5 \text{ eV}$ is smaller than $\chi(\text{Cl})$.

IV. SOME THERMAL AND PHOTOCHEMICAL REACTIONS AMONG HOLE CENTERS

In order to obtain more detailed information concerning thermal and photochemical reactions involving hole centers, some additional pulse annealing and photoexcitation experiments were carried out. The result of pulse annealing a $\text{KCl}:\text{KBr}:\text{PbCl}_2$ crystal containing Cl_2^- is shown in Fig. 6 in which the ordinate indicates the normalized intensity of the particular EPR spectrum. The Cl_2^- is observed to decay between 180 and 210 °K, and as it decays BrCl^- is observed to form. It is well known^{1,2} that in this temperature range, Cl_2^- in KCl is thermally unstable and can migrate through the crystal.¹⁸ The formation of BrCl^- results from the encounter between a migrating Cl_2^- and a substitutional Br^- . Upon continuing the pulse annealing above 220 °K, it is observed that BrCl^- decays in two steps, at approximately 235 and 270 °K. Clearly these two steps result from two different modes of decay of BrCl^- . During the

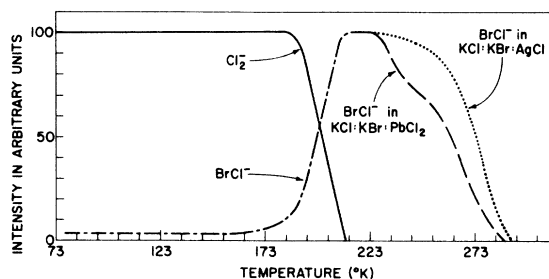


FIG. 6. EPR study of the decay of Cl_2^- and the formation and decay of BrCl^- as a function of temperature using a pulse annealing technique. The crystal was warmed to an annealing temperature and kept there for 2 min before cooling to 77 °K for measurement. The annealing temperatures were spaced at 10 °K intervals. The intensities of the Cl_2^- and BrCl^- signals have been normalized.

decay of BrCl^- , a second type of BrCl^- is formed.¹⁴ This second BrCl^- will be discussed in a subsequent paper.

The decay of BrCl^- in a $\text{KCl}:\text{KBr}:\text{AgCl}$ crystal occurs in a single step as shown in Fig. 6. The gradual onset of decay in this crystal between 220 and 250 °K is believed to arise from the varying thermal stabilities of nearby pairs of Ag^0 and BrCl^- caused by attractive electrostatic forces. Above 250 °K, as the BrCl^- decays, the Ag^0 decreases and Ag^{++} is formed.

V. THERMAL REORIENTATION KINETICS

It is possible in a short time to produce a considerable change in the population of V_K centers among the six $\langle 110 \rangle$ directions by excitation with an intense beam of polarized light. At sufficiently low temperatures the anisotropy produced by the polarized light will persist. However, if the crystal is warmed sufficiently, it is found that a random distribution of the V_K centers among the six $\langle 110 \rangle$ directions again is obtained. Figure 7 shows the change at 382 nm in the $[0\bar{1}1]$ spectrum of BrCl^- during a continuous warm up, after an anisotropy had been produced at 77 °K by exciting with $[01\bar{1}]$ light at 760 nm. The disorientation temperature of BrCl^- is 94 °K for a warming rate of 0.75 °K/min. Within experimental error, the same disorientation temperature is obtained when BrCl^- is studied with EPR techniques using a pulse anneal procedure. The thermal reorientation is studied by following what has been called the disorientation¹¹ of the preferentially oriented molecules. The definition which has been given for the disorientation temperature T_D has not been very precise. In some instances when we have used pulse annealing experiments, it has been defined as the temperature at which the loss in anisotropy shows a maximum rate of change.¹¹ More recently, on continuous warming at a constant rate it is defined as the temperature at which half the anisotropy has disappeared.^{19,20}

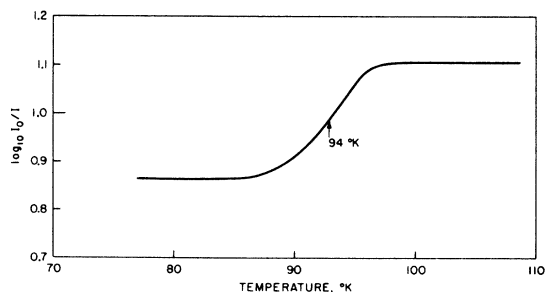


FIG. 7. Disorientation of BrCl^- showing the change at 382 nm in the $[0\bar{1}1]$ optical absorption spectrum during a continuous warmup at a rate of 0.75 °K/min. The anisotropy had been produced at 77 °K by exciting with $[01\bar{1}]$ light at 760 nm.

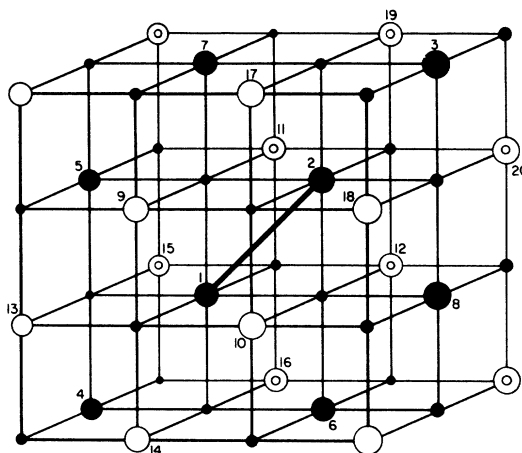


FIG. 8. Schematic representation of an X_2^- molecule located in the (1, 2) position in the lattice. Open circles, closed circles, and double circles indicate halide ions in the front, middle, and rear planes, respectively.

In general, because of the warming rates used, these two methods, applied to a particular species, lead to disorientation temperatures that differ by no more than 5 °K. In order to be consistent, the anisotropy in all experiments used to determine T_D was produced by $\langle 110 \rangle$ exciting light.

Figure 8 shows a schematic representation of an X_2^- halogen molecule ion in the lattice. No adjustments of the positions of the nuclei of the center itself or the surrounding lattice have been made. The thermal reorientation of an X_2^- ion is believed to occur because of a jumping motion involving an interchange of nuclear partners; the new molecule ion contains one of the original nuclei, and therefore this interchange results in a limited translation of position of the new ion. Keller and Murray,^{21,22} and Keller, Murray, Abraham, and Weeks²³ have studied the kinetics of reorientation of I_2^- in KI and Cl_2^- in KCl, respectively. They conclude that these two molecule ions change orientations only by 60° jumps, the probability of a 90° jump being very low. We have used the same techniques to examine the reorientation of BrCl^- , but have used a somewhat more detailed analysis which will now be described.

Nuclei 1 and 2 of Fig. 8 are the two central nuclei of the typical X_2^- molecule ion which will undergo reorientation. Under the assumption that the new X_2^- which exists after reorientation shall contain either nucleus 1 or 2, there are 18 neighbors to 1 and 2 which can be involved in the motion of the X_2^- ion. The combinations (1, 4) and (2, 3) will contribute to the translational motion but will leave the ion in the same orientation. The combinations (2, 7), (2, 8), (1, 5), and (1, 6) involve 90° jumps; the combinations (1, 9), (1, 10), (1, 11), (1, 12), (2, 9),

(2, 10), (2, 11), and (2, 12) involve 60° jumps; the combinations (1, 13), (1, 14), (1, 15), (1, 16), (2, 17), (2, 18), (2, 19), and (2, 20) involve 120° jumps. Although 60° and 120° jumps are not equivalent in the kinetics discussion, in our optical and spin-resonance measurements they are indistinguishable, since to each 60° jump there corresponds one 120° jump which gives the same orientation of the molecule ion.

We produced the anisotropy in the crystal at a temperature low enough so that the rate of reorientation is low. The crystal was then warmed to a temperature sufficiently high that reorientation takes place at a convenient rate. As in the case of Keller and Murray,²¹ two types of experiments were conducted, (a) those in which anisotropy was produced by excitation with $[0\bar{1}1]$ light, called $\langle 110 \rangle$ experiments, and (b) those in which anisotropy was produced by excitation with $[010]$ light, called $\langle 100 \rangle$ experiments (see Fig. 4). In the $\langle 110 \rangle$ experiments, the concentration of X_2^- centers in the number 1 orientation n_1 is enhanced over that in the number 2 orientation n_2 . Since the polarized light treats orientations 3–6 exactly the same, $n_3 = n_4 = n_5 = n_6$. On thermal reorientation at a fixed temperature T , the differential equation governing the rate of change in n_1 is

$$\begin{aligned} \frac{dn_1}{dt} = & -4\phi_{90}n_1 - 8\phi_{60}n_1 - 8\phi_{120}n_1 + 4\phi_{90}n_2 \\ & + 2\phi_{60}(n_3 + n_4 + n_5 + n_6) \\ & + 2\phi_{120}(n_3 + n_4 + n_5 + n_6), \end{aligned} \quad (4)$$

where ϕ_{90} is the probability per second of any one of the 90° jumps, ϕ_{60} is the probability per second of any one of the 60° jumps, and ϕ_{120} is the probability per second of any one of the 120° jumps; these probabilities are temperature dependent.

Similarly for n_2 ,

$$\begin{aligned} \frac{dn_2}{dt} = & -4\phi_{90}n_2 - 8\phi_{60}n_2 - 8\phi_{120}n_2 + 4\phi_{90}n_1 \\ & + 2\phi_{60}(n_3 + n_4 + n_5 + n_6) \\ & + 2\phi_{120}(n_3 + n_4 + n_5 + n_6). \end{aligned} \quad (5)$$

Subtracting (5) from (4) and integrating, we obtain

$$n_1 - n_2 = [n_1(0) - n_2(0)] \exp[-(8\phi_{90} + 8\phi_{60} + 8\phi_{120})t], \quad (6)$$

where $n_i(0)$ indicates the concentration in orientation i at $t=0$. The quantity $(n_1 - n_2)$ is proportional to the anisotropy, measured as optical density, obtained experimentally when the $[0\bar{1}1]$ absorption is subtracted from the $[011]$ absorption.

In the $\langle 100 \rangle$ experiments, $(n_5 + n_6)$ will be greater than $(n_1 + n_2)$ or $(n_3 + n_4)$, $n_5 = n_6$, and $n_1 = n_2 = n_3 = n_4$.

During thermal reorientation, the following equation holds:

$$\begin{aligned} \frac{d[(n_5 + n_6) - (n_3 + n_4)]}{dt} = & -[(n_5 + n_6) - (n_3 + n_4)] \\ & \times (12\phi_{60} + 12\phi_{120}), \end{aligned}$$

which becomes, upon integrating,

$$\begin{aligned} (n_5 + n_6) - (n_3 + n_4) = & \{[n_5(0) + n_6(0)] - [n_3(0) + n_4(0)]\} \\ & \times \exp[-(12\phi_{60} + 12\phi_{120})t]. \end{aligned} \quad (7)$$

From (6) we see that a plot of the logarithm of the $\langle 110 \rangle$ anisotropy as a function of time should give a straight line with a slope

$$\mathcal{K}_{\langle 110 \rangle} = -(8\phi_{90} + 8\phi_{60} + 8\phi_{120})$$

and a similar plot of the $\langle 100 \rangle$ anisotropy gives a slope

$$\mathcal{K}_{\langle 100 \rangle} = -(12\phi_{60} + 12\phi_{120}).$$

The ratio of the slopes is then

$$\frac{\mathcal{K}_{\langle 110 \rangle}}{\mathcal{K}_{\langle 100 \rangle}} = \frac{2}{3} \frac{\phi_{90}}{\phi_{60} + \phi_{120}} + \frac{2}{3}. \quad (8)$$

In their treatment of the kinetics of the reorientation process, which did not include 120° jumps, Keller and Murray derived the expression

$$\frac{K_{\langle 110 \rangle}}{K_{\langle 100 \rangle}} = \frac{1}{3} \frac{P_{90}}{P_{60}} + \frac{2}{3}. \quad (9)$$

They defined P_{90} as the probability per second that a V_K center reorients through 90° and P_{60} as the probability per second that a V_K center reorients to any one of the equivalent 60° sites. Since there are four ways that a 90° reorientation can take place and eight ways that a 60° reorientation can take place, $P_{90} = 4\phi_{90}$ and $P_{60} = 2\phi_{60}$. If these relations are substituted into Eq. (8) and it is assumed that $P_{60} \gg P_{120}$, Eq. (9) is obtained. We have defined the probabilities in such a manner that only the statistical weight 1 is included in the probabilities.

Keller and Murray^{21,22} who studied I_2^- in KI, and Keller, Murray, Abraham, and Weeks²³ who studied Cl_2^- in KCl, observed experimentally that $K_{\langle 110 \rangle}/K_{\langle 100 \rangle}$ is very close to $\frac{2}{3}$; this result demonstrates that in the temperature range of their experiments P_{90} is near zero. Keller, Murray, Abraham, and Weeks point out that the distance the center of gravity of the Cl_2^- moves upon reorientation increases through the series 60° , 90° , and 120° jumps. In view of the fact that the probability for a 90° jump is near zero, they conclude that the probability for a 120° jump is near zero; they argued that since the 120° jump distance is farther than the 90° jump distance, it is likely that $P_{90} > P_{120}$. In Sec. VI we will suggest different parameters to determine the

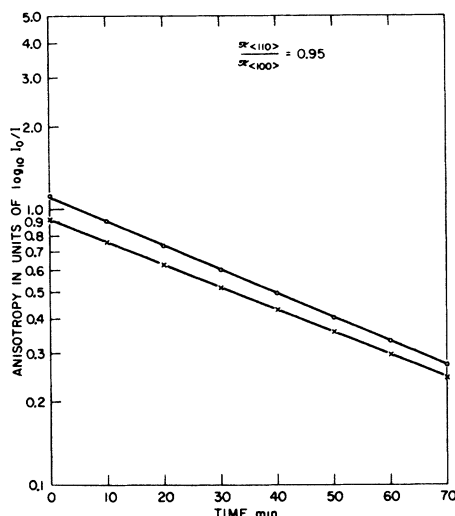


FIG. 9. Open circles and crosses indicate the $\langle 100 \rangle$ and $\langle 110 \rangle$ anisotropy, respectively, of BrCl^- as a function of time at 88°K .

relative probabilities of the various jumps.

The discussion above will now be modified to fit the case of the heteronuclear molecule BrCl^- . We will consider chloride ions to be at all halide ion sites, except that a bromine is at site 1 and the BrCl^- molecule is on site (1,2). The only thermal reorientations which we will permit will be those that maintain the species BrCl^- with the bromine remaining at its lattice site. The combination (4,1) results from a 0° jump, (5,1) and (6,1) result from 90° jumps, (9,1), (10,1), (11,1), and (12,1) from 60° jumps, and (13,1), (14,1), (15,1), and (16,1) from 120° jumps. There are just one-half the total number of combinations on reorientation, as in the case of X_2^- , and each kind of jump (0° , 60° , 90° , and 120°) is reduced in number by a factor of 2. The coefficients associated with all the probabilities in Eqs. (4)–(7) are therefore reduced by a factor of 2 and one obtains Eq. (8) again. Experimentally it is found, for BrCl^- in KCl at 88°K , that

$$\mathcal{K}_{\langle 110 \rangle} / \mathcal{K}_{\langle 100 \rangle} = 0.95$$

(see Fig. 9). This yields the result that $\phi_{90} / (\phi_{60} + \phi_{120}) = 0.42$; therefore, the 90° jump is important in the reorientation process.

In crystals of KCl containing 0.2 mole% KBr , the anisotropy of BrCl^- does not show a simple exponential decay at 88°K . A plot of the logarithm of the anisotropy against time yields a straight line in the early stages, but shows a positive curvature at high values of t . If the concentration of KBr is reduced to 0.1 mole%, a similar plot of the experimental results shows much less curvature and yields very nearly a straight line. The curvature is be-

lieved to arise because the BrCl^- molecule ions in the crystal do not all have identical surroundings. The jump frequency is very sensitive to slight perturbations in the lattice surrounding the BrCl^- molecule ion; consequently, the substitution of a Br^- for a Cl^- near a BrCl^- is enough to change measurably the rate of reorientation.

VI. DISCUSSION

A. Stability and Location of BrCl^- in a Lattice

The model for the BrCl^- center consists of a BrCl^- molecule ion with its axis exactly along a $\langle 110 \rangle$ direction, occupying two negative ion sites and not associated with any lattice defect. This model accounts for all of the experimental results and is patterned after that of the V_K center. ENDOR experiments²⁴ have helped to substantiate the model of the V_K center originally proposed by Castner and Kanzig.⁹

The Cl_2^- molecule ions formed in KCl by x-ray irradiation at 77°K are essentially immobile at this temperature, but if the crystal is warmed, they begin to diffuse very slowly in the neighborhood of the disorientation temperature 163°K .^{1,11} Between 190 and 220°K the diffusion rate is sufficiently great that the Cl_2^- ions would rapidly recombine with Pb^+ ions or react with Pb^{2+} to form Pb^{3+} , if it were not for the presence of a large concentration of substitutional Br^- ions which stabilize the holes and form BrCl^- . It is likely that one of the reasons that Br^- acts as a hole trap in KCl is that the electronegativity of bromine is less than that of chlorine, and therefore the hole prefers to be on the bromine more than on the chlorine.²⁵ The same reasoning can be used to account for the thermal stability of IBr^- in KBr ^{26,27} and ICl^- in KCl .²⁸ These molecules, like BrCl^- in KCl , occupy two halide ion sites and can be formed upon the thermal decay of the host lattice V_K center. The above argument predicts that BrCl^- will not form when KBr is doped with Cl^- ions since Br_2^- should be more stable than BrCl^- . We believe that we have confirmed this prediction since we have not observed $\langle 110 \rangle$ -oriented BrCl^- in Cl^- -doped KBr immediately after x-ray irradiation at 77°K or after thermal treatment which causes diffusion of Br_2^- through the crystal.

Although the electronegativity of the impurity plays a role in determining the stability of a heteronuclear molecule ion in a crystal, it is not the only parameter which contributes to the stability. In the case of the $\langle 111 \rangle$ -oriented center FCl^- in KCl ,^{6,7} the stability cannot come from the electronegativity alone since the electronegativity of fluorine [$\chi(\text{F}) = 11.4 \text{ eV}$] is larger than that of chlorine, and the prediction would be that Cl_2^- (in this case, the H center) is more stable than FCl^- . The FCl^- center is fundamentally different from the BrCl^- center.

The latter is a hole center, i. e., a hole stabilized on two adjoining substitutional halogen ions. The FCl^- center, on the other hand, is composed of an interstitial and a substitutional species located at a single negative ion site. Its stability very likely arises from the small size of the fluorine and the fact that the fluorine end of the molecule can extend into an interstitial position and partially relieve the lattice strain. The EPR hyperfine measurements on all of the heteronuclear molecule ions discussed in this paper, including FCl^- , agree with the prediction that the hole will spend more of its time on the constituent of the molecule ion having the lower electronegativity.

Since bromine is larger than chlorine it would be expected that the bromine end of the BrCl^- molecule ion would be larger than the chlorine end if the hole were shared equally. However, since the hole spends more time on the bromine, there would be a tendency for the bromine end to be smaller and the chlorine end to be larger than their corresponding sizes in Br_2^- and Cl_2^- . We think it probable, in spite of this compensation, that the bromine end of the molecule ion is larger.

The internuclear separation of Cl_2^- in KCl is smaller than the nearest-neighbor Cl^- - Cl^- distance; thus, the two chlorine nuclei have been displaced, along a $\langle 110 \rangle$ direction, equal distances from their normal lattice sites in forming the molecule ion. If the bromine end of BrCl^- is larger, the two nearest-neighbor potassium ions, which lie in the same $\{100\}$ plane as the molecule ion, may resist the inward displacement of the bromine and cause the molecule ion to be centered slightly toward the bromine lattice site but still orientated along $\langle 110 \rangle$. It is also possible that these same nearest-neighbor potassium ions would have a greater attraction for the chlorine end of the molecule because it has a slightly more negative charge located on it. If so, both of these effects would lead to the BrCl^- being located in the lattice with its axis along a $\langle 110 \rangle$ direction and lying in a $\{100\}$ plane, but being slightly displaced toward the bromine lattice site. The BrCl^- molecule ion and its location in the lattice are indicated in Fig. 10.

B. Reorientation of BrCl^-

Previous experiments with polarized light have shown that at a sufficiently low temperature, the axis of a Cl_2^- in KCl is fixed along a given $\langle 110 \rangle$ direction, but the mean life of a Cl_2^- in a given orientation is about 10^2 sec at $T_D = 163^\circ \text{K}$. It has been shown^{21,23} that disorientation takes place by an interchange of nuclear partners such that the new molecule ion contains one of the original nuclei and one of its nearest neighbors. This interchange probably can take place only when the vibrational modes of the lattice and the Cl_2^- , and also some

wagging motions of the Cl_2^- , are sufficiently excited. Because of these combined motions, the Cl_2^- and a third ion are placed in a favorable configuration for the interchange to take place. To describe in detail all of the processes that occur during reorientation would indeed be difficult because of all the complex motions that undoubtedly take place. However, it may be worthwhile to look at the reorientation process in a very simplified way to determine whether any correlations can be made among existing experimental results.

Since the reorientation of Cl_2^- in KCl is not unique, we will treat the general problem of the reorientation of an X_2^- molecule ion. We make the assumption that before reorientation can take place, the X_2^- molecule ion and a neighboring X^- ion must approach a configuration of an isosceles triangle. At the apex of the triangle is the nucleus which is common to both the original molecule ion and the reoriented one. In this configuration, the nuclei at the base of the triangle may be nearly equivalent, so that the hole has a nonzero probability of jumping from the original pair to the second pair.

Figure 11 shows a portion of an NaCl-type alkali-halide lattice containing an X_2^- , where M^+ represents the alkali metal ion and X^- the halide ion. In this figure, the nuclei forming the X_2^- have been allowed to pull in along a $\langle 110 \rangle$ direction from their regular lattice positions. The average distance $\bar{\delta}$ that the nuclei move depends upon the average value of the internuclear distance $\bar{r}(\text{X}_2^-)$ of X_2^- . It is assumed that $\bar{r}(\text{X}_2^-)$ for a given X_2^- is a constant independent of the host lattice. Although there will be some displacements of the ions surrounding X_2^- , we are neglecting them. Some nearest-neighbor ions involved in 60° , 90° , and 120° reorientations are shown. Assuming that the nuclei are frozen in their average positions, the average distances of these ions from one of the X_2^- nuclei are

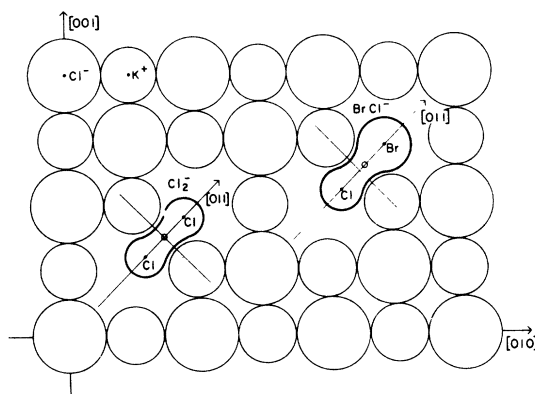


FIG. 10. Schematic representation of the Cl_2^- and BrCl^- centers in KCl.

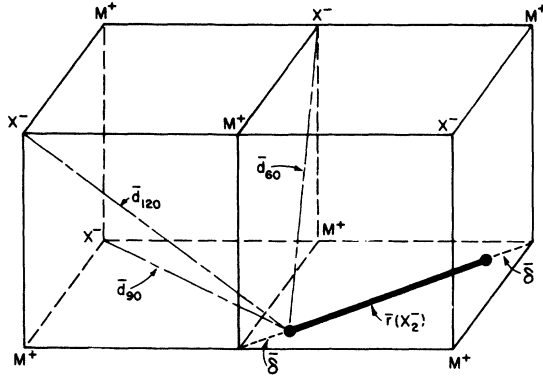


FIG. 11. Schematic representation of X_2^- in an alkali-halide lattice where the only displacement considered is the distance $\bar{\delta}$ that the two nuclei forming the X_2^- pull in from their regular lattice positions. Typical halide ions involved in 60° , 90° , and 120° jumps, and their distances from one end of the X_2^- are shown.

$$\begin{aligned}\bar{d}_{60} &= \left\{ \frac{3}{2} \left(\frac{1}{2} a \right)^2 + \left[\frac{1}{2} r(X_2^-) \right]^2 \right\}^{1/2}, \\ \bar{d}_{90} &= \left[\bar{\delta}^2 + 2 \left(\frac{1}{2} a \right)^2 \right]^{1/2}, \\ \bar{d}_{120} &= \left\{ \left[\frac{1}{2} (a + \bar{\delta}) \right]^2 + \left(\frac{1}{2} \bar{\delta} \right)^2 + \left(\frac{1}{2} a \right)^2 \right\}^{1/2},\end{aligned}\quad (10)$$

where a is the lattice constant of the alkali halide and the bar indicates the average value. It is clear that when $\bar{\delta} > 0$, $\bar{d}_{60} < \bar{d}_{90} < \bar{d}_{120}$ and that $\bar{d}_{60} = \bar{d}_{90} = \bar{d}_{120}$ when $\bar{\delta} = 0$.

We define the following parameters which we believe to be important in characterizing the reorientation process:

$$\begin{aligned}W_{60}(X_2^-) &\equiv [d_{60} - r(X_2^-)]/r(X_2^-), \\ W_{90}(X_2^-) &\equiv [d_{90} - r(X_2^-)]/r(X_2^-),\end{aligned}\quad (11)$$

and

$$W_{120}(X_2^-) \equiv [d_{120} - r(X_2^-)]/r(X_2^-),$$

where all quantities are instantaneous values. The definitions are made in the above form in order to approximate corresponding states among the various alkali halides. We also make the distinction between the instantaneous value of the parameter $W_\theta(X_2^-)$ and the average value $\bar{W}_\theta(X_2^-)$; the latter is given by substituting the values \bar{d}_θ and $\bar{r}(X_2^-)$ into (11). The criterion for a particular jump is that the corresponding isosceles triangle configuration is approached so that the instantaneous value of the parameter $W_\theta(X_2^-)$ for that particular jump approaches zero.

It seems reasonable to us that the probability of a jump through an angle θ is related to $W_\theta(X_2^-)$,²⁹ and since (10) and (11) give us the relation

$$\bar{W}_{60}(X_2^-) \leq \bar{W}_{90}(X_2^-) \leq \bar{W}_{120}(X_2^-), \quad (12)$$

we will assume that

$$\phi_{60}(X_2^-) \geq \phi_{90}(X_2^-) \geq \phi_{120}(X_2^-), \quad (13)$$

where the equality holds for $\bar{\delta} = 0$ and the inequality holds for $\bar{\delta} > 0$. Some experimental results will now be used to examine the relationship between $\phi_\theta(X_2^-)$ and $\bar{W}_\theta(X_2^-)$.

Figure 12 shows a plot of $\bar{W}_{60}(X_2^-)$ as a function of the disorientation temperature T_D . The values for $\bar{r}(X_2^-)$ were taken from Person,³⁰ and Gilbert and Wahl.³¹ The uncertainty in the $\bar{r}(X_2^-)$ values is shown in the plot. Keller *et al.*^{21,23} have determined that 60° jumps predominate in the kinetics of reorientation for I_2^- in KI and Cl_2^- in KCl. Work in our laboratory has shown this to be the case also for Br_2^- in KBr and F_2^- in LiF. The data of Delbecq, Gilbert, Hayes, and Yuster³² on T_D of Cl_2^- in LiCl, NaCl, KCl, and RbCl have been used, even though it has not been shown that the 60° jump predominates near T_D in these crystals. One observes that a straight line is a rather good fit to the data and that the line extrapolates to the origin. We believe that any curve which might fit the data should yield $\bar{W}_{60}(X_2^-) = 0$ at $T = 0^\circ \text{K}$. When $\bar{W}_{60}(X_2^-) = 0$, reorientation should take place with no activation energy; therefore, $T_D = 0^\circ \text{K}$.

It appears that the parameter $\bar{W}_{60}(X_2^-)$ can be related to the activation energy for a 60° jump. Keller *et al.*^{21,23} have shown for the cases of Cl_2^- in KCl and I_2^- in KI that the rate constant for reorientation as a function of temperature can be written as $R = se^{-E/kT}$ where R is the rate constant, s is a frequency factor, and E is an activation energy. In these two cases their data show that ϕ_{90} is very small in the temperature range studied so that the reorientation takes place by 60° and/or 120° jumps; however, (13) suggests that $\phi_{120} < \phi_{90}$ and, therefore, reorientation takes place predominately by 60° jumps, a conclusion drawn by Keller, Murray, Abraham, and Weeks.²³

In a $\langle 110 \rangle$ experiment in which 60° jumps predominate,

$$R = se^{-E_{60}/kT} = \mathcal{K}_{\langle 110 \rangle} = -8\phi_{60},$$

where E_{60} is the activation energy for a 60° jump. Thus,

$$E_{60} = [k \ln(s/\mathcal{K}_{\langle 110 \rangle})]T.$$

Our definition of T_D results in approximately equal values of R ; therefore, if we assume that s is approximately constant for all X_2^- centers, we may write

$$E_{60} = \alpha T_D.$$

This linear relationship, when compared to the plot of Fig. 11, suggests that

$$E_{60} = \beta_1 \bar{W}_{60}(X_2^-),$$

from which we extrapolate that

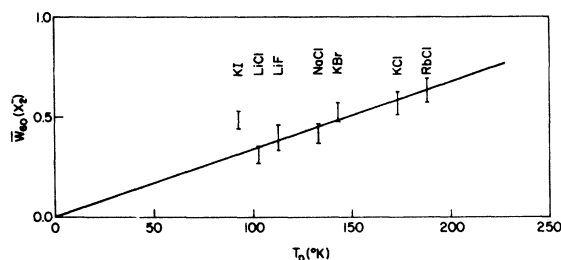


FIG. 12. Plot of the parameter $\bar{W}_{60}(X_2^-)$ vs disorientation temperature.

$$E_{90} = \beta_2 \bar{W}_{90}(X_2^-) \text{ and } E_{120} = \beta_3 \bar{W}_{120}(X_2^-), \quad (14)$$

where the β_i 's are constants. For limited differences in β_i and frequency factors, expressions (12) and (14) yield relations (13). In many cases studied, the parameter $\bar{W}_{60}(X_2^-)$ is much smaller than either $\bar{W}_{90}(X_2^-)$ or $\bar{W}_{120}(X_2^-)$. Consequently, on the basis of (14), we conclude that the activation energy for a 90° or 120° jump is so high relative to that of the 60° jump that 60° jumps predominate around T_D . However, as the value of $\bar{\delta}$ goes to zero, the 90° jumps should become more important, and finally 120° jumps should also become important.

Concurrent to this present work, Song³³ has carried out a much more elaborate treatment of the reorientation process using polaron theory. In his theory, the Huang-Rhys factor S enters the problem like an activation energy and may have been included in it a parameter similar to the ones we have discussed.

The arguments given above can be used in a qualitative way to explain why, in KCl , T_D of BrCl^- is lower than that of Cl_2^- and why ϕ_{90} of BrCl^- is greater than that of Cl_2^- . In the series Cl_2^- , BrCl^- , and Br_2^- , the dissociation energy of the molecules decreases and the internuclear distance r_e increases monotonically.³⁴ If it is assumed that the addition of an antibonding electron to produce Cl_2^- , BrCl^- , and Br_2^- reduces the dissociation energy and increases r_e , but still preserves this order, $\bar{r}(\text{BrCl}^-)$ should be greater than $\bar{r}(\text{Cl}_2^-)$ and BrCl^- should have a larger vibrational amplitude than Cl_2^- at the same temperature. Because $\bar{r}(\text{BrCl}^-) > \bar{r}(\text{Cl}_2^-)$, it follows that $\bar{W}_{60}(\text{BrCl}^-) < \bar{W}_{60}(\text{Cl}_2^-)$ and reorientation is expected to take place at a lower temperature. In addition, the fact that the amplitude of vibration of BrCl^- is expected to be greater than that of Cl_2^- at a given temperature indicates that $W_{60}(\text{BrCl}^-) < W_{60}(\text{Cl}_2^-)$, so that this effect also contributes to a reduction of T_D . These two arguments, which effectively increase $r(\text{BrCl}^-)$ over $r(\text{Cl}_2^-)$, lead to the conclusion that the 90° jump becomes more probable for BrCl^- . It was deduced in Sec. VI A that BrCl^- is slightly displaced toward the bromine lattice site. This leads to a small additional reduction in $\bar{\delta}_1$, the displacement of the bromine nucleus

for a given $\bar{r}(\text{BrCl}^-)$, and also results in both ϕ_{90} and ϕ_{120} increasing with respect to ϕ_{60} . In the limit when $\bar{\delta}_1 = 0$, $\bar{d}_{60} = \bar{d}_{90} = \bar{d}_{120}$ and all jumps become equally probable.

It was stated previously that $\mathcal{K}_{(110)}/\mathcal{K}_{(100)} = 0.95$ for BrCl^- at 88°K. Using this result one calculates from (8) that

$$\phi_{90}/(\phi_{60} + \phi_{120}) = 0.42, \quad (15)$$

which shows that ϕ_{90} is relatively large. However, (15) alone gives little information concerning ϕ_{60} and ϕ_{120} since it can be satisfied for values of ϕ_{60} and ϕ_{120} in the range from 0 to $2.38\phi_{90}$. Assuming that (13) holds for BrCl^- , we can place limits on ϕ_{120} . For the lower limit $\phi_{120} = 0$, we calculate that $\phi_{60} = 2.38\phi_{90}$ and for the upper limit $\phi_{120} = \phi_{90}$, we calculate that $\phi_{60} = 1.38\phi_{90}$. Since ϕ_{90} is so large, it is very likely that ϕ_{120} is not zero and may very well be near the middle of the range assigned to it.

Figure 12 shows that I_2^- in KI is farther from the line than the other points plotted. This suggests that the parameter $\bar{W}_\theta(X_2^-)$ in this case does not indicate corresponding states. Popp and Murray³⁵ and Keller, Murray, and Popp³⁶ have recently studied the reorientation kinetics of I_2^- in NaI and RbI . If one plots these data (they are somewhat approximate since T_D was estimated from their given data), these two points also are about the same distance from the line as I_2^- in KI . In addition, they find that the 90° jump has an appreciable probability around T_D . Our criterion for jumping could, in a qualitative way, explain the increased probability of the 90° jump in NaI since

$$\frac{\bar{W}_{90}(\text{I}_2^-)}{\bar{W}_{60}(\text{I}_2^-)} = \frac{\bar{d}_{90} - \bar{r}(\text{I}_2^-)}{\bar{d}_{60} - \bar{r}(\text{I}_2^-)}$$

decreases as the lattice constant decreases, if one assumes constant $\bar{r}(\text{I}_2^-)$. However, we are unable, on the basis of this simple criterion, to explain the relatively high probability of the 90° jump of I_2^- in RbI . Since the parameter $\bar{W}_{60}(X_2^-)$ is related to the activation energy of the 60° jump, only those systems in which reorientation by 60° jumps predominates should be expected to fall on this straight line. In view of the rather simplistic assumptions involved in our criterion for the reorientation process, it would not be surprising that all data do not fit into a simple pattern. Some points neglected that might well be important are variations from crystal to crystal in the relative relaxations of neighboring ions from their regular positions in the lattice, in the frequency factors, in the local modes, etc. The criterion for jumping, which involves what might be called corresponding states, probably works best within a series of alkali halides where the halogen ion is kept the same, e. g., Cl_2^- in LiCl , NaCl , KCl , and RbCl .

C. Decomposition of BrCl^- by Thermal and Optical Excitation

In the case of Cl_2^- in KCl , the reorientation process results in diffusion. In the case of BrCl^- , reorientation and diffusion arise from two distinctly different processes. At very low temperatures, reorientation takes place, but the exchange of partners in the BrCl^- ions is constrained to an exchange involving only the first shell of twelve Cl^- neighbors around the bromine. This is proven by the fact that we do not obtain any decomposition into Cl_2^- in a temperature region of more than 100°K above the disorientation temperature.

At temperatures above about 250°K in $\text{KCl}:\text{KBr}:\text{AgCl}$ crystals, it is observed that BrCl^- becomes unstable and disappears, destroying some Ag^0 and producing some Ag^{++} . Enough thermal energy is available to break the molecular bond and produce, with some probability, a Cl_2^- which may move away from the Br^- and then convert Ag^0 to Ag^+ as a result of electron-hole recombination or be retrapped by Ag^+ to form Ag^{++} . In the case of $\text{KCl}:\text{KBr}:\text{PbCl}_2$, it is observed that the decay of BrCl^- occurs in two steps, the first of these being at about 220°K . We do not believe that this loss in BrCl^- results from an instability of BrCl^- but rather from a positive ion vacancy moving over to the BrCl^- and producing another center. This process will be discussed in a subsequent paper. The second loss of BrCl^- in $\text{KCl}:\text{KBr}:\text{PbCl}_2$ occurs at about the same temperature as the major loss in $\text{KCl}:\text{KBr}:\text{AgCl}$ and both result from thermal decomposition of BrCl^- .

The ground-state configuration of BrCl^- is believed to be $\sigma_1^2\pi_1^4\pi_2^4\sigma_2^2(^2\Sigma_2^-)$. If we were to follow the potential energy curve of a free BrCl^- ion to very large values of the internuclear distance, we would expect to obtain the species $(\text{Br}^0 + \text{Cl}^-)$ since the energy of this system is lower than that of $(\text{Br}^- + \text{Cl}^0)$. At smaller internuclear distances, it is expected that the actual state would be a mixture of the two states $(\text{Br}^- + \text{Cl}^0)$ and $(\text{Br}^0 + \text{Cl}^-)$ with a slight preponderance of the latter state. In an excited molecular state the potential energy curves at large internuclear distances could yield either $(\text{Br}^0 + \text{Cl}^-)$ or $(\text{Br}^- + \text{Cl}^0)$. Again it would be expected that at intermediate internuclear distances, a mixture of these two states would result, but depending on the particular excitation, either of these two combinations could predominate. Examination of the results of experiments on the optical excitation of BrCl^- in the KCl crystal, in either of its two absorption

bands, does not permit us to come to unambiguous conclusions regarding which of the above-mentioned states predominates, but the following points can be made.

Excitation with polarized light absorbed in the 760-nm band leads primarily to reorientation of the axis of BrCl^- . However, prolonged exposure to this light causes some destruction of BrCl^- and the formation of Cl_2^- . It is possible that excitation in the 760-nm band leaves the distribution of the hole about the same as it was in the ground state, but the complicated collisional processes which occur after excitation allows primarily the formation of a BrCl^- molecule ion with any of the twelve chlorine neighbors surrounding the bromine. However, since the hole is on the chlorine, an appreciable part of the time it is possible to form a Cl_2^- which moves a small distance away from the Br^- . On the other hand, excitation with polarized light absorbed in the 382-nm band leads to rather comparable yields of reorientation of the axis of BrCl^- and destruction of BrCl^- to give Cl_2^- . Such excitation could yield a state where the hole distribution is now greater on the chlorine, increasing the probability of producing a Cl_2^- which can move away from the Br^- . Reorientation of the axis of BrCl^- by exchange of chlorine partners would also take place with high probability.

Thermal spikes may contribute to the photodecomposition of BrCl^- . We have already observed that BrCl^- is thermally unstable near 250°K and therefore Cl_2^- , which at this temperature is very mobile, can be produced from BrCl^- merely by heating the crystal sufficiently. We observe no luminescence, as determined by eye, when BrCl^- is excited in the 382-nm band. If we assume that no luminescence occurs for 760-nm excitation as well, then all of the excitation energy goes toward heating the lattice. These thermal spikes produced by the optical excitations involve considerable energy, and could assist in the dissociation of the BrCl^- to give Cl_2^- . It is possible that the reason we observe less Cl_2^- formation on excitation at 760 nm is that the thermal spike produced after excitation is less energetic than the one produced by 382-nm excitation.

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¹²The term "unpolarized" light in our absorption measurements refers to the light normally used in the Cary spectrophotometer with no added polarizing elements. Because of the nature of the optical elements of the spectrophotometer, the emergent light is partially polarized. However, since we only use this "unpolarized" light for absorption measurements on centers having a random distribution of orientations, we would expect to obtain the same results as those obtained with truly unpolarized light.

¹³A small amount of Cl_2^- is produced in this experiment. However, the combination of the low anisotropy of the long-wavelength transition of Cl_2^- and the low concentration of Cl_2^- results in essentially no interference of Cl_2^- with the anisotropic spectrum of BrCl^- . This lack of interference was shown in a pulse annealing experiment in which a crystal in a state indicated by curves c and d of Fig. 3 is warmed to 103°K for 5 min to disorient the BrCl^- , but not Cl_2^- ; the disorientation temperature of Cl_2^- is 170°K. The anisotropy which has disappeared gives the anisotropic spectrum of BrCl^- ; this spectrum is in good agreement with that shown in Fig. 5.

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¹⁸It is also possible, at 77°K, to produce BrCl^- from Cl_2^- by optical excitation in either the 750- or 367-nm bands of Cl_2^- . These excitations cause diffusion of the Cl_2^- ions and, when they approach substitutional Br in the lattice, BrCl^- is formed. An equilibrium is reached during the optical excitation because the absorption bands of BrCl^- overlap those of Cl_2^- , and the reverse reaction

in which BrCl^- breaks apart to give Cl_2^- occurs simultaneously. Irradiation with ultraviolet light produces an equilibrium which favors Cl_2^- more than irradiation with infrared light since BrCl^- breaks apart much more easily under ultraviolet irradiation.

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