where $\alpha=\rho_1/\rho_0$. Here $\rho_{00}\sim cA$, $\rho_0\sim cD2S/(2S+1)$, $\rho_1\sim c\delta A2S$. Figure 2 shows this function plotted for $S=4/2$ and for various values of α.

It should be remarked that where more than two levels are involved, certain special assumptions about the D_m's can result in a resistance maximum arising from the inelastic scattering alone. For example, the assumption $D_m{}^+=D_{m+1}{}^-=D-2(m+\frac{1}{2})\delta D$ yields such a result. This fact emphasizes that where ground-state degeneracy of the impurity ions is removed, there are several ways in which low-temperature resistance anomalies can arise. Until one understands better the states of the impurity ions, no useful purpose is served by developing all of the possibilities with equal vigor.

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Intensities of the R_1 and R_2 Bands in KCl Crystals*†

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Measurements have been made of the intensities of the R_1, R_2, M, and N bands in KCl crystals as functions of F light irradiation time. Both x-rayed and additively colored crystals were used. The x-raying and F light irradiation were done at room temperature. The optical absorption measurements were made at liquid nitrogen temperature to improve the resolution of the bands. In both the x-rayed and additively colored samples the ratio of the R_2 and R_1 band intensities varied by less than a factor 1.5 when the individual intensities varied by a factor 6 or greater. No other pair of bands studied showed such a small variation in their intensity ratio.

Theoretical frequencies and oscillator strengths were obtained for the $1s\,\sigma-2p\,\sigma$ and $1s\,\sigma-2p\,\pi$ transitions of $H_2{}^+$ immersed in a dielectric medium and for the $1s-2p$ transition of the hydrogen atom immersed in a dielectric medium. Frequencies were also obtained for the ${}^1\Sigma_g{}^+-{}^1\Pi_u$ and ${}^1\Sigma_g{}^+-{}^1\Sigma_u{}^+$ transitions of H_2 immersed in a dielectric medium. For KCl the computed frequencies of the last three transitions named have approximately the same magnitude and fall in the same order as the observed F, R_1, and R_2 bands, respectively. It appears possible that the observed R_1 and R_2 bands may arise from two transitions of the system of two electrons trapped at a pair of adjacent negative ion vacancies.

I. INTRODUCTION

MOLNAR[1] and Petroff[2] have found that in crystals of alkali halides such as NaCl and KCl, the F band bleaches when irradiated with F light at room temperature. As the F band intensity decreases, the R_1, R_2, M, and N bands grow. Both additively colored and heavily x-rayed crystals of NaCl and KCl exhibit this behavior. It has been stated by Molnar[1] that the R_1 and R_2 bands do not bleach when crystals exhibiting them are irradiated with R_1 and R_2 light, respectively, at room temperature. Oberly and Burstein[3] have reported that additively colored KCl crystals exhibiting R bands become photoconductive when irradiated with R light at room temperature. Similar results have been obtained by Oberly[4] for x-rayed KBr crystals exhibiting R bands.

Casler, Pringsheim, and Yuster[5] have found that R bands in crystals such as KCl and NaCl are destroyed by x-ray irradiation. These authors state that the R bands are somewhat unstable at room temperature in KCl which has been x-rayed at −195°C and irradiated at room temperature with F light. Prolonged irradiation of such crystals with F light at room temperature also causes the R bands to decrease in intensity.

Hesketh[6] has obtained curves of growth for the R_1, R_2, and M bands formed in x-rayed KCl by irradiation with F light, presumably at room temperature. Corrections were made for the overlapping of the F and R_1 bands. Hesketh found that the M and R_1 band intensities increased rather rapidly to maximum values and then decreased. The R_2 band increased more slowly and reached an intensity maximum which was less than that for the R_1 band.

Seitz[7,8] has suggested that the R_1 and R_2 bands arise

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[*] A portion of the work reported in this paper was supported by the Bureau of Ordnance, Department of the Navy.

[†] A preliminary account of this work was presented at the 1955 Thanksgiving Meeting of the American Physical Society. See Herman, Wallis, and Wallis, Phys. Rev. **100**, 1267 (A) (1955).

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[1] J. P. Molnar, thesis, Massachusetts Institute of Technology, 1940 (unpublished).

[2] S. Petroff, Z. Physik **127**, 443 (1950).

[3] J. J. Oberly and E. Burstein, Phys. Rev. **79**, 217 (1950).

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[5] Casler, Pringsheim, and Yuster, J. Chem. Phys. **18**, 1564 (1950).

[6] R. V. Hesketh, thesis, University of Durham, Durham, England, 1953 (unpublished).

[7] F. Seitz, Revs. Modern Phys. **18**, 384 (1946).

[8] F. Seitz, Revs. Modern Phys. **26**, 7 (1954).

from optical transitions of imperfection centers consisting, respectively, of one and of two electrons trapped at a pair of adjacent negative ion vacancies. These centers may be designated by the symbols F_2^+ and F_2, respectively.

Theoretical calculations of the frequencies associated with various transitions of the F_2^+ and F_2 centers have been calculated by Nagamiya and Tatsuuma[9] and by Nagamiya, Kojima, and Kondoh.[10] The work of these authors indicates that the frequencies of more than one transition of both the F_2^+ and F_2 centers lie fairly near the F band.

In the present paper results are reported for experimental measurements of the curves of growth for R_1, R_2, M, and N bands during the irradiation of both x-rayed and additively colored KCl crystals with F light at room temperature. The optical absorption measurements were made at liquid nitrogen temperature in order to obtain better resolution of the various bands than is obtainable at room temperature.

Theoretical values have been obtained for the frequencies and in some cases the oscillator strengths of several transitions of the F_2^+ and F_2 centers. The theoretical values are based on rather simple models for these centers and are believed to be nearly exact for the models as postulated.

II. EXPERIMENTAL PROCEDURE

Single crystals of KCl obtained from the Harshaw Chemical Company were used in all experiments. The additively colored KCl was prepared by heating a crystal ~1 cm×1 cm×1 cm in potassium metal vapor at ~500°C for 46 hours in a stainless steel bomb and then cooling rapidly. Immediately prior to an experiment a sample ~0.1 cm thick cleaved from the colored block was wrapped in Al foil to prevent optical bleaching and heated to 400°C in the steel bomb for one-half hour. The sample was then quenched quickly to room temperature and mounted with the aid of a very dim light in a cryostat of the type designed by Duerig and Mador.[11] The mounted crystal was kept in darkness except during the optical bleaching and optical absorption measurements. The above procedure was used so that the colored crystal samples would have a minimum concentration of R and M centers.

For the study of x-rayed KCl, an uncolored crystal ~0.1 cm thick was mounted in the cryostat and x-rayed at room temperature for a number of hours. A Machlett x-ray tube with a molybdenum target was operated at ~50 kv accelerating voltage and ~15 ma tube current. The beryllium window of the cryostat was ~1 cm from the beryllium window of the x-ray tube.

The optical absorption measurements and F light bleaching were done in a Beckman Model DU spectrophotometer modified to hold the cryostat. For bleaching, the F light spectral band pass was ~30 mμ centered about the peak of the F band at room temperature. In a typical experiment a spectrum was taken at liquid nitrogen temperature after which the cryostat was warmed up to room temperature. The colored crystal was then irradiated with F light for a measured length of time. The cryostat was refilled with liquid nitrogen and the absorption spectrum of the bleached crystal measured. This cycle was repeated for successively longer periods of F light irradiation. At the conclusion of each F light irradiation the crystal

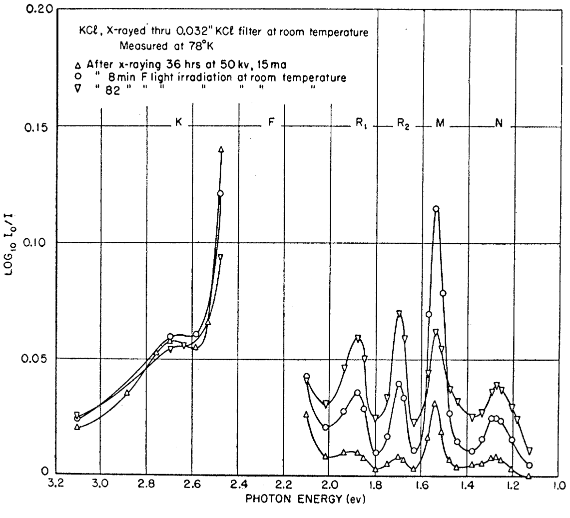

FIG. 1. Absorption spectra of an x-rayed KCl crystal after various times of F light irradiation.

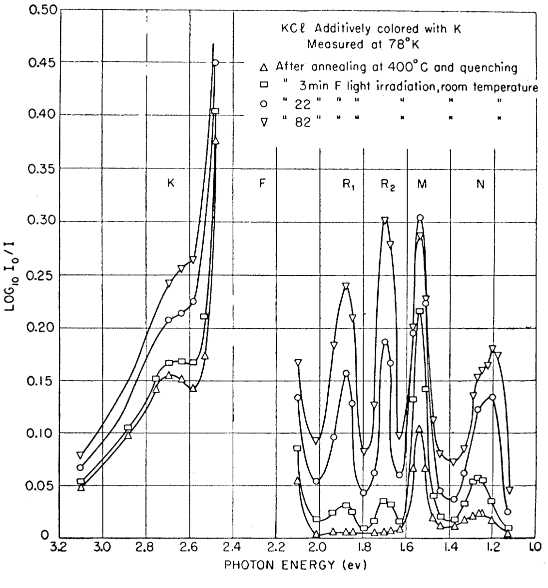

FIG. 2. Absorption spectra of an additively colored KCl crystal after various times of F light irradiation.

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[9] T. Nagamiya and N. Tatsuuma, J. Phys. Soc. Japan **9**, 307 (1954).

[10] Tagamiya, Kojima, and Kondoh, J. Phys. Soc. Japan **9**, 310 (1954).

[11] W. H. Duerig and I. L. Mador, Rev. Sci. Instr. **23**, 421 (1952).

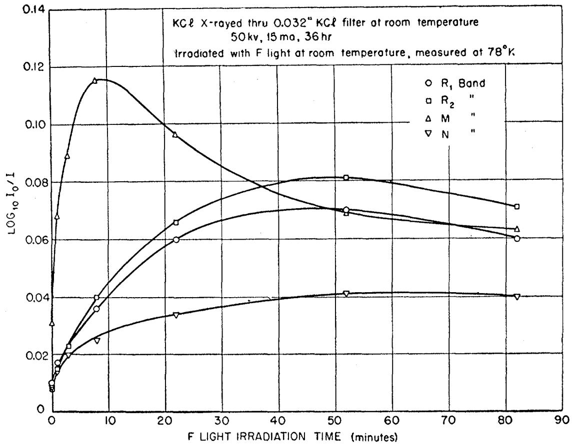

FIG. 3. Experimental intensities of the R_1, R_2, M, and N bands as functions of F light irradiation time in an x-rayed KCl crystal.

remained at room temperature for at least 15 minutes. An extrapolation of the data given by Pick[12] indicates that F' centers in KCl at room temperature have a half-life of less than one second. Accordingly, in the present experiments it appears that practically all the F' centers produced during the F light irradiation had decayed before the crystal was cooled.

III. EXPERIMENTAL RESULTS

Figures 1 and 2 show the absorption spectra of two colored KCl crystals in the vicinity of the R bands before and after various times of F light irradiation. Figure 1 refers to an x-rayed crystal; Fig. 2 to an additively colored crystal. In each case the F band maximum, which is outside the limits of the figures, decreased continuously with increasing F light irradiation time. Absorption measurements were made down to a wavelength of ~208 mμ. The additively colored KCl showed a very small band with a maximum at ~211 mμ while the x-rayed KCl showed a considerably stronger band at this wavelength. In neither case did the band at 211 mμ change appreciably during the F light irradiation.

The KCl crystal considered in Fig. 1 was x-rayed through a KCl filter 0.032 inch thick and showed very little change in the K band after F-light irradiation. The optical density of the F-band maximum decreased continuously from 1.10 to 0.28. Prominent R_1, R_2, M, and N bands developed during the F-light irradiation.

A run was made with a KCl crystal x-rayed without a filter. The results were nearly the same as in the case just discussed. The principal difference was an appreciable growth of the K band during the F-light irradiation. The spectrum of another KCl crystal x-rayed without a filter and irradiated with F light was determined at room temperature out as far as 2.5μ.[13] No appreciable absorption beyond the N band was observed.

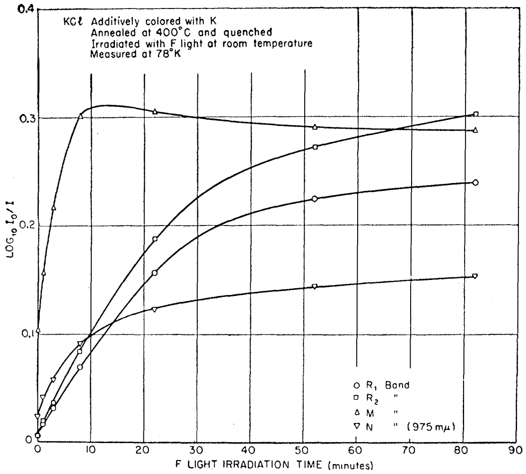

FIG. 4. Experimental intensities of the R_1, R_2, M, and N bands as functions of F light irradiation time in an additively colored KCl crystal.

The spectra of the additively colored KCl crystal shown in Fig. 2 differ in several details from those of the x-rayed crystal given in Fig. 1. Both the K band and the long wavelength tail of the F band increased markedly in the additively colored crystal during F light irradiation. The optical density of the F band maximum decreased from >2.0 to 1.26. The peak of the N band shifted slightly to the red after prolonged F light irradiation, indicating the possibility of unresolved structure within the N band.[14]

In Fig. 3 the optical densities at the band maxima of the R_1, R_2, M, and N bands are plotted against F light irradiation time for the x-rayed KCl crystal whose absorption spectra are given in Fig. 1. The M band intensity increased rapidly to a maximum and then decreased. The R_1 and R_2 band intensities increased together to a maximum and then decreased slightly. The N band increased fairly rapidly at first and then more slowly.

The variations of the M and R_2 band intensities with F light irradiation time shown in Fig. 3 are qualitatively similar to those found by Hesketh[6] in KCl x-rayed at 220 kv accelerating voltage and 15 ma tube current and irradiated with F light at room temperature. Hesketh, however, found that the R_1 band behaved more like the M band than the R_2 band during the F light irradiation. In contrast with the present work Hesketh apparently made his optical absorption measurements at room temperature where it is difficult to resolve the R_1 band from the F and R_2 bands. This

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[12] H. Pick, Ann. Physik **31**, 365 (1938).

[13] We wish to thank Dr. R. M. Talley for permitting us to make these measurements on the Perkin-Elmer double beam spectrometer at the U. S. Naval Ordnance Laboratory.

[14] In the course of a different investigation a NaCl crystal was heavily x-rayed and then exposed to room light at room temperature. The absorption spectrum was then determined at liquid helium temperature and was found to have two resolved peaks in the N-band region. Since only a single run was made this observation would require further confirmation.

TABLE I. Experimental intensities[a] of R_1, R_2, and N bands for various times of F light irradiation in x-rayed KCl.

Time (minutes)	R_1	R_2	N	R_2/R_1	N/R_1
0.0	0.010	0.008	0.008	0.8	0.8
0.5	0.013	0.011	0.012	0.8	0.9
3.0	0.023	0.023	0.020	1.0	0.9
22.0	0.060	0.066	0.034	1.10	0.57
82.0	0.060	0.071	0.040	1.18	0.67

[a] Optical densities at the band maxima.

difference in experimental procedure may be responsible for the difference in the R_1 band behavior observed.

In Fig. 4 the optical densities at the band maxima of the R_1, R_2, M, and N bands are plotted against F light irradiation time for the additively colored crystal whose absorption spectra are given in Fig. 2. In this case the R bands did not reach maxima. The M band decreased relatively little after reaching its maximum.

Table I gives the intensities (i.e., optical densities at the band maxima) of the R_1, R_2, and N bands after various times of F light irradiation for the x-rayed crystal of Figs. 1 and 3. The ratio of the R_2 band intensity to the R_1 band intensity and the ratio of the N band intensity to the R_1 band intensity are also given in Table I. The R_2 to R_1 ratio varies by a factor ~1.5. The R_1 band intensity itself varies by a factor ~6. The N to R_1 ratio varies by a factor ~1.6.

Table II gives the intensities of the R_1, R_2, and N bands as well as the R_2 to R_1 and N to R_1 intensity ratios after various times of F light irradiation for the additively colored crystal of Figs. 2 and 4. The R_1 band intensity varies by a factor greater than 25. The R_2 to R_1 intensity ratio varies by a factor ~1.3, while the N to R_1 intensity ratio changes by a factor ~7.

An interesting feature of the results given in Tables I and II is the near constancy of the R_2 to R_1 intensity ratio. A constant intensity ratio for two bands is evidence that the bands may correspond to two transitions of the same center.

IV. THEORETICAL METHODS

The purpose of the theoretical work reported in this paper is to obtain approximate values for the frequencies and oscillator strengths of various transitions of the F_2^+ and F_2 centers proposed by Seitz[8] to be responsible for the R_1 and R_2 absorption bands, respectively. The F_2^+ and F_2 centers consist of one and of two electrons, respectively, trapped at a pair of adjacent negative ion vacancies. Our models for the F_2^+ and F_2 centers consist of one and of two electrons, respectively, moving in the field of two point positive unit charges immersed in a dielectric medium. In other words our models consist of a hydrogen molecular ion and a hydrogen molecule immersed in a dielectric medium.

Various properties of either a hydrogen molecular ion or a hydrogen molecule immersed in a dielectric medium can be obtained from the properties of the corresponding model without the dielectric medium. As an example we shall consider in detail the hydrogen molecular ion immersed in a dielectric medium characterized by a dielectric constant κ_0. The Schrödinger equation satisfied by the electronic wave function ψ is given by[15]

$$\nabla^2\psi+\frac{2}{\kappa_0}\left[\frac{1}{r_a}+\frac{1}{r_b}\right]\psi+E\psi=0, \tag{1}$$

where r_a and r_b are the distances, measured in units of $a_0=\hbar^2/(me^2)$, of the electron from the positive point charges a and b and E is the energy measured in units of $e^2/(2a_0)$. In terms of confocal elliptical coordinates defined by

$$\lambda=(r_a+r_b)/r_{ab},$$
$$\mu=(r_a-r_b)/r_{ab},$$
$$\varphi=\text{azimuth about the internuclear axis,}$$

Eq. (1) can be rewritten as

$$\left\{\frac{\partial}{\partial\lambda}\left[(\lambda^2-1)\frac{\partial}{\partial\lambda}\right]+\frac{\partial}{\partial\mu}\left[(1-\mu^2)\frac{\partial}{\partial\mu}\right]+\frac{\lambda^2-\mu^2}{(\lambda^2-1)(1-\mu^2)}\frac{\partial^2}{\partial\varphi^2}\right\}\psi+\left[-p^2(\lambda^2-\mu^2)+2R\lambda\right]\psi=0, \tag{2}$$

where r_{ab} is the distance between the positive charges,

$$R=r_{ab}/\kappa_0, \tag{2a}$$

and

$$p^2=-\kappa_0^2R^2E/4. \tag{2b}$$

The eigenvalue parameter p^2 is a function only of R and of the particular eigenstate. The energy $E(r_{ab},\kappa_0)$ of a given electronic state of the hydrogen molecular ion in a dielectric medium can be related to the energy $E'(R)$ of the same state of the same molecule in free space by noting that

$$\kappa_0^2R^2E(r_{ab},\kappa_0)=-4p^2=R^2E'(R), \tag{3a}$$

or

$$E(r_{ab},\kappa_0)=\frac{1}{\kappa_0^2}E'(R). \tag{3b}$$

A rather extensive tabulation of the energy of the hydrogen molecular ion in free space for various bound electronic states over a range of internuclear distances has been given by Bates, Ledsham, and Stewart.[16] For given values of κ_0 and r_{ab}, one obtains R from Eq. (2a),

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[15] The formulation given below assumes that the effective mass of the electron is the ordinary electron mass. The generalization to an arbitrary effective electron mass, m^*, is accomplished by replacing E with ρE and by replacing κ_0 with κ_0/ρ where $\rho=m^*/m$.

[16] Bates, Ledsham, and Stewart, Trans. Roy. Soc. (London) **A246**, 215 (1953).

then $E'(R)$ from these tables and finally $E(r_{ab},\kappa_0)$ using Eq. (3b).

Equation (3b) is also found to be valid for the case of the hydrogen molecule immersed in a dielectric medium. Mulliken[17] has given electronic energy *vs* internuclear distance curves for many electronic states of the hydrogen molecule. Using these curves one can obtain $E'(R)$ and then $E(r_{ab},\kappa_0)$ by means of Eq. (3b).

For a hydrogen atom immersed in a dielectric medium, the quantity $1/\kappa_0$ plays the role of an effective nuclear charge. The energy E for a given state is related to the energy E' of the same state of a hydrogen atom in free space by the relation

$$E=(1/\kappa_0^2)E'. \tag{3c}$$

The absorption coefficient $\sigma_{\alpha\beta}(\nu)$ for a transition of frequency ν between two states α and β of a system immersed in a dielectric medium has been discussed by Lax.[18] The magnitude of the absorption coefficient is determined to a large extent by the oscillator strength $f_{\alpha,\beta}$ defined by the equation

$$f_{\alpha,\beta}=[8\pi^2m^*/(3h)]\nu G|\mathbf{Q}_{\alpha,\beta}|^2, \tag{4}$$

where m^* is the effective mass of an electron in the medium, G is the orbital degeneracy factor, and

$$|\mathbf{Q}_{\alpha,\beta}|^2=|Q_{\alpha,\beta}(x)|^2+|Q_{\alpha,\beta}(y)|^2+|Q_{\alpha,\beta}(z)|^2. \tag{4a}$$

The quantity $Q_{\alpha,\beta}(x)$ is defined by the equation

$$Q_{\alpha,\beta}(x)=\int\cdots\int\psi_\alpha[\sum_i x_i]\psi_\beta\prod_i dv_i, \tag{4b}$$

where x_i is the x-coordinate of the ith electron, dv_i is the volume element for the ith electron, and the sums and products are over all electrons of the system which is immersed in the dielectric medium. Defining equations for $Q_{\alpha,\beta}(y)$ and $Q_{\alpha,\beta}(z)$ may be obtained from Eq. (4b) by replacing x by y and z, respectively.

We now consider the determination of the oscillator strength for transitions between bound electronic states of the hydrogen molecular ion immersed in a dielectric medium. The wave function ψ_α for a particular state α is a solution of Eq. (2). For a particular internuclear distance r_{ab} and dielectric constant κ_0 the function $\psi_\alpha(r_{ab},\kappa_0)$ is the same, aside from a constant of proportionality, as the wave function $\psi_\alpha'(R)$ for the same state of the hydrogen molecular ion in free space with internuclear distance $R=r_{ab}/\kappa_0$. The requirement that ψ_α and ψ_α' be normalized to unity enables one to evaluate the constant of proportionality. Let

$$\psi_\alpha(r_{ab},\kappa_0)=N\psi_\alpha'(R). \tag{5a}$$

The normalization conditions for ψ_α and ψ_α' are

$$\tfrac{1}{8}r_{ab}^3\int\psi_\alpha^2(\lambda^2-\mu^2)d\lambda d\mu d\varphi=1, \tag{5b}$$

and

$$\tfrac{1}{8}R^3\int\psi_\alpha'^2(\lambda^2-\mu^2)d\lambda d\mu d\varphi=1. \tag{5c}$$

TABLE II. Experimental intensities[a] of R_1, R_2, and N bands for various times of F light irradiation in additively colored KCl.

Time (minutes)	R_1	R_2	N	R_2/R_1	N/R_1
0.0	0.005	0.005	0.022	1.0	4.4
0.5	0.009	0.010	0.030	1.1	3.3
3.0	0.031	0.036	0.057	1.2	1.8
22.0	0.157	0.188	0.123	1.20	0.78
82.0	0.240	0.303	0.154	1.26	0.64

[a] Optical densities at the band maxima.

Using Eqs. (5a), (5b), and (5c) one can show that

$$N=1/\kappa_0^{3/2}. \tag{5d}$$

If the z coordinate of the electron is expressed in terms of elliptic coordinates, $z=r_{ab}\lambda\mu/2$, the quantity $Q_{\alpha,\beta}(z)$ is given by

$$Q_{\alpha,\beta}(z;r_{ab},\kappa_0)=\tfrac{1}{16}r_{ab}^4\int\psi_\alpha(\lambda\mu)\psi_\beta(\lambda^2-\mu^2)d\lambda d\mu d\varphi. \tag{6a}$$

Using Eqs. (2a) and (5a), Eq. (6a) can be rewritten as

$$\begin{aligned}Q_{\alpha,\beta}(z;r_{ab},\kappa_0)&=\tfrac{1}{16}\kappa_0R^4\int\psi_\alpha'(\lambda\mu)\psi_\beta'(\lambda^2-\mu^2)d\lambda d\mu d\varphi\\&=\kappa_0Q_{\alpha,\beta}'(z,R),\end{aligned} \tag{6b}$$

where $Q_{\alpha,\beta}'(z,R)$ is the matrix element of z between states α and β of the hydrogen molecular ion in free space with internuclear distance R. Equations similar to Eq. (6b) can be developed for $Q_{\alpha,\beta}(x)$ and $Q_{\alpha,\beta}(y)$.

The frequency ν, which appears in Eq. (4) defining the oscillator strength $f_{\alpha,\beta}$, is given by

$$\nu=[E_\beta(r_{ab},\kappa_0)-E_\alpha(r_{ab},\kappa_0)]/h. \tag{7a}$$

Using Eq. (3b), Eq. (7a) can be rewritten as

$$\nu=[E_\beta'(R)-E_\alpha'(R)]/(\kappa_0^2h). \tag{7b}$$

If Eqs. (6b) and (7b) are substituted into Eq. (4), one finds that

$$\begin{aligned}f_{\alpha,\beta}(r_{ab},\kappa_0)=(8\pi^2m^*/3h^2)&[E_\beta'(R)-E_\alpha'(R)]\\&\times G|Q_{\alpha,\beta}(R)|^2=f_{\alpha,\beta}'(R),\end{aligned} \tag{8}$$

where $f_{\alpha,\beta}'(R)$ is the oscillator strength for the transition between states α and β of the hydrogen molecular ion in free space with internuclear distance R.

It has been pointed out by Lax[18] that the absorption coefficient $\sigma_{\alpha\beta}(\nu)$ is not sensitive to the value of the effective mass m^* appearing in the definition of the oscillator strength $f_{\alpha,\beta}$ given by Eq. (4). Accordingly, in the present paper the quantity m^* is taken to be equal to the ordinary electron mass m. For the case $m^*=m$, Bates and collaborators have tabulated the quantity $f_{\alpha,\beta}'(R)$ over a range of values of R for a

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[17] R. S. Mulliken, Revs. Modern Phys. 4, 1 (1932).

[18] M. Lax, in *1954 Photoconductivity Conference* (John Wiley and Sons, Inc., New York, 1956).

TABLE III. Theoretical frequencies (expressed as energy differences) and oscillator strengths for various transitions of the F, F_2^+, and F_2 centers for $r_{ab}=8.39$ au and $\kappa_0=2.22$. Experimental. frequencies of the F, R_1, and R_2 bands in KCl are also given

		Theoretical		Experimental	
Center	Transition	ΔE(ev)	f	Band	ΔE(ev)
F	$1s-2p$	2.07	0.42	F	2.30
F_2	${}^1\Sigma_g{}^+-{}^1\Pi_u$	2.01	···	R_1	1.88
F_2	${}^1\Sigma_g{}^+-{}^1\Sigma_u{}^+$	1.62	···	R_2	1.70
F_2^+	$1s\,\sigma-2p\,\pi$	2.52	0.47		
F_2^+	$1s\,\sigma-2p\,\sigma$	0.64	0.24		

number of electronic transitions. From these tables it is then a relatively simple matter to obtain $f_{\alpha,\beta}(r_{ab},\kappa_0)$ using Eq. (8).

V. THEORETICAL RESULTS

The models discussed in the preceding section have been used as a basis for a theoretical study of the F, F_2^+, and F_2 centers in KCl. The results are given in Table III under the heading "Theoretical." The frequencies (expressed as energy differences between states) for the $1s\,\sigma-2p\,\sigma$ and $1s\,\sigma-2p\,\pi$ transitions of the F_2^+ center were computed using Eq. (3b) and the tables of $E'(R)$ given by Bates, Ledsham, and Stewart.[16] The oscillator strength for the $1s\,\sigma-2p\,\sigma$ transition was obtained with the aid of Eq. (8) and the table computed by Bates.[19] The oscillator strength for the $1s\,\sigma-2p\,\pi$ transition was obtained with the aid of the table computed by Bates, Darling, Hawe, and Stewart.[20]

The frequencies of the ${}^1\Sigma_g{}^+-{}^1\Sigma_u{}^+$ and ${}^1\Sigma_g{}^+-{}^1\Pi_u$ transitions of the F_2 center approximated by a hydrogen molecule immersed in a dielectric medium were obtained using Eq. (3b) and the energy curves given by Mulliken.[17] No values appear to be available for the oscillator strengths $f_{\alpha,\beta'}(R)$ for the ${}^1\Sigma_g{}^+-{}^1\Sigma_u{}^+$ and ${}^1\Sigma_g{}^+-{}^1\Pi_u$ transitions of the hydrogen molecule in free space with the required values of the internuclear distance R. In addition, no reasonably accurate wave functions seem to be available for the excited states involved in these transitions. It would therefore be a very laborious task to calculate the oscillator strengths for the transitions of the F_2 center. Accordingly, no values of these oscillator strengths are given in Table III.

The frequency for the $1s-2p$ transition of the F center approximated by a hydrogen atom immersed in a dielectric medium was obtained using Eq. (3c). The corresponding oscillator strength is identical to the known[21] oscillator strength of the $1s-2p$ transition of the hydrogen atom in free space.

In all of the calculations just discussed κ_0, the high-frequency dielectric constant for KCl, was taken to be 2.22. In the calculations on the F_2^+ and F_2 centers, the distance r_{ab} between the point positive charges was taken to be 8.39 au which is the distance between nearest neighbor chloride ions in the perfect KCl lattice at room temperature.

For comparison purposes experimental values of the frequencies at the band maxima (measured at liquid nitrogen temperature) of the F, R_1, and R_2 bands are given in Table III. It may be seen that the observed frequencies of these bands have approximately the same magnitude and fall in the same order as the computed frequencies for the $1s-2p$ transition of the F center and the ${}^1\Sigma_g{}^+-{}^1\Pi_u$ and ${}^1\Sigma_g{}^+-{}^1\Sigma_u{}^+$ transitions of the F_2 center, respectively.

VI. DISCUSSION

The experimental and theoretical work reported in this paper indicates that the observed R_1 and R_2 bands possibly may arise from two transitions from the ground state of the F_2 center consisting of two electrons trapped at a pair of adjacent negative ion vacancies. In order for this interpretation to be valid the ratio of the intensities of the R_1 and R_2 bands should be a constant independent of the absolute intensity of either band, provided the absolute intensities are not too great. If the intensities are very large, effects due to the interaction of centers may arise. The observed R_2 to R_1 band intensity ratio (as determined from the optical densities at the band maxima) is not constant, but increases somewhat with increasing F light irradiation time. Experimental error may be responsible for part of this variation in the intensity ratio.

Another contributing factor to the variation may be the overlapping of the F and R_1 bands and of the M and R_2 bands. The decrease in the F-band intensity and the increase in the M band intensity during the first few minutes of F light irradiation tend to cause an increase in the R_2 to R_1 band intensity ratio. The decrease of the M band during the later part of the F light irradiation tends to reduce the rate of increase of the R_2 to R_1 band intensity ratio. It may be seen from Tables I and II that the increase in the latter ratio during the first three minutes of F-light irradiation is equal to or greater than the increase during the next 79 minutes.

The rather small variation in the intensity ratio of the R_1 and R_2 bands is perhaps surprising if one associates the R_1 band with a transition of the F_2^+ center and the R_2 band with a transition of the F_2 center. The F_2^+ center has a net positive charge and would attract a conduction electron with a force that is Coulomb-like at large distances. Capture of a conduction electron by an F_2^+ center would lead to the formation of an F_2 center. This process would tend to increase the intensities of the bands corresponding to the F_2 center and decrease the intensities of bands corresponding to the F_2^+ center.

Although the models employed in the theoretical

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[19] D. R. Bates, J. Chem. Phys. **19**, 1122 (1951).

[20] Bates, Darling, Hawe, and Stewart, Proc. Phys. Soc. (London) **A66**, 1124 (1953).

[21] See reference 18, p. 9.

calculations are considerably simplified versions of the F_2^+ and F_2 centers, they nevertheless possess a number of the gross features of these centers. The models have the advantage that their properties can be determined fairly exactly without excessive labor. The use of similar physical assumptions in the two cases provides a basis for comparing their properties. In addition, the calculated properties of the F_2^+ and F_2 centers can be compared with those of the F center treated as a hydrogen atom immersed in a dielectric medium.

It might be worthwhile to indicate the sensitivity of the calculated values of the oscillator strength and frequency with respect to the variation of the separation, r_{ab}, of the negative ion vacancy pair and to variation of the dielectric constant κ_0. It seems probable that the best values of the parameter r_{ab} are not the same in the F_2^+ and F_2 centers. The net positive charge on the F_2^+ center would tend to increase the distance between the positive charges relative to the corresponding distance in the F_2 center. In addition, it seems unlikely that the best value of r_{ab} in either the F_2^+ or the F_2 center is the same as the distance between adjacent negative ions in the perfect crystal.

The frequencies and oscillator strengths for various transitions of the F, F_2^+, and F_2 centers are given in Table IV for $r_{ab}=6.44$ au and $\kappa_0=2.22$ and for $r_{ab}=8.39$ au and $\kappa_0=2.73$. These sets of values for r_{ab} and κ_0 were chosen so that for the first set the frequency of the $1s\,\sigma-2p\,\sigma$ transition of the F_2^+ center would coincide with the observed N-band maximum and for the second set the frequency of the $1s\,\sigma-2p\,\pi$ transition of the F_2^+ center would coincide with the observed R_1-band maximum.

A comparison of the calculations given in Tables III and IV shows that a relatively large decrease of r_{ab}, ~25 percent, produces a relatively small change in the frequencies of the $^1\Sigma_g{}^+-{}^1\Pi_u$ and $^1\Sigma_g{}^+-{}^1\Sigma_u{}^+$ transitions of the F_2 center. The major effect of the change in r_{ab} appears to be the shift of the $1s\,\sigma-2p\,\sigma$ transition of the F_2^+ center toward the ultraviolet. The principal effect of increasing κ_0 is to shift the frequencies of all transitions listed toward the infrared with the exception of the $1s\,\sigma-2p\,\sigma$ transition of the F_2^+ center.

TABLE IV. Theoretical frequencies and oscillator strengths for various transitions of the F, F_2^+, and F_2 centers.

Center	Transition	r_{ab}(au)	κ_0	ΔE(ev)	f
F	$1s-2p$		2.22	2.07	0.42
F_2	$^1\Sigma_g{}^+-{}^1\Pi_u$	6.44	2.22	2.05	...
F_2	$^1\Sigma_g{}^+-{}^1\Sigma_u{}^+$	6.44	2.22	1.74	...
F_2^+	$1s\,\sigma-2p\,\pi$	6.44	2.22	2.95	0.48
F_2^+	$1s\,\sigma-2p\,\sigma$	6.44	2.22	1.27	0.29
F	$1s-2p$		2.73	1.37	0.42
F_2	$^1\Sigma_g{}^+-{}^1\Pi_u$	8.39	2.73	1.34	...
F_2	$^1\Sigma_g{}^+-{}^1\Sigma_u{}^+$	8.39	2.73	1.11	...
F_2^+	$1s\,\sigma-2p\,\pi$	8.39	2.73	1.88	0.48
F_2^+	$1s\,\sigma-2p\,\sigma$	8.39	2.73	0.71	0.28

The calculations just given indicate that over a rather wide range of values for the parameters r_{ab} and κ_0 the model employed for the F_2^+ center exhibits an absorption band somewhat to the ultraviolet of the F band and a second absorption band considerably to the infrared of the F band. The model employed for the F_2 center shows two absorption bands rather close to and most likely to the red of the F band.

It may be mentioned that both the $1s\,\sigma-2p\,\pi$ transition of the F_2^+ center and the $^1\Sigma_g{}^+-{}^1\Pi_u$ transition of the F_2 center are doubly degenerate for the models employed in this paper. In more refined models this degeneracy would be removed, and the corresponding bands would each be split into two bands.

The models employed for the calculations are probably most appropriate for treating crystals such as KCl, NaF, and RbBr in each of which the cation and anion have the same number of electrons and nearly the same polarizability. The electron or electrons of the F, F_2^+, and F_2 centers probably spend the greater portion of their time near the cations adjacent to the negative ion vacancy or vacancies. The polarizability of the cation might then be expected to be most significant in determining the proper value of the dielectric constant to be used in the calculations. This best value of the dielectric constant is probably close to the gross observed high frequency dielectric constant (which was the value of κ_0 employed in the calculations on KCl) when the cation and anion have nearly the same polarizability.