A study of the F-center in several alkali halides

David Atherton Robinson

Iowa State University

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A STUDY OF THE F' CENTER IN SEVERAL ALKALI HALIDES

by

David Atherton Robinson

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Approved:

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In Charge of Major Work

Signature was redacted for privacy.

Head of Major Department

Signature was redacted for privacy.

Dean of Graduate College

Iowa State University
Of Science and Technology
Ames, Iowa

1967
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ABSTRACT

The F' band has been produced and measured in the following alkali halides: NaCl, KCl, KBr, KI, RbCl, RbI, CsBr, and CsI. The spectra consisted of a single main peak and either a shoulder or a distinct second peak to the high energy side of it. The main peak in NaCl had a symmetrical bell shape, whereas in the remainder of the salts it showed some structure. The potassium and rubidium salts showed a shoulder located on the high energy side of the main peak. The cesium halides showed a more complex structure. The structure in the main peak may be attributed to differences in band structure between the sodium halides and the other alkali halides. The shoulder, or second peak, to the high energy side of the main peak has been assigned tentatively to F' center absorption where the F center is left in an excited 2p state.

A semicontinuum model variational calculation has also been carried out using a correlated Hylleraas wave function. The F' binding energies were calculated in a self-consistent a priori fashion for $m^* = m_e$ and $0.6m_e$. ($m^*$ is the conduction band effective mass.) Generally good agreement with experimental binding energies was achieved for the $m^* = 0.6m_e$ case. Also the potential well was adjusted to force agreement with experimental binding energies for the $m^* = m_e$ case. The resulting wave functions were used to calculate the absorption coefficients for the F' centers. Generally good agreement was obtained concerning the positions and sizes of the main peaks and their half-widths. The second absorption edges, corresponding to leaving the F center in an excited 2p state, were calculated. Good agreement with the experimental second edges was
obtained. A preliminary calculation, concerning the peak height and half-width of this second band, yielded results in fair agreement with data on KBr.
INTRODUCTION

Purpose of this Investigation

Extensive work has been done in the general area of color centers in alkali halides (30,48,49). In general, attention has been given mainly to the F center with little experimental or theoretical work being done on the F' center. To our knowledge the most recently published data on the optical absorption of the F' center in several salts is that of Pick (40,41) taken in 1938 and 1940. Several more recent papers (11,18,24) show the F' band in KBr and KCl but do not deal with the optical absorption of the F' band explicitly or investigate other crystals. A few recent calculations (7,28,42,44) have been done using the continuum, semicontinuum, and point-ion models. These calculations all employed simple product wave functions and did not explicitly include any electron-electron correlation effects. In the light of this previous work, therefore, it was decided to obtain new optical absorption data on the F' center in as many alkali halides as possible and to calculate a priori, using a correlated wave function, the F' binding energies for these salts. It was also decided to calculate theoretical absorption curves which could be compared with experiment.

The F Center and Smakula's Equation

Several reviews have been published concerning the field of color centers in alkali halides (30,48,49). These reviews form the basis of this introductory discussion. The most extensively examined defect in the alkali halides is the F center, which is accepted as being an electron trapped at a negative ion vacancy. F centers are usually produced in the
alkali halides by exposing them to ionizing radiation or by heating them in alkali metal vapor. Either process results in the addition of negative ion vacancies and free electrons, and hence F centers, to the salt. The two lowest bound electronic states of the F center can be described by s-like and p-like wave functions (17), and the difference in energy between these levels for the various salts is on the order of 2-4 eV. Photons of this energy correspond to the visible spectrum, hence F centers in a particular salt give it a characteristic color.

Experimentally, the F centers produce a bell-shaped F absorption band which is approximately Gaussian in shape. Traditionally, the F band has been assigned a Lorentzian shape, and the equation given here applies to this case. Classical dispersion theory was first applied to the F center by Smakula (48) who obtained a relationship between the density of F centers and the size of the absorption band. The result, commonly known as "Smakula's equation", is (48)

\[ N_f = 1.29 \times 10^{17} \frac{n}{(n^2 + 2)^2} \alpha_{\text{max}} W \] (1)

where

- \( N \) = the number of F centers per cm\(^3\)
- \( f \) = the "oscillator strength"
- \( n \) = the index of refraction of the crystal at the peak of the absorption band
- \( \alpha_{\text{max}} \) = the absorption coefficient in cm\(^{-1}\) at the peak of the absorption band
- \( W \) = the half-width of the absorption band in electron volts.
The oscillator strength (f) has both a classical and quantum mechanical definition. Classically, for a system of N oscillators, \( f_{\omega_k} \) represents the fraction of oscillators in the system of frequency \( \omega_k \). The quantum mechanical f is found from the classical f by equating the classical and quantum mechanical expressions for the polarizability of an atom (12). The actual broadening of the F band absorption does not result from a damped classical oscillator but results, as shown by Dexter (12), from lattice vibrations. However, it turns out, as shown by Dexter, that if a correct calculation involving the lattice vibrations is done and that if the absorption is assumed to be Lorentzian, then Smakula's equation is reproduced. In practice \( N \) and \( \alpha_{max} \) are measured for a particular system, and Equation 1 is "calibrated" to agree with the measurements by adjusting f. If a Gaussian band shape is assumed the numerical factor in Equation 1 is 0.87 rather than 1.29 (12). The oscillator strengths for three alkali halides as given by Schulman and Compton (48) for use in Equation 1 are shown in Table 1.

Table 1. Oscillator strengths for the F center

<table>
<thead>
<tr>
<th>Salt</th>
<th>f</th>
</tr>
</thead>
<tbody>
<tr>
<td>KCl</td>
<td>0.90</td>
</tr>
<tr>
<td>KBr</td>
<td>0.80</td>
</tr>
<tr>
<td>NaCl</td>
<td>0.81</td>
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</table>

Smakula's equation was required for finding the concentration of F' centers in the samples used.
The F' center

The F' center is accepted as being two electrons trapped at a negative ion vacancy, hence an F center which has trapped one additional electron. F' centers can usually be produced in a crystal containing F centers by optically bleaching the F band at temperatures between liquid nitrogen temperature and dry ice temperature. The F' centers produce an F' absorption band which is located to the low energy side of the F band. Figure 1 shows a KCl crystal before and after optical bleaching in the F band at T = 183°K. The spectra were measured at liquid nitrogen temperature.

The two-electron model of the F' center is supported by several experimental results. Pick (40) measured the quantum yield for F to F' and F' to F conversion and found that the reaction could be described by the equation 2F → F'. His data are reproduced in Figure 2. Here two different quantum yields are shown. The two quantum yields are defined as

\[ \eta(2F \rightarrow F') = \frac{\text{number of F centers destroyed}}{\text{number of F quanta absorbed}} \]

and

\[ \eta(F' \rightarrow 2F) = \frac{\text{number of F centers created}}{\text{number of F' quanta absorbed}} \]

At low temperatures \( \eta(2F \rightarrow F') \) is small, since the probability of thermal ionization of the excited F center is small. As the temperature increases, the probability that the excited F centers will be thermally ionized increases, hence \( \eta \) increases. At temperatures where the ionization probability is unity, \( \eta = 2 \). Each F quantum destroys two F centers, since
Figure 1. Absorption spectra of KCl before and after optical bleaching of the F band at $T = 183^\circ K$
Figure 2. Quantum yields for $F$ to $F'$ and $F'$ to $F$ conversion in KCl (after Pick)
one center is destroyed by ionization, and another is destroyed when it captures the free electron to form an F' center. At low temperatures \( \eta(F' \rightarrow 2F) \), on the other hand, becomes equal to two. Here just the opposite process is taking place, with one F center being created by the ionization of the F' center, and another being created when a vacancy traps the free electron. The \( \eta(F' \rightarrow 2F) \) curve shows two interesting features. The first is that the F' centers can be optically bleached at very low temperatures (Pick bleached them at 23°K) with a quantum yield of two. This indicates that the F' center has no bound excited state, and that the F' band corresponds to an optical absorption arising from a transition from a single bound state to a continuum. The second feature is that the quantum yield drops off at higher temperatures. This is due to the decreasing capture cross section of the negative ion vacancies in the crystal \((10,48)\). The idea that the F' center has only one bound state is further supported by photoconductivity measurements made by Domanic \((13)\). Domanic measured the photocurrent due to F' center electrons in KCl and KBr over a wide range of temperatures and observed a photocurrent down to 20°K. Thus it is generally concluded that the absorption of a photon by an F' center results in direct ionization of the center.

As shown in Figure 1, it is not possible to remove totally the F band by bleaching. This occurs for two reasons. The first is that, as the F band is bleached, negative ion vacancies are formed, and these act as additional electron traps which compete with the F center. The second is that the F and F' bands overlap, and the radiation used to bleach the F band will also bleach the F' band and thus establish an equilibrium.
between the two. F' centers are very weakly bound and thus are thermally unstable at temperatures above about 200°K. Because of this, and the temperature dependence of the quantum yield \( \eta(2F \rightarrow F') \), as discussed before, there exists a temperature for each salt at which maximum F to F' conversion can be obtained. That is, the F to F' conversion depends on two competing thermal ionization probabilities, one for the excited F center and another for the F' center, and a temperature must be chosen such that the reaction \( F + hv \xrightarrow{kT} F' \) proceeds as far to the right as possible. Pick (41) plotted the amount of F center conversion against the bleaching temperature and obtained the temperatures for maximum conversion in KCl, KBr, and NaCl. His values are listed in Table 2.

Table 2. Temperature for maximum F to F' conversion (after Pick)

<table>
<thead>
<tr>
<th>Salt</th>
<th>( T(\text{°K}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>KCl</td>
<td>183</td>
</tr>
<tr>
<td>KBr</td>
<td>133</td>
</tr>
<tr>
<td>NaCl</td>
<td>153</td>
</tr>
</tbody>
</table>

Previous Calculations

Several theoretical calculations have been done on the F' center using the continuum, point-ion, and semicontinuum models. These calculations are briefly described below.

The continuum model represents the lattice vacancy by a simple Coulomb potential \( Z/kr \), where \( k \) is the static dielectric constant of the medium. The electron is then allowed to interact with this potential and
the potential produced by the polarization of the lattice. Although this model has had very good success at predicting the half-width of the F band and its dependence on temperature, it is not a particularly physical model in that it ignores all short range interactions between the defect and the lattice. Cheban (7) calculated the ionization probability of the F' center using a continuum theory due to Pekar (38). Cheban calculated the F' photoionization probability for a final state consisting of either a polaron or a conduction band electron and found that to get agreement with experimental absorption curves that the final state had to consist of a conduction band electron.

The point-ion model represents the lattice as an array of point ions and describes the potential at the lattice vacancy as a sum of the Coulomb potentials due to each point ion. Raveche (44) used the results of Gourary and Adrian's (21) point-ion model calculation for the F center to calculate the F' binding energy in KCl. He used a product of their F center wave functions to describe his system and treated the electron-electron interaction as a perturbation. Although he obtained fair agreement with experiment (within 0.3 eV), the method is questionable since his perturbation is about 40% of the total Hamiltonian.

The semicontinuum model represents the lattice vacancy by a cavity in a dielectric continuum. This model is somewhat more physical than the others because it allows for short range interactions due to the vacancy and also longer range interactions due to polarization around the vacancy. This model was chosen as the basis for our calculation and will be explained in detail later. Pincherle (42) used the semicontinuum
model to calculate the F" binding energies in NaCl and KCl. He used a
simple product function and treated the electron-electron energy term by
considering two interpenetrating electron charge clouds. His calculated
values are also in fair agreement with experiment (within 0.1 - 0.3 eV).
La and Bartram (28) combined the features of several models in their
calculation. Using the Hartree-Fock method they found the wave functions
and energy levels for two electrons in a square well. They then corrected
for the effect of the lattice by treating the difference between the
square well potential and Gourary and Adrian's point-ion potential as a
perturbation. Finally they corrected for polarization effects by using
the semicontinuum model. These corrections were the same as used in the
present calculation. Here again the perturbation added was about 40% of
the total Hamiltonian. Their calculated binding energies for NaCl, KCl,
and KBr were within 0.6 to 1.5 eV of the experimental values.
THEORY AND CALCULATIONS

In this section the variational method will be applied to semi-continuum models for the F and F' center. The ground and first excited state energies for the F center and the ground state energy for the F' center will be found. From these energy values and wave functions the absorption coefficient for the F' center for a final state consisting of a plane wave electron and an F center in the ground state will be calculated.

In this discussion all quantities will be expressed in atomic units, except when noted otherwise. In this system of units the unit of charge is e, the electron charge, the unit of mass is the electron mass, and the unit of action is h. The unit of length is then the first Bohr radius (0.53 Angstroms) and the unit of energy is two Rydbergs (27.2 eV).

Semicontinuum Model

Description of model

The semicontinuum model which was used for the F and F' centers is based on the work of Krumhansl and Schwartz (27) as expanded in the review by Gourary and Adrian (20). In this approximation the periodic lattice is ignored and is replaced by a dielectric continuum. The negative ion vacancy is then represented by a spherical cavity in the dielectric continuum and is assigned some positive effective charge Z. The radius of the cavity, or well, R, is roughly the nearest neighbor distance of the ionic solid, and Z is about 1. The spherically symmetric potential represented by this model is shown in Figure 3. To discuss this potential in general we take the origin of a spherical polar coordinate system to be
Figure 3. Potential well for semicontinuum model.
at the center of the cavity and divide the space into two regions:
1) \( r > R \), and 2) \( r < R \). Inside the well, \( r < R \), the potential is constant and is equal to \( V_o \). \( V_o \) is the sum of the following terms:
1) \( V_m \), the Madelung potential which equals \(-\alpha_m/a\), where \( \alpha_m \) is the Madelung constant for the particular crystal structure and \( a \) is the nearest neighbor distance; 2) \( \chi \), the electron affinity, the energy required to take an electron from the bottom of the conduction band to the vacuum; and 3) \( W \), the polarization correction to be discussed in detail later. Outside the well, \( r > R \), the potential is

\[
-\frac{1}{K_{eff} r}
\]

where \( K_{eff} \) is an effective dielectric constant to be discussed in detail later. To find the F and F' energies the Schrödinger equation is then solved for this potential. The calculated binding energies will then be measured from the bottom of the conduction band. This particular model was chosen for several reasons: 1) it has yielded reasonable results for the F center problem (48), 2) it contains the important bulk parameters of the particular alkali halide being examined, and 3) it is an easy potential to use in a variational calculation.

Polarization effects

Before a detailed discussion of the semicontinuum model can be done the Jost cavity model and the work of Mott and Littleton should be reviewed (20). We consider an infinite medium of dielectric constant \( K \) containing a spherical cavity of radius \( R \). A charge \( Z \) is placed with a symmetrical distribution in the cavity and the polarization of the dielectric is calculated. Outside the cavity the electric displacement
and electric field vectors are both radial and are as follows:

\[
D_x(r) = \frac{Z}{r^2} \quad \text{and} \quad E_x(r) = \frac{Z}{Kr^2}.
\]

Therefore the polarization vector is radial and is

\[
P_x(r) = \frac{(D_x(r) - E_x(r))}{4\pi} = \frac{Z}{4\pi} \left( 1 - \frac{1}{K} \right) \frac{1}{r^2}.
\]

This polarization produces the following surface charge density on the cavity wall

\[
\sigma(R) = - P_x(R).
\]

This charge density integrated over the surface area of the cavity yields the following total charge

\[
q_{\text{total}} = \sigma(R) 4\pi R^2 = - Z \left( 1 - \frac{1}{K} \right).
\]

The electrostatic potential at any point in the cavity due to this polarization charge is

\[
\phi = - Z \left( 1 - \frac{1}{K} \right) \frac{1}{R}.
\]

The work of Mott and Littleton consists of calculating \( \phi \) in a detailed manner for a negative ion vacancy in a perfect lattice. Their complex calculation involving detailed sums over a lattice of point dipoles is then expressed by Equation 4 where \( K = k_o \), the optical dielectric constant, and where \( R \) is chosen to make \( \phi \) fit their result and is called the Mott-Littleton radius. In their calculation Mott and Littleton consider most of the ions to be fixed and consider only the electronic polarizability of the lattice. From Equation 3 they calculate the field seen by the
distant ions. They represent each distant ion as a point dipole and calculate its dipole moment from their knowledge of the field. They then represent each of the nearest neighbor ions by an unknown dipole and solve self-consistently for the dipole moment, taking into account the other nearest neighbor ions and all the distant ions. Finally the polarizations of the distant and nearest neighbor ions are all summed over to yield $\phi$, and therefore $R$. Their results for several salts are listed in Table 3. Here $a$ is the nearest neighbor distance.

Table 3. Mott-Littleton radii

<table>
<thead>
<tr>
<th>Salt</th>
<th>$R/a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>KCl</td>
<td>0.55</td>
</tr>
<tr>
<td>KBr</td>
<td>0.88</td>
</tr>
<tr>
<td>NaCl</td>
<td>0.95</td>
</tr>
</tbody>
</table>

It should be noted that the $\phi$ obtained from the above values of $R$ and Equation 4 will yield the correct Mott-Littleton value only at the center of the cavity.

Krumhansl and Schwartz (27) treat the semicontinuum model in detail for one electron in the well. For the $F^\prime$ center there are two electrons in the well and some details will be different. In this section the details for both one and two electrons in the well will be worked out. Krumhansl and Schwartz proceed as follows. Inside the cavity the potential energy is assumed to be constant and, as stated before, is divided into three parts: 1) the Madelung energy $-\frac{a_m}{a}$, 2) the electron affinity $x$, and 3) the polarization energy $W$. $W$ may be divided into ionic and optical parts as below.
\[ W = W_{\text{ion}} + W_{\text{opt}} \]

Krumhansl and Schwartz then use the quasi-adiabatic approximation to calculate \( W_{\text{opt}} \). In this approximation the core electrons are allowed to follow the motion of the trapped electron. If the trapped electron is at infinity the potential due to the optical polarization can be written from Equation 4 to yield

\[ \phi_{r \to \infty} = -Z(1 - \frac{1}{k_o}) \frac{1}{R} \]

If the trapped electron is confined to the well the potential due to the optical polarization becomes

\[ \phi_{r<R} = -(Z-1)(1 - \frac{1}{k_o}) \frac{1}{R} \]

We now have a potential, \( \phi(q) \), which is linear in \( q \). To find the total potential energy of the electron due to the optical polarization Krumhansl and Schwartz integrate \( \phi(q) \). The result for one electron trapped by the well is

\[ W_{\text{opt}} = (-1)(- \int_{-\infty}^{\infty} \phi(q) \, dq) = (Z - \frac{1}{2})(1 - \frac{1}{k_o}) \frac{1}{R} \]  \hspace{1cm} (5a)

If two electrons are trapped by the well the result is

\[ W_{\text{opt}} = \int_{-\infty}^{\infty} \left( 1 - \frac{1}{k_o} \right) \frac{1}{R} \, dq = (Z-1)(1 - \frac{1}{k_o}) \frac{2}{R} \]  \hspace{1cm} (5b)

Krumhansl and Schwartz also calculate the ionic part of the polarization energy, \( W_{\text{ion}} \), using the quasi-adiabatic approximation. In order to do this a general formula will be developed using a continuum treatment (20). Consider a perfect crystal which contains some sort of trap, say
a negative ion vacancy. The potential for an electron in this trap consists of two terms: 1) a spherically symmetric one due to the trap, and 2) a periodic one due to the rest of the lattice. The periodic potential may be accounted for by giving the electron some effective mass $m^*$. The potential due to the trap may be described by a potential $Z/r$, where $Z$ is the effective charge of the trap. The polarization of the lattice about the trap may be described by $k_0$, the optical dielectric constant, which gives the core polarization of the ions, and $k$, the static dielectric constant, which gives the total polarization due to both core polarization and ionic displacement polarization. We now consider a dielectric continuum with dielectric constants $k_0$ and $k$ and find the potential energy of an electron trapped by a potential $Z/r$. Contributions to the field that the electron sees will be added up and integrated to get the required potential energy. Since the potential $Z/r$ is constant in time, the lattice can come to equilibrium, and the contribution of this potential to the field is

$$\frac{Z}{kr^2}$$

The average distribution of the electron will also produce a polarization field. Let $\psi(r)$ be the normalized one-electron wave function describing the system. Now define $p(r)$ and $q(r)$ as being the fraction of a one-electron distribution which is inside or outside a sphere of radius $r$ respectively. Writing $p(r)$ and $q(r)$ in terms of $\psi(r)$ yields

$$p(r) = \int_0^r |\psi(r)|^2 \, dr , \quad q(r) = \int_r^\infty |\psi(r)|^2 \, dr ,$$

and
\[ p(r) + q(r) = 1 \]

For a one-electron system the charge distribution inside and outside a sphere of radius \( r \) is \(-p(r)\) and \(-q(r)\) respectively, while for a two-electron system the charge distribution inside and outside a sphere of radius \( r \) is \(-2p(r)\) and \(-2q(r)\) respectively. Over a long period of time the charge distribution \(-p(r)\) is also constant and produces the field

\[ -\frac{p(r)}{kr^2} \]

In the quasi-adiabatic approximation the optical polarization is allowed to follow the motion of the electron. Since we want the field the electron sees instantaneously at \( r \) we must add the term

\[ +\frac{p(r)}{k_0 r^2} \]

The total field seen by the trapped electron is

\[ E_r(r) = \frac{Z}{kr^2} + \left( \frac{1}{k_0} - \frac{1}{k} \right) \frac{p(r)}{r^2} \]

The required potential energy becomes

\[ \phi(r) = (-1) \left[ -\int_0^r E_r \cdot \mathbf{dr} \right] = -\frac{Z}{kr} - \left( \frac{1}{k_0} - \frac{1}{k} \right) \int_0^r \frac{p(r)}{r^2} \mathbf{dr} \quad (6) \]

This equation will also be useful for describing an effective dielectric constant for the semicontinuum model.

\( W_{\text{ion}} \) may now be written from Equation 6. \( W_{\text{ion}} \) is the potential energy the electron sees inside the well due to ionic polarization and is equal to the work done due to the ionic polarization in removing the electron from the well while the ions are held fixed. Krumhansl and Schwartz then write \( W_{\text{ion}} \) from the last term in Equation 6 to yield
\[ W_{\text{ion}} = \left( \frac{1}{k_0} - \frac{1}{k} \right) \int_{R}^{\infty} \frac{Z - p(r)}{r^2} \, dr . \]

\[ W_{\text{ion}} = \left( \frac{1}{k_0} - \frac{1}{k} \right) \left[ \frac{Z-1}{R} + \int_{R}^{\infty} \frac{q(r)}{r^2} \, dr \right] . \]

Here the charge +Z has been added to -p(r) to yield the total charge inside a sphere of radius r where \( r \geq R \), the well radius. It should be noted that Equation 6 describes the continuum model, and Z represents an effective point charge; while Equation 7a describes the semicontinuum model, and Z represents the effective charge of the cavity. Equation 7a has been worked out for one electron in the well. For two electrons in the well \( W_{\text{ion}} \) is written as

\[ W_{\text{ion}} = \left( \frac{1}{k_0} - \frac{1}{k} \right) \int_{R}^{\infty} \frac{Z-2p(r)}{r^2} \, dr . \]

Writing this in terms of \( q(r) \) yields

\[ W_{\text{ion}} = \left( \frac{1}{k_0} - \frac{1}{k} \right) \left[ \frac{Z-2}{R} + 2 \int_{R}^{\infty} \frac{q(r)}{r^2} \, dr \right] . \]

This concludes the discussion concerning the inside of the well.

Outside the well Equation 6 is used to yield an effective dielectric constant. For the one-electron case the formula given by Fowler (17) is obtained. From Equation 6 we write

\[ \phi(r) = - \frac{1}{k_{\text{eff}} r} = - \frac{Z}{k r} - \left( \frac{1}{k_0} - \frac{1}{k} \right) \int_{R}^{\infty} \frac{1-q(r)}{r^2} \, dr , \]

which yields

\[ - \frac{1}{k_{\text{eff}} r} = \frac{1-Z}{k r} - \frac{1}{k_0 r} + \left( \frac{1}{k_0} - \frac{1}{k} \right) \int_{R}^{\infty} \frac{q(r)}{r^2} \, dr . \]
For two electrons in the well Equation 6 yields:

\[ \psi(r) = -\frac{i}{K'_{\text{eff}}} r = -\frac{2}{kr} - \left(\frac{1}{k_o} - \frac{1}{k} \right) \int_0^\infty \frac{a(r)}{r^2} dr , \]

which reduces to

\[ -\frac{1}{K'_{\text{eff}}} r = 2 - \frac{2}{kr} + 2\left[ -\frac{1}{k_o r} + \left(\frac{1}{k_o} - \frac{1}{k} \right) \int_0^\infty \frac{a(r)}{r^2} dr \right] . \]

(8c)

All of the important polarization effects for the model are now done. Our results may be summarized by listing the well parameters which are appropriate just before and just after optical excitation of the F' center. To do this the Franck-Condon principle is employed which, in its simplest form, says that the ions do not move during an electronic transition (20). The appropriate well parameters are listed in Table 4. We let \( Z = 1 \) throughout.

Table 4. Well parameters for F and F' center

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Before absorption</th>
<th>After absorption</th>
</tr>
</thead>
<tbody>
<tr>
<td>( W_{\text{opt}} )</td>
<td>( (1 - \frac{1}{k_o}) \frac{1}{2R} ) (one electron in well)</td>
<td>( (1 - \frac{1}{k_o}) \frac{1}{2R} )</td>
</tr>
<tr>
<td>( W_{\text{ion}} )</td>
<td>( \frac{1}{k_o} - \frac{1}{k} \left[ -\frac{1}{R} + 2 \int \frac{a(r)}{r^2} dr \right] )</td>
<td>Same as before absorption</td>
</tr>
<tr>
<td>( \chi )</td>
<td>experimental number</td>
<td>Same as before absorption</td>
</tr>
<tr>
<td>( V_o )</td>
<td>( -\frac{a_m}{a} + W_{\text{ion}} + \chi + W_{\text{opt}} )</td>
<td>( -\frac{a_m}{a} + W_{\text{ion}} + \chi + W_{\text{opt}} )</td>
</tr>
<tr>
<td>(-\frac{1}{K'_{\text{eff}}})</td>
<td>( \frac{1}{kr} + 2\left[ -\frac{1}{k_o r} + \left(\frac{1}{k_o} - \frac{1}{k} \right) \int_0^\infty \frac{a(r)}{r^2} dr \right] )</td>
<td>Same as before absorption</td>
</tr>
</tbody>
</table>
Here, according to the Franck-Condon principle, \( q(r) \) is to be calculated from the one-electron \( F' \) wave function.

### Variational Method

The variational method for finding the lowest energy state of a system is discussed by Schiff (47). The basic result is that, given some wave function \( \psi \), the expectation value of the Hamiltonian, \( H \), of a system is an upper bound to the ground state or lowest energy of the system. That is,

\[
E_0 \leq \frac{\int \psi^* H \psi \, dr}{\int |\psi|^2 \, dr}
\]

where \( E_0 \) is the ground state energy of the system. A variational calculation then consists of choosing a reasonable wave function with several variable parameters. These parameters are then varied such that the expectation value of the Hamiltonian is a minimum. The closer \( \psi \) is to the true ground state wave function, the closer the expectation value will be to the true ground state energy.

### F Center and F' Center Variational Wave Functions

The wave functions used for the F center have been given by Fowler (17). These are

\[
\psi_{1s} = \left( \frac{\alpha}{\pi} \right)^{1/2} (1 + \alpha r) e^{-\alpha r}
\]

and

\[
\psi_{2p} = \left( \frac{\beta}{\pi} \right)^{1/2} r e^{-\beta r} \cos \theta
\]

Here \( \alpha \) and \( \beta \) are variational parameters and \( r \) and \( \theta \) are the usual spherical polar coordinates. It should be noted that \( \psi_{1s} \) is not a true hydrogenic 1s wave function but is labeled "1s" because it represents the lowest state.
of the F center and is spherically symmetrical.

In order to choose a suitable wave function for the F' problem, its atomic analog, the H⁻ ion, was examined. Considerable work has been done on the H⁻ ion because of its importance in producing absorption in the solar atmosphere (6,4,31,58). The important analogy between the F' center and the H⁻ ion is that both have a rather diffuse structure since one electron can provide almost complete shielding for the second. That is, each represents adding a second electron to a configuration which is almost electrostatically neutral. Because of this fact, correlation effects between the two electrons are very important. Previous work done on the H⁻ ion has employed wave functions consisting of power series of the Hylleraas coordinates s,t, and u. If \( r_1 \) and \( r_2 \) are the radial distances to electron 1 and electron 2 respectively, then s,t, and u are defined as

\[
s = r_1 + r_2, \quad t = r_1 - r_2, \quad u = r_{12}.
\]

The success of this approach for solving the H⁻ ion problem is shown in Table 5 (6,58). Here the Greek letters represent variational parameters. These values of the electron affinity can be compared with that due to Pekeris (39) who, using a different wave function, calculated a value of 0.0277509 a.u. This seems to be the best calculation to date (19). An exact experimental value for the ionization potential could not be found (39,52). However, Geltman (19) makes a comparison between the experimental absorption coefficient due to Smith and Burch and the absorption coefficients calculated by using the Hart-Herzberg bound state wave function and a plane-wave outgoing electron. The agreement is found to be satisfactory. It was felt, therefore, that by using the above type wave function that
the $F'$ problem could be reasonably described. For this work the three parameter wave function was chosen for several reasons. From Table 5 it is seen that at least three parameters are required to yield even modest accuracy for the $H^-$ ion problem. Also both radial and angular correlation are explicitly present as represented by $\tau^2$ and $u$ respectively. Finally with more than three parameters the calculation would have been excessively long.

For this problem the wave function was then written as

$$\psi = e^{-\frac{\alpha}{2} s} (1 + \beta u + \gamma \tau^2) , \quad (12)$$

and the normalization constant was written as

$$N = \int |\psi|^2 \, d\tau \quad . \quad (13)$$
This wave function is symmetric in its space coordinates \( r_1 \) and \( r_2 \), hence it must be anti-symmetric in its spin coordinates to satisfy the Pauli exclusion principle. These spin coordinates will not be explicitly written out, but they should be kept in mind when the expectation value of the Hamiltonian is calculated. This wave function, therefore, represents two electrons in a singlet state. At any instant of time the motion of the two electrons will be correlated due to the explicit appearance of \( r_{12} \) and \( (r_1 - r_2)^2 \) in the wave function, while over a long period of time each electron will have an s-like symmetry about the origin.

The F Center and F' Center Hamiltonians

We now follow a discussion due to Fowler (17) and write the Hamiltonian for the F center. His ideas will then be extended, and the Hamiltonian written for the F' center. In general for an F center in an ionic crystal the one-electron Hamiltonian is

\[
\hat{H} = -\frac{1}{2} \nabla^2 + \sum_n V_{\text{perf}}(\vec{r} - \vec{R}_n) + V_{\text{pol}}(\vec{r})
\]  

(14)

Here the first term is the kinetic energy. The second term is the perfect crystal potential, where \( \vec{r} \) and \( \vec{R}_n \) are the radius vectors from the center of the vacancy to the F electron and to the neighboring ions respectively. \( V_{\text{perf}}(\vec{r} - \vec{R}_n) \) is the potential at \( \vec{r} \) due to the nth ion centered at \( \vec{R}_n \). The prime indicates that the value \( V_{\text{perf}}(\vec{r}) \) is to be excluded from the sum. The third term includes all polarization effects. For the semi-continuum model we must now consider how to write this expression for the regions \( r > R \) and \( r < R \), where \( R \) is the well radius. Inside the well Equation 14 is approximated by
\[ H = -\frac{1}{2}v^2 + V_0 \quad \text{for} \quad r < R \quad (15) \]

where \( V_0 \) is the well depth as discussed in the section on polarization effects. Outside the well Equation 14 may be written as

\[ H = -\frac{1}{2}v^2 + \sum_n V_{\text{perf}}(\vec{r} - \vec{R}_n) - V_{\text{perf}}(\vec{r}) + V_{\text{pol}}(\vec{r}) \]

where \( V_{\text{perf}}(\vec{r}) \) has been added and subtracted. By making the effective mass approximation, the first two terms may be written as

\[ -\frac{1}{2m^*}v^2 \]

Also, the last two terms may be approximated by using an effective dielectric constant and written as

\[ -\frac{1}{K_{\text{eff}}} \]

where \( K_{\text{eff}} \) was discussed in the section on polarization effects. Therefore, outside the well the Hamiltonian is

\[ H = -\frac{1}{2m^*}v^2 - \frac{1}{K_{\text{eff}}} \quad \text{where} \quad r > R \quad (16) \]

From the above results an analogous Hamiltonian was written for the F' center. Since there are two electrons in two regions of space, there will be four cases. These are:
\[ H = - \frac{1}{2} \psi_1^2 - \frac{1}{2} \psi_2^2 + V_o + \frac{1}{K r_{12}^*}, \quad r_1 < R, \quad r_2 < R \]

\[ H = - \frac{1}{2} \psi_1^2 - \frac{1}{2} \psi_2^2 + V_o - \frac{1}{K'_{\text{eff}} r_2^*} + \frac{1}{K r_{12}^*}, \quad r_1 < R, \quad r_2 > R \]

\[ H = - \frac{1}{2} \psi_1^2 - \frac{1}{2} \psi_2^2 - \frac{1}{K'_{\text{eff}} r_1^*} + V_o + \frac{1}{K'_{\text{eff}} r_2^*} + \frac{1}{K r_{12}^*}, \quad r_1 > R, \quad r_2 < R \]

\[ H = - \frac{1}{2} \psi_1^2 - \frac{1}{2} \psi_2^2 - \frac{1}{K'_{\text{eff}} r_1^*} - \frac{1}{K'_{\text{eff}} r_2^*} + \frac{1}{K r_{12}^*}, \quad r_1 > R, \quad r_2 > R. \]

Here \( R \) is the potential well radius, \( K'_{\text{eff}} \) is the effective dielectric constant outside the well, \( K^* \) is the dielectric constant for the Coulombic correlation potential between the two electrons, and \( V_o \) is the square well potential each electron sees. \( K'_{\text{eff}} \) was discussed in the section on polarization effects, and \( K^* \) and \( V_o \) will be discussed in more detail when the expectation values of these terms are computed.

**Variational Calculations**

**F center calculation**

For the F center Equation 9 was written as

\[ E_i = - \frac{1}{2} \int_0^R \int_0^{2\pi} \int_0^\pi r^2 \sin\theta \psi_i \psi_i^* \]

\[ + \int_0^R \int_0^{2\pi} \int_0^\pi r^2 \sin\theta |\psi_i|^2 \]

\[ - \frac{1}{2m} \int_0^\infty \int_0^\pi \int_0^{2\pi} r^2 \sin\theta \psi_i \psi_i^* \]

\[ \frac{1}{2m} \int_0^R \int_0^{2\pi} \int_0^\pi r^2 \sin\theta \psi_i \psi_i^* \]
where Equations 15 and 16 have been used for the F center Hamiltonian. Here the subscript i refers to either the 1s or 2p state. The well parameters used in Equation 18 are shown in the last column of Table 4.

Using Equations 10 and 11 for the F center wave functions yielded

\[
E_{1s} = \frac{a^2}{28}[6 - (1 - \frac{1}{m})(-\frac{\alpha^4}{4} + 3a^2 + 6a + 6)e^{-a}]
\]

\[
+ V_o \left(1 - \left[14(l+a) + 7a^2 + 2a^3 + \frac{\alpha^4}{4} - e^{-a}\right]\right)
\]

\[
- \left[\frac{\alpha^4}{2} + \frac{7a^3}{2} + 9a^2 + 9a\right] \frac{e^{-a}}{28 K_{eff}^R}
\]

\[
E_{2p} = \frac{b^2}{8R^2} \left(1 - \left(\frac{1}{m}\right)^2\left[-\frac{\alpha^4}{2} + 2b^3 + 6b^2 + 12(b+1)\right] \frac{e^{-b}}{12}\right)
\]

\[
+ V_o \left(1 - \left[24(b+1) + 4b^2 + b^4\right] \frac{e^{-b}}{24}\right)
\]

\[
- \frac{3b^2 + 6(b+1)}{12K_{eff}} e^{-b}
\]

where \(a=2\alpha R\) and \(b=2\beta R\). These results are the same as those obtained by Fowler (17).

F' center calculation

The F' center calculation was similar to, but much more complex than, the F center calculation. The expectation value of the Hamiltonian was calculated in four steps by considering the following terms one at a time: 1) the square well potential, 2) the Coulomb shoulder potential, 3) the Coulomb correlation potential, and 4) the kinetic energy. Each of these
terms could be done in closed form in a straightforward but tedious fashion. The greatest difficulty was produced by the appearance of factors like \( r_{12} \) and \( 1/r_{12} \) in the various integrals. However, these could be handled by expanding them in terms of Legendre polynomials. Therefore, before describing the details of the problem, the formulas required to perform the integrations will be given.

To do the required integrals a coordinate system is needed in which the surfaces \( r_1 = R \) and \( r_2 = R \) can be described in a natural way. We choose as our three coordinates \( r_1, r_2, \) and \( \theta_{12} \), where \( \theta_{12} \) is the angle between \( \hat{r}_1 \) and \( \hat{r}_2 \). The differential element, \( dx^6 \), for these coordinates is derived by Morse and Feshbach (33) and is

\[
dx^6 = 8\pi^2 \sin \theta_{12} \, d\theta_{12} \, r_1^2 \, dr_1 \, r_2^2 \, dr_2 (19)\]

where

\[0 < r_1 < \infty, \quad 0 < r_2 < \infty \quad \text{and} \quad 0 \leq \theta_{12} \leq \pi.\]

This formula is derived by starting with the product of the usual spherical polar coordinates and then referring the direction of \( \hat{r}_2 \) to \( \hat{r}_1 \) and integrating over all angles except \( \theta_{12} \) to get the factor \( 8\pi^2 \). These coordinates are shown in Figure 4.

The normalization factor \( (N) \) given by Equation 13 can be more easily worked out using the Hylleraas coordinates \( s, t, \) and \( u \), since here we integrate over all space. Morse and Feshbach continue from the intermediate result given by Equation 19 and give as a final result

\[
dx^6 = \pi^2 \, u \, (s^2 - t^2) \, du \, ds \, dt (20)\]

where

\[-u \leq t \leq u, \quad 0 \leq u \leq s < \infty.\]
Figure 4. Coordinate system used for integration
The expressions for $1/r_{12}^2$, the Legendre polynomials, and the necessary orthogonality relations are given by Jackson (23). These are

$$\frac{1}{r_{12}^2} = \frac{1}{r_>^2} \sum_{n=0}^{\infty} \left( \frac{r_<}{r_>^n} \right)^n P_n(\cos \theta_{12})$$

(21)

where

$$P_0(\cos \theta_{12}) = 1 \quad P_1(\cos \theta_{12}) = \cos \theta_{12}$$

(22)

and

$$\int_0^\pi P_n'(\cos \theta_{12}) P_n(\cos \theta_{12}) \sin \theta_{12} d\theta_{12} = \frac{2}{2n+1} \delta_{n,n}. \quad (23)$$

Here $r_>$ is the larger of $r_1$ and $r_2$, and $r_<$ is the smaller of $r_1$ and $r_2$. Only the values $n=0,1$ entered into the calculation. Williamson (58) gives the following expansion for $r_{12}^2$

$$r_{12}^2 = r_> \sum_{n=0}^{\infty} \left[ \left( \frac{1}{2n+3} \right) \left( \frac{r_<}{r_>^n} \right)^2 - \left( \frac{1}{2n-1} \right) P_n(\cos \theta_{12}) \left( \frac{r_<}{r_>^n} \right)^n \right]$$

(24)

This relation, as shown in Appendix A, can be obtained by assuming it to be of the form

$$r_{12}^2 = r_> \sum_{n=0}^{\infty} a_n \left( \frac{r_<}{r_>^n} \right)^n$$

differentiating this form with respect to $\cos \theta_{12}$, and making a term-by-term comparison with Equation 21. For terms containing factors like $r_{12}^2$ the law of cosines,

$$r_{12}^2 = r_1^2 + r_2^2 - 2 r_1 r_2 \cos \theta_{12}$$

(25)

is used.

With the aid of these formulas Equation 9 can be written for the $F'$ center. First the normalization constant given by Equation 13 will be
calculated and then the terms in Equation 17 will be treated one at a time, starting with the square well portion of the potential.

Normalization constant We follow Bethe and Salpeter (4) and write \( N \) from Equation 13 using Equations 12 and 20 to get

\[
N = \pi^2 \int_0^\infty ds \int_0^u du \int_0^{-u} dt \, u(s^2-t^2)e^{-as}(1 + \beta u + \gamma t^2)^2.
\]

The integrand is an even function of \( t \), so we can write

\[
N = 2\pi^2 \int_0^\infty ds \int_0^u du \int_0^{-u} dt \, u(s^2-t^2)e^{-as}(1 + \beta u + \gamma t^2)^2.
\]

Integration yields

\[
N = 2\pi^2 \left( \frac{32}{a^6} + \frac{768}{a^8} + \frac{4608}{a^{10}} + \frac{384}{a^8} + \frac{280}{a^7} + \frac{2464}{a^9} \right). \tag{26}
\]

Square well potential Using Table 4 and Equations 19 and 17, Equation 9 is written as

\[
V_{\text{sq well}} = 8\pi^2 \left[ \int_0^R dr_1 \int_0^R dr_2 \int_0^\pi d\theta_{12} \, r_1^2 r_2^2 \sin \theta_{12} \, \psi(V_1+V_2) \psi
\]

\[
+ \int_0^R dr_1 \int_0^\infty dr_2 \int_0^\pi d\theta_{12} \, r_1^2 r_2^2 \sin \theta_{12} \, \psi(V_1+\omega_{\text{opt}}) \psi
\]

\[
+ \int_0^\infty dr_1 \int_0^R dr_2 \int_0^\pi d\theta_{12} \, r_1^2 r_2^2 \sin \theta_{12} \, \psi(V_2+\omega_{\text{opt}}) \psi
\]

\[
+ \int_0^\infty dr_1 \int_0^\infty dr_2 \int_0^\pi d\theta_{12} \, r_1^2 r_2^2 \sin \theta_{12} \, \psi(0+0) \psi
\]

where

\[
V_1 = V_2 = -\frac{\alpha}{a} + \omega_{\text{ion}} + \chi
\]

and
\[ W_{\text{opt}} = \left(1 - \frac{1}{k_0}\right) \frac{1}{2R}. \]

The F' center wave function, \( \psi(r_1, r_2, \theta_{12}) \), in this equation and in the ones to follow is given by Equation 12. Combining terms yields

\[ V_{\text{sq well}} = 8\pi^2 [2V_1 \int_0^R \int_0^{\pi} r_1 r_2 \sin \theta_{12} |\psi|^2 \]

\[ + 2(V_1 + W_{\text{opt}}) \int_0^R \int_0^{\pi} r_1 r_2 \sin \theta_{12} |\psi|^2] \]

since \( \psi(r_1, r_2, \theta_{12}) \) as given by Equation 12 is symmetric in \( r_1 \) and \( r_2 \). It should be pointed out that in this integral and in the ones to follow that the operators are functions of only \( r_1 \), \( r_2 \), and \( \theta_{12} \). That is, none of the variables previously integrated over appear in any terms of the Hamiltonian. The first integral was not directly calculated, but the integral

\[ \int_0^R \int_0^{\pi} r_1 r_2 \sin \theta_{12} |\psi|^2 \]

was done instead. The second integral was then done and subtracted from Equation 27 to yield the first integral. Equation 27 proved useful in calculating the kinetic energy term and in describing polarization effects. These integrals were done in the following manner. For each term in the integrals the integration on \( \theta_{12} \) was done first with the help of Equations 22, 23, and 24. The remaining integrals were then of the form (5, #305)

\[ \int x^n e^{-ax} dx = -\frac{a^{-ax}}{a+n+1} [(ax)^n + n(ax)^{n-1} + n(n-1)(ax)^{n-2} + \cdots + n!] \]

where \( n \) is a positive integer. The results of this integration appear, highly disguised however, in the FORTRAN program listed in Appendix B.

Coulomb potential Using Equations 19 and 17 again, we write
Equation 9 for this term as

\[
V_{\text{coul}} = 8\pi^2 \int_0^\infty \int_0^\infty \int_0^\pi \frac{r_1 r_2}{r_{12}} \sin \theta_{12} \sin \theta_1 \sin \theta_2 \left( 2 \sum_{i=1}^{2} \psi_i \frac{1}{K_{\text{eff}} r_1^2} \left( r_i r_2^2 \right) \right)
\]

which becomes

\[
V_{\text{coul}} = -\frac{16\pi^2}{K_{\text{eff}}} \int_{r_1}^{R} \int_0^\pi \int_0^\pi \frac{r_1 r_2}{r_{12}} \sin \theta_{12} \sin \theta_1 \sin \theta_2 \psi^2
\]

since again \(\psi(r_1, r_2, \theta_{12})\) is symmetric in \(r_1\) and \(r_2\). This integral was done in the same manner as that of Equation 27. The result of this integration also appears in the FORTRAN program of Appendix B.

**Correlation potential.** Writing from Equations 19, 17, and 9 yields

\[
V_{\text{corr}} = 8\pi^2 \int_0^\infty \int_0^R \int_0^\pi \frac{r_1 r_2}{r_{12}} \sin \theta_{12} \sin \theta_1 \sin \theta_2 \psi \frac{1}{K r_{12}} \psi
\]

where \(K^* = 1\) or \(K_0\), depending on the region of integration. Inside the well \(K^* = 1\), and outside the well \(K^* = K_0\) since only the electronic polarization can follow the instantaneous motion of the two electrons. This integral is considered to be the mutual electrostatic potential between two overlapping charge distributions. The correct \(K^*\) for each region of integration is found by considering two cases: 1) the potential of electron 2 due to that portion of electron 1 which is in the potential well, and 2) the potential of electron 2 due to that portion of electron 1 which is outside the potential well. Using Gauss' law the above integral becomes

\[
V_{\text{corr}} = \frac{8\pi^2}{K_0} \int_0^R \int_0^\pi \int_0^\pi \frac{r_1 r_2}{r_{12}} \sin \theta_{12} \frac{r_1^2 r_2^2}{r_{12}^2} \psi^2
\]
where Equations 30 and 31 come from case 1 and Equations 32 and 33 from case 2. Only the integral in Equation 31 needs to be done since the integrals in Equations 30, 32, and 33 can be obtained by subtracting the integral in Equation 31 from the integral over all space which is readily obtained using Hylleraas coordinates. This integral is

\[ 2\pi^2 \int_0^\infty ds \int_0^\infty du \int_0^\infty dt (s^2-t^2)e^{-as}(1+\beta u + \gamma t^2)^2 . \]  

(34)

Again these terms appear in Appendix B.

**Kinetic energy** For this term the variational equation yields

\[ T = 8\pi^2 \int_0^\infty dr_2 \int_0^\infty dr_1 \int_0^\pi d\theta_{12} \sin \theta_{12} \frac{r_2^2}{r_1^2} \left[ -\frac{1}{2} \frac{V_i^2}{(r_i < R)} \right] \psi \]  

\[ + \sum_{i=1}^\infty \frac{1}{2m} \left[ \psi_i \left( \frac{1}{r_i} \right) \right] \psi \]  

(35)

This integral was done by using Green's theorem to convert the \( V_i^2 \) operators to \( (\nabla_i \psi)^2 \) operators. The standard 3-dimensional Green's theorem is

\[ \int \psi \frac{V_i^2}{V_i} \psi_i \, dv_i = \int \psi \nabla_i \psi \cdot \hat{n} \, da_i - \int |\nabla_i \psi|^2 \, dv_i \]  

(36)

where \( s_i \) is the surface enclosing volume \( v_i \), and \( \hat{n} \) is the outward normal
vector from volume \( v_1 \). Here it is required that \( \psi \), its first derivative, and its second derivative be continuous. For this problem we performed a second volume integration over Equation 36 to get

\[
\int_{v_i} \int_{v_j} \psi \frac{\partial^2 \psi}{\partial x^2} \text{d}v_i \text{d}v_j = \int_{v_i} \int_{v_j} \frac{\partial}{\partial x} \frac{\partial^2 \psi}{\partial x^2} \text{d}v_i \text{d}v_j - \int_{v_i} \int_{v_j} \left| \frac{\partial}{\partial x} \right| \psi \text{d}v_i \text{d}v_j. \tag{37}
\]

where \( i,j = 1,2; i \neq j \). The required differential elements can be written from Equation 19 as

\[
\text{d}v_i \text{d}v_j = dx^6 = 8\pi^2 \sin \theta_{ij} \text{d}q_{ij} r_1^2 \text{d}r_1 r_2^2 \text{d}r_2 \tag{38}
\]

and

\[
\text{d}a_i \text{d}v_j = dx^5 = 8\pi^2 \sin \theta_{ij} \text{d}q_{ij} R^2 r_j^2 \text{d}r_j \tag{38}
\]

where \( R \) is the well radius, and \( i \) and \( j \) are the same as in Equation 37.

Using Equations 37 and 38, Equation 35 becomes

\[
T = 4\pi^2 \left[ \int_0^\infty \int_0^{R} \int_0^{\pi} \int_0^{\pi} \int_0^{R} \int_0^{R} \right. \sin \theta_{12} r_1^2 r_2^2 \left| \frac{\partial}{\partial x} \psi \right|^2 \\
- \int_0^\infty \int_0^{R} \int_0^{\pi} \int_0^{\pi} \int_0^{R} \int_0^{R} \sin \theta_{12} \psi \frac{\partial^2 \psi}{\partial x^2} \left| \frac{\partial}{\partial x} \psi \right| \\
+ \int_0^\infty \int_0^{R} \int_0^{\pi} \int_0^{\pi} \int_0^{R} \int_0^{R} \sin \theta_{12} R^2 r_1^2 r_2^2 \left| \frac{\partial}{\partial x} \psi \right|^2 \\
- \int_0^\infty \int_0^{R} \int_0^{\pi} \int_0^{\pi} \int_0^{R} \int_0^{R} \sin \theta_{12} R^2 r_1^2 \psi \frac{\partial}{\partial x} \psi \frac{\partial}{\partial x} \frac{\partial}{\partial x} \psi \right]_{r_1=R} \\
+ \frac{1}{m} \int_0^\infty \int_0^{R} \int_0^{\pi} \int_0^{\pi} \int_0^{R} \int_0^{R} \sin \theta_{12} r_1^2 r_2^2 \left| \frac{\partial}{\partial x} \psi \right|^2 \\
- \frac{1}{m} \int_0^\infty \int_0^{R} \int_0^{\pi} \int_0^{\pi} \int_0^{R} \int_0^{R} \sin \theta_{12} R^2 r_1^2 \psi \frac{\partial}{\partial x} \psi \frac{\partial}{\partial x} \psi \right| \left| \frac{\partial}{\partial x} \psi \right|_{r_1=R}.
where \( \hat{r}_1 \) and \( \hat{r}_2 \) are radial unit vectors outward from the origin. The quantities

\[
|\hat{\psi}_1|^2, \quad |\hat{\psi}_2|^2, \quad \psi \hat{\psi}_1 \hat{r}_1, \text{ and } \psi \hat{\psi}_2 \hat{r}_2.
\]

are worked out in detail in Appendix C. It should be noted that these expressions are also functions of only \( \theta_{12}, r_1, \) and \( r_2, \) hence it is still valid to use the differential elements given in Equation 38. We also note that

\[
|\hat{\psi}_1|^2 + |\hat{\psi}_2|^2 \quad \text{if} \quad r_1 \neq r_2
\]

and

\[
\psi \hat{\psi}_1 \hat{r}_1 \neq \psi \hat{\psi}_2 \hat{r}_2 \quad \text{if} \quad r_1 \neq r_2
\]

Because of these symmetries in the operators, Equation 39 can be simplified to

\[
T = 4\pi \frac{1}{m} \int \int \int \sin \theta_{12} \frac{\partial}{\partial \theta_{12}} \frac{\partial}{\partial \theta_{12}} \sin \theta_{12} \left( |\hat{\psi}_1|^2 + |\hat{\psi}_2|^2 \right)
\]

\[
+ \frac{1}{m} \int \int \int \sin \theta_{12} \left( |\hat{\psi}_1|^2 + |\hat{\psi}_2|^2 \right)
\]

\[
+ (1 - \frac{1}{m}) \int \int \int \sin \theta_{12} \left( |\hat{\psi}_1|^2 - |\hat{\psi}_2|^2 \right)
\]

\[
- 2(1 - \frac{1}{m}) \int \int \int \sin \theta_{12} R^2 \frac{\partial}{\partial \theta_{12}} \frac{\partial}{\partial \theta_{12}} \psi \hat{\psi}_1 \hat{r}_1 \hat{r}_2 \left| \frac{r_1}{r_2} \right| \quad .\]

(40)
This equation was evaluated by calculating directly the first integral and subtracting this expression from the integral over all space to obtain the second integral. The third and fourth integrals also were calculated directly. The operator

\[ |\vec{V}_1\psi|^2 + |\vec{V}_2\psi|^2 \]

can be readily found in Hylleraas coordinates (33), and when integrated over all space yields

\[ T_m^* = \frac{N}{8\pi^2} a^2 + 768 \frac{Y^2}{8} + 32 \frac{E^2}{a^6} - 20 \frac{E}{a^5} - 96 \frac{E^2}{a^6} - 32 \frac{EY}{a^7}, \]

where \( N \) is the normalization constant given by Equation 26. This term also appears in the FORTRAN program of Appendix B.

The above results can be summarized by writing the total energy as a function of the variational parameters \( \alpha, \beta, \) and \( \gamma \) as below

\[ E(\alpha, \beta, \gamma) = \frac{V_{\text{so well}} + V_{\text{coul}} + V_{\text{corr}} + T}{N}. \]

The minimization of \( E \) was then done using a computer program.

Absorption Coefficient Calculation

In this section the formula for the cross section for optical absorption by an atomic system will be developed. The optical absorption for the \( F' \) center will be found where the initial state is described by Equation 12, and where the final state consists of one bound and one free electron. In this section cgs units will be used.

Time dependent perturbation theory and absorption cross section

We consider a group of identical atomic systems (\( F' \) centers) which
38

are being disturbed by the harmonic perturbation

\[ \hat{E}(\mathbf{r}_1, t) = \hat{e} E_0 \cos(k' \mathbf{r}_1 - \omega t), \quad (41) \]

where \( \hat{e} \) is a unit vector in the direction of the polarization. For the present this derivation will be confined to the case of a group of atomic systems in a vacuum. At the end corrections will be made for a dielectric medium. The derivation here is based on the "golden rule #2" for a harmonic perturbation as given by Powell and Crasemann (43). The probability per unit time for a transition between the initial state I and the final state F of a system is given by

\[ \omega_{FI} = \frac{2\pi}{\hbar} |V_{FI}^+|^2 \rho(E_F) \quad (42) \]

evaluated at

\[ E_F = \hbar \omega + E_I \]

where

\[ V_{FI}^+ = (\psi_F, V^+ \psi_I) \quad (43) \]

is the matrix element between the final and initial state, and \( \rho(E_F) \) is the density of final states. To find the operator \( V^+ \) in Equation 43, the Hamiltonian for two particles in interaction with an electromagnetic field is examined. The Hamiltonian is

\[ H = \sum_{i=1}^{2} \left[ \frac{1}{2m_i} \left( \hat{p}_i^2 - \frac{e_i}{c} \hat{A}_i \right)^2 + e_i \phi_i \right] \quad (44) \]

where \( \hat{A}_i \) and \( \phi_i \) are the vector and scalar potentials describing the incident radiation. The potentials for the perturbation given by Equation 41 are
\[ \tilde{h}(\tilde{r}, t) = \tilde{e} \frac{e}{k} \sin(k \cdot \tilde{r} - \omega t) \]  
(45)

and
\[ \phi(\tilde{r}, t) = 0 \]

where
\[ \tilde{E} = -\nabla \psi - \frac{1}{c} \frac{\partial \tilde{A}}{\partial t} . \]

Multiplying out Equation 44 and keeping only first order terms in \( \tilde{A} \) yields for the perturbation
\[ E'(t) = -\frac{e}{2mc} \sum_{i=1}^{2} (\hat{p}_1 \cdot \tilde{A}_i + \tilde{A}_i \cdot \hat{p}_1) \]

\[ = -\frac{e}{mc} \sum_{i=1}^{2} \tilde{A}(\tilde{r}_i, t) \cdot \hat{p}_1 \]

since
\[ \tilde{k} \cdot \hat{e} = 0 . \]

Now the total perturbation can be written as
\[ E'(t) = V^+ e^{-i\omega t} + V e^{i\omega t} \]

where \( V^+ \) is the operator corresponding to absorption of a photon, and \( V \) is the operator corresponding to emission of a photon. Evaluating \( V^+ \) yields
\[ V^+ = \frac{ek}{2m\omega} E_o \sum_{i=1}^{2} e^{ik \cdot \tilde{r}_i} \hat{e} \cdot \hat{\tilde{r}}_i . \]

For wavelengths on the order of visible light the dipole approximation,
\[ e^{ik \cdot \tilde{r}} = 1 , \]

can be made and
The matrix element is
\[ \gamma^+_{FI} = \frac{e^2}{2\hbar} E_0 \hat{e} \cdot \sum_{i=1}^{2} \hat{v}_i. \]

For this problem the density of final states is that for a free electron.

If the free electron or plane wave wave function is normalized to one particle in a cubical box of volume \( L^3 \) it is written as
\[ \phi_{k_e} = \frac{1}{\sqrt{L^3}} e^{i \hat{k}_e \cdot \vec{r}} \]

where \( \hat{k}_e \) is the electron wave vector. The density of final states is then
\[ \rho(E) = \frac{mk_e L^3}{\hbar^2 (2\pi)^3} d\Omega \quad (4.7) \]

where \( \rho(E)d\Omega \) is the number of electrons with energy between \( E \) and \( E + dE \) traveling out in solid angle \( d\Omega \). Spin has been neglected in both \( \phi_{k_e} \) and \( \rho(E) \).

The differential cross section, \( \sigma(\theta) \), is defined as
\[ Probability \ per \ unit \ time \ for \ transition \ from \ I \ to \ F \ \left( \frac{\#}{sec} \right) \]
\[ \sigma(\theta)d\Omega(\text{cm}^2) = \frac{\text{with outgoing electron emitted into } d\Omega \text{ at angle } \theta}{\text{Incident photon flux } (\#/\text{cm}^2 \text{ sec})} \quad (4.8) \]

where \( \theta \) is measured with respect to \( \hat{k} \). To calculate the photon flux the average value of the Poynting vector is found:
\[ \langle \vec{S} \rangle = \frac{c}{4\pi} \langle \vec{E} \times \vec{B} \rangle \]

where
\[ \vec{B} = \vec{V} \times \vec{A} = \hat{k} \times \vec{E}. \]
Using Equation 41 yields
\[ <\mathbf{S}> = \frac{c}{4\pi} E_o^2 \]
where we have multiplied by two to account for two independent polarizations. The incident photon flux becomes

\[ \text{Incident photon flux (#/cm}^2 \text{sec)} = \]

\[ \frac{\text{Incident energy/unit area unit time (ergs/cm}^2 \text{sec)}}{\text{Energy/photon (ergs/#)}} \]

\[ = \frac{c}{4\pi} \frac{E_o^2}{2\omega} . \]

Substituting into Equation 48 yields
\[ \sigma(\theta) \, d\Omega = \frac{\omega_F}{\text{Incident photon flux}} \]

\[ = \frac{e^2}{4\pi mc^2k} |\hat{e} \cdot (\psi_F, \sum_{i=1}^{2} \hat{\psi}_i)|^2 k_e L^2 \, d\Omega \]

Since \( \psi_i \) is a bound state we may integrate by parts to get
\[ \sigma(\theta) \, d\Omega = \frac{e^2}{4\pi mc^2k} \left| \hat{e} \cdot (\psi_I, \sum_{i=1}^{2} \hat{\psi}_i) \right|^2 k_e L^2 \, d\Omega \quad \text{(49)} \]

To get the total cross section, the two independent polarization directions must be summed over, and \( \hat{k}_e \) must be integrated over \( d\Omega \). The two independent polarizations can be represented by the unit vectors \( \hat{e}_1 \) and \( \hat{e}_2 \) where \( \hat{e}_1, \hat{e}_2, \) and \( \hat{k} \) form an orthogonal triplet. Let
\[ \mathbf{\hat{D}} = (\psi_I, \sum_{i=1}^{2} \hat{\psi}_i) \quad \text{(50)} \]

and write
\[ \sum_{i=1}^{2} |\hat{e}_i \cdot \mathbf{\hat{D}}|^2 = |\hat{e}_1 \cdot \mathbf{\hat{D}}|^2 + |\hat{e}_2 \cdot \mathbf{\hat{D}}|^2 = |\mathbf{\hat{D}}|^2 - |\hat{k} \cdot \mathbf{\hat{D}}|^2 . \]
If the bound part of the final state is an s state, \( \hat{D} \) will "point" along the direction of \( \hat{k}_e \) since the bound initial and final states will be symmetrical about \( \hat{k}_e \). Therefore, the angle between \( \hat{k} \) and \( \hat{D} \) is also the scattering angle, and we may integrate over \( \theta \). Integration yields:

\[
\sigma = \int \sum_\Omega \text{ polarizations} \ |\hat{e} \cdot \hat{D}|^2 \, d\Omega = |\hat{D}|^2 \int (1 - \cos^2 \theta) \, d\Omega = \frac{2\pi}{3} |\hat{D}|^2.
\]

Finally Equation 49 becomes

\[
\sigma_{\text{vacuum}} = \frac{2e^2}{3mc^2k} \left| \langle \psi_i, \sum_\mathbf{\mathbf{v}_i} \psi_f \rangle \right|^2 k e L^3
\]

where \( \sigma_{\text{vacuum}} \) indicates that this equation has been derived for absorbing centers in a vacuum.

Final state wave function and evaluation of matrix element

The final state of the F' center after absorption of a photon consists, as said before, of one bound and one free electron. Since \( \hat{v}_1 \) operates only on the space coordinates of the final state wave function, the spins must remain unchanged. Thus the final state wave function is also symmetric in its space coordinates and is written as

\[
\psi_f(\vec{r}_1, \vec{r}_2) = \frac{1}{\sqrt{2L^3}} \left[ \phi_{n\ell m}(\vec{r}_1)e^{i\vec{k} \cdot \vec{r}_2} + \phi_{n\ell m}(\vec{r}_2)e^{i\vec{k} \cdot \vec{r}_1} \right].
\]

For our calculation we chose \( \psi_f(\vec{r}_1, \vec{r}_2) \) to be

\[
\psi_f(\vec{r}_1, \vec{r}_2) = \frac{1}{\sqrt{2L^3}} \left[ \phi_{1s}(\vec{r}_1)e^{ikz_2} + \phi_{1s}(\vec{r}_2)e^{ikz_1} \right]
\]

where \( \phi_{1s}(\vec{r}) \) is the F center wave function as given by Fowler, and the free electron is assumed to move out along the z axis. Using Equation 12 for the initial state, Equation 50 for the momentum dipole matrix
\[ \mathbf{D} = \frac{k}{2} \int \int e^{-\frac{\alpha}{2}(r_1^2 + r_2^2)} \left[ 1 + \beta r_{12} + \gamma (r_1 - r_2)^2 \right] \times \]
\[ \frac{2}{3} \sum_{i=1}^{\frac{3}{2}} \left[ \phi_{1s}(\mathbf{r}_1) e^{i k \mathbf{z}_2} + \phi_{1s}(\mathbf{r}_2) e^{i k \mathbf{z}_1} \right] \, d\mathbf{v}_1 \, d\mathbf{v}_2 \] (53)
where the \( \hat{i} \) and \( \hat{j} \) components vanish because of axial symmetry about \( \hat{k}_e \).

This integral may be done in a straightforward but tedious manner if the usual expansion of the plane wave is done (58). The required expansion is

\[ e^{i k z} = \sum_{n=0}^{\infty} (2n+1) i^n P_n(\cos \theta) \sqrt{\frac{n}{2 k r}} J_{n+\frac{1}{2}}(k r) \]
where \( J_{n+\frac{1}{2}}(k r) \) are the Bessel functions of half integer order. The required \( J_{n+\frac{1}{2}}(k r) \) are tabulated by Jackson (23). The other formulas needed to do this integration have been previously given in the section on the variational calculation. For this integral \( d\mathbf{v}_1 \) and \( d\mathbf{v}_2 \) must be integrated over explicitly, and the \( P_n(\cos \theta_{12}) \) which appears due to the \( r_{12} \) factor in the initial state wave function must be written using the addition formula for the spherical harmonics. The required form is (23)

\[ P_n(\cos \theta_{12}) = P_n(\cos \theta_1) P_n(\cos \theta_2) \]
\[ + 2 \sum_{m=1}^{n} \frac{(n-m)!}{(n+m)!} P_m^m(\cos \theta_1) P_n(\cos \theta_2) \cos[m(\phi_1 - \phi_2)] \]

where \( P_m^m(\cos \theta) \) are the associated Legendre functions. Since

\[ \psi_{1s}(\mathbf{r}_1, \mathbf{r}_2) = \psi_{1s}(\mathbf{r}_2, \mathbf{r}_1) \]
the integral can be done by multiplying it by two and using only half of the symmetrical wave function given by Equation 52. Here the selection
rule for dipole transitions, $\Delta \lambda = \pm 1$, says that the outgoing plane wave will have only a $p$-wave component. That is, in the expansion for the plane wave only the $n = 1$ term will come into the calculation.

Connection between cross section and measurable quantities

Experimentally the optical density of a sample is measured. The relation between $\sigma$ and the optical density is found as follows. Let the sample have an area $A$, a thickness $dx$, and contain $N$ absorbing centers per unit volume. Let the incident beam intensity falling perpendicularly on $A$ be $I$. We now make the fundamental assumption that for a thin sample of thickness $dx$ the fractional change in $I$, $-dI/I$, is equal to the ratio of the effective area of the absorbing centers to the total area $A$. That is,

$$\frac{dI}{I} = -\frac{\sigma N A}{A} dx = -\sigma N dx$$

(54)

If we assume that the photons do not change energy as they move through the sample, $\sigma$ will be independent of $x$, and Equation 54 may be integrated to get

$$I = I_0 e^{-N \sigma x}$$

where $I_0$ is the intensity of the incident beam, and $x$ is the total thickness of the sample. The absorption coefficient is defined as

$$\alpha = N \sigma$$

The optical density is defined as

$$\text{Optical density} = -\log_{10} \frac{I}{I_0} = \frac{N \sigma x}{2.303}$$

(55)

Equation 55 was the fundamental equation for comparing our calculated and experimental values for the F' absorption.
To find the dependence of \( \sigma \) on wavelength we consider conservation of energy and write

\[
\varepsilon_0 c k = W + \frac{h^2 k^2}{2m}
\]  

(56)

where \( W \) is the electron affinity of the F center, and \( k \) and \( k_e \) are the magnitudes of the incident photon and emitted electron wave vectors respectively. To evaluate \( \sigma \) easily it is best to write it as a function of \( k_e \) only, since \( |\mathbf{D}|^2 \) is a function of \( k_e \) only. If Equation 56 is solved for \( k \) and substituted into Equation 51 for the cross section leaving \( \sigma_{\text{vacuum}} \) in cgs units, but writing everything else in atomic units, the result is

\[
\sigma_{\text{vacuum}} = 2.71 \times 10^{-19} \frac{k_e}{(k_e^2 + 2W)} |\mathbf{D}|^2 \text{ cm}^2
\]

(57)

where \( k_e \) and \( W \) are in atomic units, and \( |\mathbf{D}|^2 \) is to be evaluated in atomic units. This formula agrees with that given by Chandrasekhar (6). The relation between \( k_e \) and the energy of the photon, \( E \), needed to produce it can be obtained from Equation 56 and is

\[
E = 13.6(k_e^2 + 2W) \text{ eV}
\]

(58)

where \( E \) is in eV and \( k_e \) and \( W \) are in atomic units.

As stated previously, the absorption cross section (\( \sigma_{\text{vacuum}} \)) must be corrected for a dielectric medium. Two corrections must be distinguished. The first is the local field correction which gives the local electric field the center sees in terms of the electric field in the dielectric. Dexter (12) discusses this correction and states the following result for localized centers in crystals of cubic symmetry.
\[
\frac{E_{\text{eff}}}{E_0} = \frac{n^2 + 2}{3}
\]

This is the Lorentz-Lorenz local field ratio and takes into account dipole-dipole interactions between the medium and the defect. It is nicely described by Panofsky and Phillips (37). The second correction involves renormalization of the incident photon flux. For a dielectric medium the average value of the Poynting vector for two polarizations is (23)

\[
\langle S \rangle = n \frac{c}{4\pi} |E_0|^2
\]

where \( n \) is the index of refraction of the dielectric, and

\[
n^2 = k_0.
\]

Combining these corrections yields

\[
\sigma_{\text{dielectric}} = \frac{(n^2 + 2)^2}{9n} \sigma_{\text{vacuum}}.
\]

A FORTRAN program was used to evaluate Equation 57 and plot the corrected absorption constant versus energy for \( N \) normalized to \( 10^{16} \) F' centers per cm\(^3\). Using Equation 55 our data were renormalized to \( N = 10^{16} \) F' centers per cm\(^3\) and plotted on the absorption versus energy computer plots. These plots appear in Figures 6 through 13.

Selection of Physical Parameters

The various physical parameters selected for the model are discussed below. Fowler (17) discusses previous data regarding band effective masses for the alkali halides and concludes that \( m^* = 0.6m_e \) is a reasonable choice for NaCl. Here \( m_e \) is the free electron mass. More recent data due to Mikkor et al. (32), obtained by a cyclotron resonance technique, list
a value of $m^* = 0.55m_e$ for KBr. In our calculation we chose $m^* = 0.6m_e$ for all the salts calculated. For comparison purposes we also used $m^* = m_e$.

The well radius was chosen to be 90% of the nearest neighbor distance mainly because it seemed reasonable. Fowler (17) discusses the nearest neighbor ion movement for the case of the F center in NaCl. He concludes that 10% outward motion of the nearest neighbors between the ground and relaxed excited state configuration of the center is reasonable. From our calculation about 50-60% of the electron distribution is inside the vacancy such that the effective positive charge of the vacancy is more than compensated for. Also, since the negative ion is missing the repulsive potential on the nearest neighbors is missing. Hence it is felt that a 10% inward movement of the nearest neighbors is not unrealistic. It should be said that the full value of the nearest neighbor distance was still used to calculate the Madelung potential, however.

The values of $\chi$, the electron affinity, were taken from Eby et al. (15) and Mott and Gurney (34). They are shown in Table 6. It should be noted that the values quoted by Eby et al. are obtained from photoelectric data taken at 300°K and optical absorption data taken at 80°K. Because of this, 0.2 eV was added to each of Eby et al. values as a rough correction. This was done, since the optical absorption edge corresponding to interband transitions shifts by about 0.2 eV between 80 and 300°K. These values appear in Table 6.

The values for the optical dielectric constant, $k_o$; the static dielectric constant, $k$; and the nearest neighbor distance, $a$; were taken
Table 6. Values of the electron affinity

<table>
<thead>
<tr>
<th>Salt</th>
<th>$x$(eV)</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiF</td>
<td>0.1</td>
<td>-a</td>
</tr>
<tr>
<td>NaF</td>
<td>0.1</td>
<td>-a</td>
</tr>
<tr>
<td>NaCl</td>
<td>0.1</td>
<td>-b</td>
</tr>
<tr>
<td>KCl</td>
<td>0.4</td>
<td>-b</td>
</tr>
<tr>
<td>KBr</td>
<td>0.5</td>
<td>-b</td>
</tr>
<tr>
<td>KI</td>
<td>1.3</td>
<td>-b</td>
</tr>
<tr>
<td>RbCl</td>
<td>0.4</td>
<td>-c</td>
</tr>
<tr>
<td>RbI</td>
<td>1.4</td>
<td>-b</td>
</tr>
<tr>
<td>CsBr</td>
<td>0.1</td>
<td>-d</td>
</tr>
<tr>
<td>CsI</td>
<td>0.3</td>
<td>-b</td>
</tr>
</tbody>
</table>

*a* None-estimated value only  
*b* Eby, Teegarden, and Dutton (15)  
*c* Mott and Gurney (34)  
*d* Extrapolated from Eby et al. with the use of Taft and Philipp (55).

from the review by Schulman and Compton (48). The values of $n$ required for Equation 59 and Smakula's equation were obtained from the "state-of-the-art" report on optical materials for infrared instrumentation (3).

Computer Calculations

A single program was used to find the minimum in the variational energy for the $F$ and $F'$ center problems. These values were then used to calculate the $F'$ binding energy using the following relation

$$ E_{\text{binding}} = E_F - E_{F'} $$

The program was written to solve the variational problem using two methods as discussed below. The first was an a priori calculation of $E_{\text{binding}}$. To do this the charge-distribution-dependent well parameters as listed in Table 4 were determined in a self consistent fashion. The well
parameters of Table 4 are all easy to solve for in a self consistent fashion, except for $K'_\text{eff}$ which is the distance-dependent effective dielectric constant. From the knowledge of the electron distribution function, as shown in Figure 15, it was known that outside the well the electrons spent most of their time at the well edge. In Figure 15 the well radii are given by the tick marks on the curves. Since it seems important that the majority of the electron distribution outside the well sees the correct $K'_\text{eff}$, we let $K'_\text{eff}$ be a constant and evaluated it at $r = R$, the well radius. With these simplifying assumptions the self consistent variational problem could be readily solved. Therefore, for both $W_\text{ion}$ and $K'_\text{eff}$ the following integral was needed

$$\int_0^\infty \frac{a(r)}{r^2} \, dr \quad .$$

This integral was readily evaluated by integrating over the result of the integration given in Equation 27 to get

$$\int_0^\infty \frac{p(r)}{r^2} \, dr \quad .$$

Equation 60 was then obtained from Equation 61 by using the relation $p(r) + q(r) = 1$. Initially the parameters were set as below

$$K'_\text{eff} = k_0$$

$$W_\text{ion} = 0 \quad .$$

The variational energy was then minimized for this well, and $K'_\text{eff}$ and $W_\text{ion}$ solved for using the calculated wave function. These values were then used for the second iteration, and new $K'_\text{eff}$ and $W_\text{ion}$ were again calculated, and so forth. Self consistency could be readily obtained;
and, after five iterations, the greatest error in $W_{\text{ion}}$ in any particular salt was less than 0.25%. The errors in the $K'_{\text{eff}}$'s were even less than this value.

The second part of the variational program adjusted the value of the integral in Equation 60 to force agreement between the experimental and calculated values of the $F'$ binding energies. This part of the program was used to calculate the wave function parameters which were used in calculating the absorption coefficients for the various salts.

Finally, a program was written to calculate the one-electron radial distribution function. Using Equation 19 the one-electron radial distribution function $|\psi(r)|^2 4\pi r^2$ was written as

$$|\psi(r)|^2 4\pi r^2 = \frac{8\pi^2}{N} r^2 \int_0^\infty \int_0^\pi \rho^2 \sin \theta \rho \frac{d\theta}{\rho} |\psi(r,\rho)|^2$$

where $\psi(r,\rho)$ and $N$ were written from Equations 12 and 13 respectively.

The following computer calculations were then done. The a priori or self-consistent calculation was done using $m^* = m_e$ and $0.6m_e$. The results of this calculation appear in Figure 14 and Table 8. The calculation to force a fit to the $F'$ binding energies was done using $m^* = m_e$ only, except for KI where $m^* = 0.6m_e$ and $0.45m_e$ were also used. The results of this calculation for $m^* = m_e$ are shown in Table 7. The wave functions obtained from this calculation were then used in the calculation of the absorption constants and the radial distribution functions.
EXPERIMENTAL PROCEDURE

In this section the apparatus and techniques used for producing and measuring the F' band spectra will be discussed.

Spectrophotometer

All spectral data were taken on a Cary model 14R recording spectrophotometer, which yielded optical density plots linear in wavelength. The machine was used in its standard configuration, except in the spectral region between 0.7 and 2.5μ. In its usual operating mode the source and detector are placed such that undispersed white light falls on the sample. Since the F' band that was being measured would be radically changed, if not completely destroyed, by the optical bleaching effect of the source light, the spectrophotometer was modified such that only dispersed radiation fell on the sample. This was done by operating the machine in the same mode as used from .6 to 1.7μ and replacing the standard PbS detector by a PbS detector without the infrared filter in front of it. Normally the warm parts of the spectrophotometer, in particular the chopper, emit black body radiation which, if undispersed, will produce errors in absorption measurements. Because of this the PbS detector is normally equipped with a long wavelength cut filter which will not pass radiation longer in wavelength than 1.7μ. However, if the optical densities to be measured are small, as ours were, then the chopper radiation is small compared to the radiation transmitted by the sample, and little error is introduced if the filter is left off the detector. This then allows the spectrophotometer to be used from 1.7 to 2.5μ with dispersed radiation falling on the sample. To make this modification a PbS detector without the
infrared filter was purchased from the manufacturer. In measuring an optical density of 1.2 using the detector without a filter an error of 3% was introduced. For our measurements the optical densities were in the range of 0 - 0.5, and this error would be 0.5% or less. In order to reduce mismatch between the spectra as measured with different detectors, the slit heights were set to their minimum value.

Optical Cryostat

An optical cryostat of standard design, as shown in Figure 5, was built for making measurements at liquid nitrogen temperature and above. The cryostat was equipped with a heater and could hold the sample, to within a few degrees, at any temperature between liquid nitrogen temperature and ice temperature. Design ideas for the heater were taken from the book by A. C. Rose-Innes (45). The sample was supported in a copper holder which was attached to the liquid nitrogen bath by way of a brass rod. The lower end of the brass rod was wound with a manganin wire heater coil which was held in place with G.E. 7031 varnish. The temperature of the copper sample holder was measured with a copper-constantan thermocouple. The cryostat windows were chosen to transmit from 0.2 to 2.6μ.

Sample Preparation

All alkali halides used were purchased from commercial suppliers. Crystals manufactured by the Harshaw Chemical Company, Optovac Inc., and the Karl Korth Laboratory were used. All samples prepared, except for NaF, were additively colored using the method of van Doorn (14). NaF was
Figure 5. Optical cryostat
colored by x ray ing. After coloring, the samples were cleaved (NaCl structure samples) or sawed and polished (CsCl structure samples) to proper size, then quenched from their coloring temperatures in the dark, and loaded into the cryostat under a safe light. All samples that were additively colored were colored with potassium, except for NaCl, which was colored with sodium.

Producing and Measuring the F' Spectra

The absorption spectra of the prepared samples were first measured at liquid nitrogen temperature to determine an absorption baseline and to measure the F band absorption. The samples were then optically bleached with F band light at a variety of temperatures to find the temperature at which maximum F to F' conversion occurred. All spectra were measured at liquid nitrogen temperature, therefore the sample was allowed to cool to this temperature after optical bleaching. During cooling it was very important that the sample be kept in the dark to keep the F' centers from optically bleaching, since the F and F' absorptions overlapped. Optical bleaching was done in the Cary spectrophotometer using a high intensity quartz iodine light source supplied by the manufacturer. During bleaching the high intensity source was set for its maximum output, and the slits and slit heights were open to their maximum positions. With the slits wide open (3mm), the typical band pass of the monochromator was on the order of 20% of the F band half-width. The samples were optically bleached between 30 and 45 minutes. When the temperature for maximum F to F' conversion had been found, detailed measurements were made to determine the shape of the F' absorption.
The above method for finding the temperature for maximum F to F' conversion was applied to all the salts except KBr, KCl, and NaCl, for which Pick's values as listed in Table 2 were accepted. In NaF the F' band was formed directly by X raying. By making measurements before and after bleaching it was possible to determine the F' band spectra. In all cases care was taken to use a high enough gain on the spectrophotometer detectors and a fast enough scanning speed such that the F' band would not be optically bleached during the measurement. Repeated measurements on KCl and NaCl reproduced the same band shape and size and indicated that no appreciable bleaching had taken place. Not all the crystals were checked for this effect. However, since KCl had to be bleached at the highest temperature, it would have had the greatest F' to F quantum yield at liquid nitrogen temperature and would have been most easily bleached by the measuring light. It was thus concluded that our absorption spectra represented true band shapes for the F' center. For a few salts the onset of absorption (absorption edge) occurred at wavelengths where there was absorption due to water, which obscured the edge. In these cases the spectrophotometer was flushed with dry nitrogen.

The F' band shapes were obtained by carefully subtracting the spectra after bleaching from the spectra before bleaching. To do this the F' band in the region of the F band was extrapolated, and a baseline was determined for the F band after bleaching. Having this, the ratio of the F band peak after bleaching to the F band peak before bleaching was found. Knowing this ratio a point-by-point subtraction was done where the size of the F band after absorption was determined by multiplying this ratio times the
F band before absorption. By subtracting the F band portion from the curve obtained after bleaching, the F' band could be obtained. Here a self consistent check could be made, since the subtraction should yield a smooth F' band in the region of the F band. If the initial baseline taken for the F band after bleaching was too high or too low, a new ratio was determined and the subtraction done again. In this way a smooth F' absorption curve was obtained.

Here it should be noted that our samples showed absorption due to K and L bands also. The K band is on the high energy side of the F band and is believed to be due to transitions from the ground state of the F center to higher excited states of the F center (51). The L bands lie to higher energies than the K band and have been measured by Lüty (29). They are believed to be due to transitions from the F center ground state to conduction band states (8,9). In subtracting to get the F' band the K band was treated the same as the F band. In each case where data were available the spectra were carefully checked for L bands (16,29). In all spectra checked, the L bands were found to be very small and were thus ignored in the subtraction process.

The number of F' centers was calculated using the assumption that the relation $2 \, F \rightarrow \, F'$ was strictly true. That is, there were no electron traps present other than F centers and vacancies. The number of F centers before and after bleaching was calculated using Smakula's equation, and the number of F' centers created calculated from the following relationship

$$N_{F'} = \frac{1}{2} \left( N_{F\text{ before}} - N_{F\text{ after}} \right)$$
where

\[ N_{F'} = \text{the number of } F' \text{ centers created} \]

\[ N_{F\text{ before}} = \text{the number of } F \text{ centers before optical bleaching} \]

\[ N_{F\text{ after}} = \text{the number of } F \text{ centers after optical bleaching} \]

For the salts not listed in Table 1 the oscillator strengths were all taken to be .80.
RESULTS AND DISCUSSION

In this section the experimental and calculated absorption curves and the results of the variational calculation for the $F'$ energies will be presented.

The calculated and experimental absorption curves are shown in Figures 6 through 13. The solid line represents the calculated absorption, and the circles are the experimental data. As stated before, the theoretical absorption curves were calculated using the wave functions from the variational problem where $m^* = m_e$, and where the ionic polarization was varied to achieve agreement with experiment. The plots were then made by setting the $F'$ ionization energy, $W$, in Equation 58 equal to the experimental value. Thus the calculated and experimental curves coincide at the absorption edge. This is self consistent within the idea that the potential well was chosen such that the calculated and experimental $F'$ energies would be equal. There is generally good agreement between the calculated and experimental absorptions concerning both the maximum value and the energy at which the maximum value occurs. It should be pointed out here that this good agreement has only involved fitting the absorption edge to the experimental value. The peak height and half-width of the band have not been adjusted in any manner. It should be noted that Figures 11, 12, and 13 have a different vertical scale than the other absorption plots.

One systematic feature is quite apparent, and this is the second absorption shoulder to the high energy side of the $F'$ band in each of the salts. One mechanism which can be proposed for this absorption is that
Figure 6. $F^*$ center absorption in NaCl
Figure 7. P' center absorption in KCl.
Figure 8. F⁺ center absorption in KBr
Figure 9. $F'_1$ center absorption in KI
Figure 10. $F'$ center absorption in RbCl
Figure 11. F' center absorption in RbI
Figure 12. F' center absorption in CsBr
Figure 13. F' center absorption in CsI
it corresponds to a final state of the ionized F' center consisting of a free electron and an F center in the first excited (2p) state. The excited state energy was calculated for the F center for each salt, and the absorption edge energies corresponding to this mechanism are shown by the arrows in Figures 6 through 13. Partial work was done to calculate the absorption curve for this mechanism. The matrix element in Equation 53 was worked out using Fowler's 2p F center wave function rather than his 1s wave function. Since an averaging over the angles between the p state and the outgoing electron was required in this case, only the final state consisting of a p state oriented along the z axis (the axis of the outgoing electron) was considered. Evaluation of this absorption cross section for KBr yielded a band whose half-width and peak value were in fair agreement with the observed experimental curve. The agreement is good enough to warrant continuation of the calculation. It is also possible that this absorption could correspond to leaving the F center in a 2s rather than a 2p state. Here a variational calculation to obtain the 2s energy for one electron would be difficult, since the final 2s wave function would have to be orthogonalized to the 1s F center wave function.

The calculated and experimental F' absorption edges are shown in Figure 14. The calculated values are the F' binding energies and these are identified as being the low energy thresholds for optical absorption in each salt. As stated before, these calculated values were found from the a priori or self-consistent calculation using $m^* = m_e$ and 0.6$m_e$. The experimental edges were found by a detailed reploting of the raw data on an optical density versus energy scale. From these plots the edge energy
Figure 14. Calculated and experimental $F'$ absorption edges
was found for each salt examined. For each alkali halide several (two
to six) runs were made and the edge energy determined for each. The
average of these values for each salt appears in Figure 14. The error
bars are larger than the actual scatter in the data and represent the
largest error that could occur in the subjective judgment of the edge in
each of the several runs for the various salts. The error bars were
chosen in this way since, even on an expanded energy plot, the edges were
not extremely well defined. A good improvement on this scheme would be
to fit a simple analytical curve to the points and take the edge as the
point where the curve crosses the x axis (57). Attempts at finding such
a function for the present case were not successful. The edges for RbI,
CsBr, and CsI could only be assigned an upper bound, since the Cary
spectrophotometer was only reliable down to 0.485 eV. It is felt, however,
that the circles are fairly close to the real values for these salts. In
Figure 14 the nearest neighbor distance was chosen simply as a parameter
which could be used to order the salts for presentation of the energy data.
The lines between the points are drawn to aid the reader in following the
general trend of the energies and are not intended to indicate any sort
of analytical relation between the edge energies and the nearest neighbor
distance. A smooth dependence is not to be expected since the energies
are very sensitive to the dielectric constants and electron affinities
for the various salts, and these parameters at best are simply monotonic
functions of the nearest neighbor distance.

The one-electron radial distribution function is plotted in Figure
15. These distribution functions were all calculated with \( m^* = m_e \) wave
Figure 15. $F^1$ center radial distribution function
functions. The wave function for LiF was calculated by the self-consistent method and the wave functions for the remaining salts were calculated by using the edge fitting routine.

Table 7 lists the well parameters which yielded the correct experimental F' binding energies. The experimental F' binding energies are also shown. Thermal depths for the F' centers in a few salts as measured by Scaramelli (46) are shown in the last column. These thermal depths are each about one-half the energy of the corresponding optical edges. This is reasonable since the thermal depth corresponds to the binding energy of two electrons in an F' center with an ionic polarization corresponding to an F center, while the optical depth corresponds to the binding energy of two electrons in an F' center including additional ionic polarization corresponding to an F' center. This additional ionic polarization produces a self-trapping effect which causes the optical depth to be larger than the thermal depth. Scaramelli's thermal depth for KCl as measured by photostimulated thermoluminescence can be compared to that of Tomura et al. (56) who obtained a value of 0.62 eV by measuring the temperature dependence of the F' center lifetime. Table 8 lists the well parameters which resulted from the self consistent solution of the variational problem for the F' binding energies.

Table 9 lists the temperature at which maximum F to F' conversion occurred during optical bleaching of the F band. Also listed are the quantum efficiencies for optical bleaching of the F band and the fraction of the original F band destroyed. The quantum efficiencies were found by using Spinolo's (53) data to evaluate (54)
Table 7. Well data for experimental fit of F' binding energy for $m^* = m_e$

<table>
<thead>
<tr>
<th>Salt</th>
<th>$R$(Å)</th>
<th>$V_0$(eV)</th>
<th>$K_{eff}$</th>
<th>$W_{ion}$(eV) F' binding energy (eV)</th>
<th>Thermal depth (eV) $^a$</th>
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</thead>
<tbody>
<tr>
<td></td>
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<td></td>
</tr>
<tr>
<td>NaF</td>
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<td>1.17</td>
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<td>NaCl</td>
<td>2.83</td>
<td>-7.62</td>
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<td>0.904</td>
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<td>KCl</td>
<td>2.97</td>
<td>-6.87</td>
<td>2.63</td>
<td>0.24</td>
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<tr>
<td>KBr</td>
<td>3.17</td>
<td>-6.05</td>
<td>2.38</td>
<td>-0.22</td>
<td>0.695</td>
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<tr>
<td>KI</td>
<td>3.29</td>
<td>-5.58</td>
<td>2.45</td>
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<tr>
<td>RbCl</td>
<td>3.34</td>
<td>-6.07</td>
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<td>CsBr</td>
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<td>0.544</td>
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$^a$After Scaramelli (46)

Table 8. Well data for self consistent solution of F' binding energy

<table>
<thead>
<tr>
<th>Salt</th>
<th>$m^*(m_e)$</th>
<th>$R$(Å)</th>
<th>$V_0$(eV)</th>
<th>$K_{eff}$</th>
<th>$W_{ion}$(eV)</th>
<th>Calculated F' binding energy (eV)</th>
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<tr>
<td>LiF</td>
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<tr>
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<td>KCl</td>
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<tr>
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<tr>
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</tr>
<tr>
<td>RbCl</td>
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<td>2.94</td>
<td>-8.32</td>
<td>1.49</td>
<td>-1.04</td>
<td>1.77</td>
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<td></td>
</tr>
<tr>
<td>RbI</td>
<td>1.0</td>
<td>3.29</td>
<td>-6.24</td>
<td>1.53</td>
<td>-0.97</td>
<td>1.02</td>
</tr>
<tr>
<td></td>
<td>0.6</td>
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<tr>
<td>CsBr</td>
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<td>-7.52</td>
<td>1.86</td>
<td>-0.77</td>
<td>1.82</td>
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<tr>
<td>CsI</td>
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<td>0.828</td>
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Table 9. Optical bleaching data

<table>
<thead>
<tr>
<th>Salt</th>
<th>Bleaching temperature (°K)</th>
<th>Fraction of F centers destroyed</th>
<th>Quantum efficiency</th>
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<tbody>
<tr>
<td>NaF</td>
<td>x rayed</td>
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<tr>
<td>NaCl</td>
<td>153</td>
<td>.39</td>
<td>.99</td>
</tr>
<tr>
<td>KCl</td>
<td>183</td>
<td>.76</td>
<td>.99</td>
</tr>
<tr>
<td>KBr</td>
<td>133</td>
<td>.58</td>
<td>.99</td>
</tr>
<tr>
<td>KI</td>
<td>143</td>
<td>.83</td>
<td>.99</td>
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<tr>
<td>RbCl</td>
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<td>.54</td>
<td>.92</td>
</tr>
<tr>
<td>RbI</td>
<td>103</td>
<td>.25</td>
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</tr>
<tr>
<td>CsBr</td>
<td>103</td>
<td>.80</td>
<td>.99</td>
</tr>
<tr>
<td>CsI</td>
<td>87</td>
<td>.84</td>
<td></td>
</tr>
</tbody>
</table>

\(^{a}\)After data due to Spinolo (47)

\[ \eta_i = \frac{1}{1 + \left(\frac{1}{\tau_o} / \tau_R\right) e^{\Delta E / kT}} \]

where

\( \eta_i \) = the probability that an excited F center will be thermally ionized

\( 1 / \tau_o \) = the frequency factor for thermal ionization

\( \tau_R \) = the radiative lifetime

\( \Delta E \) = the thermal depth of an excited F center below the conduction band

\( k \) = the Boltzmann constant

\( T \) = the temperature in °K

Finally Table 10 lists the thickness, F' center concentration, and the manufacturer for the samples used to produce the absorption curves in Figures 6 through 13.
Table 10. Sample data

<table>
<thead>
<tr>
<th>Salt</th>
<th>Sample thickness (cm)</th>
<th>Number of $F'$ centers/cm$^2$ x10$^{16}$</th>
<th>Manufacturer</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaF</td>
<td>.27</td>
<td></td>
<td>Harshaw</td>
</tr>
<tr>
<td>NaCl</td>
<td>.44</td>
<td>0.82</td>
<td>Optovac</td>
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<td>KCl</td>
<td>.20</td>
<td>2.1</td>
<td>Harshaw</td>
</tr>
<tr>
<td>KBr</td>
<td>.28</td>
<td>1.4</td>
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</tr>
<tr>
<td>KI</td>
<td>.32</td>
<td>1.2</td>
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</tr>
<tr>
<td>RbCl</td>
<td>.52</td>
<td>0.73</td>
<td>Korth</td>
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<tr>
<td>RbI</td>
<td>.63</td>
<td>0.22</td>
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</tr>
<tr>
<td>CsBr</td>
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<td>Korth</td>
</tr>
<tr>
<td>CsI</td>
<td>.20</td>
<td>1.1</td>
<td>Harshaw</td>
</tr>
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</table>

The above general results will now be discussed in more detail.

NaCl (Figure 6) shows a symmetrical $F'$ band with a very broad high energy tail. It is not obvious that a second distinct absorption curve could be present in the high energy tail, however, the small shoulder at about 4 eV appeared consistently in the raw data for four different runs. Optovac crystals were chosen over Harshaw in this case because the $M$ band (optical absorption due to an aggregate of two $F$ centers) could be more readily quenched out. This was necessary since the $M$ band was located at the $F'$ edge and tended to obscure it. The existence of $L$ bands (16) in the high energy part of the raw absorption curves could not be detected, thus they were neglected in the analysis of the data. The agreement between the second edge (arrow) and the shoulder at 4 eV is quite poor. The energy of our peak absorption, 2.7 eV, does not agree well with that due to Pick (41) whose value is 2.4 eV.

The three potassium salts (Figures 7, 8, and 9) will be discussed.
together. In each of these crystals the second absorption is very clear. It is difficult to compare the calculated and experimental second edges since the shape of the second absorption is not known. In general, the agreement is good enough to indicate that the mechanism given for it is a reasonable one. Compared to NaCl the F' bands in the potassium halides are not symmetrical. KCl and KBr both show a large shoulder on the high energy side of the main peak, and the entire peak in KI is skewed to the high energy side. This difference in symmetry between the absorption bands for the potassium salts, as compared to that for NaCl, may be due to a difference in band structure between the potassium and sodium halides. In the free sodium atom all states up to the final 3s are filled, whereas in the free potassium atom all states up to the final 4s are filled, except for the 3d states. These empty states affect the conduction band energy levels when the atom is incorporated into a crystal. Band structure calculations on KCl (36) and KI (35) indicate that for both crystals the s-like states are lowest, and the d-like states are second lowest in the conduction band. Presumably there would be no low lying d-like conduction band states in NaCl. These extra d-like levels could readily change the density of final states in the conduction band and thus produce the observed asymmetry.

The band effective mass for KI is on the order of 0.5m_e (1), one of the smallest for the alkali halides. To check the dependence of the absorption constant on the effective mass, absorption curves were calculated for KI using m* = 0.6m_e and 0.45m_e. The results of using an effective mass were two-fold. First, the density of final states,
Equation 47, was reduced by the factor \( m^*/m_e \); and second, the energy scale was shifted by including \( m^* \) in Equation 58. The mass appearing in the momentum operator matrix element, Equation 46, was not altered. Since the well depth for KI was too shallow to permit edge fitting by the usual method of varying the polarization, it was made artificially deep by changing the electron affinity from 1.3 to 0.5 eV. The usual edge fitting routine could then be used, and the required wave functions were determined. These wave functions were then used to calculate the required absorption curves. These curves, as well as those for \( m^* = m_e \) and the experimental data, are shown in Figure 16. The use of the effective mass moves the maximum in the correct direction, but only about half of the discrepancy is removed. Making the effective mass smaller than \( 0.45m_e \) does not seem as if it would improve agreement much either. As the effective mass gets smaller, the wave function moves outward in the potential well. This causes all the wave function parameters to get smaller in absolute value. These new parameters, in turn, have a tendency to make the absorption curve peak at lower energies. It is this competition between the changing wave function parameters and the energy scale shift which produces the same energies for the maxima for \( m^* = 0.6m_e \) and \( 0.45m_e \).

It was first thought that the shifted experimental peak in KI could be due to \( F_A \) centers. \( F_A \) centers are F centers in which one of the nearest neighbor alkali ions is replaced with an alkali ion foreign to the host crystal (25). Because of the [100] symmetry of this defect it can be detected by optically bleaching it with polarized light and then examining it for any anisotropy. In our case the F band was bleached to form the F'
Figure 16. F' center absorption in KI calculated for three effective masses
band using [100] polarized light. The F' band was then examined using [100] and [010] polarized light, and no anisotropy was detected. It was concluded that the F' band shown in Figure 9 was the true band shape. The presence of the L bands (29) could not be detected in any of the salts, therefore they were neglected in the analysis of the data.

As was found in NaCl, the energies of the peak absorptions do not agree well with those of Pick (41). For KCl and KBr the values measured here were 1.5 eV and 1.2 eV respectively. These are to be compared with Pick's values of 1.75 eV and 1.35 eV respectively. The high energy edges are not clearly shown by Pick and cannot be compared with the present work. Smakula et al. (50) formed the F' band in KCl and KBr by irradiating their samples with 3-mev electrons. The energies of their F' peaks are in agreement with those found here. Kingsley (24) shows the F' band in KCl. His curve peaks at 1.5 eV like ours, but does not show a second absorption shoulder. Crandall and Mikkor (11) show the F' band in KBr. Their curve agrees excellently with ours concerning all the important features. However, if their curve is renormalized to $10^{16}$ F' centers per cm$^3$, its peak value is about five times too small. Averaging over all the runs made on KBr yielded the same peak absorption as that shown in Figure 8 to within a few percent. Konitzer and Hersh (26) show the spectral photoconductivity of the F' center in additively colored KI. Their curve shows an edge for photoconductivity at about 0.78 eV. This agrees fairly well with our optical edge of 0.70 eV.

RbCl (Figure 10) is similar to KBr with respect to its lattice parameter and dielectric constants. Thus we might expect their F' bands
to be somewhat similar also. This was found to be the case for the present data. The F' bands in RbCl and KBr both have nearly the same optical absorption edges and peak absorption values. RbCl also shows, as did the potassium salts, a shoulder on the high energy side of the main absorption band. Rubidium, in a way similar to potassium, has unoccupied 4d and 4f levels which presumably could contribute to conduction band levels in a crystalline structure. Again these levels may be responsible for the high energy shoulder of the main peak. Smakula et al. (50) also irradiated RbCl. The energy for their F' peak is 1.1 eV in agreement with that found here. The calculated position of the second absorption edge agrees well with the observed absorption.

The absorption for RbI (Figure 11) is anomalous in that its peak seems to be truncated. Several runs on RbI all yielded the same "flat spot" on the absorption curve. Since all wavelengths in the F' band bleach it with equal efficiency it does not appear as if the band could have been optically bleached during measurement. Because of the flat appearance it is difficult to say if a shoulder is present on the high energy side of the main peak. Again the calculated second edge agrees well with the observed absorption. Attempts were made at x raying both uncolored and additively colored RbI in order to produce a larger F' concentration (see Table 10), however, concentrations greater than those produced by optical bleaching of additively colored samples could not be achieved.

Data are presented on the CsCl-structured salts (Figures 12 and 13) for the sake of completeness. The F' absorptions for CsBr and CsI are somewhat similar in their general features and are both different than the
previous salts which had the NaCl structure. The sharp shoulder at 1.6 eV in CsBr was again thought to be due to $F_A$ centers. The $F_A$ band, like the $F$ band, has a temperature dependent half-width, and this fact was used to test for the presence of $F_A$ centers in the sample. The $F'$ centers were initially formed and the spectra measured at liquid nitrogen temperature using a helium cryostat. The sample was then cooled to liquid helium temperature and the spectra measured again. No change was apparent in the $F'$ band. This particular run was made using a Harshaw sample. The $F'$ spectra for Korth and Harshaw CsBr were identical. Colloids of alkali metal can give rise to absorption bands whose half-widths are temperature independent (48), however, in CsBr the only products of optical bleaching at 133°K were $F$-aggregate bands and not colloids. Also $F$-aggregate centers were not formed during optical bleaching at $T = 103°K$, the temperature for maximum $F$ to $F'$ conversion. The second absorption starting at about 2 eV is much larger in proportion to the $F'$ band than those appearing in the NaCl structure salts.

Generally the same comments apply to CsI as to CsBr. The presence of the $F_A$ band was not checked for here, but bleaching at several temperatures between 87°K and 133°K produced different size $F'$ bands of constant shape. That is, there was no indication of an overlapping absorption due to a second center. Again, in a manner similar to the previous two alkali metals discussed, cesium has empty 4f, 5d, 5f, and 5g levels which could contribute low lying conduction bands to the band structure of the cesium salts.

The calculated $F'$ energies in Figure 14 and Table 8 depend to a large
extent on the values of the electron affinities. This is most evident for
the cesium salts where $\chi = 0.2$ compared to KI and RbI where $\chi = 1.3$. This
sudden change in the electron affinity produced the sudden change in the
calculated absorption energy between RbI and CsBr. A similar, but smaller,
change occurred between RbCl and KBr. Because the electron affinities
are not well known, and the calculated energies are sensitive to these
values, good agreement with experiment cannot be expected. Also, the
experimental edges are not strictly sharp but are broadened by lattice
vibrations. This broadening is on the order of 0.2 eV. The calculated
tedge energies tend to get smaller with increasing lattice parameter, and
this agrees with the curve for the experimental edges. Also there is
generally better agreement with the curve calculated using $m^* = 0.6m_e$.
This agrees with the previous argument concerning the selection of an
effective mass for the calculation. La and Bartram's calculation using
$m^* = m_e$ yielded values somewhat larger than those obtained in the present
calculation. Their results are also shown in Figure 14.

In addition to the salts previously discussed, the experimental edge
for NaF is shown. This edge was found in the following manner. Harshaw
NaF was x rayed at liquid nitrogen temperature for 5 hours to form the F
and F' bands. At this temperature a fairly pure F' band can be obtained
(2). The F and F' spectra were then measured and the F' band bleached
using a tungsten lamp and a long wavelength pass sharp cut filter. The
spectra of the remaining F band was then measured. By subtracting the
spectra, the F' edge was determined. Due to absorption bands on the high
energy side of the F band arising from hole centers and uncertainty in the
F' to F conversion ratio an absorption plot was not obtained. X raying NaF at dry ice temperature produces a large F band with very little absorption on the low energy side (2). Attempts at optically bleaching the F band in a sample prepared like this at a variety of temperatures between liquid nitrogen and room temperature did not produce an F' band. Attempts were made at electrolytically coloring (22) NaF but these failed. Attempts to form the F' band in NaBr and RbBr were not successful. Additively colored Harshaw NaBr was optically bleached with F light between 50°K (pumped liquid nitrogen) and 193°K, but no F' band was formed. Here again there appeared to be an F_A band, however, bleaching it with polarized light did not introduce any anisotropy into the band. Additively colored Isomet RbBr was optically bleached in the F band between liquid nitrogen temperature and room temperature, but no F' band was formed. Again an F_A band appeared but polarized bleaching did produce an anisotropy in the band in this case. It was concluded that a true F_A band was formed in RbBr. Using Spinolo's (53) data the quantum efficiency for thermal ionization of an excited F center in RbBr at liquid nitrogen temperature was found to be about 0.2. Therefore, bleaching in the F band at temperatures below liquid nitrogen temperature was not attempted.
SUMMARY

Experimental Measurements

The F' band was produced and measured in the following salts: NaCl, KCl, KBr, KI, RbCl, RbI, CsBr, and CsI. The spectra consisted of a single main peak and either a shoulder or a distinct second peak to the high energy side of it. The main peak in NaCl had a symmetrical bell shape, whereas in the remainder of the salts it showed some structure. The potassium and rubidium salts showed a shoulder located on the high energy side of the main peak. The cesium halides showed a more complex structure. The structure in the main peak can be attributed to differences in band structure between the sodium halides and the other alkali halides. Here it is thought that unoccupied levels occurring before the final s level in the various alkali metals contribute low lying conduction band levels to the band structure. These levels could produce the observed structure.

The shoulder, or second peak, to the high energy side of the main peak has been assigned tentatively to F' center absorption where the F center is left in an excited (2p) state. The consistency with which it appeared in the salts would tend to indicate that it is a property of the F' center itself and not the host lattice.

The temperatures for maximum F to F' conversion were found for the salts, and quantum efficiencies for F center bleaching were calculated where data were available. At the temperatures for maximum F to F' conversion all quantum efficiencies calculated were greater than 0.9. The $F_A$ band, or what appeared to be the $F_A$ band, was examined in several of
the crystals. A true $F_A$ band was found only in RbBr.

Calculations

A semicontinuum model variational calculation was done using a correlated Hylleraas wave function. The F' binding energies were calculated in a self-consistent a priori fashion for $m^* = m_e$ and $0.6m_e$. Generally good agreement was obtained for the $m^* = 0.6m_e$ case. Also the potential well was adjusted to force agreement with experimental binding energies for the $m^* = m_e$ case. The resulting wave functions were used to calculate the absorption cross sections for the F' centers. Generally good agreement was obtained concerning the positions and sizes of the peaks and the half-widths of the bands. The second edges, corresponding to leaving the F center in an excited state, were calculated. Good agreement with the experimental second edges was obtained. A preliminary calculation concerning the peak height and half-width of the band yielded results in fair agreement with data on KBr.

Future Work

The complex structure obtained in the cesium salts requires more investigation. Bleaching experiments at lower temperatures than that of liquid nitrogen may reveal that the F' band shown here is not a pure F' band. Photoconductivity measurements at liquid helium temperature would most likely reveal the true F' band shape.

The near infrared edges in CsBr, CsI, and RbI should be remeasured using an infrared monochromator. Again photoconductivity would be a sensitive way to measure the optical absorption edge.
Further attempts at forming the F' band in RbBr and NaBr could be done using a combination of optical bleaching and high electric fields to place F center electrons in the conduction band. However, any external mechanism that frees excited F center electrons would most likely ionize the F' center too, and a favorable F' equilibrium would be required for the process. Attempts at x ray these samples would be worthwhile.

The semicontinuum calculation which has been done is felt to be a "balanced" one in that it could not be improved much without being completely redone. Improvement in any one area, the semicontinuum potential, the polarization corrections, or the variational wave functions would probably not be worthwhile. It would be worthwhile, however, to complete the work done on the absorption cross section for the second peak found. Good agreement concerning a shape could not be expected. However, it would be helpful in assigning a mechanism to the absorption if the peak height and half-width were calculated.
LITERATURE CITED


ACKNOWLEDGEMENTS

The author would like to thank Dr. David W. Lynch for the suggestion of this problem and for many helpful discussions throughout the course of this work. He also wishes to thank Mr. A. D. Brothers for construction of the optical cryostat used in the investigation and Mr. B. F. Schmidt for extensive help in the early part of the work.
APPENDIX A: DERIVATION OF EXPANSION FOR \( r_{12} \)

We now derive Equation 24 using the method stated by Williamson. Assume we can write \( r_{12} \) as a series of the form

\[
 r_{12} = r > \sum_{n=0}^{\infty} a_n \frac{r_<}{r_>^n} \tag{62}
\]

where \( a_n \) is an unknown coefficient. Differentiating Equation 62 with respect to \( \cos \theta_{12} \) yields

\[
 \frac{d}{d(\cos \theta_{12})} \frac{r_{12}}{r} = \frac{-r^2 r_{12}}{r_{12}} \sum_{n=0}^{\infty} \frac{d(a_n)}{d(\cos \theta_{12})} \left( \frac{r_<}{r_>^n} \right) \tag{63}
\]

where we have used the law of cosines,

\[
 r_{12} = \left( r_1^2 + r_2^2 - 2 r_1 r_2 \cos \theta_{12} \right)^{\frac{1}{2}}
\]

to obtain

\[
 \frac{d(r_{12})}{d(\cos \theta_{12})}.
\]

Equation 63 can be written as

\[
 \frac{1}{r_{12}} = \frac{-1}{r} \sum_{n=-1}^{\infty} \frac{d(a_{n+1})}{d(\cos \theta_{12})} \left( \frac{r_<}{r_>^n} \right) \tag{64}
\]

Comparing Equation 64 with Equation 21 term by term yields

\[
 P_n(\cos \theta_{12}) = -\frac{d(a_{n+1})}{d(\cos \theta_{12})}.
\]

Using the following recurrence relation from Jackson (23)

\[
 \frac{d(P_{n+1})}{d(\cos \theta_{12})} - \frac{d(P_{n-1})}{d(\cos \theta_{12})} - (2n+1) P_n = 0
\]

yields
\[ a_n = \left( \frac{1}{2n-1} \right)(P_{n-2} - P_n) + C_n \]

where the constants of integration, \( C_n \), must all be zero for the sum in Equation 62 to converge properly as \( \theta_{12} \) goes to zero. Writing out Equation 62 yields

\[ r_{12} = r > \sum_{n=0}^{\infty} \left( \frac{1}{2n-1} \right)(P_{n-2} - P_n) \left( \frac{r}{r} \right)^n \]

which finally becomes

\[ r_{12} = r > \sum_{n=0}^{\infty} \left[ \left( \frac{1}{2n+3} \right)(\frac{r}{r})^2 - \left( \frac{1}{2n-1} \right) \right] P_n (\cos \theta_{12}) \left( \frac{r}{r} \right)^n. \]  (65)
APPENDIX B: COMPUTER SUBPROGRAM TO CALCULATE THE TOTAL ENERGY OF THE F' CENTER

The FUNCTION subprogram shown in Figure 17 was used to evaluate the expectation value of the Hamiltonian for the F' center given a particular set of variational parameters and a particular potential well. The variables of the program are identified in Table 11. All variables are in atomic units except where noted.

Table 11. Identification of program variables

<table>
<thead>
<tr>
<th>Variable</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>R</td>
<td>radius of potential well</td>
</tr>
<tr>
<td>V0</td>
<td>depth of potential well</td>
</tr>
<tr>
<td>DIE1</td>
<td>coulomb shoulder dielectric constant</td>
</tr>
<tr>
<td>DIE2</td>
<td>optical dielectric constant</td>
</tr>
<tr>
<td>EFFM</td>
<td>effective mass</td>
</tr>
<tr>
<td>ALPHA</td>
<td>variational parameters a, b, γ</td>
</tr>
<tr>
<td>BETA</td>
<td>variational parameters a, b, γ</td>
</tr>
<tr>
<td>GAMMA</td>
<td>variational parameters a, b, γ</td>
</tr>
<tr>
<td>N</td>
<td>an integer which tells what value of ENERGY is returned to the main program as listed below</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Value of N</th>
<th>Returned value of ENERGY</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>F' energy in eV</td>
</tr>
<tr>
<td>1</td>
<td>electron correlation energy in eV</td>
</tr>
<tr>
<td>2</td>
<td>fraction of total electron distribution in potential well</td>
</tr>
</tbody>
</table>

This program directly includes only the effect of optical polarization on the depth of the potential well. Other polarization effects were calculated in the main program and appeared in the potential well variables.
Figure 17. FUNCTION subprogram to calculate the F' center energy
Figure 17. (Continued)
\[ T = T + T_C + T_S \]
\[ T = 1 / \text{CONST} \]

\[ \text{WOPT} = \text{CORRECTION FOR OPTICAL POLARIZATION} \]
\[ \text{WOPT} = (1 - 1 / \text{DIE}^2) / 2 \times R \]

\[ \text{VSOWL} = \text{SQUARE WELL POTENTIAL ENERGY} \]
\[ \text{VSOWL} = R \times (\text{VCOUL} + \text{WOPT} \times \text{VUUL}) \]
\[ \text{VSOWL} = \text{VSOWL} / \text{CONST} \]

\[ \text{VCE} = 10.0 \times \text{A} + 140.0 \times \text{B2} / \text{A7} + 624.0 \times \text{G2} / \text{A9} + 72.0 \times \text{G1} / \text{A7} + \text{G6} \times \text{G1} / \text{A6} + \text{G1} \times \text{G2} / \text{A8} \]

\[ \text{VR12} = \text{COULOMB CORRELATION POTENTIAL ENERGY} \]
\[ \text{VR12} = \text{VCOUL} / \text{DIE}^2 + (1 - 1 / \text{DIE}^2) \times (16 \times \text{VR1} / \text{A5} + 16 \times \text{B2} \times \text{V47} / \text{A7} + 16 \times \text{B2} \times \text{VR3} / \text{A9} + 32 \times \text{G1} \times \text{VR4} / \text{A7} + 16 \times \text{G1} \times \text{VR5} / \text{A6} + 32 \times \text{G1} \times \text{VR6} / \text{A8} \}
\[ \text{VR12} = \text{VR12} / \text{CONST} \]

\[ \text{VCOUL} = \text{COULOMB SHOULDER POTENTIAL ENERGY} \]
\[ \text{VCOUL} = (1.0 / \text{DIE}^2) \times (4.0 \times \text{VCOUL} / \text{A5} + 8.0 \times \text{B2} \times \text{C2} / \text{A7} + 8.0 \times \text{G2} \times \text{VCOUL} / \text{A9} + 8.0 \times \text{G1} \times \text{VCOUL} / \text{A7} + 8.0 \times \text{G1} \times \text{VCOUL} / \text{A8} \]
\[ \text{VCOUL} = \text{VCOUL} / \text{CONST} \]
\[ \text{EN} = T + \text{VSOWL} + \text{VR12} \times \text{VCOUL} \]
\[ \text{IF} (\text{N} \leq 1) \]
\[ \text{ENERGY} = \text{EN} \times 27.2 \]
\[ \text{RETURN} \]
\[ \text{ENERGY} = \text{VR12} \times 27.2 \]
\[ \text{RETURN} \]
\[ \text{ENERGY} = 4 \times \text{VIN} / \text{CONST} \]
\[ \text{RETURN} \]
\[ \text{END} \]

*Figure 17. (Continued)*
APPENDIX C: DERIVATION OF VECTOR OPERATORS

The vector operators required for the kinetic energy term were evaluated by writing them in cartesian coordinates. The required scalar or dot products of these operators were then taken, and the resulting scalar operators worked out using the "chain rule" of partial differentiation.

In cartesian coordinates the needed operators are

\[ \hat{\nabla}_i \phi = \frac{\partial \phi}{\partial x_i} \hat{i} + \frac{\partial \phi}{\partial y_i} \hat{j} + \frac{\partial \phi}{\partial z_i} \hat{k} \]

and

\[ r_i = \frac{i_x i + j_y y_i + k_z z_i}{r_i} \]

which yield

\[ |\hat{\nabla}_i \phi|^2 = \left( \frac{\partial \phi}{\partial x_i} \right)^2 + \left( \frac{\partial \phi}{\partial y_i} \right)^2 + \left( \frac{\partial \phi}{\partial z_i} \right)^2 \] (66)

and

\[ \hat{\nabla}_i \phi \cdot \hat{r}_i = \frac{1}{r_i} \left( x_i \frac{\partial \phi}{\partial x_i} + y_i \frac{\partial \phi}{\partial y_i} + z_i \frac{\partial \phi}{\partial z_i} \right) \] (67)

where \( i = 1, 2 \).

In general \( \phi \) is a function of the independent variables \( r_1, r_2 \), and \( r_{12} \) where

\[ r_i = (x_i^2 + y_i^2 + z_i^2)^{\frac{1}{2}} \]

and

\[ r_{ij} = \left[ (x_i - x_j)^2 + (y_i - y_j)^2 + (z_i - z_j)^2 \right]^{\frac{1}{2}} \]
and where

\[ i, j = 1, 2; i \neq j. \]

Differentiating \( \phi(r_1, r_2, r_{12}) \) with respect to \( x_i \) yields

\[ \frac{\partial \phi}{\partial x_i} = \frac{\partial \phi}{\partial r_i} \frac{\partial r_i}{\partial x_i} + \frac{\partial \phi}{\partial r_j} \frac{\partial r_j}{\partial x_i} + \frac{\partial \phi}{\partial r_{ij}} \frac{\partial r_{ij}}{\partial x_i} \]

which becomes

\[ \frac{\partial \phi}{\partial x_i} = \frac{\partial \phi}{\partial r_i} \frac{x_i}{r_i} + \frac{\partial \phi}{\partial r_{ij}} \left( \frac{x_i - x_j}{r_{ij}} \right) \]  

(68)

where

\[ i, j = 1, 2; i \neq j. \]

The expressions for \( \frac{\partial \phi}{\partial y_1} \) and \( \frac{\partial \phi}{\partial z_1} \) are similar. Using Equation 68 to write Equations 66 and 67 yields

\[ |\hat{\nabla_i}\phi|^2 = (\frac{\partial \phi}{\partial r_i})^2 + (\frac{\partial \phi}{\partial r_{ij}})^2 + 2(\frac{\partial \phi}{\partial r_i})(\frac{\partial \phi}{\partial r_{ij}})(\frac{r_i - r_j \cos \theta_i}{r_{ij}}) \]

and

\[ \hat{\nabla_i}\phi \cdot \hat{r_i} = \frac{\partial \phi}{\partial r_i} + \frac{\partial \phi}{\partial r_{ij}} \left( \frac{r_i - r_j \cos \theta_i}{r_{ij}} \right) \]

where again

\[ i, j = 1, 2; i \neq j. \]