

Electronic Structure and Optical Transition of R Centers

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We have constructed the low-lying wave functions for R center in the molecular orbital approach employing the projection operator technique. Using these wave functions, the electronic states of R center in alkali halides with NaCl structure have been calculated. The calculations have been done in the quasi-continuum model and the effect of configuration interaction has been investigated. Our calculations show that the ground state of R center is of E symmetry and the low-lying excited states to which transitions take place are, respectively, of E, A_2 , A_1 and E symmetries.

Construímos as funções de onda de baixas energias para centro-R pelo método de orbitais moleculares empregando a técnica de operadores de projeção. Usando estas funções de onda, calcularam-se os estados eletrônicos do centro-R nos haletos alcalinos com estrutura NaCl. Os cálculos foram feitos no modelo quai e contínuo e o efeito da interação de configurações foi investigado. Os resultados mostram que o estado fundamental do centro-R é de simetria E enquanto que os estados excitados de mais baixas energias, para os quais as transições se realizam, são respectivamente de simetrias E, A_2 , A_1 e E.

1. Introduction

Three F centers forming an equilateral triangle lying in a (III) plane give rise to an R center. This model of R center as a F_3 center was proposed by Van Doorn¹ and has been confirmed by the experimental works of Silsbee², Krupka and Silsbee³, Shepherd⁴ and others. Their work also implies that the ground state of R center is a 2E state. Experimentally observed R, and R_2 absorption bands lie on the longer wave length side of F band. A host of alkali halide crystals, KCl, KBr, NaCl, NaF (Refs. 5, 6) etc, exhibit R_1 and R_2 absorption peaks. In addition, in KCl crystal, other absorption peaks associated with R center have also been observed².

On the theoretical side, work has been done on R center in KCl by Silsbee² and by Wang and Chu⁷. The work of Silsbee is a qualitative one and is based on the calculation of Hirschfelder⁸ for the H_3 molecule. The low-lying excited states with respect to the ground state were

calculated for KCl by extending Hirschfelder's linear combination of atomic orbitals calculations. Wang and Chu used Heitler-London type wave functions, built from the 1s hydrogenic atomic orbitals, for the ground and the excited states. Their calculations are done in the continuum approximation on the polaron model. They have calculated the transition energies of R center in KCl crystal and the theoretical results are in good agreement with the experimental ones.

In the present work, we have studied the electronic structure of R center in a host of alkali halide crystals with NaCl structure. To this end, projection operator technique has been used to construct all the low lying symmetry adopted wave functions in the Molecular Orbital approach. The different electronic energy states of R center have been determined using the quasicontinuum model of F aggregate centers. The effect of configuration interaction on the electronic states has been investigated.

2. Wave Functions and Electronic States of R Center

R center has C_{3v} point group symmetry. For the C_{3v} point group, the wave functions belong to A_1 , A , and E irreducible representations. To construct the wave functions for R center, Molecular Orbital approach has been adopted. Molecular Orbitals are one electron eigenfunctions satisfying the symmetry conditions. These can be formed by taking the right linear combinations of hydrogenic 1s wave functions. The use of p, d, ..., wave functions are not considered, as these will presumably give states of higher energies and are, therefore, relatively unimportant⁸.

For one electron in the field of three defect centers arranged in an equilateral triangle, the following three independent symmetry adopted molecular orbitals are obtained

$$g = \frac{1}{\sqrt{3(1+2\Delta)}} \{a(\mathbf{r}_i) + b(\mathbf{r}_i) + c(\mathbf{r}_i)\}, \quad (1)$$

$$E = \frac{1}{\sqrt{6(1-\Delta)}} \{2b(\mathbf{r}_i) - a(\mathbf{r}_i) - c(\mathbf{r}_i)\}, \quad (2)$$

$$e = \frac{1}{\sqrt{2(1-\Delta)}} \{a(\mathbf{r}_i) - c(\mathbf{r}_i)\}. \quad (3)$$

Here, $a(\mathbf{r}_i)$, $b(\mathbf{r}_i)$ and $c(\mathbf{r}_i)$ are 1s hydrogenic eigenfunctions, centered on the respective trapping centers a, b and c, i.e.,

$$\eta(\mathbf{r}_i) = (\lambda^3/\pi)^{1/2} \exp(-\lambda r_{in}), \quad y = a, b, c, \quad (4)$$

where λ is a variational parameter and A is the overlap integral between any two of the centers. g forms a basis for the A_1 irreducible representation whereas E and \mathcal{E} are basis functions for the doubly degenerate E irreducible representation.

The configurational wave functions are obtained by adding three electrons to the three molecular orbitals g, E and \mathcal{E} taking into account the Pauli principle. Three possible configurational states i.e., $g^2(E\mathcal{E})^1$, $g^1(E\mathcal{E})^2$ and $(E\mathcal{E})^3$ are obtained using the six possible spin orbitals viz.,

$$\begin{pmatrix} g \\ \alpha \end{pmatrix}, \begin{pmatrix} g \\ \beta \end{pmatrix}, \begin{pmatrix} E \\ \alpha \end{pmatrix}, \begin{pmatrix} E \\ \beta \end{pmatrix}, \begin{pmatrix} \mathcal{E} \\ \alpha \end{pmatrix} \text{ and } \begin{pmatrix} \mathcal{E} \\ \beta \end{pmatrix}.$$

α is the electronic spin functions in the preferred direction and β corresponds to an spin in the opposite direction. All possible symmetry adopted wave functions, for the R center, are then constructed by employing the Projection Operator technique^{9,10} and using the above obtained three configurational states, 2E , 2A_1 , 2A_2 and 4A_2 states are obtained. We are not interested in the spin quartet state 4A_2 as transitions between this and the spin doublet states are highly forbidden². We, therefore, shall confine ourselves in the present work only to the spin doublet 2E , 2A_1 and 2A_2 states. The configurational states, different wave functions and their symmetries are given in table I. The wavefunctions are given for $S = 1/2$ and $S_z = 1/2$ and the bracket notation denotes the Slater determinant.

The quasicontinuum model of F aggregate centers has been applied successfully to study the electronic structures for the M' and R' centers^{11,12}. We use the same model to study the R center. Accordingly, the Hamiltonian describing the low-lying states of R centers can be written as

$$H = \sum_{i=1}^3 \frac{P_i^2}{2m} - \sum_{i=1}^3 \sum_{v=a}^c \frac{e^2}{K_D r_{i2}} + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{\epsilon_\infty r_{ij}} = \quad (5)$$

$$= \sum_{i=1}^3 H(r_i) + \frac{1}{2} \frac{e^2}{\epsilon_\infty} \sum_{i \neq j} \frac{1}{r_{ij}}. \quad (6)$$

The interaction among the trapping centers is a constant during the optical transitions and hence is omitted in (6). P_i , m and r_{ij} refer, res-

Symmetry	Configuration	Wave Functions
2A_1	$g^1(E \mathcal{E})^2$	$(2 \times 3!)^{-1/2} \left[\begin{pmatrix} g & E & E \\ \alpha & \beta & \alpha \end{pmatrix} + \begin{pmatrix} g & \mathcal{E} & \mathcal{E} \\ \alpha & \beta & \alpha \end{pmatrix} \right]$
2A_2	$g^1(E \mathcal{E})^2$	$(6 \times 3!)^{-1/2} \left[\begin{pmatrix} g & \mathcal{E} & E \\ \alpha & \beta & \alpha \end{pmatrix} - \begin{pmatrix} g & E & \mathcal{E} \\ \alpha & \beta & \alpha \end{pmatrix} + 2 \begin{pmatrix} \mathcal{E} & g & E \\ \alpha & \beta & \alpha \end{pmatrix} \right]$
	$g^2(E \mathcal{E})^1$	$(3!)^{-1/2} \begin{pmatrix} g & g & E \\ \alpha & \beta & \alpha \end{pmatrix}$ $(3!)^{-1/2} \begin{pmatrix} g & g & \mathcal{E} \\ \alpha & \beta & \alpha \end{pmatrix}$
2E	$g^1(E \mathcal{E})^2$	$(2 \times 3!)^{-1/2} \left[\begin{pmatrix} g & \mathcal{E} & \mathcal{E} \\ \alpha & \beta & \alpha \end{pmatrix} - \begin{pmatrix} g & E & E \\ \alpha & \beta & \alpha \end{pmatrix} \right]$ $(2 \times 3!)^{-1/2} \left[\begin{pmatrix} g & E & \mathcal{E} \\ \alpha & \beta & \alpha \end{pmatrix} + \begin{pmatrix} g & \mathcal{E} & E \\ \alpha & \beta & \alpha \end{pmatrix} \right]$
	$(E \mathcal{E})^3$	$(3!)^{-1/2} \begin{pmatrix} \mathcal{E} & \mathcal{E} & E \\ \alpha & \beta & \alpha \end{pmatrix}$ $(3!)^{-1/2} \begin{pmatrix} E & E & \mathcal{E} \\ \alpha & \beta & \alpha \end{pmatrix}$

Table I – The configurational wave functions for R centers; $S = 1/2$, $S_z = 1/2$

pectively, to the i^{th} electronic momentum, the electronic mass and the distance between the j^{th} center and the i^{th} electron. K_D is a parameter and is determined by fitting the energy of the F center electron. ϵ_∞ is the high frequency dielectric constant.

Next, the energy expressions have been determined for all the five configurational states given in table I. The obtained expressions are:

$$E({}^2A_1) = T(g) + 2T(\mathcal{E}) - \frac{e^2}{K_D} [A(g) + 2A(\mathcal{E})] + \frac{1}{\epsilon_\infty} \{2R[\mathcal{E}, g] + 3J[\mathcal{E}, E] + R[E, \mathcal{E}] - J[\mathcal{E}, g]\}, \quad (7)$$

$$E_1(^2A_2) = T(g) + 2T(\mathcal{E}) - \frac{e^2}{K_D} [A(g) + 2A(\mathcal{E})] + \frac{1}{\varepsilon_\infty} \{J[\mathcal{E}, E] - 2R[\mathcal{E}, g] - J[\mathcal{E}, g] - R[E, \mathcal{E}]\}, \quad (8)$$

$$E_1(^2E) = 2T(g) + T(\mathcal{E}) - \frac{e^2}{K_D} [2A(g) + A(\mathcal{E})] + \frac{1}{\varepsilon_\infty} \{2R[\mathcal{E}, g] + R[g, g] - J[\mathcal{E}, g]\}, \quad (9)$$

$$E_2(^2E) = T(g) + 2T(\mathcal{E}) - \frac{e^2}{K_D} [A(g) + 2A(\mathcal{E})] + \frac{1}{\varepsilon_\infty} \{2R[\mathcal{E}, g] - J[\mathcal{E}, g] + R[E, \mathcal{E}] + J[\mathcal{E}, E]\}, \quad (10)$$

$$E_3(^2E) = 3T(\mathcal{E}) - \frac{3e^2}{K_D} A(\mathcal{E}) + \frac{1}{\varepsilon_\infty} \{3R[E, \mathcal{E}] + J[E, \mathcal{E}]\}. \quad (11)$$

The subscripts 1, 2 and 3 to E in Eq.s (9) to (11) distinguish the three 2E states. Here $T(g)$ and $T(\mathcal{E})$ represent the Kinetic energy term of an electron when it is in the orbitals g and \mathcal{E} respectively. $A(g)$ and $A(\mathcal{E})$ denote the attractive energy terms between an electron and the trap centers, the electron being, respectively, in the orbitals g and \mathcal{E} . The different R and J's stand for the repulsive energies between two electrons. Thus,

$$T(g) = \frac{\hbar^2 \lambda^2}{2m} \frac{1}{(1+2\Delta)} \left[1 + 2e^{-\lambda b} \left(1 + \lambda b - \frac{\lambda^2 b^2}{3} \right) \right], \quad (12)$$

$$T(\mathcal{E}) = \frac{\hbar^2 \lambda^2}{2m} \frac{1}{(1-\Delta)} \left[1 - e^{-\lambda b} \left(1 + \lambda b - \frac{\lambda^2 b^2}{3} \right) \right], \quad (13)$$

$$A(g) = \frac{1}{(1+2\Delta)} [F(1) + 2F(2) + 4F(3) + 2F(4)], \quad (14)$$

$$A(\mathcal{E}) = \frac{1}{(1-\Delta)} [F(1) + 2F(2) - 2F(3) - F(4)], \quad (15)$$

$$F(1) = \int a(r_1) \frac{1}{r_{1a}} a(r_1) dr_1 = \lambda, \quad (16)$$

$$F(2) = \int a(r_1) \frac{1}{r_{1b}} a(r_1) dr_1 = \frac{1}{b} [1 - (1 + \lambda b) e^{-2\lambda b}], \quad (17)$$

$$F(3) = \int a(r_1) \frac{1}{r_{1a}} b(r_1) dr_1 = \Delta(1 + \lambda b) e^{-\lambda b} \quad (18)$$

$$F(4) = \int a(r_1) \frac{1}{r_{1c}} b(r_1) dr_1, \quad (19)$$

b is the distance between any two trap centers and Δ , the overlap integral, is given by

$$\Delta = \left[1 + \lambda b + \frac{1}{3} \lambda^2 b^2 \right] e^{-\lambda b}. \quad (20)$$

The repulsive energy terms R and J between two electrons are defined by

$$R[m, n] = \iint |m(r_1)|^2 \frac{e^2}{r_{12}} |n(r_2)|^2 dr_1 dr_2 \quad (21)$$

$$J[m, n] = \iint m(r_1) n(r_1) \frac{e^2}{r_{12}} m(r_2) n(r_2) dr_1 dr_2. \quad (22)$$

The integral $R[m, n]$ represents the natural potential energy of two charge distributions calculated in a classical way and is called Coulomb integral. $J[m, n]$ is called the Exchange integral as in this, the charge density is represented by $m(r_1) n(r_1)$, in which both the orbitals m and n are involved. The Coulomb and Exchange integrals given by (21) and (22), respectively, can be expanded into integrals over atomic orbitals. The numerical values of these integrals as well as of $F(4)$ can be obtained from the works of Hirschfelder¹³ and Hirschfelder *et al*¹⁴. Thus using expressions (12) to (22), we have minimized the energies for each states of R center as given by (7) to (11) for KCl crystal using λ as a variational parameter. The value of K has been determined from the calculated ground state energy of F center for the KCl crystal. The obtained minimum energies for different states and their symmetries are given in Table II. We note that the 2E state is

Electronic Configurations	Symmetry of States	$\lambda(\text{\AA}^{-1})$	Energy (eV)
$g^2(E)^1$	2E	0.675	-10.11
$g^1(E)^2$	2E	0.675	-9.29
$g^1(E)^2$	2A_2	0.698	-8.82
$(E\mathcal{E})^3$	2E	0.788	-8.77
$g^1(E\mathcal{E})^2$	2A_1	0.619	-8.71

Table II – R center electronic energy states in KCl crystal

the lowest i.e., the ground energy state. Next, we have calculated the optical transition energies to different excited states. In the numerical calculations of the excited state energies, the values of constants used for the lattice are the same as those used in the ground state calculation. This is in accordance with the Franck – Condon principle. Furthermore, as during the optical transitions the lattice remains virtually unchanged, the value of λ used for the calculation of excited state energies is the same as that obtained by minimizing the ground state energy¹².

In table III, we give the different, theoretically obtained, optical transition energies for R center in KCl crystal. Comparison of these results with the experimental R transition energies shows that the agreement between the theoretical and experimental results are, in general, not good. This lack of good agreement may be due to the fact that configuration interaction has not been taken into consideration. Hence, next we consider the effect of configuration interaction on the R center transition energies.

Present Calculations			Experimental Results ⁽²⁾		
Symmetry of State	Energy of State (eV)	Transition energy (eV)	Symmetry of transition	Bund	Transition energy (eV)
2E (Ground State)	-10.11				
2E	-9.29	0.82	${}^2E \rightarrow {}^2E$	R_N	1.22/1.28
2A_2	-8.80	1.31	$\rightarrow {}^2A_2$	R_2	1.70
2A_1	-8.68	1.43	$\rightarrow {}^2A_1$	R_M	1.52
2E	-8.45	1.66	$\rightarrow {}^2E$	R_1	1.89

Table III – Theoretical energies for R center in KCl crystal without configuration interaction and the corresponding experimental transition energies and symmetries. Values of Constants are $\lambda(\text{\AA}^{-1}) = 0.675$, $K_p = 2.39$

3. Configuration Interaction

The electronic wave functions of different states are given by Slater determinants made up of orbital wave functions. The Slater determinant neglects the finer interaction of the electrons and so it represents only a first approximation to the true electronic wave function. The Molecular Orbital method does not take into account properly the electron correlation due to the Coulomb repulsion between electrons. Theoretically, it is possible to take electron correlation fully into account if we include into our calculations the configuration interaction¹⁵.

The configuration interaction or superposition of configurations occurs only between different configurations belonging to the same irreducible representation. It leads to a change in the energy states as well as corresponding modifications in the electronic wave functions. The magnitude of this effect depends on the energy matrix elements between configurations as well as on the energy differences between them. We know examples in which configuration interaction has been shown to be essential in the assignment of ground state and the identification of the calculated energies with the experimental ones. In the calculation of absorption spectrum of an isolated vacancy in an otherwise perfect diamond lattice, it has been shown by Coulson and Kearsley¹⁶ that configuration interaction inverts the sequence of energy levels. In the case of MgI, the configuration interaction between two ¹D states arising out of 3s3d and 3p² has been shown to play an important role. Taking the configuration interaction into account, a very good agreement between the theoretical and experimental values is obtained¹⁷.

From the above discussions, it seems reasonable to investigate the effect of configuration interaction on the R center transition energy in KCl. From table I we see that there are three ²E state wave functions $\psi_1(^2E)$, $\psi_2(^2E)$ and $\psi_3(^2E)$ arising respectively, from the electronic configurations $g^2(\mathcal{E}E)^1$, $g^1(\mathcal{E}E)^2$ and $(\mathcal{E}E)^3$. The state $\psi_1(^2E)$ is the ground state. We consider the interaction of this state with the next higher ²E state i.e., the state $\psi_2(^2E)$. The interaction of the state $\psi_1(^2E)$ with the state $\psi_3(^2E)$ is neglected in the first approximation. This is because the configuration interaction is the most important with the lowest lying configuration which is closest in energy¹⁵.

Considering the effect of configuration interaction, the obtained energies are

$$E_{\text{CON}}[{}^2E] = \frac{1}{2} \{ [E_1({}^2E) + E_2({}^2E)] \pm [(E_1({}^2E) - E_2({}^2E))^2 + 4H_{12}^2({}^2E)]^{\frac{1}{2}} \}. \quad (23)$$

Here $E_1({}^2E)$ and $E_2({}^2E)$ are the energies of the states $\psi_1({}^2E)$ and $\psi_2({}^2E)$ and are given, respectively, by (9) and (10). In (23), the corresponding components of the states $\psi_1({}^2E)$ and $\psi_2({}^2E)$ have been combined.

$H_{12}({}^2E)$ is the off-diagonal matrix element between the states $\psi_1({}^2E)$ and $\psi_2({}^2E)$ and is

$$\begin{aligned} H_{12}({}^2E) &= \sqrt{2} K(g_1 E_1, \mathcal{E}_2 \mathcal{E}_2) \\ &= \sqrt{2} \iint (\mathbf{r}) E \quad \frac{e^2}{r_{12}} |\mathcal{E}(r_2)|^2 dr_1 dr_2 \quad (24) \end{aligned}$$

Equation (23) has been minimized with respect to λ and the plus and minus signs in it give us the higher and lower energy states with E symmetry. We find that the configuration interaction lowers the ground state energy of R center in KCl by 0.28 eV. We further find that the sequence of energy states is not altered by the configuration interaction. Table IV gives the theoretically calculated transition energy for R center in KCl. We also list the experimental values. We note that the agreement between the theoretically predicted transition energies and the experimental values are quite good and reasonable.

Symmetry of State	Energy of State (eV)	Transition energy (eV)	Band
2E	-10.39		
2E	-9.01	1.38	R_N
2A_2	-8.80	1.59	R_2
2A_1	-8.68	1.71	R_M
2E	-8.45	1.94	R_1

Table IV – Calculated energy for R center transitions in KCl crystal taking configuration interaction into consideration. Experimental Values are given in table III. Values of constants are same as in Table III.

We have, next, calculated the R center transition energies, taking into consideration configuration interaction, in KBr, LiF, NaCl and NaF crystals. The calculated values for the R_1 and R_2 bands in these crystals as well as the corresponding experimental results are given in table V.

Crystal	$\lambda(\text{\AA}^{-1})$	κ_D	Calculated energies of different States (eV)			Calculated Transition energy (eV)		Experimental Band (Ref. 6)	
			2E (ground State)	E (Excited State)	2A_2 (Excited State)	R , Band ${}^2E \rightarrow {}^2E$	R_2 Band ${}^2E \rightarrow {}^2A_2$	R_1	R_2
KBr	0.666	2.46	-9.99	-8.32	-8.60	1.67	1.39	1.69	1.57
NaCl	0.780	2.25	-12.31	-9.95	-10.51	2.36	1.80	2.27	2.08
LiF	0.918	2.24	-13.38	-8.88	-10.23	4.50	3.15	4.05	3.29
NaF	0.829	2.17	-13.06	9.50	-10.37	3.56	2.69	3.14	2.85

Table V – Calculated energies for R , and R_1 transitions in KBr, LiF, NaCl and NaF considering the configuration interaction. The corresponding experimental values are also given.

4. Results and Conclusions

We find in the present calculations that the ground state of R center in KCl, KBr, LiF, NaCl and NaF crystals with NaCl structure is lowered by the order of 0.3 eV due to the configuration interaction. We further find that the configuration interaction does not alter the sequence of energy levels and that all these crystals have the same sequence of energy levels for R center. Our calculations also show that 2E state is the ground state of R center not only in KCl (shown experimentally in Ref. 2) but also in KBr, LiF, NaCl and NaF crystals.

The quasi continuum model has been successfully applied before in predicting the optical transition energies of F-aggregate centers^{11,12}. Thus, the calculated optical transitions for R center in the present work (Tables IV and V) seem quite reasonable. A comparison of the theoretical and experimental values shows that R_1 and R_2 bands not only in KCl (Refs. 2,7), but also in KBr, LiF, NaCl and NaF crystals are due to the optical transitions from the 2E ground state to the low lying doublet states of 2E and 2A_2 symmetries, respectively, of the F_3 center. We further conclude from table IV that R_M and R_N bands in KCl are due to ${}^2E \rightarrow {}^2A_1$ and ${}^2E \rightarrow {}^2E$ electronic transitions, respectively, of the F_3 center in agreement with the experimental results.

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