A study of the structure of the self-trapped exciton in alkali halides by ab initio methods

A study of the structure of the self-trapped exciton in alkali halides by *ab initio* methods

R C Baetzold† and K S Song‡

‡ Corporate Research Laboratories, Eastman Kodak Company, Rochester, NY 14650, USA
‡ Department of Physics, University of Ottawa, Ontario, Canada K1N 6N5

Abstract. Hartree–Fock calculations have been performed for various possible geometries of the self-trapped exciton (STE) in several alkali halide crystals. The computations treat a four- to twelve-ion cluster embedded within an ionic lattice representation that may or may not respond self-consistently to the charge distribution in the cluster. Both the triplet and open-shell singlet excited states of the exciton are considered. The energy of each state decreases as the molecular component of the exciton moves from the on-centre D_{2h} symmetry to an off-centre C_{2v} symmetry site. This distortion is accompanied by a separation of the electron and hole components of the exciton leading to a nearest neighbour F–H pair. These findings are in general accord with earlier analyses and one-electron calculations presented by K S Song and co-workers.

1. Introduction

In alkali halide crystals and in many other ionic crystals the exciton becomes self-trapped very soon after the crystal is excited optically or by other ionizing irradiation. Since formation of the STE (self-trapped exciton) is a necessary step in many electronic excitations of pure and doped crystals before the system returns to the ground state, the STE has been studied extensively [1, 2]. Self-trapping leads to drastic changes in some properties of the crystals. These include the luminescence (Stokes shift, band shape and lifetime), energy transport (thermally activated hopping motion), and lattice defect creation of the vacancy–interstitial pair in the anion sublattice.

Recent studies published by Song and co-workers [3–5] predicted that the STE in alkali halide crystals is not in the assumed symmetry of the D_{2h} point group, which has the same symmetry as the self-trapped hole (the so-called V_k centre), but occupies a lower symmetry: C_{2v}. According to this theory the STE is more like a primitive vacancy–interstitial pair in the anion sublattice (nearest neighbour F–H pair). This new structure is attributed to an instability of the system in the D_{2h} symmetry which can be explained by a pseudo Jahn–Teller effect [3]. This new view can explain a host of data which remained a puzzle for a long time.

It appeared from this series of works that there are two groups of alkali halides as far as several important properties of the STE are concerned [4, 5]. This distinction includes the efficiency of F-centre creation at very low temperature (the so-called Rabin–Klick criterion [6]), and the large variation of the Stokes shift as well as the lifetime of the

intrinsic π-polarized emission bands. One group is represented by NaF for which the molecule ion F_2^- is relatively small compared with the lattice constant. In this group the V_k core undergoes a large axial shift and the STE is equivalent to a nearest-neighbour F–H pair. The second is typified by NaBr with a large molecule ion Br_2^- in a small lattice, and results in a relatively small off-centre shift. Although the axial shift of the V_k core (Br_2^- in this case) is relatively small, the electron and hole distribution spontaneously break the inversion symmetry thereby resulting in C_{2v} symmetry. There are several experiments which are more or less directly related to the question of the symmetry of the STE. These include the ENDOR measurement made in KCl [7] and the optically detected magnetic resonance [8] (especially the determination of the zero-field splitting parameter D).

    The need for a more sophisticated calculation to determine the overall structure of the STE has been known since the first studies were published in 1985. In this paper we determine whether the off-centre STE is energetically more stable than the on-centre STE using two distinct *ab initio* computer codes for automated defect structure calculation. They are CADPAC [9] (Cambridge analytic derivatives package) and ICECAP [10] (ionic crystal with electronic cluster: automatic program). Both methods treat a relatively small cluster of atoms quantum mechanically and differ in their treatment of the rest of the crystal. Both methods confirm that the STE is strongly unstable in the D_{2h} symmetry (so-called on-centre structure), undergoing a spontaneous off-centre distortion and ending in the C_{2v} symmetry in accord with predictions of the earlier works. These also provide clear evidence that there are two distinct groups among the alkali halide crystals with respect to the off-centre distortion. Another interesting point noted is that the spin triplet and singlet states behave differently in terms of the off-centre shift and this may offer some clue regarding the origin of the σ bands. In section 2 a brief description of the methods is given. In section 3 the results obtained by the two different methods followed by a discussion are presented.

2. Method

We have employed Hartree–Fock computations for a cluster of ions which are embedded within the remaining lattice ions. Two different procedures are employed. In the first, a spherical array of fixed point charges arranged in the sodium chloride structure with appropriate lattice constant is considered. We employ 884 ions in this array which was centred about the midpoint of the on-centre V_k molecule. This computation employs the CADPAC [9] computer program where both restricted and unrestricted Hartree–Fock methods are used to treat the open-shell singlet and triplet exciton in different positions. Recently the CADPAC program has been applied successfully in the study of the self-trapped exciton in SiO_2 [11]. In addition to these Coulombic interactions between the embedding ions and cluster ions, standard Born–Mayer potentials are employed.

    The second method of embedding employs the ICECAP [10] program which we use to treat some of the smaller quantum mechanical clusters. In this method the lattice ions are represented by the shell model and they are free to polarize and distort in the presence of the quantum mechanical cluster. We employ parameters of the shell model and short-range Buckingham potentials from other work [11]. Self-consistency between the quantum mechanical cluster and the embedding lattice is achieved by comparison of multipole moments in a procedure which has been described previously [11].
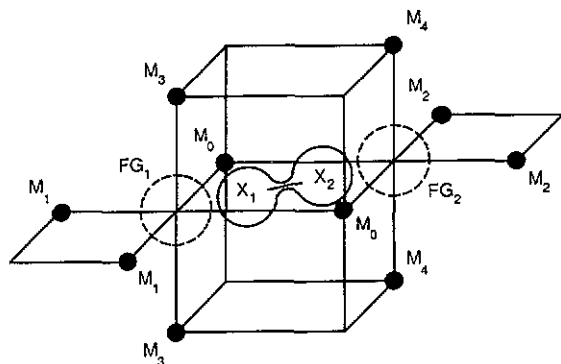
Figure 1. The cluster of atoms included in the quantum mechanical calculations of the STE. Ms represent the 10 cations and Xs the two anions which form the V_k centre. FG$_1$ and FG$_2$ are the two floating Gaussian basis functions which take part in representing the excited electron. (In the four-atom cluster $M_1 \ldots M_4$ are missing.) This cluster is embedded inside an array of 884 point ions centred about the mid point of X_1 and X_2 before the off-centre shift.

Gaussian basis sets are employed in both of the computational procedures. We employ neutral atom basis sets taken from the compilation of Huzinaga [13] with and without split valence orbitals for the CADPAC calculations. The actual basis sets are: Na (533/5), K (4333/43), F (6111/41), Cl (6631/631) and Br (4333/433/4) where the number of primitive Gaussians per orbital are listed for (s/p/d) orbitals, respectively. In the case of ICECAP we employ norm-conserving pseudopotentials [14] with the valence set given above for K and the above basis set for F. Floating Gaussian (FG) orbitals are placed near the virtual sites on either side of the V_k molecule to permit the formation of the F centre.

3. Results and discussion

We were more successful with the CADPAC code than with the ICECAP code. In fact, most of the results reported here were obtained with the former method. The ICECAP code, nevertheless, has confirmed the same result for a small size cluster, and this was encouraging.

In the following, we first report results obtained for a small cluster of four atoms (two alkali plus two halogen atoms) embedded in the 884 point ions that symmetrically surround the small cluster. This cluster is used to study the STE in KF and NaBr with the V_k core at the on-centre position. The pair of alkali atoms, see figure 1, are displaced outward by 0.42 au. For discussions below, the atoms and the floating Gaussians are numbered as in figure 1. The next geometry examined corresponds to that of the V_k core shifted axially by the vector (1.0, 1.0, 0.0) (in au). No Born–Mayer repulsive potential was provided between the atoms of the cluster and the surrounding atoms in this case. Therefore, the total energy change between the on-centre and the off-centre geometry does not reflect correctly the energy changes. However, as the only ions which move between the two geometries are the ions of the V_k core, this is not considered to be critical.

Table 1 summarizes the results for the four-atom clusters in KF and NaBr and contains the total energy of the triplet and singlet states in the on-centre and off-centre geometries. In addition to the energy, the charge distribution on the four atoms and on the pair of optimized floating Gaussians (Gaussian factor $\alpha = 0.08$ for $\exp(-\alpha r^2)$ placed on the two halogen atom sites in the perfect lattice position) are given. The charges are represented by the Mulliken population given by the cluster calculation. As the X_2^-

Table 1. Results of four-atom clusters of the STE in NaBr and KF. The total energy of the cluster and the electronic charge on each atom, halide (X_i), metal (M_0) and at the floating basis (FG$_i$) are given (in units of $-e$). ΔQ_2 represents the shift (in au) of the V_k core from the on-centre position along the (110) direction. d_0 is the bond length of the V_k molecule ion.

Charges	X_1	X_2	FG$_1$	FG$_2$	M_0	Energy (eV)
NaBr	$d_0 = 5.3$ (au)					
$\Delta Q_2 = 0$: on centre						
$S = 1$	35.38	35.38	0.27	0.27	10.38	-148683.42
$S = 0$	35.39	35.39	0.22	0.22	10.39	-148683.17
$\Delta Q_2 = 1.4$: off centre						
$S = 1$	35.62	35.13	0.20	0.93	10.06	-148683.95
$S = 0$	35.43	35.33	0.21	0.43	10.30	-148682.93
KF	$d_0 = 3.6$ (au)					
$\Delta Q_2 = 0$: on centre						
$S = 1$	9.44	9.44	0.19	0.19	18.36	-37993.95
$S = 0$	9.45	9.45	0.17	0.17	18.39	-37993.52
$\Delta Q_2 = 1.4$: off centre						
$S = 1$	9.79	9.10	0.06	0.83	18.11	-37994.77
$S = 0$	9.79	9.10	0.06	0.71	18.17	-37993.73

molecule is displaced to the left along the molecular axis by ΔQ_2, see figure 1, it becomes immediately clear that the lowering of the symmetry is accompanied by a drop in total energy as well as by the shift of the electron and hole charges. It is interesting to note that the hole and the electron are strongly correlated in the off-centre geometry, namely that the electron and hole attract each other (more electron on FG$_2$ and more hole on X_2, see figure 1). These results are a confirmation of earlier results obtained with the extended-ion method in combination with a CNDO code which was interfaced to represent the hole [5].

A comparison of KF and NaBr is significant. The energy drop accompanying the off-centre motion is smaller for NaBr than for KF. Similar distinctions have been noted in the earlier works too and will be discussed in further details below for twelve atom clusters. The spin singlet states are always higher than the triplet state, as expected. The energy difference is generally not large. There is, however, an interesting difference in the off-centre trend between the two spin states. The singlet state has less strongly polarized hole population than the triplet state.

For a larger cluster, we included ten alkali atoms: the first nearest neighbours of the two halogen atoms. For this case we introduced Born–Mayer repulsive potentials between the atoms immediately bordering the cluster and all the atoms of the cluster. Although the pair potential is only meant to be used between the nearest-neighbour anion and cation pairs, because of the fast decay with distance, we do not feel this introduces significant error. First, the on-centre geometry is studied as in the case of the four-atom cluster. Although the code has an option for geometry optimization (lattice relaxation), we have not attempted in this preliminary study to determine the lattice relaxation at equilibrium using this code, except in one test case for the NaF triplet state, because of the amount of computing time required. Instead, the off-centre geometry is studied with the V_k core shifted by ΔQ_2 as given in table 2 (near the values previously

Table 2. Results of twelve-atom cluster of the STE in NaF, NaCl and NaBr. Electronic charges for atoms and basis as defined in figure 1.

Charges	X_1	X_2	FG_1	FG_2	M_0	M_1	M_2	M_3	M_4	Energy (eV)
NaF $d_0 = 3.4$										
$\Delta Q_2 = 0$: on centre										
$S = 1$	9.38	9.38	0.08	0.08	10.10	10.15	10.15	10.07	10.07	−49535.49
$S = 0$	9.38	9.38	0.05	0.05	10.11	10.15	10.15	10.08	10.08	−49535.18
$\Delta Q_2 = 2.1$: off centre										
$S = 1$	9.60	9.21	0.06	0.90	10.02	10.02	10.04	10.02	10.02	−49536.85
$S = 0$	9.56	9.27	0.06	0.75	10.01	10.02	10.11	10.02	10.04	−49535.63
NaCl $d_0 = 4.9$										
$\Delta Q_2 = 0$: on centre										
$S = 1$	17.43	17.43	0.25	0.25	10.00	10.12	10.12	10.03	10.03	−69130.75
$S = 0$	17.44	17.44	0.17	0.17	10.00	10.15	10.15	10.05	10.05	−69130.08
$\Delta Q_2 = 1.0$: off centre										
$S = 1$	17.81	17.05	0.00	0.76	10.01	10.00	10.12	10.00	10.05	−69132.18
$S = 0$	17.77	17.12	0.00	0.59	10.02	10.01	10.17	10.01	10.07	−69131.45
BaBr $d_0 = 5.4$										
$\Delta Q_2 = 0$: on centre										
$S = 1$	35.38	35.38	0.17	0.17	10.06	10.10	10.10	10.08	10.08	−183991.25
$S = 0$	35.39	35.39	0.13	0.13	10.11	10.10	10.10	10.08	10.08	−183991.06
$\Delta Q_2 = 0.5$: off centre										
$S = 1$	35.58	35.18	0.17	0.34	10.04	10.01	10.22	10.02	10.09	−183991.64
$S = 0$	35.51	35.28	0.13	0.16	10.07	10.02	10.23	10.03	10.12	−183991.13

obtained in [4] and [5]). For NaF a smaller value is used because of the small cluster size used in the present work. The central cations, M_0 of figure 1, are shifted outward by 0.42 au, as described above, while all other cations are held at their perfect lattice positions. The on-centre case is studied similarly with $\Delta Q_2 = 0.0$. We have studied the triplet and singlet states of STE for NaF, NaCl and NaBr. The number of electrons included in these works is respectively 120, 136, and 172 for the three systems. The results are presented in table 2, which is organized as in table 1. The atoms inside the cluster are numbered in figure 1. Again there is a pair of floating Gaussians near the regular anion sites to give further variational freedom to the excited electron.

The main results are the following. First, there is generally a spontaneous loss of inversion symmetry in all cases, leading to the C_{2v} symmetry. In NaF, this is accompanied by a large off-centre shift of the F_2^-. In NaBr, the off-centre shift seems to be small. This has already been observed in earlier work using the extended-ion method. NaCl may be regarded as an intermediate case. In all cases we observe that the excited electron becomes localized on the nascent vacancy (FG_2 and surrounding cations of figure 1). We observe a strong correlation between the electron and the hole: the electron and hole tend to pull together. The electron is concentrated on M_2 and the basis FG_2 while the hole is shifted on X_2 in all cases (refer to figure 1).

There is a noticeable difference between the spin singlet and triplet states. The singlet-state energy is always higher than that for the triplet state. Also, it seems that

Table 3. Results of four-atom cluster of the STE in KF, obtained with the ICECAP code. Charges and total energy are given for the on-centre and off-centre geometry ($S = 1$). $d_0 = 3.71$ (au).

Charges	X_1	X_2	FG_1	FG_2	M_0	Energy (eV)
$\Delta Q_2 = 0$: on centre						
	9.41	9.41	0.54	0.54	18.06	−5407.77
$\Delta Q_2 = 1.1$ au: off centre						
	9.75	8.99	0.20	0.54	18.26	−5411.66

the singlet state experiences a weaker tendency toward lower symmetry. This point was also noted in an earlier work using the extended-ion method [15]. There are new intriguing data concerning the emission of the singlet STE. In NaBr, NaI and others such as NaBr:I (I_2^- plus electron) the π band is found to contain a weak component with lifetime in the range of a nanosecond, which is the typical lifetime of the singlet state [16]. Further studies are in progress using the present method in order to shed new light on this intriguing problem.

As we mentioned in section 2, the ICECAP code is capable of handling the relaxation and polarization outside the quantum mechanical cluster in a consistent manner. In the following, we present the result on the four-atom cluster STE in KF obtained by optimizing the positions of the pairs of anions and cations separately a few times in sequence. A relatively rudimentary level of the multipole consistency was achieved in this work. The result should, therefore, be considered as preliminary. Table 3 gives the charge distribution and the total energy of the triplet STE state for on-centre and off-centre geometries. The total energy drops by about 4 eV when the V_k core has slipped out of the on-centre position by about 1.1 au.

We note some general agreements and differences on comparing the two works on the K_2F_2 cluster made with the CADPAC and ICECAP codes. Both indicate a clear off-centre trend for the STE and a strong electron–hole correlation as indicated by the Mulliken populations. On the other hand, the total energy change corresponding to comparable values of ΔQ_2 is greater with the ICECAP method. There are also some differences in the distribution of the excited electron charge on the floating basis FGs and the cations M_0. These differences are probably attributable to the differences in K ion positions, pseudopotential versus full basis treatment of K ions and the fundamentally different treatment of the lattice outside the quantum mechanical region in the two approaches. We have not investigated these possible effects further since they are outside the scope of the present work. Rather, we stress that the main points of each calculation are in accord with one another and with earlier extended-ion calculations. Indeed, this is quite satisfactory considering the difference of the methods used.

In this paper we reported the preliminary results on the structure of the STE in three sodium halides (NaF, NaCl and NaBr) and KF obtained with two distinct *ab initio* computer codes. Although the size of the cluster treated quantum mechanically is rather small because of the time required in such work, all major results obtained in earlier works based on extended-ion methods are confirmed. Our results also indicate the possibility of studying different spin states as a function of the lowered lattice symmetry which would be crucial in understanding the mechanism of the σ emission bands. Such

work is now under way. Future work will include basis set optimization, which is not studied here.

References

[1] Itoh N 1982 *Adv. Phys.* **31** 491
[2] Williams R T, Song K S, Faust W L and Leung C H 1986 *Phys. Rev.* B **33** 7232
[3] Leung C H, Brunet G and Song K S 1985 *J. Phys. C: Solid State Phys.* **18** 4459
[4] Song K S, Leung C H and Williams R T 1989 *J. Phys.: Condens. Matter* **1** 683
[5] Song K S and Leung C H 1989 *J. Phys.: Condens. Matter* **1** 8425
[6] Rabin H and Klick C C 1960 *Phys. Rev.* **117** 1005
[7] Block D, Wasiela A and Merle d'Aubigné Y 1978 *J. Phys. C: Solid State Phys.* **11** 4201
[8] Block D and Wasiela A 1979 *Solid State Commun.* **28** 455
[9] Amos R D and Rice J E 1987 *CADPAC: The Cambridge Analytical Derivatives Package* issue 4.0 (Cambridge)
[10] Harding J H, Harker A H, Keegstra P B, Pandey R, Vail J M and Woodward C 1985 *Physica* B **131** 151
[11] Fisher A J, Hayes W and Stoneham A M 1990 *Phys. Rev. Lett.* **64** 2667
[12] Catlow C R A, Diller K M, Norgett M J, Corish J, Parker B M C and Jacobs P W M 1978 *Phys. Rev.* B **18** 2739
[13] Huzinaga S 1984 *Gaussian Basis Sets for Molecular Calculations* (New York: Elsevier)
[14] Bachelet G B, Hamann D R and Schluter M 1982 *Phys. Rev.* B **26** 4199
[15] Song K S and Leung C H unpublished
[16] Kan'no K, Tanaka K, Kosaka H, Mukai T, Nakai Y, Itoh M, Miyanage T, Fukui K and Watanabe M 1990 *Phys. Scr.* **41** 120