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## Decay of the self-trapped exciton near the (001) surface in NaBr and KBr

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Received 26 April 1999

**Abstract.** The adiabatic instability of the self-trapped exciton near the (001) surface in NaBr and KBr leading to Br atom desorption is studied. It is shown that in the first two layers below a (001) surface, the exciton relaxes backward to the bulk; no desorption may result thereby. Only from deeper layers does the instability propel the  $\text{Br}_2^-$  molecule toward the surface as well as backward. The relaxation toward the surface is strong in KBr, making energetic Br desorption likely. Similar strong relaxation is not found in NaBr, by contrast. These results are discussed in comparison with experimental data on energetic halogen atom desorption upon electronic excitation.

### 1. Introduction

Recent progress in the study of halogen atom desorption from the surface of alkali halide crystals has established several interesting points. Time-of-flight (TOF) studies [1] have shown that in a number of crystals there is a non-thermal energy component of halogen atom desorption beside the thermal component which is observed in all crystals. In KBr, which is a typical example with a non-thermal component, the hyperthermal emission energy is centred around 0.3 eV and can be as large as 1 eV. While the thermal component yield depends on the temperature, that of the energetic emission does not. Compounds having an energetic component include KCl, RbCl, KBr, RbBr, KI and RbI [2]. This group of alkali halides is known for its efficient low-temperature F-centre formation under ionizing irradiation [3, 4]. Also, this group of alkali halides is characterized by a large off-centre axial relaxation of the self-trapped excitons (STEs) according to recent theoretical work [5, 6]. NaF, which belongs to the above group, has only a weak hyperthermal halogen emission, however.

The energetic emission of the halogen atom is characterized by its direction of emission, which is perpendicular to the (001) surface [1]. Earlier, it was argued that the halogen desorption is the consequence of the STE relaxation near the surface [7]. The later observation that the direction of emission is not along the molecular axis of the STE in the bulk seemed to contradict this interpretation. Recently, theoretical studies based on two different approaches have been made. Puchin *et al* [8] have studied the STE decay near the (001) surface in NaCl employing an embedded-cluster quantum chemical method, while Song *et al* [9] have studied the STE decay near the surface of NaBr, KBr and RbBr on the basis of the extended-ion approach combined with classical treatment of the lattice. Both studies predicted the correct direction of emission. According to these studies, the STE undergoes an axial instability near a (001) surface, as in the bulk. The excited electron of the STE localizes at an anion site, thereby becoming an F centre. This localization is accompanied with the release of a large

relaxation energy which propels the H centre, the halogen molecular ion  $X_2^-$ , along the (110) axes. However, as the head halogen atom emerges from the surface, there is a correction of the trajectory which brings it toward the normal to the (001) surface. Song *et al* have also found that energetic desorption of Br atoms was possible not only in KBr and RbBr, but also in NaBr, which has never been observed. The result on NaBr presents therefore a troubling question.

We have made new careful studies of the subject, including aspects which have not been adequately attended to in earlier work. Earlier theoretical calculations have been performed with samples of limited thickness. A five-monolayers NaCl sample was used in [8] and a hemispherical sample with about 2500 ions was used in [9]. In the present work, we have studied the STE decay near a (001) surface in NaBr and KBr using a larger number of layers. Each monolayer is represented by an infinite two-dimensional lattice.

The main results obtained are as follows.

- (1) The STE near the (001) surface induces a lattice instability similar to that in the bulk. However, when the STE is created in the first two layers below the (001) surface, the excited electron localizes at the site nearer to the surface (the proximal site) and propels the H centre into the bulk.
- (2) Only from the third layer and below can the electron localization take place with equal probability at the distal (away from the surface) and proximal sites. This is observed for both KBr and NaBr.
- (3) From the third layer and below, the relaxation of the STE is similar to that in the bulk. In particular, there is a substantive energy barrier for the H-centre propulsion in NaBr. On the other hand, there is no such barrier in the case of KBr and an energetic Br desorption is possible with a kinetic energy of the order of 1 eV.

In section 2 we present some details of the method used. Section 3 presents the results obtained followed by a discussion of the new results compared with experiments as well as earlier calculations.

## 2. Method of calculation

The excited electron and the self-trapped hole are treated by the extended-ion method and CNDO code respectively as in the earlier work on the STE in the bulk crystal [5, 10] and other excited-state studies [11]. The use of a floating 1s Gaussian orbital (FGO) makes it practical to evaluate various short-range terms (screened Coulomb, exchange and overlap integrals) efficiently. It also gives us the flexibility of placing the Gaussians at appropriate positions in the crystal to best represent the defect electron states.

The Hamiltonian of the excited electron is given as

$$H = -\frac{1}{2}\Delta^2 + V_{pi}(\vec{r}) + V_{sc}(\vec{r}) + V_{ex}(\vec{r}) \quad (1)$$

where  $V_{pi}$ ,  $V_{sc}$  and  $V_{ex}$  are point ion potential, screened Coulomb potential and exchange potential, respectively.

The defect electron wavefunction is represented by  $\psi$ , which is orthogonal to all of the occupied ionic orbitals  $\chi_{\gamma,\lambda}$  ( $\chi_{\gamma,\lambda}$  is the  $\lambda$ th occupied atomic orbital on the  $\gamma$ th atom):

$$|\psi\rangle = \sum_i c_i \left[ |\phi_i\rangle - \sum_{\gamma,\lambda} |\chi_{\gamma,\lambda}\rangle \langle \chi_{\gamma,\lambda} | \phi_i \rangle \right]. \quad (2)$$

$\phi_i$  is a floating 1s Gaussian ( $\exp(-\alpha_i(r - R_i)^2)$ ). The problem now is solving the secular equation for the state  $\psi$  and its energy  $E$ :

$$|H_{i,j} - ES_{i,j}| = 0. \quad (3)$$

With the introduction of the ion-size parameters for the deep core and the interpolation formulae for the short-range energy terms and overlap integrals, we can easily obtain the electronic energy, which is a part of the total system energy. The details of the extended-ion approach are given in [5, 10]. (The parameters used in this work can be obtained from the authors upon request.)

In calculating the adiabatic potential energies, the lattice deformation and polarization energies are evaluated using classical approaches. Pair potentials published in reference [12] are used for host atoms. As for the polarization energy, the point polarizable dipole approach is used. The  $\text{Br}_2^-$  molecular ion on which the hole is localized interacts strongly with the excited electron and undergoes a large relaxation including a bond-switching sequence before the Br atom reaches the surface. This part is represented by a CNDO code with up to five Br atoms. The parameters of the pair potential, and the polarizability of the atoms and the CNDO code are given in table 1 and table 2. The various parts are interfaced in such a way that the charges on the Br atom cluster are input into the calculation of the excited electron energy as well as the potential due to the excited electron in the calculation of the hole centre by the CNDO code. The details of this part including the various approximations used are given in our recent paper on the STEs in pure and doped caesium halides [10]. Generally, two or three pairs of FGOs:  $\exp(-\alpha|\vec{r} - \vec{R}_i|^2)$ , with optimized damping constant  $\alpha$ , are placed at the two semi-vacancies created when the self-trapped hole, a  $\text{Br}_2^-$  molecular ion, is formed near the surface. Typically, the optimized  $\alpha$  (in atomic units) is around 0.03–0.04. In order to provide enough variational flexibility for the excited electron wavefunction, both a diffuse basis and a compact basis are used. In evaluating the electronic energy, over 400 ions contribute to the short-range energy terms. These include the screened Coulomb energy, exchange interaction and orthogonalization terms for the occupied levels.

**Table 1.** Pair potential coefficients:  $V(r) = Ae^{-r/\rho} - C/r^6 - D/r^8$  (atomic units).

Coefficient	$\text{Na}^+-\text{Na}^+$	$\text{Na}^+-\text{Br}^-$	$\text{K}^+-\text{K}^+$	$\text{K}^+-\text{Br}^-$	$\text{Br}^--\text{Br}^-$
$A$	$3.3489 \times 10^8$	185.18	$2.2682 \times 10^{10}$	161.62	100.88
$\rho$	0.1368	0.5367	0.2050	0.6193	0.7532
$C$	5.188	57.989	60.616	210.99	761.30
$D$	9.562	173.793	171.76	736.41	3157.92

**Table 2.** Polarizability and CNDO parameters for Br.

Polarizability ( $a_0^{-3}$ )			CNDO parameters			
$\text{Na}^+$	$\text{K}^+$	$\text{Br}^-$	$I_s$ (eV)	$I_p$ (eV)	$\beta$ (eV)	$\alpha$ ( $\text{\AA}$ )
1.957	8.980	28.073	-25.2	-6.37	-6.9	2.20

The long-range electrostatic energies are calculated by the Ewald method. In the present work, we simulated the semi-infinite crystal with a (001) surface by a finite number of monolayers. The Madelung potential for the two-dimensional infinite lattice has been treated in several papers [13, 14]. Here, we have used the approach presented in [14].

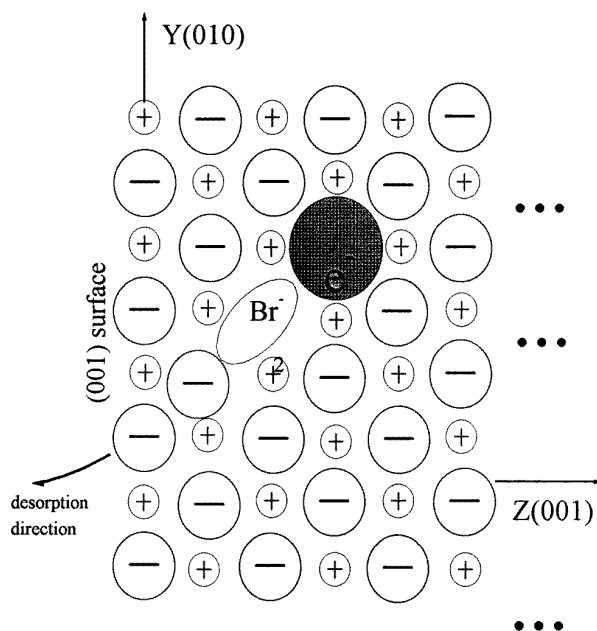
The total system energy  $E_{total}$  is therefore represented as

$$E_{total} = E_{coul} + E_{rep} + E_{elec} + E_{pol} + E_{CNDO} \quad (4)$$

where  $E_{coul}$ ,  $E_{rep}$ ,  $E_{elec}$ ,  $E_{pol}$  and  $E_{CNDO}$  are the lattice electrostatic energy, pair potential energy, electronic energy, polarization energy and CNDO energy, respectively.

In determining the equilibrium structure or the adiabatic potential energy surface (APES) of a given species of localized exciton, a finite number of ions are explicitly allowed to relax in minimizing the total energy of the system. The number of relaxing ions depended on the number of Br atoms in the part treated by the CNDO code, and varied between three and five dozen ions. In our previous work on excited defect calculations [5, 9, 11], we have optimized the positions of several dozens of atoms by evaluating the energy gradient and determining the local energy minimum one atom at a time. This sequence was repeated a number of times until the total energy of the system satisfied a predetermined threshold of convergence. In the present work, we improved the minimization routine by relaxing all atoms at the same time or groups of atoms by symmetry. Energy gradients for all atoms were evaluated before moving any atoms. Then the energy surface was fitted to a quadratic form and all atoms were displaced to the new positions. The cycle was repeated until the largest energy gradient and the energy change both became smaller than a preset value (e.g., 0.01 eV/Bohr radius and 0.005 eV respectively). This approach leads to an improved symmetry of the atomic displacement around the defect and also resulted in a shorter computing time being required to reach the equilibrium geometry. The details are given in the appendix.

The first investigation was to study the site of the excited electron localization near a (001) surface. This electron localization determines the way in which the molecular ion will be relaxed: either forward (toward the surface) or backward (away from the surface into the bulk). In order to study the dynamics of  $\text{Br}^0$  desorption, we then determined the APES of the forward-relaxing STEs in both NaBr and KBr. This was done as follows. For the third-layer STE, four Br atoms (at (000), (011), (022) and (033), as shown in figure 1) are treated in



**Figure 1.** A schematic illustration of halogen atom desorption. In this case, the STE is formed by Br atoms in the third and fourth layers, i.e., atoms (022) and (033), and the electron is localized at site (033).

the CNDO cluster. A forward relaxation follows a localization of the excited electron at the vacated site (033). First, the Br at (033) is given a series of fixed positions along the [011] axis until it reaches the site (022). At each step, all other atoms are relaxed by the process described above. After this, the Br atom originally at (022) is moved to a number of fixed positions along the axis [011] leading to the site (011), and so forth. At the end, when the Br atom originally at the surface site (000) leaves the surface, its position as well as the direction is determined by minimizing the total energy. This process allows the hole to be transferred from one pair of Br atoms to the next pair. In drawing an APES, we found it more convenient to use  $R$ , the distance of the hole centre from the surface, than  $Q_2$  previously used [5] which designated the hole position measured from the localized electron site.

### 3. Results

We have studied several situations in which a STE can induce Br desorption from the (001) surface of NaBr and KBr. This work has two parts. The first part is the study of the exciton relaxation as a function of the depth from the (001) surface. We analysed the decay of the STE formed in the first four layers below the surface in KBr and NaBr. In the second part we study those cases of the STE decay which lead to the off-centre relaxation toward the surface, with possible desorption of  $\text{Br}^0$ . For all of the work presented here, the sample consists of 14 layers of an infinite two-dimensional lattice.

#### 3.1. Decay of the self-trapped excitons near a (001) surface in NaBr and KBr

The STEs created below the surface at a depth of up to four layers are considered. Only those STEs which are formed between two adjacent monolayers are studied. The strongest relaxation found in the bulk involves the off-centre axial transport of the hole along the [011] axis. Only those axial relaxations heading toward the (001) surface are considered to lead to dynamic Br atom desorption. Other systems of interest include the STE formed on the surface or on a plane parallel to the surface. In those cases, a more complex relaxation including reorientation of the hole centre might be involved. Such cases can best be handled in molecular dynamics studies, and have therefore been left out. In this work the first-layer STE corresponds to  $\text{Br}_2^-$  formed between the surface and the next monolayer. The second-layer STE is between the first and the second monolayers, and so forth. We started by placing a  $V_K$  centre at a pair of adjacent halogen sites of two layers and relaxed the lattice. After this preliminary step, floating Gaussian functions are placed at the two anion sites which are vacated by the two Br atoms forming the  $V_K$  centre. At this point, we have to determine the direction of the off-centre relaxation of the STE (forward or backward). The total system energy is minimized by relaxing all atoms without constraint, and allowing the excited electron to freely find its localization site. Due to the Coulomb attraction between the hole and the electron, the site of the electron localization determines which way the hole centre undergoes off-centre relaxation. The results are very different depending on the layers where the STE was formed initially. The main points are as follows.

- (a) With the first- and second-layer STEs, the excited electron is found to localize at the anion site nearer to the surface (proximal site) in both KBr and NaBr. As a result, the  $\text{Br}_2^-$  was propelled toward the bulk. To verify any dependence on the choice of basis sets used, a number of sets of FGOs have been used both with varying  $\alpha$  as well as varying size of the basis. In all cases we found that the excited electron localized at the proximal site to the surface. For a flexible set of basis functions which does not favour either of the two sites

( $\alpha = 0.02$  at the two Br sites, and  $\alpha = 0.01$  and  $0.03$  at the mid-point of the  $\text{Br}_2^-$  molecule), a typical result is shown in table 3. The total system energy, the bond length, the hole charge distribution and the net off-centre displacement of  $\text{Br}_2^-$  at the energy minimum are given. In our earlier preliminary work [9], we assumed that both backward (toward the bulk) and forward (toward the surface) off-centre relaxations were equally likely at any depth. As we were primarily interested in the desorption energetics, we provided the FGO basis only at the deeper anion site (distal site), thereby preventing the molecular ion from ever relaxing backward.

- (b) With the third- and the fourth-layer STEs, we observed the molecular ions to undergo relaxation forward as well as backward in both NaBr and KBr. The difference between the layers close to the surface and the deeper layers can be seen in the Madelung potential at different layers as shown in table 4. In a bulk crystal, the relaxation in one or the other direction is equally probable. In this sense, the third and deeper layers hence approach the bulk.

**Table 3.** The localization of the excited electron in the first and second layers.  $E$  and  $d_0$  are respectively the system energy and molecular bond length;  $q_{prox}$  and  $q_{dist}$  are the charges on the proximal and distal ions;  $\Delta Q_2$  is the shift of the molecular centre. ‘Back’ means that the molecule moves backward.

	Molecular position	$E$ (eV)	$d_0$ (Å)	$q_{prox}/q_{dist}$	$\Delta Q_2$ (Å)	Motion
NaBr	1st layer: (000)/(011)	7.58	2.75	-0.45/-0.55	0.3	Back
	2nd layer: (011)/(022)	9.36	2.73	-0.51/-0.49	0.4	Back
KBr	1st layer: (000)/(011)	7.18	2.78	-0.42/-0.58	0.4	Back
	2nd layer: (011)/(022)	8.84	2.75	-0.46/-0.56	0.5	Back

**Table 4.** The Madelung potential in the 14-layer lattice and in the bulk (in rydbergs).

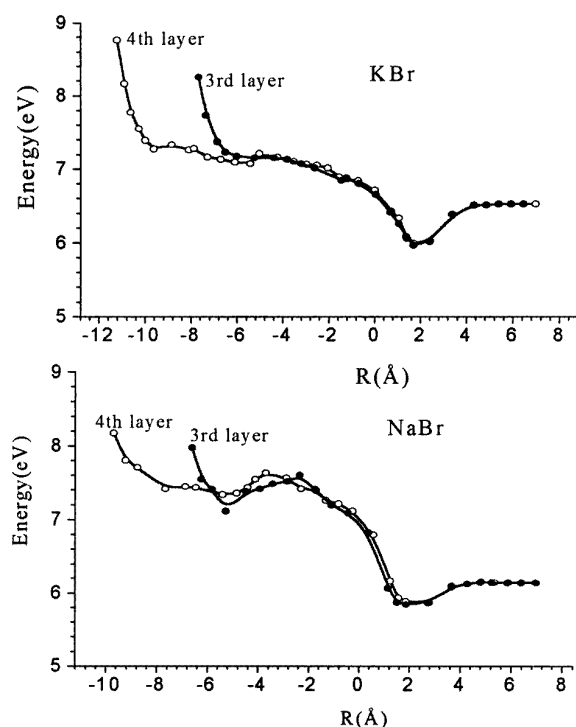
	Front surface	2nd	3rd	4th–11th	12th	13th	Back surface	<b>Bulk</b>
KBr	0.272789	0.283623	0.283496	0.283498	0.283496	0.283623	0.272789	<b>0.283498</b>
NaBr	0.301233	0.313197	0.313057	0.313058	0.313057	0.313197	0.301233	<b>0.313058</b>

### 3.2. The third- and fourth-layer STEs and desorption of Br

From the above result it appears that only the third- or deeper-layer excitation can lead to Br desorption. We have therefore determined the APES of the STE relaxation with the electron localized at (033). The result for the fourth layer is similar to that for the third layer; therefore, we describe here mainly the results for the third-layer STE. In order to provide a flexible basis for the excited electron which is rather diffuse before it localizes more strongly at the anion vacancy, we have employed a set of three FGOs comprising both diffuse and compact components ( $\alpha = 0.01, 0.02$  and  $0.03$  for KBr, and  $\alpha = 0.01, 0.02$  and  $0.035$  for NaBr). As described above, a set of four Br atoms from (000) to (033) are treated by the CNDO code. At the beginning the Br atoms at (022) and (033) are relaxed to form a  $V_K$  centre. A cluster of 47 atoms are explicitly relaxed. Three FGOs are placed at the anion site at (033). The first Br atom to take discrete steps along the axis [011] is the one at (033) until it reaches the next site (022). All other ions are relaxed by the gradient method as described in section 2. At the end of the first track, the next Br atom from the site (022) takes discrete positions while other ions

are relaxed. This sequence allows the hole to diffuse along the row of Br atoms. At the end the Br atom from the site (011) reaches the site (000), at which time the Br atom from the site (000) is found to leave the surface along a trajectory very nearly perpendicular to the (001) surface. At a distance of about 4 Å from the surface, the desorbing Br atom is close to being neutral and its direction from the normal is about 19°. While the molecular ion  $\text{Br}_2^-$  remains below the surface, the motion is more or less along the [011] direction as in the bulk. As the head Br atom clears the surface, there is a clear sign of trajectory correction toward the normal to the surface according to calculations. The trajectory correction is attributed to the symmetry of the various forces of both short and long ranges acting on the desorbing atom. At this point it is very difficult to minimize the energy relative to the angle. We simply pulled the desorbing atom perpendicularly until it reached about 8 Å from the surface. These results are shown in figure 2 for NaBr and KBr. The configuration coordinate  $R$  represents the position of the centre of the hole population from the surface projected along the normal (the  $z$ -component). There are several features which are of particular interest.

- (1) In both NaBr and KBr the localized electron propels the hole centre along the [011] axis. As has been seen in the bulk, associated with such relaxation is a package of energy which can be converted into kinetic energy of the Br atom. The nominal energy drop from the early stage of the relaxation is quite considerable. It is, however, reasonable to



**Figure 2.** The calculated adiabatic potential energies of the STE in the third and fourth layers below a (001) surface are shown for KBr and NaBr. The coordinate  $R$  (Å) gives the distance between the (001) surface and the centre of gravity of the hole charge distributed on the bromine ions.  $R = 0$  represents the surface.



assume that only a fraction of this energy drop can effectively be converted to produce a sequence of bond-switching events leading to the desorption from the surface. The entire relaxation involves not only the translational motion along the [011] axis, but also many other modes. In this regard it is interesting to refer to recent work by Meise *et al* on the ODMR (optically detected magnetic resonance) of the STE in KBr at liquid He temperature [15]. From an analysis of the resonance spectra it was concluded that the hole and electron centres—respectively the H and F centres—are correlated in space and their separation was estimated to be the fourth-nearest-neighbour distance. Assuming that a ballistic model of the process is reasonable, it was argued that an initial kinetic energy of about 1 eV could lead to such a separation. We could apply a similar reasoning here and say that an energy of about 1 eV is available at the start of relaxation for the dynamic process along the [011] axis, compared with a nominal energy drop of about 2.5 eV for KBr. As can be seen in figure 2, the fourth-layer STE undergoes quite similar relaxation to the third-layer STE. The difference is in the longer relaxation path to the surface. Future molecular dynamics simulation of the STE relaxation could deal more directly with some of the points presented above.

- (2) There is a significant difference between NaBr and KBr, however. Just as was seen in the bulk [5, 6], there appears in NaBr a substantial barrier at around  $R = -3 \text{ \AA}$  on the path for further separation of the hole centre from the electron centre. It is concluded that in NaBr the bond-switching sequence may not reach the surface, or even if it did there may not be sufficient kinetic energy left on reaching the surface, as can be seen in figure 2.
- (3) In all cases studied, there is a dip in the energy, at about  $R \approx 2 \text{ \AA}$  from the surface, before a plateau appears. Our calculation shows that this is related to the dissociation of  $\text{Br}_2^-$ .

The above results are now compared with the experimental data obtained through TOF measurements made by Szymonski *et al* [1, 2]. No hyperthermal energy Br atom desorption has been observed in NaBr, while in KBr an average kinetic energy of about 0.3 eV is observed in the fast temperature-independent component. A maximum energy of up to 1 eV is observed. Generally, alkali halides are divided in two groups according to their sensitivity to radiation damage at very low temperature. Rabin and Klick [3], and later Townsend [4], have shown that NaBr, NaI, KI, LiCl and LiI have very low F-centre formation yield at liquid He temperature under x-ray or electron beam irradiation. They have also shown that CsF, RbF, KF, RbCl, NaF, KCl, RbBr, KBr and RbI are among those where there is an efficient channel of dynamic F-centre formation. Such division has been correlated with the degree of off-centre relaxation of the STE [5, 6] as predicted by theory. Large off-centre relaxation is also correlated with large Stokes shift of the triplet STE luminescence (the  $\pi$ -band) [6, 16]. In recent work [2], Szymonski *et al* have shown that the efficient F-centre production at low temperature and the hyperthermal energy halogen desorption are observed in the same group of alkali halides, but possibly excluding NaF which has a weak component of hyperthermal energy halogen emission.

The result obtained in the present work is therefore in qualitative agreement with the experimental data of reference [2] as well as with the overall view of the defect creation induced by exciton decay. In our earlier preliminary work [9], we assumed incorrectly that the STE relaxes off-centre with equal probability both forward and backward, irrespective of the proximity of the (001) surface. As we were interested in the forward relaxation leading to desorption, we placed the floating Gaussian basis only at the deep end of the hole centre which automatically propelled the hole centre toward the surface. In this way, we found that an energetic Br emission was possible even in NaBr if the excitation takes place from the first two layers. This result was in disagreement with the experimental observation of reference [2]

and was very puzzling. We now understand how this conclusion was reached. It should be mentioned that Puchin *et al* [8] in their work on NaCl had made a similar assumption and provided a floating basis only on the deeper end of the Cl row, thereby propelling the molecule to relax toward the surface in all layers studied.

We have examined the influence of the sample thickness on the relaxation of the STE near the surface. Employing the same set of Gaussians, we varied the number of layers between 8 and 14. No significant difference was observed, either in the pattern of forward and backward relaxation, nor in the amount of relaxation energy. It is nevertheless to be noted that there is a minimum number of layers required for a given depth from the surface where the STE is created. For example, it is clearly incorrect to study a fourth-layer STE with less than eight layers, as the back surface is closer.

#### 4. Conclusions

We have reported that near a (001) surface of alkali halides, there is a clear indication of adiabatic instability of the STE. In the first two layers, the STE relaxes backward into the bulk and no halogen is emitted from the surface in both NaBr and KBr. From the third and deeper layers, the STE can relax in both directions with equal probability and therefore can lead to desorption of halogen atoms. However, only in KBr and presumably in others of the same group is an energetic halogen atom emission expected. The Madelung potential is considered to be the principal cause of this effect near the surface.

#### Appendix

The quadratic form  $E(\alpha)$  is constructed in terms of a non-negative variable  $\alpha$ :

$$E(\alpha) = E_0 + \alpha E_1 + \alpha(\alpha - \alpha_1)E_2 \quad (\text{A.1})$$

which interpolates between the system energies at  $\alpha = 0$ ,  $\alpha_1$  and  $\alpha_2$ . The displacement of the whole system is determined by  $\alpha \mathbf{G}$ , where

$$\mathbf{G} = \left( \sqrt{\sum_{i=1}^N |g_i|^2} \right)^{-1} \begin{pmatrix} g_1 \\ g_2 \\ \vdots \\ g_N \end{pmatrix} \quad (\text{A.2})$$

represents the direction of the system energy gradient.  $N$  is the number of relaxing atoms and  $g_i$  the energy gradient vector of the  $i$ th atom.

On setting  $dE/d\alpha = 0$ , we obtain

$$\alpha_{min} = \frac{1}{2}(\alpha_1 - E_1/E_2). \quad (\text{A.3})$$

$E_1$  and  $E_2$  are given as

$$E_1 = \frac{(E(\alpha_1) - E_0)}{\alpha_1} \quad E_2 = \frac{(E(\alpha_2) - E_0 - \alpha_2 E_1)}{\alpha_2(\alpha_2 - \alpha_1)} \quad (\text{A.4})$$

where  $E_0$  is the system energy for atoms at position  $\mathbf{X}_0$  (a  $3 \times N$  matrix representing the geometrical configuration of the lattice), and  $E(\alpha_1)$  and  $E(\alpha_2)$  are the system energies respectively at two different positions  $\mathbf{X}_0 - \alpha_1 \mathbf{G}$  and  $\mathbf{X}_0 - \alpha_2 \mathbf{G}$ . Finally, the new position  $\mathbf{X}$  of relaxing atoms is given as

$$\mathbf{X} = \mathbf{X}_0 - \alpha_{min} \mathbf{G}. \quad (\text{A.5})$$

In each optimizing step, the maximum  $\alpha$  is restricted to within 0.25 au to ensure reasonable relaxation for all movable ions.

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