Relaxation of excitons in ionic halides: a molecular dynamics study[†]

Relaxation of excitons in ionic halides: a molecular dynamics study†

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Abstract
We report here the results of molecular dynamics simulation of hole and exciton relaxation in KBr and NaBr. The semi-classical program previously used for study of static properties has been modified to implement the solutions of Newton's equations with a time step of 0.50 femtosecond. The hole self-trapping process is studied at 80 K. A rapid bond-length oscillation is observed which damps out very fast in NaBr (in about 0.5 picosecond). The relaxation of a Frenkel-type exciton (localized on a single site) is studied at 10 K. It is found that the localization of the excited electron at an anion site drives the relaxation process, resulting in the simultaneous formation of H and F centres. In KBr, the F–H pair created has the F and H about 14 Å apart (third neighbours). In NaBr, the separation is about 4 Å. The maximum relaxation is achieved in about 1.5 ps in KBr, and in about 0.75 ps in NaBr. These results are discussed in comparison with recent femtosecond spectroscopic work.

1. Introduction

In a number of insulators the exciton–phonon coupling can be significant and as a result the exciton may be localized in the lattice spontaneously, leading to the formation of self-trapped excitons (STE). Associated with a STE, an energy package of a few electron volts is confined within a volume of the order of a unit cell. Such system can induce large-scale atomic displacements leading to energetic atom desorption [1] or permanent lattice defects [2].

Of the many materials in which the STE is observed, the most extensively studied are the family of ionic halides [3]. The primary radiation defect formed following electronic excitation is a pair of electron and hole centres. The electron centre, known as the F centre, is an anion vacancy with an electron bound to it. The hole centre is a pair of halogen ions sharing a hole between them. Depending on whether it occupies a single anion site or a pair of anion sites, the hole centre is called an H centre or a V_K centre. The H centre is viewed as an interstitial halogen atom, while the F centre represents an anion vacancy. The V_K centre on the other hand describes a state of the self-trapped hole, not directly associated with the lattice defect.

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Experiments have shown that F centres are created as early as two picoseconds after excitation in KBr at room temperature [4]. More recent ultra-fast spectroscopic studies have shown that the processes taking place even earlier are quite complex [5–7]. For example, it is observed [6, 7] that the F centres are produced within a timescale of the order of a picosecond at low temperature in KBr and RbBr under band-to-band excitation. Also, that the stable form of the hole, the V_K centre, takes a substantially longer time to form in KBr (of the order of ten picoseconds) compared with in NaBr where it is achieved within a picosecond.

It is therefore clear that it is important to understand the dynamic aspects of exciton relaxation. A series of calculations, of both semi-classical [8, 9] and *ab initio* types [10, 11], have established the presence of a strong trend toward so-called off-centre relaxation. In this work we present the results of a molecular dynamics (MD) study of hole and STE relaxation in NaBr and KBr. The main results are: starting from a one-centre hole state the V_K centre forms quite quickly (within less than one picosecond), but undergoes a rapid oscillation which can last up to about 3 ps or more in KBr while in NaBr it damps out in less than 1 ps; starting from a one-centre exciton (such as a Frenkel-type exciton), the off-centre relaxation is found to be vigorous in KBr and reaches the maximum F–H separation (the third-neighbour separation) in about 1–2 ps depending on temperature; a similar off-centre relaxation is much weaker in NaBr; there is a slow oscillation of the H centre after it has reached the maximum relaxation; during an exciton relaxation no fast oscillation of the hole centre is observed. A brief description of the method used is given in section 2, followed by a presentation of the results in section 3.

2. Method

The cluster of atoms considered for the MD simulation is of finite size, in the range between 120 and 160, and is embedded in an infinite static lattice. All atoms within the first five neighbouring shells of a string of halogen atoms are included in the MD study. The choice of the string of halogen atoms in fact restricts the kind of hole motion that can follow in the MD. For example, up to five halogen atoms along a (110) axis are taken in the study of the exciton relaxation. When a rotational diffusion of the hole centre is being studied, the halogen atoms are along two pieces of the strings joined at a certain angle. Such a restriction is inevitable in our approximation in which the hole is treated by the CNDO (complete neglect of differential overlap) code for a limited number of halogen atoms while the excited electron is treated in the extended-ion approximation (or one-electron Hartree–Fock approximation) interacting with about 600 atoms. The polarization and the atom–atom interactions are treated classically. The details were given earlier [9]. At the beginning of the MD study, the cluster of atoms is equilibrated at a specified temperature in the ground state. This is achieved within about one thousand time steps (about 0.5 ps). After this, the excited species under consideration, such as a Frenkel-type exciton (described as a Br^0 plus an excited electron), is introduced. For each of the atoms in the MD cluster the forces $\mathbf{F}$ are evaluated numerically from the calculated potential energies:

$$\mathbf{F} = -\nabla E(\{\mathbf{R}_i\})$$

where E is the total potential energy of the system and $\{\mathbf{R}_i\}$ the coordinates of the MD atoms.

The potential energy E is evaluated in a semi-classical way:

(1) The excited electron is given the privileged status of quantum treatment (extended-ion approximation) as it is the origin of the driving force of the large atomic rearrangement. All short-range terms in the Hartree–Fock equation are evaluated using accurate and efficient interpolation formulae. A large number of atoms are included: between 300 and 600 atoms. This is made practical by using the floating Gaussians as the basis [8, 9].

(2) Atom–atom interaction is included via a pair potential of Buckingham type [12].
(3) Electronic polarization is included via a point polarizable model.
(4) The semi-empirical CNDO code (only for the halide atoms) is employed to treat the self-trapped hole. The parameters used are fitted to the bond length, the stretching mode frequency and the ionization potential of the molecule ion X_2^-.

Various parts are interfaced consistently (in particular, the charges on the CNDO atoms and the electrostatic potential acting on the CNDO atoms are updated as frequently as is needed) in the evaluation of the total energy E:

$$E = E_{el} + E_{CNDO} + E_{pol} + E_{latt}.$$

Taking a time step of 0.48 femtosecond for the bromides, the relaxation is left to run for about 6000 steps.

As the relaxation proceeds, part of the potential energy is converted into kinetic energy of the atoms. The thermodynamic temperature is calculated from the average kinetic energy of participating atoms at each time step. In view of the limited number of atoms taking part in the MD, there is a need to simulate artificially the dissipation of kinetic energies to the surroundings. This was done by reducing the kinetic energy by a fixed fraction for all atoms. In general the temperature rises first and then gradually stabilizes. In the self-trapping of the hole the released energy is relatively small compared with the relaxation of the STE. For the hole centre we have kept the total energy constant (no dissipation). For the exciton we have tried several variation rates for the energy dissipation and found that scaling down the kinetic energies of all MD atoms by 0.85 every ten steps, for example, keeps the temperature at the desired value.

3. Results

A MD study of exciton relaxation presents some basic problems regarding the choice of initial state for starting the dynamics. Ideally, one should start from a plane-wave-like free-exciton state and proceed to self-trapping of charges at particular sites accompanied by lattice relaxation, eventually ending at a stable (the recombined ground state) or a metastable state (the Frenkel defect pair: an electronically excited state). This is not only a complex chain of processes, but also one that is not convenient to consider, as we are primarily interested in the transient triplet STE states as well as the F–H pairs. We have therefore adopted two idealized localized 'initial' states in this study. One is a Frenkel-like exciton state in which the hole is represented by a Br^0 in a lattice under thermal fluctuation. The electron is relatively compact and bound to the hole. This process will show the competition between the electron localization and the V_K-centre bond formation. It is considered that this may represent the experiment with a fast band-to-band pulse at a very early stage, in the first few picoseconds [6, 7]. The other case considered assumes a pre-existing V_K centre which attracts an electron nearby. This may describe the experiment based on double excitation with the pump/probe method [5], or a later stage in the fast band-to-band pulse experiment [6, 7]. In addition to the two cases, we have also studied the dynamics of hole self-trapping, as experiment has shown significant differences at 80 K between NaBr and KBr [6, 7].

3.1. Relaxation of the hole

Relaxation of a single hole (a Br^0 atom) in NaBr and KBr lattices equilibrated to have the ground state at 80 K has been studied. The energy dissipation is varied between no variation and scaling to 85% every ten time steps with the results remaining very similar. The variation

of the bond length with time is shown in figure 1 for the first case. The hole is initially located on one of the two Br atoms. The number of atoms included in the MD simulation is 166. The covalent molecule bond is formed very quickly, within about 0.5 ps. This is accompanied with a rapid oscillation of the bond length which persists in KBr beyond 3 ps. However, in NaBr the oscillation cools off within about 1 ps. The equilibrium bond length is around 2.6 Å and compares well with the results of a static calculation by Cade *et al* [13]. It has been noted that the bond length is remarkably stable for a given halogen species in various matrices [14]. The speed of damping observed is dependent to some degree on the kinetic energy dissipation rate used. There is about 1 eV of energy which is released when a V_K centre is formed. For the result shown in figure 1 the average kinetic energy of atoms near the end of the relaxation is about 90 K in KBr and 100 K in NaBr.
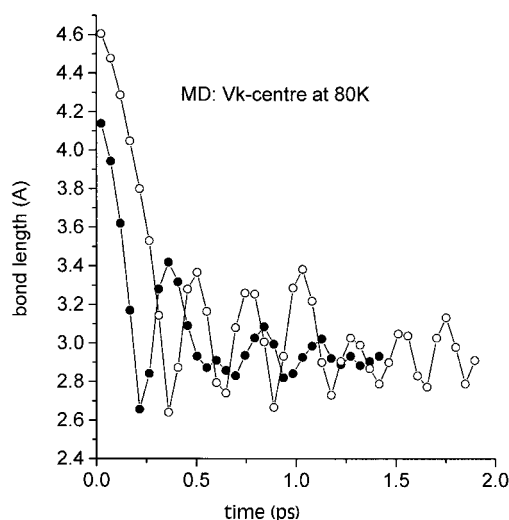
Figure 1. Time evolution of the V_K-centre bond length (in Å) at 80 K in NaBr (solid circles) and KBr (open circles).

It is interesting to compare the present work with a recent report which shows that at 80 K the V_K centre stabilizes much more quickly in NaBr (at about 0.5 ps) than in KBr (occurring after more than 4 ps) [6, 7]. Our work is therefore in qualitative agreement with the experiment. The difference between NaBr and KBr can be understood by comparing the V_K-centre stretching mode frequency (145 cm^{-1}) [15] with the Debye frequencies (129 cm^{-1} and 160 cm^{-1}, respectively, for KBr and NaBr). A localized mode with frequency outside the lattice mode spectrum may take a longer time to dissipate its excess kinetic energy. When we present below the relaxation of a one-centre exciton, we will see the striking effect of the excited electron in the bond formation for the V_K centre.

3.2. Relaxation of the Frenkel-type (one-centre) exciton

One of our objectives is to compare the result of MD simulation with the available low-temperature (10 K) femtosecond spectroscopic data of references [6, 7]. The main point is that the F centre is formed very early, within about 1 ps after the fast band-to-band excitation; this is earlier than the formation of the V_K centre. Together with the appearance of the F centre, an early hole-centre (H-centre) absorption is observed.

The ground-state lattice is first equilibrated at 10 K. Then a Frenkel-type exciton is implanted as the initial state. To simulate the relaxation of a one-centre exciton in KBr, we have started from a string of five Br atoms, with the first one represented by an excited Br atom. The excited electron is described by a Gaussian ($\alpha = 0.025$, in atomic units) centred on Br^0. The number of atoms in the MD simulation is 149 in this study.

Figure 2(a) shows the temporal evolution of the positions (actually the x-coordinates, with the dynamic process taking place along the (110) axis) of the five Br atoms as well as that of the centre of gravity of the hole distribution for KBr. This result was obtained at 10 K with a kinetic energy dissipation of 15% every five time steps. As a result of this dissipation, the average kinetic energy of the atoms in the cluster is kept near 10 K. The variation of the temperature during relaxation is shown in figure 2(b). The bond formation takes place at about 0.5 ps. However, no fast oscillation like that for the V_K centre is seen. This is one of the unexpected observations. On the other hand, the off-centre relaxation begins while the bond is still forming. At about 2 ps, the system relaxes to reach the third-neighbour F–H pair geometry (with the separation of about 14 Å). A similar study conducted at 30 K resulted in a faster relaxation, in about 1.5 ps.
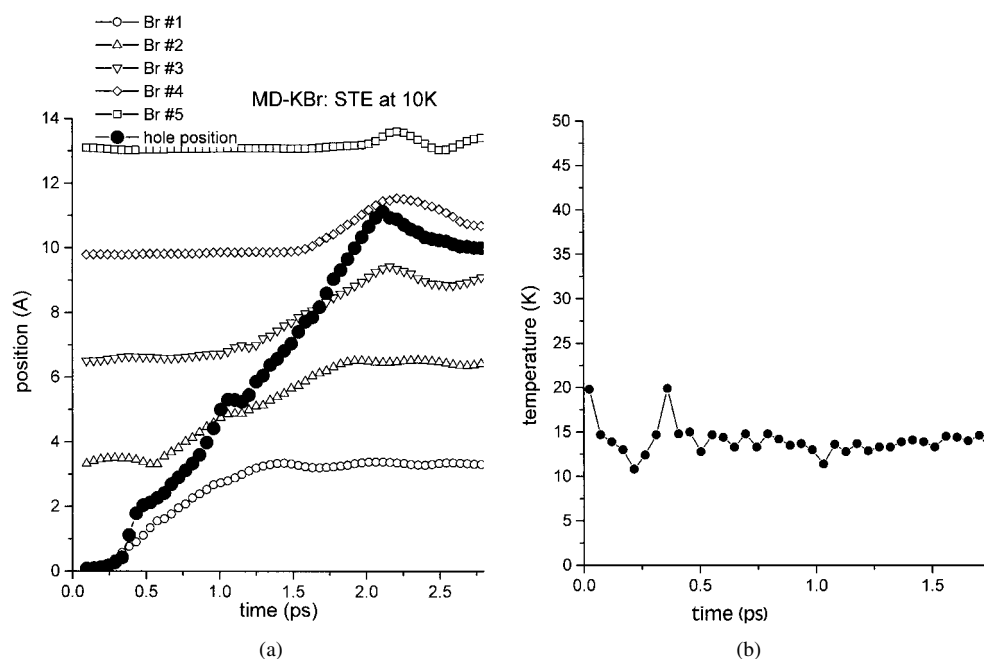
Figure 2. (a) Positions (the coordinates x on the (110) plane in Å) of the five Br atoms and the centre of gravity of the hole distribution as functions of time in KBr at 10 K (with the Frenkel exciton as the initial state). (b) Variation of the average kinetic energy (in K) of the MD atoms (in K) of (a).

In figure 3(a) we show the result for NaBr at 10 K under the same conditions as for KBr. A string of four Br atoms is employed in this case, as it was expected that the hole centre would not diffuse beyond this number. Figure 3(b) presents the variation of the temperature during relaxation. There are several differences from the case of KBr. The range of the hole-centre diffusion is the first thing to notice. At the maximum relaxation, the electron and hole centres are like those in a primitive Frenkel pair (nearest neighbours). There is also some suggestion of early difficulty in achieving the off-centre relaxation—at about 0.25 ps. The
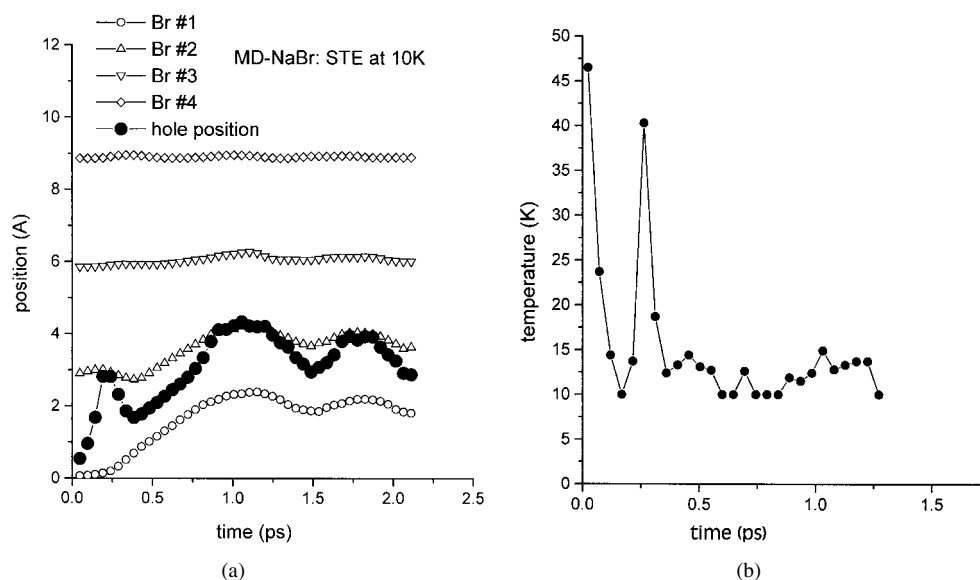
Figure 3. (a) Positions (the coordinates x on the (110) plane in Å) of the four Br atoms and the centre of gravity of the hole distribution as functions of time in NaBr at 10 K (with the Frenkel exciton as the initial state). (b) Variation of the average kinetic energy (in K) of the MD atoms (in K) of (a).

statistical temperature undergoes a fast fluctuation in NaBr compared with KBr in the early stages. In both systems, however, the hole centre oscillates with a period of about 1 ps after reaching the maximum relaxation. It is tempting to associate this slow oscillation between two local minima on the potential energy surface with that observed in NaCl [5], attributed to two minima of the STE energy surface. It is estimated that the electron and hole centres separate with an apparent speed of about 1000 m s^{-1}.

It is to be noted that during the hole diffusion along the (110) Br-atom row, no Br atom is actually transported beyond the next halogen site. The hole is transported in a sequence of Br$_2^-$ bond-switching reactions. In the case of KBr the end product of the relaxation is close to a stable Frenkel defect pair, probably safe from annihilation via recombination, comparable to the result of optically detected magnetic resonance [16]. On the other hand, in NaBr the end product is a weakly off-centre STE. Whether or not the triplet STE in NaBr is truly off-centre or a metastable on-centre entity is not clear, and requires further study [17, 18].

3.3. Relaxation of the two-centre exciton

In this study, the starting configuration is a V_K centre, such as was obtained above for 10 K. A floating Gaussian basis ($\alpha = 0.03$) is placed on one anion site which is now vacated with the self-trapped hole in place. This case could simulate those situations in which an electron becomes attracted to the hole after it has had time to form the V_K centre, or the experiment based on double excitation with the pump/probe technique [5]. In this study the kinetic energies of atoms are reduced by 10% every five time steps. The average temperature of the atoms fluctuated between 10 K and 15 K, except in the first 0.2 ps when it was higher. The results for KBr and NaBr are quite similar to those presented for the relaxation of the Frenkel-type exciton, in section 3.2 above. The differences are in some of the details at early stages. The final

relaxation product in KBr, the third-nearest-neighbour F–H pair, is reached about 0.5 ps earlier. In NaBr we do not observe the apparent hesitation before achieving off-centre relaxation at around 0.25 ps, seen in figure 3(a).

We now discuss the V_K-centre bond formation with and without the accompaniment of an excited electron. In the absence of the excited electron, the bond formation is simply due to the covalent attraction, and the hole is equally distributed on the two Br atoms from the very earliest instant. As there is a modest amount of excess kinetic energy, the oscillation persists until it dissipates. In the presence of an excited electron, the situation is quite different because of several factors: different symmetry of relaxation (combination of bond formation and axial off-centre motion); much larger relaxation energy available; and a strong interaction between the hole and the electron. The process is a superposition of electron localization, hole bond formation and the off-centre axial relaxation along the (110) axis. As a result, the strong oscillation of the bond is suppressed. It is not surprising that the excited electron not only drives the off-centre relaxation, but also has a strong influence on the bond formation of the hole centre.

We have briefly described the results of the MD studies. There are already some new observations which were not foreseen before this study. One is regarding the hole bond formation and its rapid oscillation: the difference between NaBr and KBr; and the absence of similar oscillation during the exciton relaxation. The other is that the F centre, or a primitive form of it, is created very early following the formation of an exciton (of Frenkel type). This is clearly the consequence of the dynamic process induced by the localizing excited electron. A well-separated F–H pair can be formed in KBr within about 1–2 ps following one-centre exciton creation at low temperature. In contrast to the case in ground-state MD studies, the relaxation in an excited state is driven by the conversion of part of the electronic excitation energy into kinetic energy of the atomic subsystem. Part of the electronic energy is spent in creating large atomic rearrangements which may be metastable with very long lifetime, while another part is dissipated into the rest of the crystal. As we have not considered in the present study the radiative recombination channel within the MD simulation, the system remains in the excited state.

Molecular dynamics study of exciton relaxation is only at its beginning. The present work relies on a semi-classical method and there are a number of limitations. There is a need to learn about various aspects such as the rate of energy dissipation for a finite cluster of atoms, especially in the case of an exciton. In view of the many limitations associated with *ab initio* calculations for relaxed excited systems, a molecular dynamics study based on an *ab initio* approach seems quite daunting at present. However, this will have to be undertaken eventually within some approximations acceptable both theoretically as well as computationally. In the meantime we can explore this new field on the basis of more approximate approaches.

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