Simulation of Coherent Dissociation of the Self-Trapped Exciton in Alkali Halides

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Abstract

One of the best-studied point defect in ionic crystals is the self-trapped exciton in alkali halides. We have used existing theoretical and experimental results to parameterise a generic model potential and performed nuclear quantum dynamics simulations with this model using grid-based wave function propagation techniques. A photoinduced reaction is sought that separates the self-trapped exciton into a pair of point defects. A purely vibrational excitation scheme is excluded due to the difficulty of finding a resonant excitation for the double minimum potential. A control scheme based on purely vibrational excitation would also have a time scale that invites dissipative quenching of the process. However, an electronically excited state can be used to take the wave packet to a dissociative flank of the model potential, thereby separating the exciton into the defect pair. A double-pump, double-dump pulse scheme is proposed to attain a satisfactory yield of separated defect pairs. A pump-dump time delay minimising the population of the barrier area in the two-dimensional potential is proposed to avoid quenching of the process due to non-radiative coupling.
I. INTRODUCTION

Among the best studied crystalline defects are the Frenkel defects in alkali halides, most prominently the self-trapped exciton (STE). The current qualitative atomistic model of the triplet STE in alkali halides (MX, where M denotes the metal and X the halogen compound) was proposed by Song and co-workers.\textsuperscript{1} It has been developed further using effective potential and embedded cluster ab-initio Hartree-Fock calculations\textsuperscript{2–4}. Experimental evidence\textsuperscript{4} supports the following currently accepted model.

According to this model, the STE consists of a pair of halide ions with an excited electron localised on them. The excitation can follow one of two pathways: Either it decays non-radiatively back into the ground state of the crystal or the di-haloid separates from the electron location. This process forms a pair of point defects, the F centre (the electron localised at the anion vacancy) and the H centre, an interstitial halogen atom forming a chemical bond with a halogen ion away from the vacancy.

Recently, Gavartin and Shluger\textsuperscript{5} simulated adiabatic snapshots of the separation process using ab initio GGA plane-wave DFT calculations performed on a $6\times6\times4$ unit cell of sodium chloride. Only the coordinate of one anion relative to the vacancy was fixed, while the rest of the system was fully relaxed. We will use these results to illustrate the STE separation process. Fig. 1 shows the spin densities from the calculation corresponding to some key configurations alongside cartoons of their atomic geometries. The spin density is used because it yields the best contrast, showing approximately the changes in charge density and omitting the constant background consisting of the chlorine valence electrons not involved in the process.

The stable configurations of the triplet excited state of NaCl shown in fig. 1 are: A vertical transition from the ground state minimum leads to the triplet excited state MX* state shown in the upper panel of fig. 1.\textsuperscript{11} This state is also referred to as free exciton. It can be seen in the spin density plot that the charge of the excited electron is delocalised over all anions (illustrated by the dashed line encompassing the entire unit cell in the cartoon).

After some time, the system can thermally fluctuate over, or tunnel through, a small barrier of about 0.1 eV and a Self-Trapped Exciton (STE) forms. This happens when anion 1 moves towards anion 2 along the (110) direction of the lattice and the electron localises near the vacancy, as shown in the middle panel of fig. 1. The anion pair 1-2 has donated an electron charge to the vacancy (illustrated by the dashed oval in the accompanying cartoon), and hence is regarded as
a hole, which is illustrated by the colouring of the anion pair. The visible \( p \) orbitals in the spin density plot on the right demonstrate the bond formation between the halide ions 1 and 2.

As a next step, the pair 1-2 may approach anion 3, so that it gets polarised. Then anion 2 carries most of the hole, (this is a barrier configuration and not shown). The halide 2 is now atomic, and when it moves further to anion 3 it binds to it, as shown in the lower panel of fig. 1. Again, the spin density demonstrates the newly formed bond. Anion 1 remains at the former lattice position of anion 2. This process can in principle continue with the pair 2-3 approaching anion 4 and so on. This way the \( \text{X}_2^- \) di-haloid (H-centre) ion can successively separate from the electron in the vacancy (F-centre), forming an F-H centre pair of point defects. The hole separation from the vacancy can thus be regarded as reaction coordinate.

In this geometry, the lattice sites carry the same charges as in the ground state, as an electron is localised at the anion vacancy and the \( \text{X}_2^- \) di-haloid is situated at an anion site, carrying a single negative charge. However, the spin density shows a clear contrast to the ground state and therefore we will keep using the label hole for the di-haloid.

According to experimental results and theoretical predictions\(^3,4\), the potential energy dependence on the distance between the hole and the vacancy in most alkali halides should qualitatively resemble the sketch in fig. 2. This figure also contains the cartoons corresponding to the STE and the separated F-H centre pair state to indicate the geometry at the potential minima. There is theoretical evidence\(^4\) for an excited state of the exciton (top line in fig. 2) which has its minimum at the minimum of the ground state and is shown as the top potential line in fig. 2.

A model will be described in the following that is meant to describe the STE potential in a generic alkali halide. This model potential will be used to obtain a proof-of-principle and demonstrate a mechanism for coherent control of the STE separation. It is in no way meant to simulate the dynamics in a particular alkali halide crystal, although the mass and distance relations will be based on NaCl.

### A. Reaction Coordinates

Fig. 3 shows some vibrational modes of the di-haloid that are important for the STE separation. As indicated above, the main reaction coordinate is the distance between the F-centre and H-centre. Rather than jumping from one anion to the next (as we have shown in the discussion of fig. 1), the distance between the vacancy and the centre of mass of the hole can be used as the coordinate.
This changes smoothly during the separation process, as the polarisation of the di-haloid changes according to its distance from a neighbouring anion.

We will call this the \textit{x coordinate} in the following, which is illustrated in fig. 3a. The \textit{x coordinate} alone can be used for a first approximate study of the STE dissociation process.

Besides this, the stretching mode of the di-haloid ion (or \textit{y coordinate}, fig. 3b) and the three-dimensional rotation of the di-haloid ion (fig. 3c) can play a role in the considered reaction. The reaction may then proceed along a minimum energy line in the PES spanned by these coordinates.

According to Puchin et al.\textsuperscript{3}, the rotation plays an important role in the H-centre diffusion in NaCl. In other crystals, such as KBr, it appears to play a lesser role\textsuperscript{6}. However, as we aim at a first study of the STE dissociation in a generic alkali halide, this distinction and the rotational mode is omitted from further considerations in order to avoid overcomplicating the task in hand. The \textit{x} and \textit{y} coordinates will appear in dynamical simulations reported below.

\textbf{B. Model Dipole Moment}

An important condition for the direct vibrational response of the system to infrared laser radiation via the coupling Hamiltonian \(\varepsilon\mu\), where \(\varepsilon\) is the time-dependent electric field of the laser pulse and \(\mu\) is the dipole moment, is the coordinate-dependence of the dipole moment. Although experimental evidence has to be employed in constructing the model potential, \textit{ab initio} results\textsuperscript{7} can be used to fit a model dipole moment.

The data points of this calculation of the dipole moment dependence on the di-haloid position are shown in fig. 4. For dynamics, this result needs to be parameterised as a fit to a smooth function. We used the function

\[
\mu (x) = A_\mu \cdot (x - x_\mu) \cdot e^{-\frac{x-x_\mu}{r}}.
\]

This function has been used previously to parameterise the dipole moment of diatomic molecules\textsuperscript{8} and was demonstrated to show the correct tendency in the coordinate dependence. At large separation the F-centre and the H-centre are neutral defects, so the dipole should approach zero asymptotically.

A least-squares fit of the parameters of eq. (1) yields \(A_\mu=18\ \text{e}\cdot\text{Å}, \ x_\mu=-3\text{Å}, \ r_\mu=2\text{Å}\).
C. Reaction Scenario

A sketch of the potential energy dependence on the distance between the hole and the vacancy was already shown in fig. 2. On the basis of this sketch, two possible scenarios of coherent control of the separation of the STE into the F-H-pair can be proposed:

1. On the STE electronic state, purely vibrational excitation using IR pulses (fig. 5a) and

2. via excitation to the electronically excited state of the STE (fig. 5b). Instead of dissociating immediately, the excited (step 1) wave-packet is accelerated in the opposite direction (step 2) and consequently dumped on the dissociative flank of the STE potential (step 3). From there the system can then dissociate (step 4).

If the system has enough momentum when it reaches the right-hand potential minimum, it can travel to potential minima further away from the STE minimum in some alkali halides. At large enough distances, recombination is then no longer ruled by the attraction between F-centre and H-centre but becomes subject to a random meeting of the two due to diffusion. The lifetime of the F-H centre pair is then greatly increased. The feasibility of this process will be demonstrated by the preparation of a transient state with non-zero momentum at the right-hand potential minimum.

D. Model PESs

A considerable part of the work presented in this article has been to find an analytic expression mimicking the known properties of the STE potential energy surface and to explore the dynamics on this surface in order to become able to propose heuristically a reaction scheme that was later demonstrated in the simulation. For the purpose of constructing a one-dimensional model potential along the x coordinate, the following assumptions were used:

1. The depths of the minima at the STE minimum and the F-H centre pair are 0.20 eV and 0.18 eV, respectively.

2. The distance between the minima is about one lattice diagonal, i.e. 2.94Å.

3. The barrier height is 0.1 eV above the STE minimum.
To extend the model to two dimensions, the following considerations are made: The barrier configuration between the STE (fig. 1, middle panel) and the next-nearest neighbour F-H centre pair (fig. 1, lower panel), is at a configuration where anion 2 has equal distances to its neighbour halide ions, 1 and 3. Any break of the symmetry where two of the ions pair up, leaving the other one at a larger distance, lowers the energy.

This means that, although the potential has single minima along the y coordinate at the x coordinates corresponding to the STE and the F-H centre pair, it has a double well structure in y direction at the barrier between these. Hence the following assumptions are used to extend the model to two dimensions:

A. The minima in x direction are also minima in y direction.

B. The barrier in x direction is also a barrier for the double-minimum potential in y direction.

C. At the barrier in x direction, the y coordinate wells are one sixth lattice diagonal away from the barrier between them.

D. The minima in y direction at the barrier in x direction are about 0.1 eV below the barrier energy.

1. One-Dimensional Model Potential

We have modelled the potential energy surface (PES) of the exciton along the x coordinate over the range from the STE to the F-H centre pair by the sum of two Gaussian functions with negative coefficients,

$$U_1(x) = C_1 \cdot e^{-\frac{1}{2} \left( \frac{x-x_{m1}}{\sigma_1} \right)^2} + C_2 \cdot e^{-\frac{1}{2} \left( \frac{x-x_{m2}}{\sigma_2} \right)^2}.$$  \hspace{1cm} (2)

When this model is subjected to the assumptions ID 1–3, the parameters shown in table I result. A graph of the resulting potential energy curve is shown in fig. 6. This model contains only the two minima, $x_{m1}$ at the STE and $x_{m2}$ at the F-H centre pair. The minimum corresponding to the free exciton MX* is not taken into account, i.e. the formation of the STE is assumed to be completed at the start of the dynamics simulation.

We have chosen the widths $\sigma_j$ of the Gaussians forming the potential such that $x_{m1} \approx \mu_1$ and $x_{m2} \approx \mu_2$ and a local maximum at $x_M = 1.4\text{Å}$, $U_1(x_M) = -0.09\text{ eV}$ results. For $x \to \pm \infty$, the model potential goes to zero asymptotically.
2. Extension of the Model Potential to Two Dimensions

The one-dimensional model potential is extended to two dimensions by using a double Gaussian potential in y-direction such that the one-dimensional model potential is reproduced and the PES topology as given by the conditions ID A–D is preserved. Fig. 7 shows an image of the resulting model potential.

To extend the model potential to two dimensions, we have represented the dependence of the potential on the y coordinate as the sum of two Gaussian functions:

\[ U(x, y) = C_y(x) \cdot \left( e^{-\frac{1}{2} \left( \frac{y-\mu_1(x)}{\sigma_y} \right)^2} + e^{-\frac{1}{2} \left( \frac{y+\mu_2(x)}{\sigma_y} \right)^2} \right) \]  

(3)

The positions of the two Gaussians \( \mu_1(x) \) and \( \mu_2(x) \) are close together at \( x_{m1} \) and \( x_{m2} \), resulting in single wells, but further apart at \( x_M \), creating a double well. This behaviour can be achieved by parameterising

\[ \mu_y(x) = C_{\mu} \cdot e^{-\frac{1}{2} \left( \frac{x-\mu}{\sigma_\mu} \right)^2} \]  

(4)

where \( \mu = x_M \) and \( C_{\mu} = \frac{1}{6} \sqrt{2 \omega_0} \). \( \sigma_\mu \) must be chosen such that the transition between the different parts of the potential (single well to double well to single well) is smooth enough, here \( \sigma_\mu = 1.0 \text{Å} \). For this model, we set the value of the minima of the double well in y direction at \( x = x_M \) to the average of the maximum and the larger minimum of the one-dimensional model, i.e.

\[ U(x_M, \mu_y(x_M)) = \frac{1}{2} \left( U_1(x_M) + U_1(x_{m2}) \right) \]  

(5)

This fixes the depth of the paths around the local maximum at \( x_M \).

3. Model Potential for the Electronically Excited State

Embedded cluster calculations and experimental work suggest that a bound excited state with a minimum at the equilibrium geometry of KBr exists. We put the crystal equilibrium geometry at the reasonable estimate of \( x = -1 \text{ au} \approx -0.53 \text{Å}, y = 0 \) relative to the minimum of the STE potential (see Fig. 2 for an illustration of how the potentials are related). As minimum energy for the harmonic model potential we used 1.2 eV, which results in an STE excitation energy of 1.5 eV which is in the range reported in experimental results.

Theoretical results predict the excited state energy at the STE geometry to be about 0.1 eV higher than at the equilibrium geometry. We use a harmonic potential, hence this energy change
corresponds to a spring constant of $k_x = 0.71 \text{ eVÅ}^{-2}$. For the y coordinate, we used a harmonic potential with a spring constant corresponding to that of the STE state at the minimum, $k_y = 0.76 \text{ eVÅ}^{-2}$. This assumption makes use of the fact that the Gaussian potential for the STE is almost harmonic near the minimum. The excited state potential surface will then preserve the shape in y direction of an STE vibrational ground state wave function that is electronically excited.

II. RESULTS OF WAVE-PACKET PROPAGATION SIMULATIONS

Definitive statements about the coherence time for the STE separation dynamics cannot be made at this time, as a long-time simulation of the dynamics of such a system may only be performed classically, which is complicated by the continuous charge transfer processes involved. However, the separation of the STE is observed experimentally so that, while dissipation may affect the quantitative yield of the coherent dynamical processes proposed in this article, it should not affect the qualitative outcome.

A mechanism for control will be proposed based on wave-packet dynamics simulations without taking vibrational energy dissipation into account. Due to the effects of dissipation, such an approach is more likely to yield realistic predictions at shorter time scales.

It is instructive to characterise the one-dimensional model potential $U_1(x)$ by calculating its eigenstates. Fig. 8 shows the energy levels of the 20 lowest eigenstates of $U_1(x)$, eq. (2).

It can be seen that the lowest 20 eigenstates of the one-dimensional model potential $U_1(x)$ are each localised in one of the two potential wells. Their energy levels are, due to the anharmonic nature of the potential, not equidistant. Only near the minimum the quanta are approximately equally spaced because there the Gaussian potential is a very good approximation to a harmonic potential. Table II shows the lowest vibrational transition energies and periods in the two minima of the model STE and separated F-H centre pair wells of the potential.

The lowest (and largest) quantum in the left well is 4 meV, i.e. at room temperature (300 K $\simeq$ 13 meV) only a few eigenstates are accessible. This means that the higher states, to which F-H centre pair separation by tunnelling through the barrier is available, are populated very little at room temperature which explains why spontaneous F-H centre pair separation only has relatively low yields (depending on the material).

Fig. 8 also shows the lowest non-localised vibrational state, $\nu = 64$, $\Delta E = 108$ meV, and the highest vibrational eigenstate calculated ($\nu = 100$, $\Delta E = 240$ meV).
A. F-H Centre Pair Separation by Vibrational Excitation

As a first step, we explored the purely vibrational transition scheme devised for the one-dimensional one-state model (fig. 5a). Time is plotted along the ordinate. The laser field used has a Gaussian envelope. Its parameters are shown in table III. The coordinate dependence of the vibrational dipole moment operator from section IB was used. Fig. 9 shows the result of a simulated vibrational excitation of the STE with an infrared pulse.

The laser field is indicated at the left border of the diagram. The wave function snapshots are shown at a height corresponding to the time at which the snapshot was taken.

The initial wave function (the vibrational ground state) starts oscillating synchronously with the electric field in the STE potential well. As the wave function crosses the potential barrier between 22 and 24 ps, the total energy and the coordinate expectation values increase abruptly. This means that, rather than resulting in a globally bound wave function that has slightly higher energy than the barrier and is thus able to cross it, the electric field produces a free wave state (with energy above zero) that fills the whole simulation region. This can be seen by looking at the topmost snapshots of the wave function.

This demonstrates how difficult it is to purely by vibrational means generate a state that is energetically between the barrier and the vacuum level.

It may be noted by inspecting fig. 9 that the barrier energy is crossed just as the laser reaches its maximum. However, using a shorter field with smaller intensity at this time, the wave function never reaches the barrier energy and remains trapped in the STE potential minimum.

Selective excitation of the STE vibrational coordinate relies on resonance of the laser field with this mode only. As the vibrational frequency of the STE (1.1THz) is not untypical for alkali halide bulk crystals, it is quite likely that a frequency-swept laser pulse will be resonant with a larger number of normal modes, either directly or via multi-photon processes. The model for the vibrational response of the STE to infrared radiation used here that relies on specific excitation of the STE is therefore questionable at best.

Adding to these problems, the vibrationally resonant process considered here has to be several ten ps long due to the about one picosecond vibrational period of the STE (see table II). This is a time scale at which dissipation (which has been neglected here) becomes non-negligible. This was demonstrated in a previous publication\(^9\) on the dissociation of the hydroxyl ion formed by HCl adsorption on the MgO(001) surface. A considerable falloff of the yield due to dissipation
was seen, although the process studied there is shorter than 1 ps. This means that a process proposed from a wave packet propagation simulation of a purely vibrational infrared excitation is not realistic.

Due to these problems, we have decided to abandon the attempt to separate the F and H centres vibrationally and pursue a much more promising path, the separation by electronic excitation.

### B. F-H Centre Pair Separation by Electronic Excitation

The electronic excitation scheme for separating the F-H centre pair we would like to suggest is the pump-dump scheme illustrated in fig. 5b. This reaction will not, as is often done, rely on the presence of a dissociative excited state, so that the wave packet could be excited and, after some evolution in the excited state, just dumped in the lower electronic surface minimum one would like to reach.

Instead, the excited state is bound and the geometry change in the excited state is away from the one we would like to achieve (the right-hand minimum on the STE electronic surface in fig. 6 which corresponds to separated F-H centre pair). However, a dump pulse can drop the wave packet onto a dissociative flank of the STE potential surface, from which it can then pick up momentum to pass the potential barrier and subsequently reach the F-H centre pair well.

Reaction schemes involving electronic excitation will be presented based on both the one-dimensional model potential $U_1(x)$ and the two-dimensional one, $U(x, y)$.

Calculations of the eigenstates of the two-dimensional model potential $U(x, y)$ are computationally far more demanding than for the one-dimensional model potential $U_1(x)$. We have therefore calculated only the first ten two-dimensional eigenstates; their appearance is more or less that of products of eigenstates of the x and y coordinates. However, of the lowest eigenstates only the vibrational ground state is relevant for the proposed dynamics, as it is used as initial state. It will be seen that motion along the y coordinate only becomes relevant as the wave packet approaches the barrier. We will therefore not present the two-dimensional eigenstates in detail.

1. **Electronic Excitation Simulated with the Surface Hopping Method**

The simplest model for electronic excitation is the surface hopping method$^{10}$. According to this, the entire wave function is translated by a sudden excitation to a different electronic state.
The vibrational ground state wave function of the STE when displaced to the electronically excited state of the STE will become subject to the excited state’s potential energy surface. According to this, it will pick up momentum towards the vibrational minimum of the electronically excited state.\textsuperscript{12}

Subsequent de-excitation puts the wave packet onto the left-hand flank of the STE potential where it will climb further until the momentum built up on the electronically excited state is exhausted. At this point, the wave function resembles the ground state displaced to the left. We can therefore assume the displaced vibrational ground state of the STE as approximate transient state of the pump-dump process for the purpose of a wave-packet propagation simulation on a single electronic surface (that of the STE).

Since the surface hopping method is quite simplistic, we present the results of the dynamics calculations using this method on the two-dimensional model potential rather than starting with the one-dimensional model potential. In the next section that treats excitation explicitly, we will compare the results according to the one- and two-dimensional models in greater detail.

Fig. 10a shows the STE ground state in the two-dimensional model potential. Fig. 10b shows the same state displaced to the left by 0.8Å. We have performed wave packet propagation simulations taking this displaced STE ground state as initial condition.

Fig. 10c shows how this state has evolved after 1 ps. After 2.3 ps (fig. 10d), the transition probability into the separated state, i.e. the population to the right of the barrier is 64%.

The structure seen in the wave functions is due to the collision of the wave packet with the anharmonic barrier – incoming and backscattered parts of the wave function interfere with each other. Note that these interference effects are impossible to represent with a set of classical particle dynamics and are difficult to predict with frozen Gaussian techniques, as complicated structures evolve that require a large set of Gaussian basis functions to represent. This lends support to the choice of propagation method taken to study this subject.

The wave packet travels \textit{around} the local maximum in the middle of the model potential, thereby avoiding the point where the coupling to the electronic ground state is likely to be maximal. This means that in this process the non-radiative decay into the ground state would be smaller than for processes where the barrier area is populated strongly, increasing the yield of separated F-H centre pairs.

This statement can be quantified by considering the population of the area near the barrier. We define this area as the area where the potential energy is higher than half the difference between
the barrier energy and the lowest energy at $x = x_M$. Fig. 11 shows the evolution of this population along with the evolution of the population of the target area (i.e. the area to the right of the barrier). The target area population decreases at the end of the simulation due to reflection at the barrier limiting the simulation area on the right (see fig. 10). It can be seen that the barrier population remains below 10% throughout the simulation, while the population of the target area to the right of the barrier reaches more than 70%.

2. Electronic Excitation Simulated with a Field-Dependent Electronic Transition Operator

In contrast to the surface hopping approach above, a more accurate description of the electronic transition process is the first-order perturbation approach involving the operator

$$
\hat{X} = \varepsilon (t) \mu_{ij} (x, y) (|\psi_j \rangle \langle \psi_i | + |\psi_i \rangle \langle \psi_j |)
$$

in the Hamiltonian which mediates a transition between the electronic states $\psi_i$ and $\psi_j$ (here the STE and its electronically excited state), caused by irradiation with an electric field strength $\varepsilon$ and an electronic transition dipole moment $\mu_{ij}$.

The operator $\hat{X}$ couples the populations of the STE electronic state and its electronically excited state. If no vibrational motion took place, a long-time resonant excitation process would tend to equalise the populations of the STE and its excited state, i.e. in the limit the electronically excited state of the STE would gain only 50%. Surface hopping of the full wave function between states as used above, however, assumes a transfer of 100% of the state population.

Another factor that is not taken into account by the surface hopping method is the change in shape of the vibrational wave function due to electronic excitation. Such changes are effected by the slope of the electronically excited potential surface. If the laser pulse is long enough to make vibrational dynamics on the excited state surface relevant, the shape of the ground state wave function changes as well. This is due to stimulated emission, i.e. electronic de-excitation during the pulse.

For the purpose of the present excitation calculations, the Born-Oppenheimer approximation is invoked by neglecting the coordinate dependence of the electronic states. This means that the electronic dipole moment $\mu_{ij}$ is assumed to be coordinate-independent. The value of $\mu_{ij}$ is rolled into the electric field variable, i.e. $\mu_{ij} \equiv 1 \text{ au}$ is assumed and hence $\varepsilon (t) = \varepsilon (t) \mu_{ij} = 1 \text{ au}$ corresponds to an amplitude of 27.2116 eV.
As a first step, we have performed simulations on a two-state, one-dimensional model system with a time step of 0.048 fs, which is short enough to capture the dynamics due to the interaction with the electric field (since the shortest vibrational period in the fields used is 2.75 fs, i.e. 57 time steps).

Using a single Gaussian pulse with an amplitude of $10^{-3} \text{ au} \approx 5.1 \times 10^8 \text{ V m}^{-1}$, a temporal width of $\sigma = 18 \text{ fs}$, an excitation frequency $\omega = 1.5 \text{ eV}$ and a chirp of $\Delta \omega = 0$ results in a population of the excited state of $\Delta n_1 = 26\%$. Considering that the second, de-excitation, pulse will further diminish this ratio and only some part of the dumped wave packet will be able to cross the barrier, this is not satisfactory for the purpose of separating the F and H centres.

3. The Double-Pulse Excitation Scheme

One way to increase the population of the excited state after the excitation pulse is to increase the pulse’s amplitude. This would, however, necessitate laser pulses that are less feasible experimentally and only bring the excited state population to slowly approach 50% from below.

A qualitatively different approach is to exploit the fact that the excited wave packet immediately starts moving towards the equilibrium geometry of that electronic state, while the remaining STE wave packet remains trapped in the STE state minimum. This means that after a short time the region at the STE minimum geometry becomes vacant in the excited state and hence a second excitation pulse with the same parameters will yield another considerable excitation, without suffering from stimulated emission.\(^1\)

Such a double-pulse excitation with a time delay of 24.2 fs yields an excited state population of $\Delta n_1 = 53\%$, higher than the optimum ratio of 50% for a high-amplitude single ultrashort pulse.

This technique can be generalised to multiple pump pulses applied in short succession. The increase in yield due to the application of additional pulses is only limited by the tendency of the STE vibrational wave function to acquire kinetic energy and hence move out of resonance with the laser frequency. This effect can be accounted for by decreasing the laser frequency. In order to not over-complicate matters and maintain experimental viability, however, we will continue discussing an excitation scheme based on a double pulse.

Following up on the excitation (pump) pulse we have placed de-excitation (dump) pulses following the same double-pulse scheme. Each of the dump sub-pulses has the same amplitude and width as the pump sub-pulses. We set the frequency of the dump sub-pulses according to the
nominal excitation energy at the expectation value of the excited state wave packet at the moment temporally *between* the de-excitation sub-pulses. In order to assure resonance of the dump sub-pulses with the dynamics, we employed a chirp of $-6.9 \times 10^{-2} \text{ eV ps}^{-1}$, which means a frequency change of $\pm 1.2 \text{ meV}$ at a time difference of $\sigma = 18 \text{ fs}$ (the temporal width) from the centre of each sub-pulse. The parameters of the laser pulse used are recapitulated in table IV.

Note that, as projected in section II B 1 on the surface hopping method above, the dumped wave packet moves to the left for some time after de-excitation due to the momentum it has built up while in the excited state. This means that after the first dump sub-pulse, the dumped ground state wave packet vacates the area it was dumped into so that, as in the pumping process, the second dump sub-pulse effects an appreciable increase in the dump yield ratio $\Delta n_2$.

Table V lists the time delays and frequencies of the dump pulses used along with some results: The pump yield $\Delta n_1$ is the percentage of the STE electronic state wave function that is placed on the electronically excited state by the pump pulse. The dump yield $\Delta n_2$ is the percentage of the electronically excited state wave function that is put back on the STE electronic state by the dump pulse. The product $\Delta n_1 \cdot \Delta n_2$ is the percentage of the STE electronic state wave function that has been placed back after having been excited. The target hit rate is the percentage of the ground state wave function that has crossed the ground state barrier separating the STE from the separated F-H centre pair after a propagation time of 1.74 ps.

Fig. 12 shows snapshots of the wave packet evolution for the different runs. All figures demonstrate how the de-excited wave packet travels through the STE ground state wave packet that was left behind after the excitation, causing clearly visible interference patterns. It can be seen in the upper two panels, fig. 12a and (b) that the dumped wave packet travels quite far to the left before turning around and moving into the direction of the barrier.

This is the region where the free exciton is found on the STE electronic state, about $0.6 \text{ Å}$ to the left of the STE well. See fig. 2 for an impression of its position (marked MX*) relative to the STE well. It has to be taken into account although it is not represented in the model potential. A part of the wave packet can remain in the well corresponding to the free exciton, decreasing the predicted yield of separated F-H centre pairs with respect to the values quoted in table V. To avoid this, one would like to use shorter pulse delays that yield a dumped wave packet that does not travel so far to the left.

There are pathways in the two-dimensional potential that are energetically lower than the barrier in the one-dimensional potential, since a distortion of the $X^-_2$ molecule lowers the energy around
the barrier. This has been seen already in fig. 10, where the evolution of the shifted ground state wave packet proceeded around the barrier. This allows to use short pulse delays that do not yield a barrier crossing in the one-dimensional model.

The purpose of performing the simulations with smaller pump-dump delays that did not yield large amounts of F-H separates pairs in the one-dimensional model (shown in fig. 12c and d and in the rightmost columns of table V) has been to find delays at which the energy of the dumped wave packet is just below the barrier of the one-dimensional model potential. We have subsequently used these pulses to simulate pump-dump dynamics on the two-dimensional model potential that do not cross the barrier directly but circumvent it, yielding STE dissociation without touching the free exciton minimum.

The numerical results of the two-dimensional simulations with pulses of delay 205.6 fs, 157.2 fs and 133.0 fs are listed in the lower half of table V. Fig. 13 shows the populations of the target area and the barrier area from the two-dimensional pump-dump simulation runs.

It can be seen that, while the barrier area populations of the pump-dump processes with the two longer delay times peak at around 0.05, that of the process with the shortest delay of 133 fs peaks at only 0.02. This means that non-radiative decay of the STE is less likely to occur.

Figs. 14, 15 and 16 show snapshots of the two-dimensional wave function for a pump-dump delay of 205.6 fs, 157.2 fs and 133.0 fs, respectively.

As before, it can be seen that for the longer two of the three time delays the dumped wave packet extends very far to the left of the simulation area, into the range where the presently ignored free exciton is situated. The smallest delay of 133 fs, however, yields a well-contained dumped wave packet. In all cases, it can be seen that the pathway around the barrier is the preferred one. However, the shortest time delay also yields the smallest population of the barrier area.

III. CONCLUSION

We have demonstrated the simulation of a proposed photoinduced reaction scheme for the separation of the self-trapped exciton (STE) into a pair of F- and H-centres with quantum nuclear dynamics techniques.

As a first step for the simulation of the dynamics of the STE separation in an alkali halide, the most relevant vibrational modes taking part in this reaction were selected. They are the hole separation from the vacancy and the di-haloid stretching and were labelled x and y coordinate,
respectively. Angular vibrational modes of the di-haloid may play a role in the STE separation dynamics but were not taken into account in this first study.

To achieve our goal, we have parameterised one- and two-dimensional model potential energy surfaces (PESs) based on theoretical and experimental evidence and considered a purely vibrational reaction scheme as well as one involving electronic excitation.

After ruling out the purely vibrational scheme because of its long time scale and consequent vibrational energy dissipation that is to be expected, we have devised a pump-dump laser excitation scheme involving electronic excitation that mediates the separation process.

The excitation yield can be increased considerably by using two pump and dump sub-pulses. This makes use of the immediate onset of vibrational motion of the wave packet after electronic excitation and the inertial motion after de-excitation. Both effects cause the Frank-Condon area to be vacated between the sub-pulses. Thus, the proposed scheme exploits the shapes of the PESs as well as the interplay between the timing of the sub-pulses and the vibrational motion of the system. The dynamics in the electronically excited state do not exhibit strong quantum effects such as widening or splitting of the wave packet, so that these do not adversely affect the outcome of the reaction.

It turns out that there is an optimal time delay between the pump and dump double-pulses that maximises the yield of separated F-H centre pairs. Shorter time delays effect decreased yields due to an insufficient potential energy of the dumped wave packet, while longer delays may cause trapping in the free exciton potential minimum and increased non-radiative crossing into the electronic ground state. Neither of these effects was taken into account explicitly but their importance can be gauged from the time-dependent probabilities of residence in the free exciton and barrier areas (where the crossing with the ground state is expected).

A pump-dump scheme with a delay of 133 fs, where each of the pulses consists of two sub-pulses with a width of 18 fs with an intra-pulse delay of 24.2 fs is predicted to yield 14% separated F-H centre pairs out of all present STEs by the simulation in the two-dimensional model potential.

The model used does not take into account vibrational dissipation. However, the proposed reaction is at 133 fs+2×24 fs+2×18 fs≈0.22 ps very short compared to typical dissipation lifetimes (compare also with the reaction proposed in our previous publication\textsuperscript{9}, which is 0.87 ps long and whose yield is halved by dissipation). The proposed reaction can therefore be expected to survive the adverse effects of dissipation.

As was already proposed for the reaction proposed in a previous publication\textsuperscript{9}, the yield can
be increased by repeatedly irradiating the same spot in the crystal. The proposed scheme can is readily updated according to new insights into the shape of the PESs, since it is based on the simple vertical excitation energies between the states and the motion of the wave function in the excited state.

7 J. L. Gavartin, A. L. Shluger, private communication.
11 This state must be locally stable because otherwise an excitation would instantly destabilise the crystal structure which is not observed.
12 It will also change in width and shape but this change will be small so that it can be ignored for the time being.
13 This is because the excited state population due to the first pulse is unaffected by the pulse, as will has moved out of resonance with the pulse at this moment already.
\[ \begin{array}{c|c|c|c} \hline j & C_j & \mu_j & \sigma_j \\ \hline 1 & -0.20 \text{ eV} & 0.00 \text{Å} & 0.75 \text{Å} \\ 2 & -0.18 \text{ eV} & 2.94 \text{Å} & 1.0 \text{Å} \\ \hline \end{array} \]

Table I: Parameters used for the 1D STE model potential, equation (2).

<table>
<thead>
<tr>
<th>table 1:</th>
<th>( \Delta E ) [meV]</th>
<th>T [fs]</th>
<th>table 2:</th>
<th>( \Delta E ) [meV]</th>
<th>T [fs]</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \Delta E = 0 \rightarrow 1 )</td>
<td>4.37</td>
<td>947</td>
<td>( \Delta E = 0 \rightarrow 1 )</td>
<td>3.18</td>
<td>1300</td>
</tr>
<tr>
<td>( \Delta E = 1 \rightarrow 2 )</td>
<td>4.33</td>
<td>956</td>
<td>( \Delta E = 1 \rightarrow 2 )</td>
<td>3.16</td>
<td>1310</td>
</tr>
<tr>
<td>( \Delta E = 2 \rightarrow 3 )</td>
<td>4.28</td>
<td>966</td>
<td>( \Delta E = 2 \rightarrow 3 )</td>
<td>3.13</td>
<td>1320</td>
</tr>
<tr>
<td>( \Delta E = 3 \rightarrow 4 )</td>
<td>4.23</td>
<td>978</td>
<td>( \Delta E = 3 \rightarrow 4 )</td>
<td>3.11</td>
<td>1331</td>
</tr>
</tbody>
</table>

Table II: Vibrational transition energies and transition vibrational periods of the model potential: For the left well, i.e. the STE (table 1) and the right well, i.e. the F-H centre pair (table 2).

<table>
<thead>
<tr>
<th>property</th>
<th>value</th>
</tr>
</thead>
<tbody>
<tr>
<td>maximum intensity</td>
<td>( E_{\text{max}} = 10^{-3} \text{ au} \cong 5.1 \times 10^8 \text{ Vm}^{-1} )</td>
</tr>
<tr>
<td>envelope position</td>
<td>( t_{\text{max}} = 24.2 \text{ ps} )</td>
</tr>
<tr>
<td>envelope width</td>
<td>( \sigma = 7.26 \text{ ps} )</td>
</tr>
<tr>
<td>frequency at ( t_{\text{max}} )</td>
<td>( \omega = 844 \text{ meV} )</td>
</tr>
<tr>
<td>chirp</td>
<td>( \Delta \omega = 0.02 \text{ meV ps}^{-1} )</td>
</tr>
</tbody>
</table>

Table III: Parameters of the electric field used for vibrational excitation of the STE.
Table IV: Parameters of laser double pulses proposed for the control of STE separation via electronic excitation.

<table>
<thead>
<tr>
<th></th>
<th>pump pulse</th>
<th>dump pulse</th>
</tr>
</thead>
<tbody>
<tr>
<td>amplitude [a.u.]</td>
<td>$10^{-3}$</td>
<td>$10^{-3}$</td>
</tr>
<tr>
<td>width $\sigma$ [fs]</td>
<td>18</td>
<td>18</td>
</tr>
<tr>
<td>frequency $\omega$ [eV]</td>
<td>1.5</td>
<td>table V</td>
</tr>
<tr>
<td>chirp $\Delta \omega$ [eVps$^{-1}$]</td>
<td>0 $-6.9 \times 10^{-2}$</td>
<td></td>
</tr>
<tr>
<td>intra-pulse delay [fs]</td>
<td>24.2</td>
<td>24.2</td>
</tr>
</tbody>
</table>

Table V: Parameters of the dump pulses used for the simulation of different pump-dump scenarios for the separation of the STE in KBr and dump and target yields for simulation runs in the one- and two-dimensional two-state model systems.

| time delay [fs] | 363.3 | 254.0 | 205.6 | 157.2 | 133.0 |
| frequency [eV] | 1.38  | 1.34  | 1.35  | 1.41  | 1.43  |
| 1D pump yield $\Delta n_1$ [%] | 53.4 | 53.4 | 53.4 | 53.4 | 53.4 |
| 1D dump yield $\Delta n_2$ [%] | 64.9 | 69.1 | 65.7 | 53.0 | 33.3 |
| 1D total dumped $\Delta n_1 \cdot \Delta n_2$ [%] | 34.6 | 36.9 | 35.1 | 28.3 | 17.8 |
| 1D target hitrate after 1.74 ps [%] | 35.4 | 32.2 | 32.2 | 12.1 | 2.9 |
| 2D pump yield $\Delta n_1$ [%] | 48.1 | 48.1 | 48.1 |
| 2D dump yield $\Delta n_2$ [%] | 83.5 | 52.9 | 36.8 |
| 2D total dumped $\Delta n_1 \cdot \Delta n_2$ [%] | 40.2 | 25.4 | 17.7 |
| 2D target hitrate after 1.74 ps [%] | 27.8 | 23.8 | 14.0 |

Figure captions

Figure 1: Stable configurations of the triplet excited state of NaCl. **Upper panel:** Ground state geometry of the crystal. The charge of the excited electron (illustrated by the dashed line encompassing the unit cell) is delocalised over all anions.\*

If anion 1 moves towards anion 2 and the electron localises near the vacancy a self-trapped exciton (STE) can form, shown in the **middle panel.** The anion pair 1-2 has donated an electron charge to the vacancy, and hence is regarded as a hole, which is illustrated by the colouring of the anion pair. The visible $p$ orbitals in the spin density plot on the right demonstrate the bond formation
between the halide ions 1 and 2.

As a next step, the pair 1-2 may approach anion 3, so that it gets polarised. Then anion 2 carries most of the hole, (this is a barrier configuration and not shown). The halide 2 is now atomic, and when it moves further to anion 3 it binds to it, as shown in the lower panel. Again, the spin density demonstrates the newly formed bond. Anion 1 remains at the former lattice position of anion 2. This process can in principle continue with the pair 2-3 approaching anion 4 and so on. This way the $X_2^-$ di-haloid (H-centre) ion can successively separate from the electron in the vacancy (F-centre), forming an F-H centre pair of point defects. The hole separation from the vacancy can thus be regarded as reaction coordinate. Spin densities reproduced with permission from Gavartin and Shluger.

Figure 2: Sketch of the electronic states in alkali halides. $a = \text{lattice constant}$. The abscissa is the hole displacement from the vacancy. Shown are the electronic ground state of the crystal, its excited state with the STE and separated F-H centre pair and, above that, the electronically excited state of the STE. See text for details. The first occurrence of a sketch of this type can be found in Shluger and Tanimura. Reproduced with permission.

Figure 3: Modes of the di-haloid important in the STE separation: (a) distance between electron-in-vacancy and hole, (b) stretching of the di-haloid ion, (c) 3D rotation of the di-haloid ion. The latter was not simulated.

Figure 4: Dipole moment dependence on the di-haloid position in NaCl. Result of the DFT calculations (points and lines), with spin density plots for some points, and model (smooth line) based on the functional dependence of the dipole in $H_2$.

Figure 5: Ideas proposed to control the separation of the STE into a separated F-H centre pair:
(a) By vibrational excitation. (1.) Excitation in STE well, (2.) transition between the wells, (3.) cooling in separated F-H centre pair well. Note that step (2.) requires resonance of the laser field with the motion between the two far barriers of the potential. The right-hand barrier, however, is only present in the model and is physically replaced by a succession of wells.
(b) By electronic excitation. (1.) Excitation ("pump pulse") into the excited state of the STE, (2.) free motion in the excited state, (3.) de-excitation ("dump pulse") into the STE electronic state, (4.) free motion from flank of the left-hand barrier towards the separated F-H centre pair state.

Figure 6: 1D model potential for the STE. The left well is the STE minimum; the right-hand one is the minimum of the separated F-H centre pair.
Figure 7: Two-dimensional model potential for the STE built up of a set of double Gaussian potentials in y direction that reproduce the one-dimensional double Gaussian model potential along the x coordinate. Note the change of character of the y-coordinate potential depending on the x-coordinate.

Figure 8: Lowest 20 eigenvalue levels of the one-dimensional STE model potential, with some localised and delocalised wave functions plotted to give an impression of their character. The base lines of the wave functions plotted are shifted to the state energies. Note that the levels are not equidistant. The lowest delocalised state is at $\nu = 64$ (lower red curve), the highest state calculated is $\nu = 100$ (upper red curve).

Figure 9: Vibrational excitation of the STE with an infrared pulse. Time is plotted along the y axis. Snapshots of the wave function are shown at the height corresponding to the time at which the snapshot was taken. The potential scaled to fit into the diagram is shown at the bottom to put the wave functions into perspective. Due to the large mass of the system, the vibrational period is of the order of one picosecond so that a resonant process has to be several ten ps long, a timescale at which dissipation (which has been neglected here) becomes non-negligible. Note how the total energy and the coordinate expectation values jump abruptly as the wave function crosses the potential barrier between 22 and 24 ps. The result is a free wave state (with energy above zero) that fills the whole simulation region.

Figure 10: Propagation of the STE ground state shifted 0.8\AA to the left. Coordinates are in \AA. (a) STE ground state, (b) shifted STE ground state as initial state, after propagation for (c) 1 ps, (d) 2.3 ps. The structure seen is caused by the collision of the wave function with the anharmonic barrier, interferences of backscattered with incoming parts of the wave function can be seen.

Figure 11: Population of target area and barrier area over propagation time for shifted wave packet simulation. The target area decreases at the end due to reflection at the barrier limiting the simulation area at the right (see fig. 10).

Figure 12: Snapshots of the wave packet evolution for simulation runs in the one-dimensional two-state model system. The time delays between pump and dump are (a) 254.0 fs, (b) 205.6 fs, (c) 157.2 fs, (d) 133.0 fs. The ground state wave functions are drawn with the time the snapshots were taken as their base; the excited state wave functions are slightly above for clarity.

Figure 13: Populations of target area and barrier area from two-dimensional pump-dump simulation runs. The time delays between pump and dump are (a) 205.6 fs, (b) 157.2 fs, (c) 133.0 fs.
Figure 14: Snapshots of the two-dimensional wave function for a pump-dump delay of 205.6 fs.
(a) $t = 0$, (b) 0.43 ps, (c) 1.3 ps, (d) 1.7 ps.

Figure 15: Snapshots of the two-dimensional wave function for a pump-dump delay of 157.2 fs.
(a) $t = 0$, (b) 0.43 ps, (c) 1.3 ps, (d) 1.7 ps.

Figure 16: Snapshots of the two-dimensional wave function for a pump-dump delay of 133.0 fs.
(a) $t = 0$, (b) 0.48 ps, (c) 1.2 ps, (d) 2.4 ps.
Figure 1: A. Markmann et al., ???
Figure 2: A. Markmann et al., ???
Figure 3: A. Markmann et al., ???

Figure 4: A. Markmann et al., ???
Figure 5: A. Markmann et al., ???
One-dimensional model potential

Figure 6: A. Markmann et al., ???
Results of Relaxation Method Runs: Eigenstates of X2− Displacement Potential.

Figure 8: A. Markmann et al., ???
Figure 9: A. Markmann et al., ???
Figure 10: A. Markmann et al., ???
Figure 11: A. Markmann et al., ???

Figure 12: A. Markmann et al., ???
Figure 13: A. Markmann et al., ???

Figure 14: A. Markmann et al., ???
Figure 15: A. Markmann et al., ???
Figure 16: A. Markmann et al., ???