

## Brief Reports

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### Sputtering of atoms and excimers upon self-trapping of excitons in solid krypton

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Molecular-dynamics simulations are performed to calculate the energy of krypton atoms and excimers sputtered by “cavity ejection” upon trapping of excitons at the surface of the solid. Calculated shifts in the atomic lines of the photoabsorption spectrum are compared with experimentally observed values to test the accuracy of the interaction potentials. In contrast to previous work on argon, only the excimer formed in the singlet state was ejected with a kinetic energy of 0.11 eV. Since none of the long-lived ( $10^{-6}$  sec) triplet-state excited atoms or excimers are ejected, there should be no “cavity-ejection” contribution to the luminescence plume like that observed in argon.

#### INTRODUCTION

Energy deposited electronically into a solid by incident particles may be converted into the kinetic energy of sputtered (desorbed) atoms.<sup>1</sup> Atomic and molecular ejection from condensed argon has been studied extensively.<sup>2-7</sup> This work extends previous calculations<sup>3</sup> on argon to the case of solid krypton for which there also exists experimental data on electronically induced desorption.<sup>7</sup>

Electron-hole pairs (excitons) created by ions, photons, or electrons incident on a solid are nomadic. These excitons may become trapped at a lattice site in the bulk or at the surface of a crystal.<sup>2,4,7,9</sup> Studies of the luminescence

produced by low-energy electron excitation of solid argon indicate that excited atoms and dimers were ejected<sup>2,5</sup> as well as ground-state species. Coletti, Debever, and Zimmerer<sup>5</sup> proposed a “cavity-ejection” mechanism. The “cavity” formed by the trapping of an exciton at an atom in the bulk, due to net average repulsive forces with the neighbors, is represented in Fig. 1(a). If an exciton traps at the surface<sup>8</sup> these repulsive forces may be sufficient to eject the atom or dimer, as shown in Fig. 1(b). This process was confirmed as occurring in solid Ar by the calculations of Cui *et al.*<sup>2</sup> and excited atoms with low kinetic energies were observed by Arakawa *et al.*<sup>9</sup> Such species contribute to the luminescence from rare-gas solids,<sup>4,10</sup> although Arakawa *et al.*<sup>9</sup> and Reimann *et al.*<sup>2</sup> have been shown that “cavity ejection” is not the only process and may not be the dominant process.

In the luminescence spectra of Feulner *et al.*,<sup>6</sup> very weak or no *W*-band contribution is observed for Kr and Xe, whereas the *W*-band contribution in Ar is strong. Because cavity formation is associated with the electron negativity of the atoms, “cavity ejection” in Kr and Xe is expected to be less efficient.<sup>5</sup> Here we test this by calculating the energies of ejected atoms and excimers from solid Kr using a molecular dynamics procedure with averaged interaction potentials.

#### THE MODEL

The calculation discussed in this paper uses a predictor-corrector algorithm to solve for the position and momentum vectors, given the interaction potentials for each of the atoms in the sample cell. The excited-state atomic interaction potentials used are those given

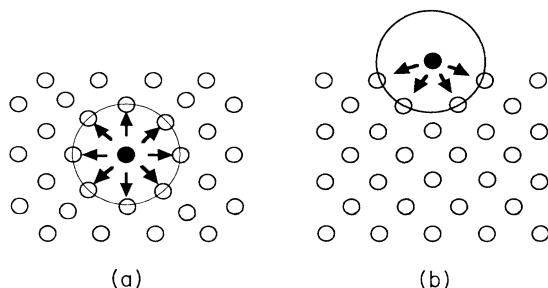


FIG. 1. (a) Two-dimensional schematic of the formation of an exciton cavity in the bulk of a crystal lattice by the repulsive interaction of the excited atom (shown in black) with its neighbors. (b) Similar schematic showing how cavity formation at the surface of the crystal leads to ejection of the excited atom.

TABLE I. Reduced parameters for Kr<sub>2</sub> interaction potential.

$A = 0.121\ 531\ 2(8)$
$\alpha = 16.496\ 763$
$C_6 = 1.156\ 173\ 9$
$C_8 = 0.541\ 492\ 3$
$C_{10} = 0.283\ 973\ 5$
$\gamma = 2.4$
$D = 1.28$
$\epsilon(k/K) = 199.9$
$r_m(\text{\AA}) = 4.012$

by Speigelmann and Gadea,<sup>11</sup> while the ground-state interactions are given by Aziz.<sup>12</sup> Since the wave function for a long-lived trapped exciton can be described by a mixture of excited states,<sup>13</sup> a static, average excited-state interaction potential is constructed by weighting these states according to their degeneracy.<sup>3</sup> The excited state potentials used in this investigation correspond to the lowest excited state, distinguished also by the spin: the triplet (<sup>3</sup>P<sub>1</sub>) and the singlet (<sup>1</sup>P<sub>1</sub>) states.

The ground-state (Kr-Kr) interaction potential as given by Aziz<sup>12</sup> is

$$V(r) = \epsilon V^*(x),$$

$$V^*(x) = Ax^\gamma \exp(-\alpha x) - \left[ \frac{C_6}{x^6} + \frac{C_8}{x^8} + \frac{C_{10}}{x^{10}} \right] F(x) \quad (1)$$

with

$$F(x) = \exp \left[ - \left[ \frac{D}{x} - 1 \right]^2 \right], \quad \text{for } x < D$$

$$= 1 \quad \text{for } x \geq D$$

and  $x = (r/r_m)$ . Values for constants in the above equation are given in Table I.

The average excited state potentials for an atomic-type trapped exciton is given by

$${}^{3,1}V = \frac{{}^{3,1}\Sigma_u^+ + {}^{3,1}\Sigma_g^+ + 2({}^{3,1}\Pi_u + {}^{3,1}\Pi_g)}{6}. \quad (2)$$

Here the  $\Sigma$  and  $\Pi$  states are the pair potentials calculated by Speigelmann and Gadea.<sup>11</sup> In the case of a self-trapped exciton leading to the formation of a dimer, the <sup>3,1</sup> $\Sigma_u^+$  state describes the interaction between the two atoms in the excimer. Therefore, the average interaction of these dimer atoms with their ground-state neighbors will not include this dimer bond interaction (<sup>3,1</sup> $\Sigma_u^+$ ). Since this covalent excitation is shared by the atoms in the dimer, the interaction potential with neighbors can be

thought of as an average of the ground-state potential and the residual in the average excited state interaction potential<sup>3</sup> given by

$${}^{3,1}V^* = \frac{{}^{3,1}\Sigma_g^+ + 2({}^{3,1}\Pi_g + {}^{3,1}\Pi_u)}{5}. \quad (3)$$

To test the validity of these interaction potentials for describing sputtering by cavity ejection, the surface and bulk photoabsorption spectra energies associated with each excitation are calculated and compared to experimentally observed data. That is, the shift in energy of the absorption in the solid is a measure of the interaction with neighbors which leads to cavity formation. The photoabsorption energy  $h\nu$  is found by  $h\nu = E_{\text{free}} + E_{\text{shift}} + L_{\perp}$ ,<sup>14</sup> where  $E_{\text{free}}$  is the atomic transition energy,  $E_{\text{shift}}$  is the photoabsorption spectra shift (calculated), and  $L_{\perp}$  is the transverse resonance interaction energy. The calculated and observed energies appear in Table II indicating reasonably good agreement.

## RESULTS

The molecular dynamics program discussed previously<sup>3</sup> using the interaction potentials described above generates the following scenarios. No atomic-type excitons are desorbed by the cavity-ejection process in the case of krypton from either the (111) or the (100) face of a crystal. Damaging the crystal weakens the repulsion further.<sup>3</sup> For both the triplet <sup>3</sup>V and singlet <sup>1</sup>V excitons, the excited atom finds an equilibrium position close to the surface of the crystal. As the approach to equilibrium is slow the molecular dynamics program cannot be run long enough to reach equilibrium. Therefore, the distance of the atom from the surface as a function of time can be roughly extrapolated using an equilibrium distance, an exponential decay, and oscillation frequency:

$$z(t) = d_{\infty} - a_i e^{-t/\tau} \cos(\omega t). \quad (4)$$

Here  $d_{\infty}$  is the equilibrium distance,  $a_i$  is the initial amplitude,  $\omega$  is the oscillator frequency,  $\tau$  is the exponential decay constant, and  $t$  is time. For the <sup>3</sup>V and <sup>1</sup>V potentials describing excitations at the surface, the values of the parameters in Eq. (4) are given in Table III. Note from Table III that these species will relax at a distance about  $d_{\infty}$  from the surface equilibrium position prior to radiative decay. Therefore, these calculations predict that the energy of the emitted photons will be 9.84 eV, for the singlet and 10.60 eV for the triplet state excitation, close to the gas-phase values.

In solid Kr and Xe dimer formation is the preferred

TABLE II. Photoabsorption energies of excitons at the surface of krypton.

	$E_{\text{free}}^a$	$E_{\text{shift}}$	$L_{\perp}^b$	$h\nu$ (calculated)	$h\nu$ (observed) <sup>c</sup>
<sup>1</sup> V	10.625	0.107	-0.030	10.70	10.68
<sup>3</sup> V	9.961	-0.027	-0.040	9.90	10.02

<sup>a</sup> Reference 15.

<sup>b</sup> Reference 4.

<sup>c</sup> Reference 10.

TABLE III. Surface dynamics constants for atomic self-trapped excitons in krypton.

	$d_{\infty}$ (Å)	$a_i$ (Å)	$\tau$ (psec)	$\omega$ (psec <sup>-1</sup> )
<sup>3</sup> V	0.55	0.67	149.48	1.1
<sup>1</sup> V	1.10	1.14	23.75	1.1

self-trapping mode. Upon forming an excimer the attractive component of the excited-state potential,<sup>3,1</sup> $\Sigma_u$ , is removed from the interaction of the self-trapped exciton and the neighboring ground-state atoms. The resulting stronger repulsion allows ejection of the singlet-state excimer. The triplet-state excimer is not ejected however. The singlet-state excimer is ejected with a kinetic energy of 0.11 eV. With this kinetic energy, the dimer moves away from the surface at 0.89 m per sec. Since the singlet-state excitation is an "allowed" transition, the excited pair will decay to the ground state in about  $10^{-9}$  sec at which time the dimer is less than 10 Å from the surface, making it difficult to distinguish spatially from surface emission. The equilibrium distance of the triplet from the surface [viz. Eq. (4)], which does not eject, is 1.1 Å. The decay of the singlet and the triplet dimer to the ground state results in repulsive separation of the two neutrals.<sup>16</sup> The ground-state neutrals so ejected will have kinetic energies indicative of gas phase decay because of their weak interaction with the surface at the time of decay, as proposed and seen by O'Shaughnessy *et al.*<sup>7</sup>

## CONCLUSIONS

Interaction potentials are constructed for a Kr atom in the lowest excited state in a solid in order to simulate the dynamics of a self-trapped exciton<sup>8</sup> at the surface of a crystal. Using a classical dynamics algorithm the atomic trajectories are numerically solved for singlet and triplet states trapping as atomic and dimer excitons. The results are most interesting in comparison to similar calculations on Ar.<sup>3</sup> In this work we find that only the singlet-state excimer of Kr is ejected for a perfect Kr crystal, whereas Ar was previously calculated to eject for all the excited species discussed here. Damaging the crystal by reducing the number of neighbors can result in the lack of ejection of the singlet species also. Since the singlet-state excitation is an "allowed" transition, for the speed determined here the ejected dimers will decay within 10 Å of the surface. Therefore, the "plume" of luminescing atoms and excimers observed<sup>2,16</sup> by electronically sputtered Ar will have a very small spatial extent for Kr if it is at all discernable from surface luminescence. As the majority of the dimers will not eject, they will relax vibrationally and in photoemission to the repulsive ground-state energetic neutrals will be ejected with energies roughly characteristic of the gas-phase dissociation process, consistent with observation.<sup>7</sup>

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