Exciton-induced desorption and surface-type luminescence of Kr atoms from Kr-doped solid Ar

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Selective excitation of Kr atoms at the surface of solid Ar with synchrotron radiation stimulates the desorption of excited Kr atoms (e.g., Kr\(^{3P_1}\)) as well as the luminescence of Kr-type surface centers at \(hv = 9.998\) eV (\(^3P_1\)) and at \(hv = 9.881\) eV (\(^3P_2\)). The high-resolution luminescence spectra and the yield curves of the radiative decay channels have been measured. They are interpreted taking into consideration ab initio KrAr pair potentials. A general correlation between the desorption mechanism and the energetic position of the vacuum level is established for pure (Ne, Ar, Kr, Xe) and doped rare gas solids.

1. Introduction

The erosion properties of rare gas solids have been studied in great detail during the last ten years. This occurred because rare gas solids are model systems for a better understanding of a variety of desorption mechanisms. The present state of the art was described in recent reviews of Johnson and Schou [1] and Brown and Johnson [2]. Whereas that work mainly concentrates on particle induced erosion, the present paper deals with desorption induced by excitonic transitions. The term "exciton" is used here for any kind of excitation which results in bound electron-hole pairs. It includes not only band-like exciton states but also excitations localized at lattice distortions, defects, impurities, and at the surface.

Desorption induced by excitonic excitations results from the peculiarities of exciton-phonon interaction in rare gas solids which lead to trapping of excitons either at a self-induced lattice distortion (self-trapped exciton, STE) at lattice defects [3-5] or at the surface [6]. Trapping is accompanied by strong lattice relaxation effects. Thus, concerning desorption, exciton-phonon interaction of rare gas solids has two essential properties. It leads to localization of an electronic excitation and to conversion of electronic energy into motional energy of atoms.

Following creation of surface excitons of the light rare-gas solids Ar and Ne, desorption of ground state atoms, electronically excited atoms (\(^3P_1, ^1P_1\)) and metastable atoms [3-5], and even of desorbed molecules [7] was observed. The desorption of excited atoms results from trapping of an exciton as an atomic species (so-called a-STE). In the bulk of the solid, the excited atom repels the lattice. The physical nature of the repulsive force is short-range repulsion due to the overlap of the excited state wavefunction with the closed electronic shells of the surrounding atoms. Short range repulsion competes with the polarization of the lattice by the excited atom. In the light rare gas solids (Ar, Ne), repulsion dominates causing a local distortion of the lattice. The new equilibrium positions of the ground-state atoms around the excited atom correspond to a balance between repulsion on one side, elastic forces and polarization on the other side. In solid Ne, e.g., in this way, a bubble is formed around the excited atom with a diameter of \(\approx 8\) Å [8] (nearest-neighbour distance of the Ne lattice 3.16 Å). It is quite natural that trapping at an atom of the crystal surface does not lead to the formation of a bubble but to the ejection of the excited atom [3-5,9].

In the present paper, the results of a systematic investigation of the desorption of Kr atoms from the surface of solid Ar are presented. The motivation for this work is as follows. In rare gas solids, a quantitative measure of the balance between short-range repulsion and long-range polarization by an electron in the conduction band is given by the so-called \(V_0\) value, \(V_0 = \)
$E_g - E_{th}$ [10]. Here, $E_g$ means the band gap energy, $E_{th}$ the threshold energy for photoelectron emission (zero point of the energy scale is the top of the valence band). A positive value of $V_0$ corresponds to a vacuum level below the bottom of the conduction band, a negative value above. In Table 1, the $V_0$ values of rare gas solids are given. A clear correlation is found between the sign of the $V_0$ value and the observation of desorbed excited atoms under primary exciton excitation. Up to now, this desorption was only observed for rare gas solids with $V_0 > 0$.

In analogy to pure rare gas solids, a $V_0$ value is also defined for doped systems, $V_0 = E_g^i - E_{th}^i$ [10]. Here, $E_g^i$ is the impurity gap energy, $E_{th}^i$ is the threshold of impurity-photoelectron emission. Both signs of $V_0$ are observed, too. The question arises whether the correlation between desorption of excited atoms and the sign of $V_0$ also holds for the doped systems. The respective values are included in Table 1. Anticipating the results of the present paper we point out that the correlation also holds for Kr doped Ar. Moreover, during the preparation of this paper, the system Xe doped Ar was measured and the correlation clearly showed up [13]. The results of the other systems mentioned in Table 1 are preliminary results of test experiments and deserve detailed experimental confirmation in future.

There are other aspects behind the subject of this paper. From solid Ne it is known that – in addition to desorption – excited atoms can also stay at the surface and emit surface-type luminescence lines [14]. Surface centers of $3P_1$ and of $1P_1$ origin were already observed. Additionally, luminescence of $3P_2$-type centers shows up (partly allowed due to the reduction of symmetry compared with the free atom). Such surface centers are also predicted from theory for solid Ar [9].

In the present study it is shown that surface centers are also observed for Kr doped solid Ar. Both, for the luminescence of Kr surface centers and for resonance fluorescence of desorbed Kr atoms, the yield spectra could be measured. The yield spectra are closely connected with the absorption cross section of the impurity absorption at the surface of the host. This is an aspect of great relevance for surface physics. However, it is also a key experiment to test interaction potentials between the impurity atom and the atoms of the host. Thus, the yield spectra provide us with a deep understanding of the microscopic nature of a particular desorption mechanism.

### Table 1

<table>
<thead>
<tr>
<th>System</th>
<th>$V_0$ [eV]</th>
<th>Desorption of electronically excited atoms</th>
<th>Refs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solid Ne</td>
<td>+1.3</td>
<td>yes</td>
<td>[3–6]</td>
</tr>
<tr>
<td>Ar/Ne</td>
<td>+1.1</td>
<td>yes</td>
<td>[11,12] a</td>
</tr>
<tr>
<td>Kr/Ne</td>
<td>+1.1</td>
<td>yes</td>
<td>[12] a</td>
</tr>
<tr>
<td>Xe/Ne</td>
<td>+1.0</td>
<td>yes</td>
<td>[12] a</td>
</tr>
<tr>
<td>Solid Ar</td>
<td>+0.4</td>
<td>yes</td>
<td>[3–6]</td>
</tr>
<tr>
<td>Kr/Ar</td>
<td>+0.3</td>
<td>yes</td>
<td>present paper</td>
</tr>
<tr>
<td>Xe/Ar</td>
<td>+0.3</td>
<td>yes</td>
<td>[13]</td>
</tr>
<tr>
<td>Solid Kr</td>
<td>−0.3</td>
<td>no</td>
<td>[3–6]</td>
</tr>
<tr>
<td>Xe/Kr</td>
<td>−0.2</td>
<td>no</td>
<td>[12] a</td>
</tr>
<tr>
<td>Solid Xe</td>
<td>−0.4</td>
<td>no</td>
<td>[3–6]</td>
</tr>
</tbody>
</table>

a Preliminary results.

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2. Experiment

The experimental method is high-resolution luminescence spectroscopy under primary selective excitation with vacuum-ultraviolet (VUV) light. The experiments were performed at the SUPERLUMI setup of the Hamburger Synchrotronstrahlungslabor HASYLAB. The setup was described recently in detail [15]. It allows for (i) selective excitation in the VUV ($8 < h\nu < 30$ eV) with $\lambda/\Delta \lambda < 10^3$, (ii) spectral analysis of luminescence in a large spectral range ($1 < h\nu < 20$ eV) with $\lambda/\Delta \lambda < 10^4$, and (iii) time resolution from the sub-ns to the ms regime. In time-resolved experiments, the pulsed nature of synchrotron radiation is exploited [16].

Only with high-resolution luminescence analysis is it possible to discriminate between the resonance fluorescence of desorbed excited Kr atoms ($^3P_1 \rightarrow ^1S_0$, $h\nu = 10.033$ eV) and, e.g., the luminescence line of $^3P_1$-type Kr centers at the surface of the Ar host ($h\nu = 9.998$ eV) However, the counting rates are extremely small ($\approx 1$ cps per resolution interval). Note, special emphasis was put on primary selective excitation of impurity atoms at the surface (some $10^{12}$ atoms/cm$^2$). The high sensitivity needed was achieved with a position-sensitive detector at the exit arm of the analyzing VUV monochromator. The detector (Surface Science Lab. Inc. model 3391A) was sensitized in our laboratory with CsI for the longer wavelengths.

An essential ingredient in our experiment is sample preparation. The Kr concentration was chosen as a compromise between two requirements: A high concentration was desirable to increase the counting rates. On the other hand, a low concentration was necessary to avoid pairing or clustering of Kr atoms at the surface of the host. It turned out, that up to 5% Kr in Ar could be used. The gases were pre-mixed in an ultrahigh vacuum gas-handling system. The samples were grown from the gas phase at $T \approx 20$ K at a rate of 200 Å/s. The rate was controlled with a needle valve between the gas handling system and the growing...
3. Results

3.1 Luminescence spectra

In fig. 1, an overview of the luminescence of Kr doped solid Ar is given for typical – however, substantially different – surface sensitive excitation conditions. Curve (1) [17] is obtained from a sample with 0.3% Kr in Ar under primary selective excitation of surface excitons of the host (hν = 11.82 eV). Curve (2) is obtained from a sample with 1% Kr in Ar under primary selective excitation with hν = 10.19 eV. This photon energy turns out to be optimal for primary selective excitation of Kr atoms at the surface.

The spectra are drastically different. Curve (1) yields a broad luminescence band centered at ~9.7 eV which stems from host luminescence centers of the molecular type (so-called m-STE, analogous to Ar2* molecules) [18]. On top of this broad band, we observe a line in perfect agreement with the energetic position of Kr3P1 → 1S0 resonance fluorescence. This line is resolution limited and stems from desorbed excited Kr atoms. Slightly red shifted are two pronounced lines (their widths are not resolution limited). They stem from Kr3P1 (hν = 9.998 eV) and Kr3P2 (hν = 9.881 eV) surface centers. Additionally, a peak at 10.38 eV is observed. It stems from 3P1 Kr atoms in the bulk of the host [17]. The narrow peak at hν = 10.62 eV originates from Kr1P1 surface centers. Desorption of Kr1P1 atoms is a very weak process. Only a tiny indication at hν = 10.644 eV is found.

Curve (2) clearly yields resonance fluorescence of desorbed Kr3P1 atoms as well as the luminescence lines which originate from Kr3P1 and Kr3P2 surface centers. The broad luminescence background is different from the one observed in curve (1). Its maximum is found at hν = 9.35 eV. In analogy to gas phase fluorescence spectra of heteronuclear ArKr* molecules [19,20] it is ascribed to a heteronuclear ArKr center.

In fig. 2, luminescence spectra of a sample with 3% Kr (excitation with hν = 10.19 eV, temperature = 6.7 K) are presented. They were measured in the first and in the second order of the monochromator. The resonance fluorescence line of desorbed Kr atoms is much narrower in second order. Its width (0.5 Å ± 4 meV) clearly demonstrates that a spectral resolution λ/Δλ = 2500 (at the given wavelength) can be obtained routinely in VUV luminescence spectroscopy under primary state-selective excitation with synchrotron radiation. The widths of the luminescence lines of the surface centers are nearly the same in first and in second order. This is of relevance from the following point of view. The Kr atoms at the surface of the host most probably occupy different sites, e.g., on top, substitutional etc. Within the measured widths, no additional structures showed up indicating that the transition energies are not sensitive to the respective site. Note, however, this statement only holds for the relaxed lattice.

In fig. 3, we present a set of spectra which were obtained for different photon energies of excitation (given at each curve). The abscissa covers only the range of the surface type luminescence lines and the
resonance fluorescence line of the desorbed Kr atoms. The results were obtained in first order from a sample with 3.3\% Krypton at a temperature $T = 6.4$ K. The curves clearly show that the relative intensities of the radiative decay channels are a sensitive function of photon energy of excitation. Details will be discussed in the next section.

### 3.2. Yield spectra

In a yield spectrum, the intensity of a spectrally selected luminescence line is measured as a function of photon energy of excitation. Such yield (excitation) spectra are presented in fig. 4 for resonance fluorescence of desorbed Krypton atoms (upper curve), for the $^3P_1$-type luminescence of Krypton surface centers (curve in middle) and for $^3P_2$-type luminescence of Krypton surface centers (3.3\% Krypton, $T = 6.4$ K). The yields are normalized to the number of photons incident on the sample per second. The reflectivity being low around 10 eV and without pronounced structures, there is practically no difference between incident and penetrating intensity.

As a consequence of the extremely low counting rates, the yield spectra were not measured in the

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**Table 2**

Comparison between experimental and theoretical values of peak positions, widths and threshold energies

<table>
<thead>
<tr>
<th></th>
<th>$^3P_1$ (atom)</th>
<th>$^3P_2$ (atom)</th>
<th>$^3P_1$ (surface)</th>
<th>$^3P_2$ (surface)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Energetic position [eV]</td>
<td>10.033&lt;sup&gt;a&lt;/sup&gt;</td>
<td>9.915&lt;sup&gt;a&lt;/sup&gt;</td>
<td>9.998&lt;sup&gt;a&lt;/sup&gt; ± 0.001</td>
<td>9.881&lt;sup&gt;a&lt;/sup&gt; ± 0.001</td>
</tr>
<tr>
<td>FWHM [meV]</td>
<td>9.90</td>
<td>9</td>
<td>18.7 ± 1.2</td>
<td>18.7 ± 1.2</td>
</tr>
<tr>
<td>Matrix shift [meV]</td>
<td>not observed</td>
<td>not observed</td>
<td>18.7 ± 1.2</td>
<td>18.7 ± 1.2</td>
</tr>
<tr>
<td>Threshold energy of the yield curve [eV]</td>
<td>desorption</td>
<td>luminescence</td>
<td>10.08</td>
<td>&lt;10.06</td>
</tr>
<tr>
<td></td>
<td>10.10</td>
<td>not observed</td>
<td>10.12</td>
<td>10.12</td>
</tr>
<tr>
<td></td>
<td>~ 10.29</td>
<td>~ 10.12</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<sup>a</sup> Ref. [20].
scanning mode (fixed wavelength at the analysing monochromator, excitation wavelength being tuned) but were constructed from luminescence spectra like those shown in fig. 3. The peak area of each radiative decay channel was plotted as a function of photon energy of excitation. The data in fig. 4 thus represent the evaluation of more than 20 luminescence spectra. In the vicinity of the maxima observed, the interval between adjacent points is only half as large as the resolution interval for the exciting light (18 meV). Note the expanded scale of photon energy of excitation. It covers only that energy range, in which primary selective excitation of Kr surface states correlating with the Kr 3P₁ and the Kr 3P₂ asymptotes is found.

The yield curves considerably differ one from another concerning (i) the threshold at the low energy side, (ii) the peak position, and (iii) the general shape. The (lowest) threshold energy for 3P₂-type surface luminescence was not covered in our experiment. The highest threshold energy is found for the desorption of Kr 3P₁ atoms. Numerical values are given in table 2.

One would like to correlate the yield spectra with the absorption cross-section σ of Kr atoms at the surface of the host. One essential condition to do so is fulfilled, the surface layer of the atoms (with n approximately equal to some 10¹³ atoms/cm²) is certainly optically thin, nσ ≪ 1. However, only the sum of all partial yields including the nonradiative decay processes would be a direct measure of σ. In the present case, one very important yield could not be measured, namely the yield of desorption of Kr 3P₂ atoms. Therefore, σ cannot be extracted directly. Nevertheless, detailed information concerning the interaction of Kr atoms with the surface of the Ar host can already be extracted.

3.3. Temperature dependence

For a sample with 3% Kr, in fig. 5 the intensities of the different radiative decay channels are plotted as a function of temperature. The photon energy of excitation, hν = 10.19 eV, approximately corresponds to the peak positions of the yield curves of fig. 4. Additionally to the intensities of the narrow lines, the values for the broad ArKr band (peak position at 9.35 eV, see fig. 1) are included. Due to the large width, the wavelength integrated intensity (peak area) is much larger than the intensities of the narrow lines.

The intensities of all radiative decay channels decrease with increasing temperature. The decrease is most pronounced for the 3P₂-center. In an Arrhenius plot, a straight line is found, indicating an (approximate) temperature dependence of the type exp (−ΔE/kT) with an activation energy ΔE ≈ 3 meV (not shown here).

Though the results of this section are not well understood, they are reported here for the following reason. A decrease of intensity of all the observed decay channels indicates that not all existing decay channels are observed. At least, desorption of Kr 3P₂ atoms should be taken into account. From pure rare gas solids (Ne, Ar), this decay channel is well known and could be analysed with time-of-flight methods and a metastable detector [5, 6]. Similar measurements will be performed for the doped systems in the future.

4. Discussion

As a guide line for a first attempt to understand the results, the ab initio pair potentials of the heteronuclear molecule ArKr may be used. The result of Spieglmann et al. [21] is reproduced in fig. 6. The ground state is strongly repulsive apart from a shallow Van der Waals minimum. Each of the excited states terminating at the Kr 3P₁ and Kr 3P₂ asymptotes exhibits a similar shallow minimum at somewhat larger internuclear distance. At shorter internuclear distance, strongly repulsive potential curves are found, some of them, however, include an additional narrow inner minimum. The double-well nature of the respective states was corroborated by fluorescence spectra in the gas phase [19].

The observed luminescence lines of those Kr atoms staying at the surface obviously originate from minima correlated with the shallow minima of the ArKr pair potentials at rather large internuclear distance. The transitions are indicated in fig. 6. The ab initio curves predict that the energetic difference of the transition energies equals the energetic difference in the asymptotic limit (atomic values). Indeed, the experimental
results are in perfect agreement with this prediction. Concerning the absolute values of the transition energies, a calculation of the energy surface of a Kr atom interacting with the Ar host is necessary. Such calculations including molecular dynamics calculations are in progress now. First results are already reported in section 5 of this paper and included in table 2. The calculated transition energies are in slight disagreement (= 70 ... 100 meV) with experiment, indicating that the well depth of the Van der Waals minima are overestimated in the work of Spiegelmann et al. [21]. For the ground state, this is quite obvious and explicitly discussed in ref. [21].

Next we discuss the threshold energies for Kr\textsuperscript{3}\textit{P\textsubscript{1}} desorption and Kr\textsuperscript{3}\textit{P\textsubscript{1}}-type surface luminescence. Again, the absolute values can only be checked with detailed calculations. However, a lower limit of the threshold of the \textit{3P\textsubscript{1}} desorption yield (experiment: 10.10 eV) can be estimated. Obviously the lower limit is given by the sum of the atomic transition energy (10.033 eV) and the binding energy of the Kr atom at the Ar host. The binding energy must be in between the value of pure Ar (80 meV [22]) and pure Kr (116 meV [22]). Taking as an estimate 96 meV, we obtain \( E_{\text{th,d}} > 10.12 \) eV. This is in surprisingly good agreement with the measured value. The threshold energy, \( E_{\text{th,d}} \), of Kr\textsuperscript{3}\textit{P\textsubscript{1}}-type surface luminescence is only slightly below \( E_{\text{th,d}} \) (see table 2 and fig 4) As it turned out in the theoretical calculations (section 5), the minima of the ground state and of the excited state are considerably shifted against each other. Therefore, direct excitation of the bound excited state well below the desorption threshold is unfavourable due to negligible Franck–Condon overlap. A similar behaviour is known from the gas phase. In absorption experiments on Kr doped Ar gas in the vicinity of the first Kr resonance line, only a “blue” wing and no “red” wing is found [19,23].

Next we want to interpret the branching ratio between desorption of Kr\textsuperscript{3}\textit{P\textsubscript{1}} atoms and luminescence of Kr\textsuperscript{3}\textit{P\textsubscript{1}}-type surface centers. For this purpose, we calculated the ratio

\[
P = \frac{Y_{\text{des}}(\text{3P\textsubscript{1}})}{Y_{\text{des}}(\text{3P\textsubscript{1}}) + Y_{\text{lum}}(\text{3P\textsubscript{1}})}
\]

from the yield curves of fig. 4. Assuming that the primary excitation leading to either \textit{3P\textsubscript{1}} desorption or \textit{3P\textsubscript{1}}-type luminescence does not feed into other decay channels, the quantity \( P \) then is the probability for desorption, \((1 - P)\) however the probability for the creation of the emitting surface center. In fig. 7, \( P^2 \) is plotted as a function of photon energy of excitation. Surprisingly enough, a straight line is found which indicates

\[
P \propto \sqrt{\hbar \nu - E_{\text{th,d}}}
\]

\( E_{\text{th,d}} \) is the intercept with the energy axis and corresponds to the threshold of desorption. The quantity \( \hbar \nu - E_{\text{th}} \) is the energy above the dissociation limit. It is a measure of the velocity of the Kr atom above the surface,

\[
\sqrt{\hbar \nu - E_{\text{th,d}}} \propto \nu \propto 1/\Delta t.
\]

The velocity can be interpreted as \( \alpha (\Delta t)^{-1} \), \( \Delta t \) being a measure of the time of the interaction of the Kr atom with the surface. The experimental result corresponds to what we intuitively expect: the probability of an
energy loss stabilizing the outward moving Kr atom in the shallow well scales with $\Delta t$. The probability of desorption, however, increases with increasing velocity of the outward moving Kr atom.

The clear and simple interpretation of the branching ratio has some hidden assumptions. Though there is a spectral overlap, the $^3P_1$-type yields have obviously nothing to do with the $^3P_2$-type yield. In other words, electronic relaxation from the $^3P_1$-type potential energy curves to the manifold correlated with the $^3P_2$ limit can be neglected. In an indirect way, this is also established by the temperature dependences in fig. 5. Only the yield of $^3P_2$-type surface luminescence is strongly quenched in favour of Kr$^3P_2$ desorption. The other yields show only a comparatively weak temperature dependence.

Another hidden assumption concerns the formation of ArKr centers emitting the broad band at 9.35 eV. The existence of this strong band was neglected in the discussion of the branching ratio. At first sight, this seems to be a strong point against our interpretation. However, from the gas-phase date it is known that the inner minima of the double-well potentials are the source of the broad luminescence features. Obviously, direct excitation to the inner minima are responsible for the molecular-type luminescence. Branching between $^3P_1$ desorption and $^3P_1$-type surface luminescence is a property of the outer repulsive part of the potential curves.

5. Molecular dynamics calculations

Using the molecular dynamics scheme described in ref. [9] for Ar and ref. [24] for Kr, we formed an fcc cubic sample containing 500 atoms with the surface (100) atoms relaxed. This defines $z = 0$ in fig. 8, where $z$ is the axis perpendicular to the surface. A surface Ar is then replaced by a Kr atom in the ground state (substitution) or a Kr atom is added onto the surface (adsorption), after which the sample is cooled to its relaxed position. A Lennard-Jones (6–12) potential is used for the Ar–Kr interaction potential ($\omega = 113.9$ cm$^{-1}$, $r_0 = 3.88$ Å) [25]. The substitutional Kr atom relaxes to a position $\approx 0.6$ Å inside the surface, and the Ar nearest neighbors relax slightly inwards, $\approx 0.04$ Å. An approximate net ground state interaction potential is then constructed by stepping the Kr atom along the $z$-direction with the Ar fixed in their relaxed positions. The potential thus constructed is shown in fig. 8. The resulting minimum is found to be shifted slightly outward from the relaxed Kr position, because the Ar positions were fixed (i.e. this is not the adiabatic potential).

An excitation is produced (viz. refs. [9, 24], assuming the Franck–Condon principle, by switching to the Ar–Kr excited state interaction potentials. We first constructed spherically symmetric excited state Kr–Ar pair interactions, as in ref. [9] for an excited Ar in an Ar matrix. Such states are, roughly, correct within the pair approximation when an excited atomic species is trapped in the bulk. However, we also used such states to describe surface desorption. These pair interaction potentials were based on the gas-phase pair potentials of Spiegelmann et al. [21] shown in fig. 6. For the $^3P_1$ and $^3P_2$ states we used the weighted mixtures $\omega = 0, 1$ and $\omega = 0, 1, 2$, respectively. Results based on the interactions were compared with those calculations shown in figs. 8 and 9 in which we simply used the $\omega = 1$ states in fig. 6. For atoms trapped far from the surface, as was found to occur when exciting pure Kr, a description based on pair potentials can be justified. However, using simultaneously the same interaction of the excited Kr with Ar in different positions is a very rough approximation for this nonspherically symmetric excited state wave function and lattice geometry. New calculations are in progress to deal with this, and the calculations described below are examples for discussions.

On exciting Kr, using one of the pair potentials discussed above, we can again construct approximate net interaction potentials along the $z$-axis, again fixing the Ar. This is done to visualize the effect produced on selectively exciting the Kr. Such potentials are shown in fig. 8, constructed using the $\omega = 1$ states only. Additional structure is seen in these potentials compared to
...in the ground state potential. Replacing the Lennard-Jones ground state interaction potential by the ground state potential of Spiegelmann et al. [21] makes the comparison to experiment worse at both the inner and outer minimum, and, in fact, at the outer minimum the shifts are in the wrong direction. Although differences from experiment are expected, because the same pair potentials are used for the Kr interacting with all of the Ar, the size of the differences found in table 2 are primarily due to the long-range well being too deep for the gas-phase pair potentials used. Following the ideas in ref. [9] a sample was also constructed in which a surface neighbour was removed, i.e. a “damaged” crystal. Allowing the substitional Kr to relax the new net interaction potentials were found to be similar but, not surprisingly, the outer minimum was somewhat shallower. Upon relaxation to the outer minimum the trapped Kr moved above the vacancy and the repulsive wall shifted outward. The calculated line shifts were in the same direction showing a slightly better agreement with experiment for the \( 3P_1 \) state using the \( \Omega = 1 \) interaction only, but a poorer agreement for the \( 3P_2 \) state.

Both for the “undamaged” and the “damaged” surface, excitation was then carried out and the motion of the system was allowed to respond to the excited state interaction potentials. This was done for Kr in the relaxed ground state position and for shifts in that positions associated with ground and possible excited vibrational states. The resulting motion of the Kr along the z-direction is shown in fig. 9 (“undamaged” surface). When there is no shift in the z-position for the fully cooled crystal (approximately a few Kelvin, our usual starting point) excitation 3 to the \( 3P_2 \) state leads to desorption, whereas excitation to the \( 3P_1 \) state leads to trapping at the outer minimum, due to the somewhat deeper well for that state and the response of the surface Ar. Fortuitously, this behavior is also the case when the spherically averaged states are used, even though the structure of the net interaction potentials differs from that obtained using the \( \Omega = 1 \) interactions only. When the Kr position is shifted inwards or outwards by \( 0.1 \) \( \text{Å} \) or by \( 0.3 \) \( \text{Å} \) for the Kr in a \( 3P_2 \) state, using the \( \Omega = 1 \) interactions, then trapping occurs for this atom also, both at the inner and outer minimum respectively. (For the spherically averaged \( 3P_2 \) interaction trapping does not occur at the inner minimum for the reasons discussed above.) This sensitivity to the initial position of the Kr atom in the lattice is, roughly, consistent with the sensitivity of the \( 3P_2 \) luminescence yield to temperature, as seen in fig. 5.

\( 3P_1 \)-type excitation of a Kr atom displaced outwards always leads to trapping. For an inward shift of the Kr atom by \( 0.1 \) \( \text{Å} \), trapping still occurs. If the Kr atom is shifted inwards by \( 0.3 \) \( \text{Å} \) during \( 3P_1 \)-type excitation, the excited atom desorbs promptly due to the increase in...
potential energy, hence, larger outward repulsion velocity (viz. eq. (3)). Because the excitation occurs to a steep repulsive wall (fig. 8), there is a transition to desorption. This is consistent with the fact that there is a threshold for desorption as shown in fig. 7. Based on these sample calculation, and the potentials in fig. 8, this threshold behavior will differ from that for substitutional Kr excited to the \( ^3P_2 \) state.

The above results should be considered as demonstrative only. Clearly using pairwise potentials and the same pair interaction with every Ar for this nonspherically symmetric geometry is not correct. Further, the spherically averaged potentials of the type used in ref. [9] miss the important case of trapping at the inner minimum. However, the results show the correct trend in the luminescence shift and a behavior (trapping vs desorption) roughly consistent with what we found experimentally. Because trapping at the outer minimum should be reasonably well described by long-range pair interactions between the excited Kr and the ground state Ar, the errors in the theoretical line shifts are primarily due to the deficiencies in the gas-phase interaction potentials used.

Acknowledgements

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