

## Formation and Dynamics of Exciton Pairs in Solid Argon Probed by Electron-Stimulated Ion Desorption

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Electron-stimulated desorption of  $\text{Ar}^+$ ,  $\text{Ar}_2^+$ ,  $\text{Ar}^{2+}$ , and  $\text{Kr}^+$  ions from solid Ar and Kr was studied for the electron energy range from 10 to 120 eV. For  $\text{Ar}^+$  and  $\text{Ar}_2^+$ , excitation resonances with onsets at 24.2, 25.4, 34, and 50 eV have been found. The two lowest thresholds cannot be explained by excitations of single Ar atoms. They are interpreted as pairs of interacting surface and bulk excitons, respectively, on neighboring atoms. The bulk species can diffuse over more than 100 layers. Novel conclusions about the desorption mechanism can be derived.

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The desorption mechanisms of atomic and cluster ions from rare-gas solids (RGSs) by electron impact are not well understood. In an investigation aimed at progress in this respect, we have found evidence for novel excitations in solid argon, exciton pairs  $[(\text{Ar}^*)_2]$  on neighboring atoms in the bulk or at the surface. These results also make conclusions about the acting desorption mechanisms possible.

All processes of DIET (desorption induced by electronic transition) involve a stage where part of the electronic excitation energy is transferred to nuclear motion. For DIET of *neutrals* from RGSs, two basic processes are considered to be important at present. The so-called *molecular mechanism* involves the formation, the vibrational relaxation, and the dissociation caused by radiative deexcitation, of a molecularly self-trapped exciton near the surface; desorption occurs either directly or due to sputtering of neighboring atoms by the fragments of this dissociating excimer.<sup>1</sup> The second process is the so-called *cavity mechanism* which is a consequence of atomic self-trapping of excitons on the surface of the RGS. Desorption of electronically excited excimers and monomers via this process has been observed for the light RGSs Ar and Ne, where the interaction between the lattice and the inflated electron distribution of these particles is repulsive, but not for the heavy rare gases Kr and Xe.<sup>2</sup> For both reaction types, the primary electronic excitations are of the exciton type; for Ar, the thresholds are at 11.8 (surface) and 12.2 eV (bulk).<sup>2</sup> The relative contributions of both mechanisms to the total desorption yield of neutrals depend on the thickness of the film.<sup>3</sup>

Studies on stimulated desorption of *ions* from RGSs are less numerous. Desorption of singly charged ions has been observed to be caused by the primary excitation of electronically excited ions  $X^{+*}$ , and primary double ionization  $X^{2+}$ ;<sup>4</sup> DIET of singly *and* doubly charged ions was obtained for core ionization from solid Ar as well as Kr.<sup>5</sup> The processes supplying kinetic energy have been interpreted as Coulomb repulsion of ion pairs which are formed by curve crossing from the initially multiply ex-

cited particles and their ground-state neighbors,<sup>4</sup> or by the radiative or recombinative decay of doubly charged ionimers.<sup>5</sup> From the comparison of the ion yields for excitonic and continuum-type core excitations it was concluded that the ion signal is at least partly due to Coulomb repulsion of pairs of ions, one partner of which is created in a secondary, electron-impact, ionization step by fast electrons originating from the Auger or autoionization decay of the core excitation, which itself supplies the second particle of the pair.<sup>6</sup> Precise data on the regime of the primary threshold for DIET of ions from RGSs, however, are missing. The intention of the present investigation was to elucidate this energy range.

The experiments were performed in a UHV system with a base pressure of  $4 \times 10^{-9}$  Pa. The system contained a cryomanipulator for the sample, equipped with a temperature controller (temperature range 10–1600 K), a quadrupole mass spectrometer for the detection of neutrals (*n*-QMS), a second QMS without ionizer for the detection of ions (*i*-QMS), and a hemispherical analyzer for electron spectroscopy (see Ref. 7 for details). A ring-shaped thoria-coated tungsten filament located between the sample and the *i*-QMS was used to irradiate the sample with electrons. The energy of the emitted electrons was set by negatively biasing the filament. The sample itself was always grounded. The spread of the kinetic energy of the electrons was approximately  $\pm 0.3$  eV; it was mainly due to the voltage drop across the filament. A retardation grid between the filament and the *i*-QMS prevented electrons from entering the detector. The Ar and Kr films were dosed onto a Pt(111) single crystal by a microchannel-plate doser. The thickness of the films was derived from temperature-programmed-desorption spectra taken with the *n*-QMS. It is given in multiples of the amount adsorbed in the first layer on the metal substrate. The substrate itself was cleaned by  $\text{Ar}^+$  sputtering and heating in  $10^{-4}$  Pa of oxygen. Its periodicity and cleanliness were checked by LEED and x-ray photoemission spectroscopy (XPS) (Al/Mg  $K\alpha$  source with hemispherical electron

energy analyzer). Dosing and measurements were done at 10 K.

The work function of the filament was obtained by measuring the kinetic energy of the emitted electrons referred to the vacuum level by the hemispherical analyzer; the work functions of the samples, the knowledge of which was necessary for the evaluation of the precise values of the electron energies at the surface of the films, were derived from the cutoff of the secondary electron peak in XPS. Because of the very low mobility of holes, charging is always a severe problem in electron and ion spectroscopy on RGSs. Here, we observed strong dependences of the threshold energies on beam current for electron fluxes in the microamp regime, especially for thick layers. For beam currents lower than  $10^{-9}$  A, however, the energetic position of the thresholds became independent of the primary electron flux. Therefore, all data presented here are recorded with such low primary electron currents.

The  $\text{Ar}_2^+$ ,  $\text{Ar}^+$ ,  $\text{Ar}^{2+}$ , and  $\text{Kr}^+$  electron-stimulated-desorption (EDS) signals obtained from solid Ar and Kr, respectively, are shown in Fig. 1. The traces for the singly charged species (which we consider first) are ap-

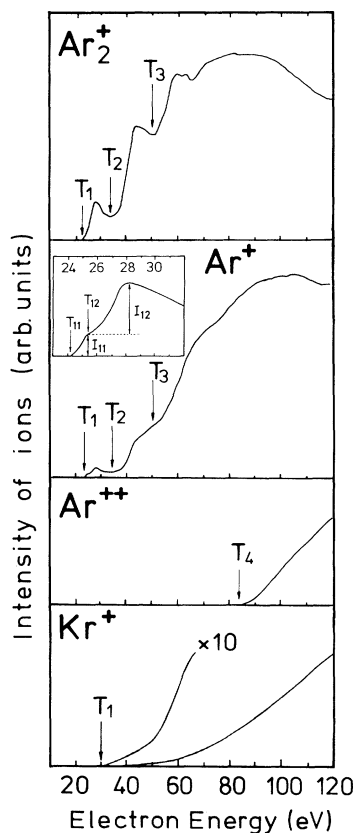


FIG. 1.  $\text{Ar}_2^+$ ,  $\text{Ar}^+$ ,  $\text{Ar}^{2+}$ , and  $\text{Kr}^+$  ESD yields vs electron energy from 40-layer-thick Ar and Kr films. Inset: The first resonance on an expanded energy scale.

parently a superposition of (a) distinct resonances, and (b) a background increasing with energy. The branching, however, varies: The resonant features are strong for the  $\text{Ar}$  ionimer, and weak for  $\text{Ar}^+$  ESD. For  $\text{Kr}^+$ , no such resonant maxima are visible. The onsets of these resonances  $T_1$  to  $T_2$  for argon (taken from the  $\text{Ar}_2^+$  trace) are at 24.2, 34, and 50 eV. Closer inspection exhibits fine structure of the first maximum: The primary threshold at 24.2 eV is followed by a second step at 25.4 eV (see the inset in Fig. 1; for clarity, we label these onsets as  $T_{11}$  and  $T_{12}$ , respectively). Data for films of different thicknesses clearly discriminate  $T_{11}$  as a surface, and  $T_{12}$  as a bulk excitation: The contribution of  $T_{11}$  to the desorption yield saturates at about 10 layers, whereas  $T_{12}$  increases with film thickness up to more than 100 layers; see Fig. 2. For Ar, no ESD of ions was obtained for excitation energies below  $T_{11}$ . For Kr, where such resonant peaks are not present, the onset of ionic ESD was found at 30 eV; see Fig. 1.

In a previous photon-stimulated-desorption study of one of the authors, the primary excitation of electronically excited singly charged ions as well as the creation of doubly charged ions was identified as the stimulus for DIET of ions.<sup>4</sup> The interpretations given in Refs. 4 and 5 imply that these multiply excited particles cause desorption either by the formation of ion pairs by curve crossing,  $X^{++}X, X^{2+}X \rightarrow X^+X^+$ , and subsequent Coulomb repulsion of the constituents of these,<sup>4</sup> or by formation of excited excimers which decay after vibrational relaxation.<sup>5</sup> For Ar, the thresholds for  $\text{Ar}^{++}$  and for  $\text{Ar}^{2+}$  formation were obtained at 32 and 40 eV, respectively.<sup>4</sup> For stimulation by electron impact as in this study, however, these excitations should be visible as broad maxima similar to the ionization-cross-section curves obtained in the gas phase, and not as narrow resonances as seen in Fig. 1. They certainly do contribute to the smooth background of the signals in Fig. 1, but they cannot be the

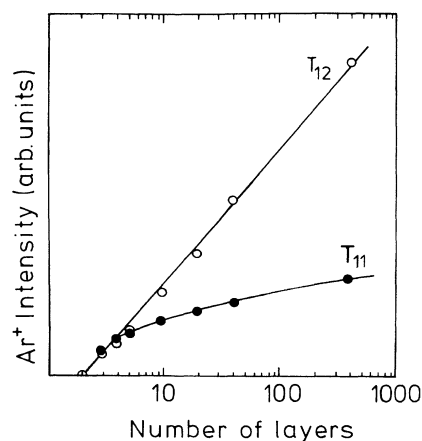


FIG. 2. Dependence of the  $\text{Ar}^+$  signals  $I_{11}$  and  $I_{12}$  which are correlated to  $T_{11}$  and  $T_{12}$  (see inset of Fig. 1) on film thickness.

cause of the resonances because the convoluted densities of states of the two free electrons in the final state should lead to maxima with widths similar to those obtained for the ionization cross section, i.e., about 80 eV for Ar.<sup>8</sup> Another contribution to the background presumably stems from ion pairs which are created by one single electron (see above). Utilizing gas-phase ionization cross sections,<sup>8</sup> we derived similar probabilities for (a) the creation of doubly charged ions, and (b) ionization of adjacent atoms by the same electron. For Ar, scenario (b) gives a broad maximum at 100 eV, in very good agreement with the trace for Ar<sup>+</sup> in Fig. 1. The background of the Ar<sub>2</sub><sup>+</sup> curve with its maximum at 80 eV resembles more closely the energy dependence observed for single ionization;<sup>8</sup> Coulomb repulsion of ion pairs apparently is not the prevalent process for desorption of ionimers. This indicates that for these species a DIET mechanism is necessary, which acts between the excited molecule and the lattice and not between separate particles.

This mechanism can be clarified by identifying the nature of the resonant excitations seen for the ion traces in Fig. 1. Focusing on the features  $T_{11}$  and  $T_{12}$ , we emphasize that these cannot be assigned to electronic excitations of one single Ar atom, since they are observed between the excitation energies for Ar  $3p$  ionization and Ar  $3s$  excitons.<sup>2,9</sup> Even the possibility of multiple bound electronic excitations of one atom is ruled out for energy reasons (for Ar gas, the lowest excitation of this type is beyond the threshold for  $3s$  excitons<sup>10</sup>). However, considering the excitation energies for  $n=1$  surface and bulk excitons of 11.8 and 12.2 in argon, we can explain these maxima as due to the simultaneous excitation of two  $3p$  excitons on neighboring atoms. On the surface, desorption of such a doubly excited excimer Ar<sub>2</sub><sup>\*\*</sup>, which resembles an alkali molecule, is expected to rapidly proceed as in the previously described cavity mechanism for Ar, but not for Kr (see above), in perfect agreement with our findings. The appearance of ionic molecules can be explained by autoionization of the highly excited entities in the gas phase after their desorption, either into Ar<sub>2</sub><sup>+</sup> in its stable ground state, or into a dissociative excited state (Ar-Ar)<sup>+</sup> leading to Ar<sup>+</sup> detection.

The most striking result is that these exciton pairs apparently have a lifetime as "free" excitations which is sufficiently long to enable their diffusion through the solid to the surface, as the data from Fig. 2 unambiguously indicate. The barrier against delocalization into separate excitons must be due to the mutual interaction energy  $\Delta E$  (from  $T_{12}$ , and the excitation energies of single excitons we derive  $\Delta E \approx 1$  eV for the bulk species), which is comparable to the width of the exciton bands; i.e., arguments similar to those used for the interpretation of the long lifetimes seen for multiply excited states in Auger spectroscopy can be applied here.<sup>11</sup> To our knowledge, this is the first observation of such an exciton dressed by an exciton in RGSs (however, holes dressed

by an exciton have been observed before in electron-scattering experiments<sup>12</sup>).

The dependence of the ESD yield on film thickness has not been recorded in detail for  $T_2$  and  $T_3$  at 34 and 50 eV. Because of their resonant shape and their energetic positions we tentatively assign them to multiple ( $n$ ) excitonic excitations at  $n(12 \text{ eV}) + \Delta E$ , for  $n=3$  and 4. The driving force for the desorption process would then be identical for  $T_1$  to  $T_3$ . The visibility of these features in the ionimer and, though depleted, in the ion yield apparently reflects different branching ratios in the autoionization process. The large nonresonant backgrounds obtained for Ar<sup>+</sup> and Ar<sub>2</sub><sup>+</sup> ESD, however, are indicative of other desorption mechanisms, probably proceeding via the creation of Ar<sup>2+</sup>, Ar<sup>+</sup>Ar<sup>+</sup>, and Ar\*Ar<sup>+</sup> excitations (see above).

The threshold at 83 eV for the desorption of Ar<sup>2+</sup> (see Fig. 1) is in good agreement with the threshold for the formation of Ar<sup>3+</sup> in the gas phase.<sup>8</sup> Obviously, DIET of this species is initiated by curve crossing from Ar<sup>3+</sup>Ar to Ar<sup>2+</sup>Ar<sup>+</sup> or Ar<sup>2+</sup>\*Ar<sup>+</sup>, and Coulomb repulsion. It is, however, still an open question why no ions are seen at the threshold for the creation of adjacent pairs of doubly and singly charged particles by one electron at about 54 eV. The probability for such an excitation should be comparable to primary triple ionization.

In summary, our threshold investigations of ionic ESD from condensed Ar and Kr have clarified the mechanisms of ion desorption and have led to the identification of new RGS excitations, exciton pairs (surface and bulk), which show up because of selective expulsion of dimers. The bulk species can migrate over more than 100 layer spacings.

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