Direct Detection of Neutral Atoms Photodesorbed from Monolayers and Multilayers of Rare Gases on a Metal Surface by Excitonic and Ionic Primary Processes

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Neutral atoms photodesorbed by monochromatic synchrotron radiation between 7 and 30 eV from monolayers and multilayers of Ar and Kr on Ru(001) have been detected by postionization and lock-in mass spectrometry. From multilayers, primary processes leading to desorption are surface and bulk excitons of various orders, ionic excitations, and two-step processes (photoelectron-induced excitons). Ar monolayers show surface excitons besides ionic excitations. The acting mechanisms are briefly discussed.

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The ability of electronic excitations to desorb rare-gas atoms from monolayers or submonolayers on metals became first obvious in LEED studies of such layers.[1,2] Electronically stimulated desorption of van der Waals–bound atoms and molecules from metals has since been purposely investigated by several groups using electron impact excitation.[2-4] The results have been discussed[2-5] in terms of a mechanism proposed in a different context by Antoniewicz.[6] In this model, the primary process is the ionization of the adatom, and the transfer of electronic excitation into atomic motion occurs in the ionic potential well which is considerably deeper than that of the ground state; neutralization by tunneling from the surface after some acceleration towards the latter brings the particle back to the ground-state curve at a too small distance and with some kinetic energy so that desorption of a neutral atom can occur after reflection. So far, evidence for this mechanism is only indirect, and, in particular, no identification of the desorption products and of the primary excitations leading to desorption exists to date.

More recently, it became obvious that electronic excitations can also lead to desorption from multilayers of rare-gas crystals.[7,8] Here, desorption has been linked to exciton-excimer conversion[8] or, for neon and argon, to relaxation at the surface of the mechanical stress induced in the lattice by an exciton.[7] Desorption of ground-state or electronically excited atoms, respectively, are the consequence. Exciton migration to the surface and slow relaxation are important aspects of these mechanisms. Again, the experimental evidence has been somewhat indirect as most investigations have used the rather unspecific excitation by electrons, often without energy variation, or by fast ions,[8] and even the investigations of luminescence light from the rare-gas film and the desorbing atoms have not observed desorption directly, but via film thickness decreases (Ref. 7; see however, Kloiber *et al.*[9]). Thus, excitation-specific measurements are of great interest here as well, even though the basic understanding is much better, as the optical excitation and decay spectra of rare-gas films and crystals have been investigated in detail over many years.[10,11] The formation, migration, self-trapping, and relaxation of surface and bulk excitons are therefore well understood, and links to absorption and luminescence spectra are possible.[7,10]

This Letter reports investigations of neutral-atom desorption after state-selective excitation with synchrotron radiation, using direct detection of the desorbing neutral atoms, for monolayers and multilayers of Ar and Kr on Ru(001). We show that for *multi*layers, the wavelength-dependent neutral-atom desorption yields correlate with absorption data, exhibiting evidence for surface and bulk excitons up to third order, but showing different, thickness-dependent weighting. Evidence for the action of ionic primary excitations and of multiple (two-step) excitations are also seen and can be understood qualitatively. For *mono*layers of Ar, the first surface exciton is resolved besides ionic excitations; for Kr, which generally exhibits much smaller desorption yields, the only discernible primary excitations are ionic. Generally, the data agree with the expectations derived from the models mentioned above, but a more direct picture of the relative importance of the various mechanisms and excitations can be developed, and a number of questions of detail are raised which require further investigation.

The experiments were performed at the Berliner Elektronenspeicherring für Synchrotronstrahlung (BESSY), with the 1-m Seya monochromator in the energy region 7–30 eV. The energy dependence of the photon flux and the contributions of higher orders were obtained from measurements of the gas-phase photoionization of Ar and Kr in the same apparatus and from published cross-section values.[12] The threshold energies agreed to 50 meV; this was also the reproducibility of the energy scale. The ultrahigh-vacuum system (working pressure 7×10^{-11} mbar) has been described before.[13] The Ru(001) crystal, prepared and cleaned as usual,[14] was mounted on a manipulator which allowed cooling to 20 K and controlled heating up to 1600 K. Desorbed neutrals were detected with a quadrupole mass spectrometer with efficient ion source which was surrounded by a glass cap with an aperture of 5 mm for increased detection efficiency,[15] with the crystal positioned in front of the aperture, about 2 mm away. Only grazing-incidence light (p polarization) was usable for neutral desorption, therefore. The light was chopped mechanically at a frequency of about 20 Hz, and the mass spectrometer signal at the selected mass was detected by lock-in techniques. A platinum shield behind the aperture suppressed signals from reflected or emitted photons. Neutral particles then entered the ionization region only after several reflections, deexciting electronically excited atoms to the ground state. Optimization led to a sensitivity of about 10^{-7} monolayer per second for neutral atoms. Multilayers of Ar, up to 6-nm thickness, and Kr, up to 15-nm thickness, were prepared by dosing through a capillary for a definite time interval from a reservoir held at constant pressure. Monolayers were prepared reproducibly from multilayers by controlled heating.[16] Dosing and desorption measurements were carried out at a crystal temperature of about 20 K.

The main results for Ar layers are summarized in Figs. 1 and 2. We shall discuss the multilayers first. The low-resolution, wide-range spectra of Fig. 1 are dominated by the sharp threshold excitation which becomes relatively less prominent, compared with the broader structures at higher energies, for thicker layers. The high-resolution spectra of Fig. 2 exhibit considerable structure which can be assigned with acceptable confidence by comparison with the absorption spectra published by Saile *et al.*[17] The first and second surface and bulk excitons can clearly be seen and their splitting is indicated (and can be increased by curve resolution techniques[18]); closer inspection also produces evidence for the bulk excitons with $n=3$ and 4 (at 13.9 and 14.0 eV). The exact energies differ slightly which may be because of the different temperatures used there and here.[19] The differences in relative intensities must be ascribed to excitation-dependent coupling to desorption. Obviously the desorption contributions of the surface excitons are constant with thickness, while those of the bulk excitons increase with thickness, with the higher excitons coming up only in the thickest layers. With prolonged measurement, signal decreases have been observed which must be due to radiation damage. In the ionic region, the first broad peak starting around the gap energy (14.2 eV) and reaching up to about 18 eV, with its maximum around 16 eV (Fig. 1), must be connected to simple ionization; its structure should be mainly caused by final-state density effects in the bulk. The peak around 27 eV is probably due to ionization with the formed photoelectron having enough energy to create a surface exciton ($14.2+11.8 \simeq 26$ eV are necessary for this) or a bulk exciton correspondingly higher.

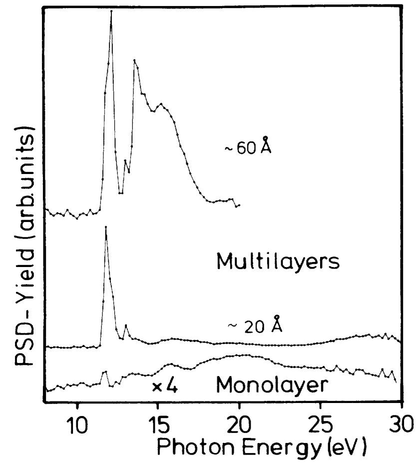

FIG. 1. Photostimulated desorption rates of Ar^0 from monolayers and multilayers of variable thickness of Ar/Ru(001), at low resolution.

For Ar *mono*layers, the spectrum clearly contains, besides ionization, contributions from desorption via the surface excitons, with only the first one clearly resolved (Fig. 1). Compared with multilayers, these are weaker, and bulk excitons are missing, of course. Interestingly, the *energy* of the first-surface exciton is found identical for monolayers and multilayers at 11.8 eV (Fig. 2) which is a surprising result.

For Kr *multi*layers, contributions from both surface and bulk excitons can be discerned again (Fig. 3), and the energy values compare very well with optical data.[17] However, the overall signal strengths are lower by a fac-

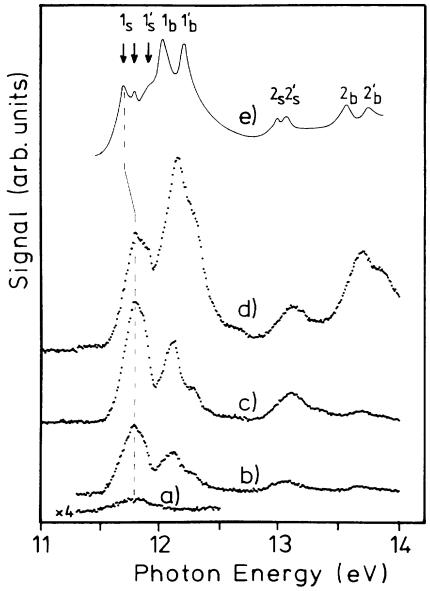

FIG. 2. "High"-resolution photo-stimulated desorption from Ar (curve *a*) monolayer and (curves *b*–*d*) multilayers (15, 25, and 60 Å, respectively) compared with (curve *e*) absorption of a 23-Å layer (from Ref. 17). Energy positions of bulk and surface excitons are indicated.

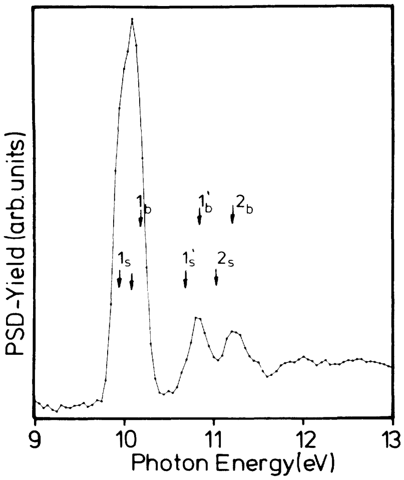

FIG. 3. Resonant photo-stimulated desorption maxima from multilayer Kr/Ru(001) (~30 Å). Exciton energies from optical data of Ref. 17 are indicated (E_{gap}: 11.6 eV).

tor of about 10 (at the first bulk exciton), compared with Ar. Again, the ionic range is weighted more strongly for thicker layers; two-step processes appear to be very strong (not shown). For Kr *mono*layers, the signal is very weak (down by a factor 8–10 compared with Ar monolayers, and by about 20 relative to Kr multilayers). Only contributions from ionization are visible here; in the excitonic range the signal cannot be distinguished from noise. In view of the interesting strong temperature dependence reported for *electron*-stimulated desorption from Kr monolayers,[2] the temperature of the substrate was varied here. A yield increase of a factor of only 1.5 was found in the range from 20 K to the onset of rapid first-layer desorption at 47 K. For Xe, *no* desorption signal could be seen from either monolayers or multilayers.

These measurements give rather direct access to the important primary excitations leading to desorption in both monolayers and multilayers. Roughly, our findings join up with the proposed mechanisms mentioned above. Thus is is clear that the bulk excitations can be summed up in multilayers; in order to become desorption active, they must be able to migrate to the surface before they decay. This must be true for both (bulk) excitonic and ionic excitations. If the relative strengths of these in the absorption spectra are taken as an indication of the intrinsic cross sections, then our data suggest that ionic excitations have a better chance to reach the surface and become converted than bulk excitons. After having arrived there and having become trapped into ionic dimers, these have to capture one of the hot electrons (photoelectrons or secondaries) to become desorption active; the further evolution parallels that of excimers which leads to desorption of ground-state atoms when fluorescent decay occurs, due to the repulsive nature of ground-state dimers at excimer distance.[8] The appearance of higher bulk excitons for our thickest layers only is understandable in terms of their "diameters"[10] which are in the range of our estimated thicknesses. As mentioned, we cannot distinguish ground-state and excited atoms so that we cannot estimate the influence of the pathway from excitons to desorption suggested by Coletti, Debever, and Zimmerer.[7]

The Ar monolayer data show clearly that even here not only ionic but also excitonic processes lead to desorption. This path must then be added to the Antoniewicz mechanism sketched above. To be sure, its overall contribution in, e.g., electron-stimulated desorption measurements, which can be roughly obtained by comparing it to yield integrals over a larger photon energy range, will be rather small and is missing in Kr monolayers. Nevertheless, it is interesting that an exciton mechanism does exist in monolayers as well. We propose that a monolayer exciton, i.e., an adsorbed $\mathrm{Ar}^*(3p^{-1}4s^{+1})$ atom, can relax into desorption because of an increased surface bond for this species, as compared the ground-state atom. An indication for this increased bond comes from the considerably higher polarizability, α, of this species (for the triplet species, α is about 7.1×10^{-24} cm^3 as compared with 1.64×10^{-24} cm^3 for the ground-state atom.[20] An increase of the van der Waals energy (which roughly scales as α for ground-state Ar, Kr, and Xe) will result; chemical effects may further enhance the bond. This should be enough for a quasi-Antoniewicz sequence, in which the role of neutralization is taken by radiationless quenching (the Penning process) of the atomic excitation into the metal. Indeed, the corresponding electron emission has been found for Xe monolayers with subthreshold photoexcitation.[21] We conclude that exciton-induced desorption from Ar *multi*layers should lead to desorption of *excited* atoms, while from monolayers the ground-state atoms should desorb. It would be interesting to check this proposition. The fact that the excitonic peak is missing for Kr-monolayer desorption is probably due to the stronger coupling between the rare-gas and metal excitations.[22] Qualitatively, this is the trend to be expected from this theory.

In conclusion we have accomplished the first direct measurements of the photon energy dependence (and therefore the dependence on primary excitation) of neutral rare-gas desorption from both monolayers and multilayers of Ar and Kr on a smooth transition metal surface, Ru(001). The results show the relative contributions of surface and bulk excitons of various order, ionic and two-step processes in multilayers, and surface excitons and ionic excitations in monolayers. A further detailed investigation of coverage and layer-thickness dependences and a detailed comparison with existing theories of the coupled optical excitations of rare-gas atoms on metals and of the transfer of excitation into the metal during evolution of the excitations should improve the understanding of excitations and their decay in van der Waals–bound surface layers.

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