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Stimulated desorption of atoms from rare-gas monolayers on metal surfaces: Dependence of yields and energy distributions on primary excitations

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Kinetic energy distributions of Ar and Kr atoms desorbed by electron impact from saturated and dilute monolayers on Ru(001) have been measured by a time-of-flight technique. Both the most-probable kinetic energies and the desorption yields are found to increase for electron energies above the thresholds for multiple ionization. This effect is particularly pronounced for Kr. Using gas-phase ionization cross sections, relative escape probabilities for single and multiple primary ionization are derived. The data can form the basis for a quantitative theory of the desorption process.

Desorption induced by electronic transitions (DIET) off physisorbed monolayers on metals has been studied experimentally—utilizing excitation by electrons [electron-stimulated desorption] (ESD) (Refs. 1–4) and photons (PSD) (Ref. 5)—and theoretically.[3,4,6–9] These investigations led to the conclusion that desorption roughly follows a so-called Antoniewicz mechanism.[10] According to this model, the adparticles are ionized and accelerated towards the surface by the image force, which is added to the attractive van der Waals interaction by ionization. For sufficiently long lifetimes of the ionic states, desorption of neutrals can occur if the particles are so close to the surface after neutralization that the sum of potential energy and accumulated kinetic energy exceeds the binding energy of the neutral ground state.[6] The complete absence of desorbing ions expected from this model has been demonstrated experimentally.[1,2,11] More detailed predictions of observables, such as the temperature dependence of the escape probability P,

$$P = \sigma_d/\sigma_p \tag{1}$$

(σ_d, desorption cross section; σ_p, primary excitation cross section[12]), and the kinetic energy distributions of desorbing particles based on this model, were not so successful. Neither classical[4,6] nor quantum-mechanical[7,8] approaches could simultaneously explain the experimental findings for the escape probabilities and the kinetic energy distributions. Calculations with parameters leading to correct energy distributions resulted in escape probabilities too low by orders of magnitude;[6,13] if the magnitude of the escape probability was reproduced correctly, the energy distributions came out too narrow. It has been suggested that this discrepancy is due to the ansatz used for the real part of the ionic potential in these calculations, i.e., the Morse equation for the ground state plus a bare image potential for the additional interaction of the ion with the surface.[8,9,14] Better agreement of experiment and theory is expected for more realistic potentials, which take into account additional chemical effects for the interaction of the ion with the surface.[9,14] Unfortunately, testing of more refined theoretical approaches suffers from the lack of pertinent experimental data. The only kinetic energy values available at present are, first, for a complex system like physisorbed N_2O,[4] which can be prepared in a matrix of chemisorbed N_2O only, and may experience internal excitations during the desorption process which are not covered by the Antoniewicz model at all.[4] Second, there are kinetic energy data taken in a very indirect way by comparing mass spectrometer readings due to thermal and stimulated desorption signals and assuming proportionality of the sensitivity to the inverse particle velocity.[2] In both studies electrons of ≥ 100 eV were used for stimulation; i.e., the nature of the primary excitations was poorly defined. We have therefore conducted measurements of escape probabilities and kinetic energy distributions by a reliable technique (time-of-flight) for well characterized physisorbates [rare gases/Ru(001)] under well-defined excitation conditions and present these in the following.

The experiments were performed in a UHV chamber with base pressure below 10^{-9} Pa. The time-of-flight apparatus for kinetic energy measurements was also used for thermal desorption (TD). It was similar to that described in Ref. 4, with some improvements: (i) A coating of activated carbon was applied to the inner parts of the liquid-nitrogen-cooled drift tube (74-K working temperature at 13 kPa in the cooling tube) for effective trapping of scattered rare-gas atoms. Trapping times above 1 min for Ar (i.e., longer by a factor of 10^5 than the average flight time) were obtained; Kr and Xe were trapped even longer. (ii) A quadrupole mass spectrometer (QMS) with very high sensitivity (10^{-4} A/Pa at the entrance of the channeltron) was used for optimum detectivity. (iii) A low-temperature electron emitter for (ESD) caused negligible heating of the sample when operated in front of it. The work function of this filament was determined to be 3.6 eV by recording the emission current to the sample vs the applied potential at constant temperature, and correlating small variations of this function to final-state effects seen in photoemission and very-low-energy electron diffraction.[15] The electron energy could be varied from 10 to 200 eV (± 0.5 eV; all electron energies are referred to the Fermi level). The excitation rates were always low enough to exclude thermal effects or interactions of the desorbing particles in the gas phase. The Ru(001) sample

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was prepared, cleaned, and mounted as described elsewhere.[15] Saturated monolayers were prepared by excess dosing (by $\approx 5\%$) through a micro-channel-plate doser, and heating beyond the trailing edge of the TD maximum related to the second layer.[16]

ESD of neutral Ar atoms was observed for electron energies above 12.5 eV. At 12.5 eV, however, the signals were too weak for energy distributions to be recorded. In PSD, the onset of desorption has been assigned to the excitation of a surface exciton at 11.7 eV.[5] This value agrees with the ESD result above, if final states close to the Fermi level for one of the two participating electrons are assumed. Similar relations between ESD and PSD thresholds have been obtained for chemisorbates.[17] This excitonic channel has minor significance for ESD, and strong desorption has only been observed for electron energies above the ionization threshold of 14 eV.[5]

Figure 1 shows kinetic energy distributions from saturated Ar monolayers obtained by stimulation with electrons of (a) 200 eV and (b) 26.5 eV. For flight times above 0.7 ms, both traces have identical shapes and can be brought to coincidence by appropriate scaling (note that the dependence of σ_p on electron energy is contained in the signal). For shorter flight times, i.e., higher kinetic energies, a slightly increased desorption yield is observed for electrons of 200 eV. From the energetic positions of the maximum and the center of gravity of the $N(E_k)$ representation (see Fig. 2) the most probable ($\hat{E}_k$), and mean ($\bar{E}_k$) kinetic energies are obtained. These are 56 and 109 meV, respectively, for 26.5 eV, and 60 and 136 meV for 200 eV. ESD by direct-momentum transfer can be excluded because even for electrons of 200 eV less than 10% of the monolayer binding energy of 110 meV (Ref. 16) is transferred by this mechanism.[12] Data on partial ionization cross sections for Ar from gas-phase measurements show that 9% Ar^{2+} and 0.5% Ar^{3+} are obtained with 200-eV electrons,[18] whereas Auger-electron spectroscopy and x-ray photoemission spectroscopy results exclude multiple ionization for an excitation energy of 26.5 eV.[11] We therefore conclude that the additional desorption yield

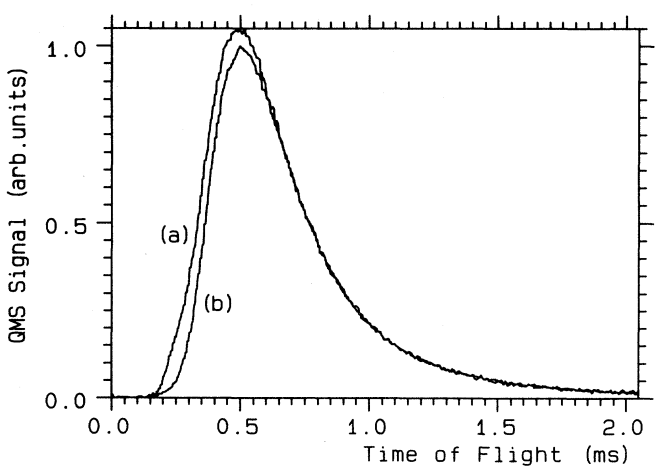

FIG. 1. Time-of-flight spectra for neutral Ar atoms desorbed from Ar monolayers for excitation with electrons of *a*, 200 and *b*, 26.5 eV.

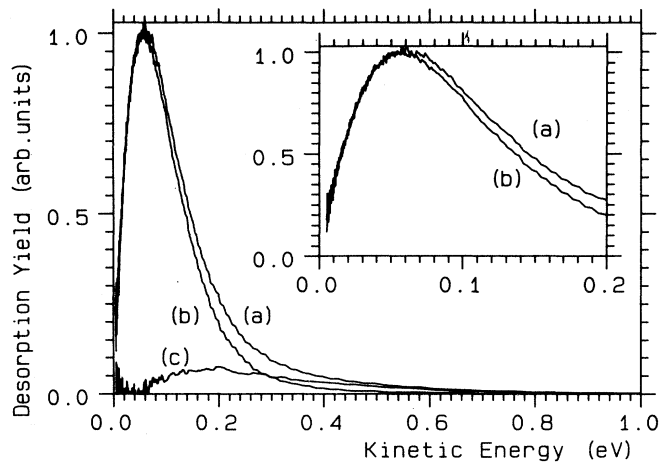

FIG. 2. Kinetic energy distributions of Ar atoms desorbed from saturated Ar monolayers on Ru(001) by electrons of *a*, 200 and *b*, 26.5 eV; the difference spectrum $a-b$ is shown in *c*. The inset shows details of $N(E_k)$ around $\hat{E}_k$.

obtained for 200-eV electrons is due to primary multiple ionization events. They contribute $\approx 14\%$ to the total area of the $N(E_k)$ representation (Fig. 2, curve *c*). For them, $\hat{E}_k$ is 185 meV (Fig. 2, curve *c*), i.e., larger by a factor of ≈ 1.7 than the binding energy of neutral Ar/Ru(001) derived from temperature-programmed desorption [110 meV (Ref. 16)]. This and the lack of particles with kinetic energies below 48 meV (i.e., flight times > 0.7 ms) indicates that the escape probability via double and higher ionization, $P(Ar^{2+,3+})$ is essentially equal to one (see also the discussion in Ref. 8). With this value, the areas under the traces *b* and *c* from Fig. 2, the partial ionization cross sections in the gas phase,[18] and the *assumption of identical angular distributions* of desorbing atoms, we calculate $P(Ar^{+}) = 0.64$ (all data are compiled in Table I). Contrary to the $Ar^{2+,3+}$ case, there was no delayed onset at the low-energy side of $N(E_k)$ here.

For Kr monolayers, the kinetic energy distributions and the desorption yields were even more strongly affected by primary multiple ionizations (Fig. 3, curves *a* vs *b*). Here, electrons of 22.5 eV were used for energy distributions consisting only of Kr^{+} excitation (Fig. 3, curve *b*). The separation procedure used for Ar could not be applied here because even multiple ionization of Kr gave rise to particle ejection with low kinetic energies (for Ar, the low-energy tail of the energy distribution is only due to single ionization, see above). Instead of this, scaling of traces *a* and *b* of Fig. 3 for identical Kr^{+} creation rates was based on gas-phase ionization cross sections.[18] Though for 200-eV electrons similar branching as for Ar is observed in the gas phase [89% Kr^{+}, 10% Kr^{2+}, and 1% Kr^{3+} (Ref. 18)], $\approx 70\%$ of the desorption signal were found to stem from multiple ionization. We assign the main peak in Fig. 3, curve *a* to the Kr^{2+} excitation. The shoulder at 140 meV, which is discernible in the Fourier smooth of trace *a*, is tentatively assigned to primary Kr^{3+} creation. This is in contradiction to former results from Kr/W(110), where influences of multiple ionization on ESD rates were excluded,[2] and corroborates conclusions

TABLE I. Most probable ($\hat{E}_k$) and mean ($\bar{E}_k$) kinetic energies and escape probabilities (P) for DIET off saturated monolayers of Ar and Kr on Ru(001) for different primary excitations ($T_{\text{sample}}=10$ K). The P values are relative to $P(\text{Ar}^{n+})=1$.

Adsorbate	Composition of the primary excitation	P	$\hat{E}_k$ (meV)	$\bar{E}_k$ (meV)
Ar/Ru(001)	Ar^+	0.64	56	109
	95% Ar^{2+}+5% Ar^{3+}	1	185	≈300
Kr/Ru(001)	Kr^+	0.007	42	140
	90% Kr^{2+}+10% Kr^{3+}	0.12	≈105	≈185

given already in Ref. 6 that multiple ionization should lead to enhanced kinetic energies. To obtain absolute values for P, we again assume $P(\text{Ar}^{2+})=1$ and identical angular distributions for both adsorbates and all excitation channels. With mass-dependent transmission data for the quadrupole mass spectrometer from auxiliary experiments and partial ionization cross sections from Ref. 18, we obtain the results compiled in Table I, which also contains the values for $\hat{E}_k$ and $\bar{E}_k$.

No ESD could be detected from Xe monolayers within the sensitivity range of our apparatus (i.e., $P<10^{-5}$) in agreement with results for Xe/Ag(111).[3] For Ar and Kr, $N(E_k)$ and P did not depend on coverage between 50% and 100% of saturation. In both cases, small amounts of preadsorbed oxygen enhanced the high-energy tail of $N(E_k)$.

The agreement of our escape probabilities for Ar with those obtained for Ag(111) in Ref. 3 is good. For Kr, the increase of P from 0.0033 at 10 K to 0.06 at 48 K obtained for monolayers on Ag(111) and Pd(100) (Ref. 3) could not be reproduced on Ru. With the composition of primary excitation expected for electron energies of 250–400 eV as used in Ref. 3, we obtain $P=0.02$ for 10 K, which is between the limits for P given in Ref. 3. As in a former PSD experiment covering the valence excitation regime,[5] this value increased by a factor of 1.8 only when the sample temperature was raised close to the onset of desorption, even for stimulation with electrons of 200 eV. The kinetic energy values obtained in the indirect way described above for Kr/W(110) (Ref. 2) appear to be much too low. This is probably due to different angular distributions in TD and ESD, contrary to the assumption made in Ref. 2.

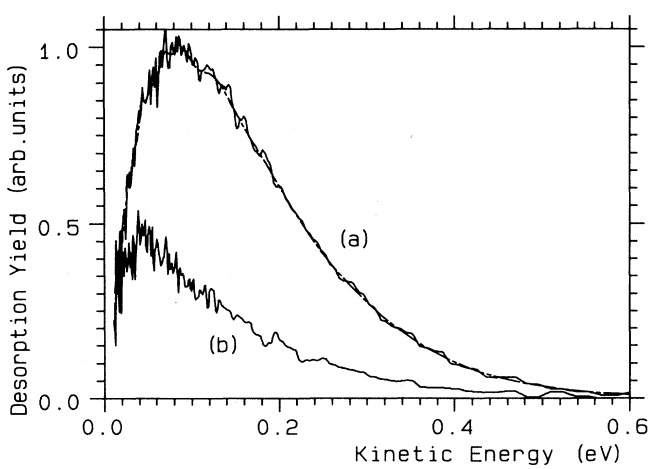

FIG. 3. Kinetic energy distributions for Kr atoms desorbed from Kr saturated monolayers on Ru(001) by electrons of *a*, 200 and *b*, 22.5 eV. Note the shoulder at 140 meV in *a*, which is discernible in the Fourier smooth of the raw data (broken line).

All theoretical results on kinetic energy distributions and on P values for ESD of rare gases obtained so far pertain to single ionization. Calculations within the classical model outlined in Ref. 6 have been performed for Ar/Ru(001) and Kr/Ru(001).[13] For the two adsorbates, the imaginary parts of the potentials[6] were chosen for best fits to the experimentally obtained energy distributions, as well as to the ratio of the P values for Ar and Kr.[13] For Ar, our energy distribution could be reproduced quite well. For Kr the calculation slightly underestimates the high-energy tail of $N(E_k)$.[13] The calculated P values are lower than the experimental ones only by a factor of 18, compared to 4 orders of magnitude in the case of N_2O.[13] This indicates that ESD of physisorbed N_2O cannot be correctly described within this framework. Even better approximation of the experimental data was obtained by a model which describes more realistically the interaction of the ion with the substrate.[14] Local-density-functional (LDF) potentials for Ag(111) as substrate are used for the ionic as well as for the neutral states.[14] For the equilibrium bond distance of the ground state, the slope of this ionic potential is smaller by a factor of 2 than for that derived under the assumption of an ideal image force.[14] For the neutralization rate, an ansatz with a functional dependence similar to the bare-metal charge density calculated with LDF was used.[14] With an appropriate choice of the parameters for the imaginary part of the potential, the agreement with the energy distributions experimentally obtained by us for Ar/Ru(001) is very good for quantum-mechanical treatment, whereas classical treatment results in too-narrow kinetic energy distributions,[14] in agreement with the conclusions from Ref. 7. The calculated P values are still lower than our experimental data by a factor of 8 (quantal treatment) to 9 (classical treatment). As shown in Ref. 14, a correct description, particularly of the slope of the ionic potential, is decisive for an exact model of the desorption process.

We have shown that DIET from physisorbates can de-

pend strongly on the charge of the primary ions, particularly if the overall escape probabilities are low. Neutralization of multiply charged ions has been shown to occur stepwise.[19] For rare gases, this evolution could also include the formation of electronically excited singly charged ions by resonance neutralization.[19] The higher escape probabilities and kinetic energies for primary multiple ionization must be due to the initially stronger image force, stronger chemical interactions with the surface, probably of the intermediate states, and, possibly, an overall longer lifetime as an ion. Detailed modeling of the desorption process is presumably much more difficult than for single ionization since more variables are involved. Our data appear certain enough to warrant efforts in this direction.

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