Substrate Mediated Suppression of Postcollision Interaction Effects

B. Kassühlke, R. Romberg, P. Averkamp, and P. Feulner
Physikdepartment E 20, Technische Universität München, 85747 Garching, Germany
(Received 31 March 1998)

The line shapes and kinetic energies of argon $2p_{3/2}$ and $2p_{1/2}$ photoelectrons from monolayers adsorbed on a Ru(001) substrate were measured with an electron time-of-flight detector in the near-threshold region. Compared with gas phase results, the two main effects due to postcollision interaction, i.e., line broadening and redshift of the kinetic energy of threshold electrons, are strongly suppressed on the surface. We show that these changes are brought about by an effective, screening induced reduction of the energy loss encountered by the threshold electron upon transition from a singly to a doubly charged central argon atom at core-hole decay. [S0031-9007(98)07162-2]

PACS numbers: 73.90.+f, 33.60.–q, 33.70.Jg

Postcollision interaction (PCI) is a well-known phenomenon in gas phase work. It occurs when one partner in a collision reaction suffers a collision induced change of charge at a time when the other (charged) partner is still close enough to be affected by the resulting change of the interaction potential. Although originally observed and described for excitation and deexcitation of autoionizing states of atoms in collisions with slow ions [1], the main interest has shifted to PCI induced phenomena associated with the decay of inner shell vacancies created either by particle or photon impact [2,3]. A particularly simple case is the *photoionization* of core level electrons in the threshold region [3]. The closer the threshold electron to the excited atom at core hole decay, the larger are the energy *gain* of the Auger electron, and the energy *loss* of the threshold electron on its residual trajectory, which is caused by the sudden increase of the central charge from X^+ to X^{2+} (or even X^{3+}, see [4]). Because of the statistical nature of core decay, distinct broadenings of the threshold and the Auger electron lines occur depending on the core-hole lifetime. This process has been experimentally studied particularly for the argon $2p$ level by various methods, including threshold electron spectroscopy [5–7], Auger electron spectroscopy (see, e.g., [8]), and photoelectron photoion coincidence [4]. PCI results have been analyzed following different approaches from purely classical [4,6] to semiclassical [2,9,10], to shakedown [11] and resonant scattering pictures [12,13], each of them at different levels of refinement, in particular for angular effects [14]. It has been shown that in the case of argon $2p$ even the classical theories suffice to reproduce the experimentally obtained line shapes [4,6].

Despite the large number of studies dedicated to PCI upon core hole decay in the gas phase, to the best of our knowledge, no data exist for atoms or molecules adsorbed on surfaces, although strong changes of the PCI effects are to be expected. The situation encountered in the gas phase, namely, the transition from a singly to a doubly charged ionic center is complicated on the metal surface by (i) polarization screening, (ii) attractive forces between the outgoing electrons and their image charges, and (iii) possible charge transfer from the metal to the singly and doubly charged centers. For our investigation we have selected a monolayer of argon adsorbed on a Ru(001) surface for several reasons. First, for an atom, additional line broadening by internal excitations is not encountered. Second, the electron affinity level of the singly charged Ar^+ is well above the Fermi edge, suppressing charge transfer screening in the primary, singly ionized state (see below). Finally, the background caused by secondary electron emission from Ru(001) is low at the vacuum level due to a large band gap in this energy range [15]. We find considerable depletions of the PCI induced *line broadening* and *line shifts* with respect to argon gas which can be explained in a simple classical model. We also argue that our data and considerations are of general importance for PCI in surface layers.

The data were obtained at the PM 5-beamline at the BESSY storage ring, Berlin. The cleanliness and crystallographic quality of the Ru(001) substrate were checked by photoelectron spectroscopy (XPS) and LEED. The Ar monolayers were prepared by partial desorption of primarily dosed multilayers monitored by thermal desorption spectroscopy. The threshold electron data were recorded with an electron time-of-flight (TOF) setup built especially for the investigation of surface systems. Its kinetic energy resolution for threshold electrons was 30 meV. The photon bandwidth of the PM 5-beamline was set at $\approx$100 meV.

A pseudo-three-dimensional spectrum of electrons emitted from a monolayer of Ar/Ru(001) along the surface normal for the Ar $2p$ threshold region is depicted in Fig. 1. (See Ref. [16] for conversion from the TOF into the kinetic energy domain.) Excitons appear as features at constant photon energy, final state effects [regions of high density of states (DOS)] as structures at constant kinetic electron energy, and photoemission is characterized by features with a slope of approximately one (see below). The prominent signatures in Fig. 1 are

1. The $2p_{3/2}^{-1}4s$ core exciton at $h\nu = 244.50$ eV.

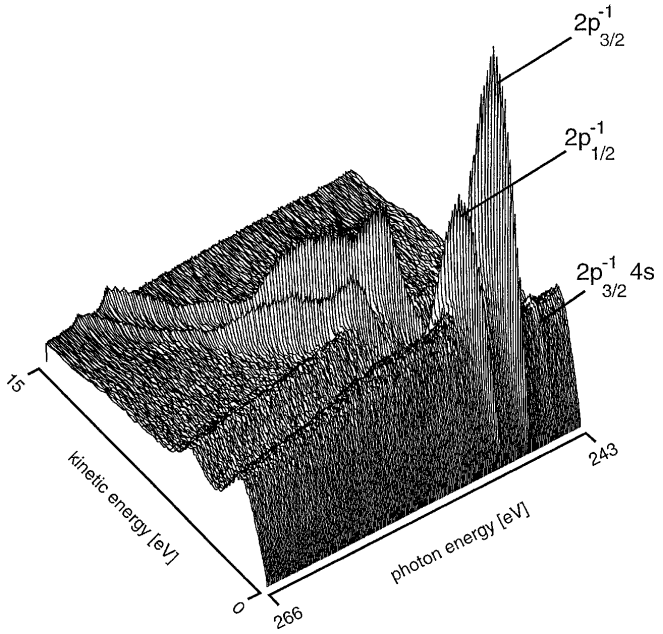

FIG. 1. Pseudo-3D plot of electron emission from one monolayer of Ar physisorbed on Ru(001) for the Ar $2p$ threshold region ($0 < E_{\mathrm{kin}} < 15$ eV; see text for details).

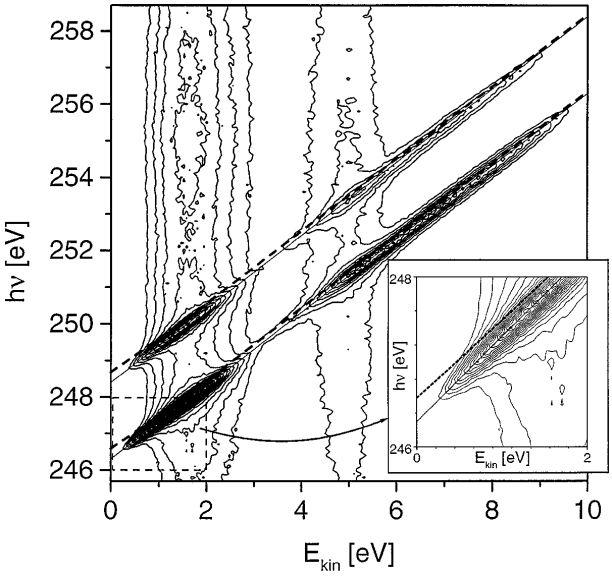

FIG. 2. 2D contour plot of a subset from the data of Fig. 1. The peak positions shifted by PCI as expected for isolated argon atoms are depicted by the broken line (the solid line indicates constant binding energy). The inset shows the $2p_{3/2}$-threshold region on an expanded scale.

2. The $2p_{3/2}^{-1}$ and $2p_{1/2}^{-1}$ photoemission maxima with thresholds at $h\nu = 246.32$ and $h\nu = 248.41$ eV, respectively.

3. Two broad peaks at 1.6 and 5 eV kinetic energy which are due to high DOS in the two-dimensional band structure of the argon monolayer. These maxima are completely missing for clean Ru(001) where the secondary electron yield is much lower, although monotonically increasing between the vacuum edge (corresponding to zero kinetic energy) and a region of high surface and bulk Ru DOS around 10 eV above E_{vac} ([15], not shown). Because of the low damping for electron energies below the (surface) plasmon energy, the Ar bands are well defined in energy and the photoemission matrix element shows strong modulations; between the two final state maxima it essentially approaches zero (Fig. 1).

To evaluate energy shifts by postcollision interaction (PCI) for isolated and physisorbed Ar atoms, a subset of the photoemission data of Fig. 1 is displayed in a 2D contour plot (Fig. 2). The dashed line in Fig. 2 corresponds to the peak positions of photoelectrons expected for the gas phase. The deviation of the dashed line from linear behavior (i.e., constant binding energy, solid line) is due to PCI. The energy shift has been calculated following the approach outlined in Ref. [4], which easily can be extended to the adsorbate case (see below). The shakedown energy $E - E'$, where E and E' correspond to the kinetic energies of the photoelectron at infinity for exclusion (inclusion) of PCI, depends on the distance between atom and electron when the central charge is changed from single to double. We obtain the photoelectron's flight time $t(E, E')$ by solving its classical equation of motion in the Coulomb potential of the singly ionized Ar^+ core. We neglect the possibility of shake-off events in core decay, which form a minority channel and would lead to even stronger line broadenings and redshifts [4]. It is not necessary to take angular effects into account, because their influence is unimportant on the scale of redshifts encountered here (see the comparison in Fig. 1 of Ref. [6]). Following standard procedure, we take one atomic unit for the initial separation of photoelectron and positive core [2]. From $t(E, E')$ and

$$P_t(t)\,dt = \frac{1}{\tau}\exp\left(-\frac{t}{\tau}\right)dt\,,$$

the probability that an Auger electron from a core-excited state with lifetime τ is emitted between t and $t + dt$, we obtain

$$P_{E'}(E)\,dE = P_t\big(t(E, E')\big)\left|\frac{dt}{dE}\right|dE$$

for the probability that a photoelectron, whose kinetic energy without PCI would be between E and $E + dE$, is redshifted to E'. Inserting $\tau = 5.5$ fs, corresponding to a linewidth of 120 meV [6], in the above formula, we obtain PCI profiles as a function of E' which we broaden by a Gaussian of 100 meV and a Lorentzian of 120 meV [6]. This approach reproduces experimentally obtained PCI shifts and PCI line broadenings for isolated atoms with a deviation of no more than 3% and 7%, respectively (see Table I and Fig. 3). Differences due to more refined calculations would be hardly noticeable on the scale of Fig. 2. Inspecting Fig. 2, it becomes obvious that the PCI induced redshift of the electron energies is absent or at least

TABLE I. Gas phase and adsorbate: Calculated (see text) and experimental Ar $2p_{3/2}$ (Ref. [4]: Ar $2p_{1/2}$, see Fig. 3) line widths and PCI induced energy shifts for photoelectrons of ≈0 and 1 eV kinetic energy.

Electron kinetic energy	PCI-shift$_{calc}$ (meV)	PCI-shift$_{exp}$ (meV)	FWHM$_{calc}$ (meV)	FWHM$_{exp}$ (meV)
Gas phase				
0 eV	287	280 [7]	480	450 [4]
1 eV	200	...	440	...
Adsorbate				
≤30 meV	60	<60	240 [17]	300
1 eV	30	<30	230	235

strongly suppressed for physisorbed argon compared with the gas phase.

In order to extend the description of PCI to atoms adsorbed on a surface, we make the following considerations. First, we account for polarization screening of the singly and doubly charged holes in the primary and final state by adding their negative images to the charged centers of the interaction potential. We position these image charges at $z = -d$, where $z = 0$ corresponds to the position of the image plane and $z = d$ to the position of the Ar atom. We use $d = 1.6$ Å, corresponding in the classical picture to our experimentally obtained physisorption shift of the Ar $2p_{3/2}$ level of 2.31 eV [4] (variations of d between 1.5 and 2 Å had no significant influence on the PCI results). Additional polarization screening by the surrounding argon atoms is clearly much weaker and is thus neglected in our calculations. Charge transfer from the metal to the adsorbate in the primary singly charged state is negligible because the electron affinity level of the Ar^+ ion lies well above the Fermi edge [we obtain $\Delta E = 3.44$ eV from the binding energy of the $2p_{3/2}\,4s$ exciton (1.82 eV, see Fig. 1) and the work function of Ar/Ru(001) (5.26 eV)]. Second, we add the positive image charge of the electron itself at $z = -r - d$, where r is the distance between electron and hole. According to our experimental boundary conditions, we then numerically calculate $t(E, E')$ and $P_{E'}(E)$ for normal emission. We find that the redshift at threshold, which for the gas phase is 280 meV [7], is reduced to about 60 meV, in good agreement with our experimental findings. We also obtain narrower lines than for the gas phase. This is illustrated in Fig. 3 where our experimentally obtained shapes of the Ar $2p_{3/2}$ peak at $E' \leq 30$ meV and 1 eV are compared with line shapes calculated for the isolated and the physisorbed atom, and with experimental gas phase data. In particular for $E' = 1$ eV the metal induced narrowing effect is strong and the agreement between experiment and simulation improves if screening is included (Fig. 3, [17]). We

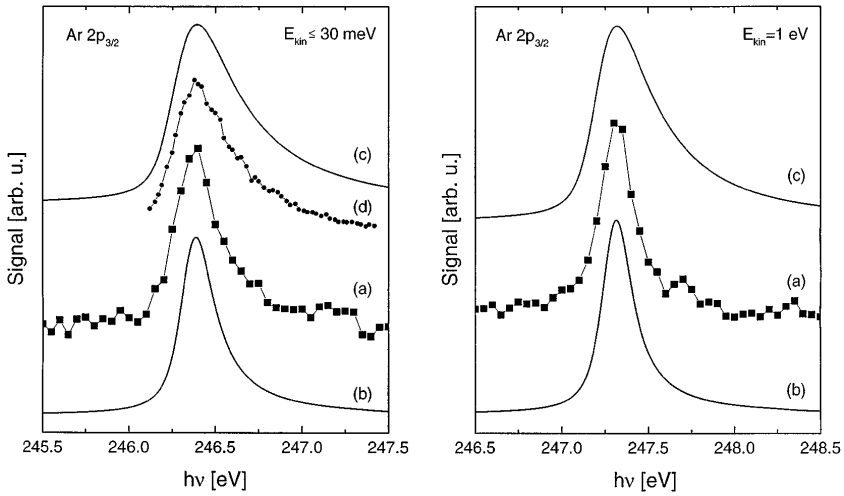

FIG. 3. Curves (a) *Experimental* threshold ($E_{kin} \leq 30$ meV) and near threshold ($E_{kin} = 1$ eV) Ar $2p_{3/2}$ photoelectron spectra of Ar/Ru(001), compared with *calculated* profiles for curves (b) the physisorbate and curves (c) the isolated atom (see text for details). A linear background has been subtracted from the experimental data. To further demonstrate the substrate mediated line narrowing, curve (d) shows *experimental* Ar $2p_{1/2}$ threshold electron/Ar^{2+} ion coincidence data obtained under identical photon energy resolution (from Ref. [4]; unfortunately, comparable Ar $2p_{3/2}$ data are not available). To ease comparison, all profiles have been shifted to the experimentally obtained $2p_{3/2}$ peak position for the surface.

note that screening of the ion *and* screening of the outgoing photoelectron itself both act in the same direction towards line narrowing. Hole screening changes the r dependence of the electron-hole interaction potential from $\sim 1/r$ into dipolar ($\sim 1/r^2$) for $r > d$, which for increasing r approaches zero more rapidly, thus strongly decreasing the energy differences for the singly and the doubly charged centers. The attractive interaction of the photoelectron with its image charge, on the other hand, requires extra kinetic energy close to the surface in order to asymptotically reach the same E' as in the gas phase. As a result, the critical region, where the energy loss is large, is crossed faster than for the isolated atom. According to our calculations hole screening is the main effect, causing about $9/10$ of the experimentally observed reduction of the PCI line shift.

We finally note that the affinity level for the doubly ionized Ar atom after core decay moves closer to the Fermi level, hence making resonant charge transfer more likely. If it were fast, PCI would not occur because of vanishing differences in potential energy as in the case of fluorescent deexcitation [18]. The finding that for Ar/Ru(001) the physisorption shift is larger by about a factor of 3 for the Auger than for the photoemission lines [19] indicates that at least on the time scale of Auger electron emission charge transfer is negligible, although we believe it will become important for slow electrons and for adsorbates more strongly coupled to the substrate.

In summary, we have shown that PCI induced effects in threshold and near threshold electron spectra, namely line broadening and energy shifts, are considerably reduced for adlayers on metals. This result is, apart from its basic importance, of interest for future spectroscopic studies of adsorbed species. In particular, it encourages investigations of the evolution of ionization satellites and of the vibrational fine structure of photoemission under high resolution conditions even in the very near threshold region. To the best of our knowledge, this is the first example that the linewidth of an electronic excitation is narrower for an adsorbed than for an isolated particle. With a simple classical model, we were able to quantitatively reproduce our experimental findings, showing the strong influence of polarization screening of the singly and doubly charged ion, and of the outgoing photoelectron's image charge on line width and shakedown energy. Because of the narrow, undamped bands for excitations below the plasmon energy, final state effects in the photoemission yield are very strong, resulting in complete suppression of core level photoemission for distinct kinetic energy values and emission angles.

We gratefully acknowledge the support and very helpful advice of D. Menzel. We thank N. Heckmair and S. Frigo, and the staff of BESSY, in particular C. Hellwig, C. Jung, and H. Pfau, for help during the experiments. This study was supported by the Deutsche Forschungsgemeinschaft (projects ME 266/21-1 and SFB 338).

[1] R. B. Barker and H. W. Berry, Phys. Rev. **151**, 14 (1966).
[2] A. Niehaus, J. Phys. B **10**, 1845 (1977).
[3] M. Yu. Kuchiev and S. A. Sheinerman, Sov. Phys. Usp. **32**, 569 (1989), and references therein.
[4] H. Kjeldsen, T. D. Thomas, P. Lablanquie, M. Lavollée, F. Penent, M. Hochlaf, and R. I. Hall, J. Phys. B **29**, 1689 (1996).
[5] P. A. Heimann, D. W. Lindle, T. A. Ferrett, S. H. Liu, L. J. Medhurst, M. N. Piancastelli, D. A. Shirley, U. Becker, H. G. Kerkhoff, B. Langer, D. Szostak, and R. Wehlitz, J. Phys. B **20**, 5005 (1987).
[6] T. D. Thomas, R. I. Hall, M. Hochlaf, H. Kjeldsen, F. Penent, P. Lablanquie, M. Lavollée, and P. Morin, J. Phys. B **29**, 3245 (1996).
[7] L. Avaldi, G. Dawber, R. Camilloni, G. C. King, M. Roper, M. R. F. Siggel, G. Stefani, and M. Zitnik, J. Phys. B **27**, 3953 (1994).
[8] H. Hanashiro, Y. Suzuki, T. Sasaki, A. Mikuni, T. Takayanagi, K. Wakiya, H. Suzuki, A. Danjo, T. Hino, and S. Ohtani, J. Phys. B **12**, L775 (1979).
[9] A. Niehaus and C. J. Zwakhals, J. Phys. B **16**, L135 (1983).
[10] A. Russek and W. Mehlhorn, J. Phys. B **19**, 911 (1986).
[11] K. Helenelund, U. Gelius, P. Froelich, and O. Goscinski, J. Phys. B **19**, 379 (1986).
[12] J. Tulkki, G. B. Armen, T. Åberg, B. Crasemann, and M. H. Chen, Z. Phys. D **5**, 241 (1987).
[13] G. B. Armen, J. Tulkki, T. Åberg, and B. Crasemann, Phys. Rev. A **36**, 5606 (1987).
[14] P. van der Straten, R. Morgenstern, and A. Niehaus, Z. Phys. D **8**, 35 (1988).
[15] M. Lindroos, P. Hofmann, and D. Menzel, Phys. Rev. B **33**, 6798 (1986).
[16] B. Kassühlke, P. Averkamp, S. Frigo, P. Feulner, and W. Berthold, Phys. Rev. B **55**, 10 854 (1997).
[17] Inclusion of surface mediated energy loss mechanisms would cause additional line broadening.
[18] J.-E. Rubensson, J. Lüning, M. Neeb, B. Küpper, S. Eisebitt, and W. Eberhardt, Phys. Rev. Lett. **76**, 3919 (1996).
[19] G. Rocker, P. Feulner, R. Scheuerer, L. Zhu, and D. Menzel, Phys. Scripta **41**, 1014 (1990).