Sharp Photon-Induced $np \rightarrow (n + 1)s$ Resonances in Xe and Kr Monolayers Observed by Spin-Resolved Electron Spectroscopy

G. Schönhense, A. Eyers,[a] and U. Heinzmann

Fakultät für Physik, Universität Bielefeld, D-4800 Bielefeld 1, Federal Republic of Germany,
and Fritz-Haber-Institut der Max-Planck-Gesellschaft, D-1000 Berlin 33,
Federal Republic of Germany

Narrow Xe $5p \rightarrow 6s$ and Kr $4p \rightarrow 5s$ resonances ($\Delta E < 80$ meV) have been observed in the adsorbate phase on Pt(111) and graphite(0001). The photon-induced transitions reveal an additional level splitting compared to the gas phase and the intensities show a significant substrate dependence. The resonances were detected via spectroscopy of the electrons emitted as a result of a subsequent relaxation decay of the excited state. Measurement of the electron-spin polarization clarified the nature of the new decay mechanism observed and furthermore provided an unambiguous quantum-number labeling of the resonances.

The existence and characteristics of the $6s$ resonance in adsorbate systems of xenon atoms (electronic ground-state configuration $5s^2p^6$) has been the subject of much controversial discussion during recent years.[1-8] $6s$ is the lowest unoccupied energy level of the Xe adatoms and should play an important role in the binding mechanism of the physisorbed atoms. Up to now, the investigation of such empty energy bands in the spectral region below the vacuum level was accessible only to optical spectroscopy, for the condensed rare gases to absorption[1,2] or reflection[3,4] measurements, to electron energy-loss spectroscopy (EELS),[5] and, more recently, to inverse photoemission.[6] In this Letter we demonstrate that under certain favorable conditions *direct spectroscopy of the primary excited electrons* is possible and bears important information—especially if besides their intensity their spin is also probed. We have employed the recently developed experimental technique of energy-, angle-, and spin-resolved electron detection combined with excitation by circularly polarized synchrotron radiation from the storage ring BESSY (Berlin).

Using reflectance spectroscopy, Cunningham, Greenlaw, and Flynn[4] studied several combinations of noble gases on metal surfaces and concluded that electronic excitations in monolayers persist only when the ionization potential I^* of the excited atom exceeds the metal work function, i.e., $I^* > \Phi$. At $I^* = \Phi$ a configurational switching should occur as a result of the instability of the excited noble-gas atom against charge transfer to the surface. Theoretical work by Lang *et al.*,[7] however, cast doubt on the interpretation of the optical experiments. By means of EELS Demuth and co-workers[5] studied Xe layers on Al, Ag, Cu, and Au and observed loss features between 8 and 12 eV energy loss, a spectral region where a number of atomic excited states are present. Employing inverse photoemission (IPE), Horn, Frank, and Reihl[6] recently ob-

served broad adsorbate-induced features for Xe on Ag(110) between 4 and 8 eV above E_F. The EELS and IPE results gave no evidence for the charge-transfer instability suggested in the optical studies.

At first sight, direct spectroscopy of the primary excited $6s$ electron seems to be impossible because the Xe $6s$ (and Kr $5s$) levels should lie below the vacuum level (E_{vac}), which is illustrated in Fig. 1 for a complete hexagonal close-packed (hcp) xenon monolayer on Pt(111). Since the vacuum level is the only relevant reference point when we compare free and adsorbed atoms we have drawn all energies with respect to $E_{vac} = 0$. The most striking difference between the two phases appears in the ionization potential: For Xe (hcp) on Pt(111) direct photoemission from the Xe $5p$ orbital sets in already at $h\nu = 9.3$ eV, whereas for the ionization of free Xe atoms photons of at least $h\nu = 12.2$ eV are needed.[9] Several mechanisms are responsible for this strong relaxation shift,[10]
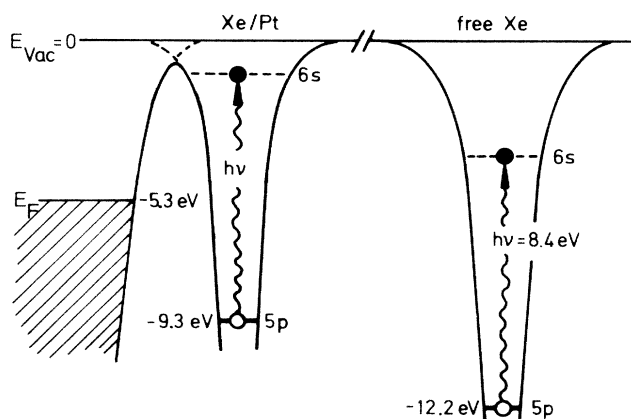

FIG. 1. Effective one-electron potential curves for xenon atoms in a monolayer on the Pt(111) face and for free xenon atoms (schematic).

the most important contributions coming from the screening of the positively charged ion by conduction electrons of the metal substrate ("image-charge") and from dielectric screening through polarization of neighboring adatoms in the close-packed overlayer. These two essential contributions are hole-screening effects in the final ionic state. The relaxation shift of the $6s$ excited level (with respect to $5p$) is considerably smaller, both the ground-state and excited atoms being electrically neutral.[11] Hence the Xe $5p \rightarrow 6s$ transition energies in free atoms and adatoms should be almost the same and the adsorbate $6s$ level should lie well below E_{vac} as shown in Fig. 1.

The favorable conditions allowing the direct spectroscopy of the primary excited electron (below E_{vac}) can occur as a consequence of a secondary relaxation process, e.g., a Penning- or Auger-type decay leading to a configuration in which the primary electron has an energy above E_{vac}. When discussing typical many-body effects like Penning or Auger transitions one usually cannot discriminate between the "primary excited electron" and other electrons involved because they are indistinguishable. In spin-resolved experiments, however, one can induce a spin-labeling of the primary electron, e.g., by optical pumping of the excited state with circularly polarized light. This spin-labeling makes the electrons distinguishable to a certain extent.[12]

The transition scheme of Fig. 2 shows the optical spin-orientation process. The important difference between the level schemes for adsorbed and free atoms is the splitting of the $p_{3/2}$ level into the magnetic
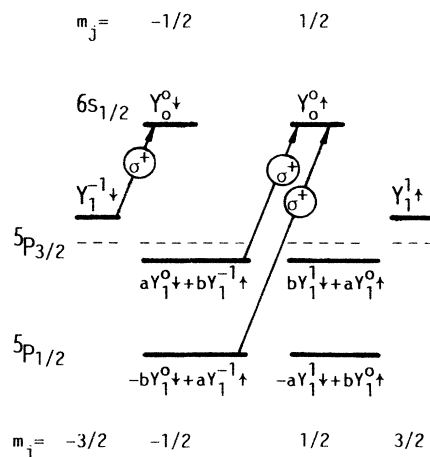
sublevels $m_j = \pm \frac{3}{2}$ and $\pm \frac{1}{2}$ due to the symmetry lowering in the adsorbate system, essentially by valence-orbital overlap of neighboring adatoms.[13, 14] As a consequence of this lifting of the $|m_j|$ degeneracy all allowed $5p \rightarrow 6s$ dipole transitions with circularly polarized light yield *completely spin-polarized 6s electrons*. Excitation by σ^+ radiation, e.g., gives rise to the three transition channels denoted by arrows in Fig. 2, because the selection rule $\Delta m_j = +1$ is compatible only with $m_j = -\frac{3}{2}$ and $-\frac{1}{2}$ in the initial state. A transition starting from the $p_{3/2}$, $|m_j| = \frac{3}{2}$ substate can only end up in the pure spin-down part ($\downarrow$) of the $6s$ state and can, as a result of this spin label, be distinguished from transitions starting from $p_{3/2}$, $|m_j| = \frac{1}{2}$ and $p_{1/2}$, both ending with spin up ($\uparrow$). It is remarkable that for free Xe atoms the four m_j levels of $p_{3/2}$ are degenerate (dashed lines) so that the left ($\downarrow$) and middle ($\uparrow$) transitions occur simultaneously, leading to a partial cancellation of the spin polarization.

The experimental setup was used recently for spin-resolved photoemission studies of rare-gas adsorbates.[14] A He-cooled manipulator allows sample transfer from a preparation chamber equipped with LEED and scanning Auger-electron spectroscopy to a separate photoemission chamber (base pressure $< 4 \times 10^{-11}$ mbar) containing the rotatable electron spectrometer and the electron-optical transport system to the ultrahigh-vacuum Mott-scattering detector for spin analysis. The apparatus is installed at the 6.5-m normal-incidence monochromator of the storage ring BESSY, which delivers high fluxes of circularly polarized off-plane synchrotron radiation. Xe or Kr was adsorbed on cleaned and well characterized substrate surfaces at temperatures around 55 or 45 K, respectively. Monolayer coverage was achieved by proper choice of the sample temperature slightly above the sublimation point of the second layer and was simultaneously controlled by photoelectron spectroscopy (see Fig. 1 of Ref. 14). After monolayer saturation the doser was closed and the temperature was lowered by 5 K to prevent sublimation. A spin-resolved electron spectrum of sixty points was sampled in about 1 h, sufficiently fast to avoid significant target contamination.

A typical example of those electron spectra which have drawn our attention to the existence of the resonances is given in Fig. 3 for a Xe monolayer on the basal plane of natural single-crystal graphite. At photon energies below or above the resonance (8.40 or 8.55 eV, respectively) the spectrum reflects a typical photoelectron spectrum of graphite with a slightly enhanced inelastic background due to the adsorbate overlayer; photoemission from the adsorbate valence orbital is not possible since $h\nu < 9.8$ eV. If, however, the photon energy matches the resonance transition (here 8.45 eV), the electron intensity of the whole spectrum is markedly enhanced. Spin-polarization
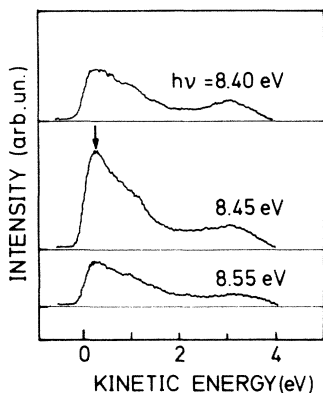

FIG. 2. Level scheme for the $5p \rightarrow 6s$ transitions in the Xe adsorbate system. Wave functions are characterized by spherical harmonics Y_l^m and spin functions $\uparrow$ and $\downarrow$, with a and b being hybridization (Clebsch-Gordan) coefficients. Arrows denote the allowed transitions for excitation by right-handed circularly polarized light. Note that all transitions yield completely spin-polarized $6s$ electrons.

FIG. 3. Electron spectra of a xenon monolayer on graphite in the region of the $5p \to 6s$ resonanes at normal incidence and emission.

analysis employing a Mott detector revealed that the additional electrons are highly polarized!

In order to scan the resonances in the usual manner versus photon energy, we have kept the analyzing energy of the electron spectrometer fixed (at maximum intensity, arrow in Fig. 3) and scanned the monochromator. The resulting spectral variations of electron intensity and polarization are summarized in Figs. 4 and 5 for Xe on graphite and Pt, and for Kr on graphite. In the photon-energy range below $h\nu = 8$ eV for Xe (9.8 eV for Kr) only a smooth background of unpolarized secondaries has been observed. The spin-polarization values plotted in Figs. 4 and 5 correspond to the total electron intensity, because no reliable background subtraction could be made. An estimation yielded values of up to $\pm 80\%$ in the resonance maxima if the underlying electron background were subtracted; hence the resonantly emitted electrons are almost completely polarized. For both rare gases the first resonance feature is a spin-down and spin-up doublet appearing close to the position of the atomic Xe 6s (Kr 5s) line[15] (left arrows). A single resonance of similar intensity with spin up appears almost exactly at the atomic Xe 6s' (Kr 5s') line position (right arrows). This experimental finding is in complete accordance with the predictions derived from the transition scheme (Fig. 2). The splitting of the magnetic sublevels $|M_J| = \frac{3}{2}$ and $|M_J| = \frac{1}{2}$ of the $^2P_{3/2}$ core configuration (= hole states) is 0.35 eV (0.22 eV) for Xe (Kr) on graphite. This splitting is a consequence of the symmetry lowering in the adsorbate system. The splitting between the $^2P_{3/2}$, $|M_J| = \frac{1}{2}$ and the $^2P_{1/2}$ core configuration is 1.06 eV (0.61 eV), almost identical to the atomic fine-structure splitting (energy difference between the arrows) induced by spin-orbit interaction.

For Xe on Pt the 6s' resonance could not be observed because of the low threshold for direct photoemission (dashed line) giving rise to a steep increase in
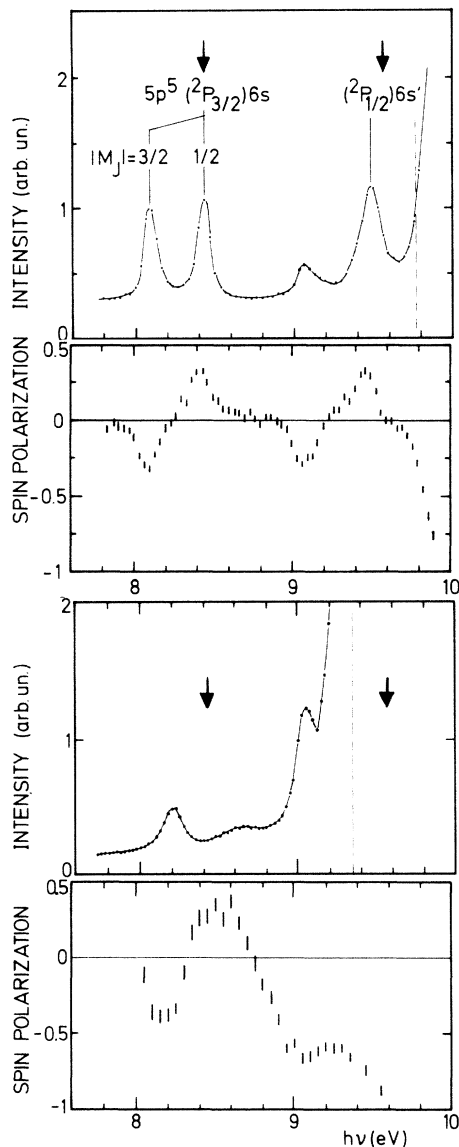

FIG. 4. Resonances in intensity and spin polarization of electron emision from a xenon monolayer on graphite (0001) (upper figures) and on Pt(111) (lower figures), for excitation by σ^+ radiation. The curves have been taken at $T = 50$ K and normal incidence and emission by our scanning the photon energy and keeping the analyzing energy fixed (arrow in Fig. 3). Error bars represent one standard deviation. Dashed lines denote the threshold positions for direct photoemission from Xe 5p; arrows indicate the 6s and 6s' resonance-line positions for free atoms (Ref. 15) ($J = 1$ for all states).

intensity and polarization.[14] Furthermore, the $^2P_{3/2}$, $|M_J| = \frac{1}{2}$ peak is smeared out and can be identified only via the positive maximum of the spin polarization around 8.5 eV. An additional spin-down peak occurs at 9.05 eV (11.1 eV) followed by a spin-up feature in the shoulder at 9.4 eV (11.3 eV) for Xe (Kr) on
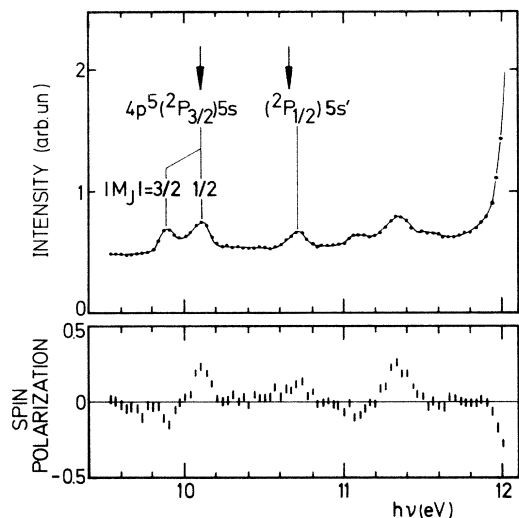
FIG. 5. Resonant electron emission from a krypton monolayer on graphite ($T = 40$ K); analogously to Fig. 4.

graphite. These resonances might give evidence of the existence of exciton series in the two-dimensional overlayer, which are of similar nature to the surface excitons detected optically in reflection and transmission by Saile et al.[2] The experimental result that the intensities of all features decrease rapidly with increasing residual gas contaminations supports the exciton hypothesis.

Although the primary $np \rightarrow (n+1)s$ excitation process is well understood, the remaining question is, How do the excited electrons surmount the potential barrier E_{vac}? Two experimental facts shed light on the relaxation mechanism. First, the resonantly emitted electrons have been in the $(n+1)s$ orbital, because of their high polarization. Second, the whole energy distribution is resonantly enhanced up to kinetic energies of nearly 4 eV (for graphite, cf. Fig. 3); hence the $(n+1)s$ electrons have gained an energy of several electronvolts. It is likely that this large energy gain results from filling up of the np core hole by a substrate electron from the valence band (via a Penning process). This observed new decay channel is competing with penetration of the $(n+1)s$ electron into the surface (resonance ionization)—the common picture of electronic deexcitation at surfaces.[16]

In conclusion, we have observed highly spin-polarized resonant electron emission from adsorbed Xe and Kr atoms following Xe $5p \rightarrow 6s, 6s'$ (Kr $4p \rightarrow 5s, 5s'$) excitation by optical pumping with σ light. The $np \rightarrow (n+1)s$ resonance line exhibits a splitting of 0.35 eV (0.22 eV) for Xe (Kr) on graphite as a consequence of the symmetry lowering in the adsorbate system. In agreement with EELS results[5,11] the transition energies show only weak relaxation shifts compared to the gas phase. Significant differ-

ences in the peak heights occur for Xe monolayers on Pt(111) and graphite(0001). The widths of the resonances ($\Delta E < 80$ meV) turned out to be considerably smaller than assumed previously. Because of their *spin label* the emitted electrons are definitely those which were primarily excited into the *s* orbital. This result gives evidence of a new (presumably Penning-type) decay channel of the excited atom by interaction with the substrate.

(a)Present address: Philips, Meiendorferstr. 205, 2000 Hamburg 73, West Germany.

[1]G. Baldini, Phys. Rev. 128, 1562 (1962).

[2]V. Saile, M. Skibowski, W. Steinmann, P. Gürtler, E. E. Koch, and A. Kozevnikov, Phys. Rev. Lett. 37, 305 (1976).

[3]P. Laporte, J. L. Subtil, U. Asaf, I. T. Steinberger, and S. Wind, Phys. Rev. Lett. 45, 2138 (1980).

[4]J. E. Cunningham, D. Greenlaw, and C. P. Flynn, Phys. Rev. B 22, 717 (1980).

[5]J. E. Demuth, Ph. Avouris, and D. Schmeisser, Phys. Rev. Lett. 50, 600 (1983); D. Schmeisser, C. M. Weinert, Ph. Avouris, and J. E. Demuth, Chem. Phys. Lett. 104, 263 (1984).

[6]K. Horn, K. H. Frank, and B. Reihl, to be published.

[7]N. D. Lang, A. R. Williams, F. J. Himpsel, B. Reihl, and D. E. Eastman, Phys. Rev. B 26, 1728 (1982).

[8]K. Wandelt and B. Gumhalter, Surf. Sci. 140, 355 (1984).

[9]It should be pointed out that because of our tunable light source we measure these ionization potentials directly without any reference to the Fermi energy and hence free of adsorbate-induced work-function changes.

[10]N. D. Lang and A. R. Williams, Phys. Rev. B 18, 616 (1978), and 25, 2940 (1982).

[11]A detailed discussion of the spectral shifts and broadening of electronic excitations of adsorbates on metal surfaces has been recently given by J. Avouris and J. E. Demuth, Surf. Sci. 158, 21 (1985).

[12]Needless to say, it is the preparation process which makes the electrons distinguishable and, strictly speaking, the argument only holds if the secondary relaxation process does not affect the electron spin significantly.

[13]M. Scheffler, K. Horn, A. M. Bradshaw, and K. Kambe, Surf. Sci. 80, 69 (1979).

[14]G. Schönhense, A. Eyers, U. Friess, F. Schäfers, and U. Heinzmann, Phys. Rev. Lett. 54, 547 (1985).

[15]C. E. Moore, Atomic Energy Levels, U. S. National Bureau of Standards Circular No. 467 (U.S. GPO, Washington, D.C., 1958), Vol. 3.

[16]W. Sesselmann, H. Conrad, G. Ertl, J. Küppers, B. Woratschek, and H. Haberland, Phys. Rev. Lett. 50, 446 (1983).