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¹D. Sherrington and S. Kirkpatrick, Phys. Rev. Lett. **35**, 1792 (1975).

²A. J. Bray and M. A. Moore, Phys. Rev. Lett. **41**, 1068 (1978); G. Parisi, J. Phys. A **13**, L115 (1980), and references therein.

³J. L. Van Hemmen, Phys. Rev. Lett. **49**, 409 (1982).

⁴D. C. Mattis, Phys. Lett. **56A**, 421 (1976).

⁵Let us remark that the physical random variables in a spin-glass are the positions x_i of the magnetic impurities; therefore the coupling constants $\lambda_{ij} = \lambda(x_i - x_j)$ must be correlated in contradistinction to what happens in the SK model.

⁶J. P. Provost and G. Vallee, Université de Nice Report No. NTH 82/12, 1982 (to be published).

Nature of the Excited States of Rare-Gas Atoms Adsorbed on Metal Surfaces

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Electron energy-loss spectroscopy has been used to study the coverage-dependent, electronic excitations of Ar and Xe adsorbed on Al(111), Ag(111), Cu, and Au surfaces. The monolayer loss features and cross sections indicate broadened atomiclike excitations with no evidence for a configurational-switching effect suggested in previous optical studies. The $np^5(n+1)s$ excited-state lifetime is found to be ~ 4 times longer than theoretically predicted for isolated adatoms.

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It has been proposed that two qualitatively different, system-dependent, excited-state configurations can occur for adsorbed atoms on metal surfaces which will affect a number of important physical processes and properties of adsorbates.¹⁻⁴ These include dipole moments, and bonding energies, as well as energy and charge transfer at surfaces. Evidence for this proposal first arose from the experimental observation of strong atomiclike excitations for nearly all the rare gases on Cs, K, Mg, and Al and their absence (at low coverages) in other cases—Xe on Al, Ti, and Au, and Kr on Au.¹⁻³ The absence of these atomic transitions is unusual and was originally interpreted to indicate strong (several electronvolts) coupling to the metallic states, associated with an "ionic" excited-state configuration. Bagchi, Barrera, and Dasgupta later showed that this absence could also be ascribed to a local-field suppression of the optical excitation.⁵ Although corroboration of two distinct configurations was subsequently inferred from the trends in dipole moments of adsorbed rare gases,⁴ recent density-functional electronic structure calculations found no significant differences for these systems and could not account for the apparent disappearance of the atomic transition.⁶

We have performed electron energy-loss and UV photoemission measurements on a variety of rare-gas/metal systems to resolve the question of whether two distinct classes of excited states occur. Our well-characterized measurements of Ar and Xe on Al(111), Ag(111), Cu, and Au show no evidence of the striking system- or coverage-dependent features observed earlier. Instead, we find relative cross sections, transition energies, and level widths of the $np^6 \rightarrow np^5(n+1)s$ excitations which indicate broadened atomiclike transitions, even for adatoms directly on the surface. The lifetimes ($\Gamma \sim 0.2$ eV) we derive for (sub)monolayer coverages are significantly longer than theoretically predicted for isolated adatoms ($\Gamma \sim 1$ eV) and may indicate excited-state delocalization phenomenon within monolayer assemblies.

These measurements were performed in a turbo-molecular, ion-getter pumped UHV chamber with base pressures of 6×10^{-11} Torr. Ultraviolet photoelectron spectroscopy (UPS), electron energy-loss spectroscopy (ELS), low-energy electron diffraction, and mass spectroscopy were performed *in situ*.^{7,8} The single-crystal samples of Al(111), Ag(111), and polycrystalline Cu were mounted on a liquid-helium-cooled,⁹ rotatable

sample manipulator coolable to ~ 15 K. The Al and Ag samples were sputtered, cleaned, and annealed to $\sim 200^\circ\text{C}$ while the sputter-cleaned Cu sample as well as freshly evaporated Au films ($\geq 1000 \text{ \AA}$ thickness) were annealed to $\sim 700^\circ\text{C}$. Surface cleanliness was monitored via vibrational ELS and UPS. Additional contamination arising from background residuals during cooldown as well as during dosage (associated with ion-pump "regurgitation") was also insignificant ($< 1\%$ monolayer). All rare-gas exposures cited account for ion-gauge correction factors of 1.2 for Ar and 2.5 for Xe.¹⁰ Nominal specular electron scattering conditions ($\theta_{\text{in}} = \theta_{\text{out}} = 45^\circ$) were used for ELS with incident electron-beam energies between 11 and 20 eV, and a resolution of ~ 25 meV (full width at half maximum). Off-specular ELS measurements on these films were indistinguishable from on-specular and were, therefore, not systematically studied.

The determination of relative coverages as well as the delineation of multilayer formation is an important aspect of these adsorption studies which we address using UPS. In Fig. 1 (left section) we show the $h\nu = 21.2$ eV photoemission spectra for clean Cu and as a function of increasing exposure to Xe. Increasing attenuation of the substrate $3d$ emission as well as the growth of the $5p_{3/2}$ and $5p_{1/2}$ Xe ionization signals at 6.05 and 7.40 ± 0.05 eV, respectively, are observed. Above ~ 1 L exposure [$1 \text{ L (langmuir)} = 10^{-6} \text{ Torr sec}$], a new set of Xe levels develop which are shifted by ~ 0.25 eV to larger binding energies as indicated by the dashed lines. This behavior arises from the different final-state screening associated with the local environment of Xe,¹¹ and allows us to delineate first and subsequent layers. From the relative intensities of these two sets of peaks we determine the relative coverages for the first and subsequent layers as shown on the right-hand side of Fig. 1. For Xe on Cu and Au, we find a nearly monotonic signal increase with coverage for the first adsorbed layer until 1.2 L whereafter the signal from the second layer increases with nearly the same slope as for the first layer. This implies a constant, near unity sticking coefficient in both the monolayers and multilayers. For Ar on Au (Fig. 1), we find clear evidence that multilayers form even at the lowest exposures, i.e., agglomeration occurs forming *three-dimensional* rare-gas clusters.¹² Such agglomeration may account for the narrow spectral features observed previously for Ar on Au.¹³ For the subsequent

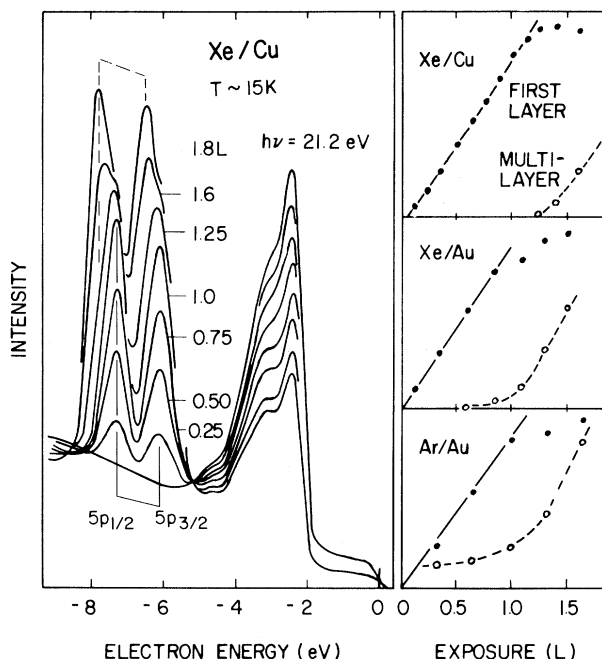


FIG. 1. Left: Photoemission spectra ($E_F = 0$) for increasing exposures of xenon to copper. Right: The deduced relative coverage of the first layer (solid line) and subsequent layers (dashed lines) for xenon on copper and gold as well as for argon on gold [$1 \text{ L (langmuir)} = 10^{-6} \text{ Torr sec}$]. The coverage determinations are based on the intensity of the Xe $5p^{1/2}$ and Ar $3p$ ionization levels.

discussions, we concentrate on Xe on Au, one of the previously studied systems which failed to exhibit atomlike spectral features¹⁻³ and which according to recent calculations should have an excited state that is strongly coupled to the surface.⁶

The coverage-dependent energy-loss spectra for Xe on Au are shown in Fig. 2. For comparison we also show a schematic of the electron-excited states of gaseous Xe obtained for similar incident energies and scattering conditions.¹³ In order to produce and define the coverage for a completely full first adsorbed layer, i.e., saturation coverage, $\theta = 1$, we have exposed the surface to 1.5 L and annealed to 90 K for ~ 1 min: Higher coverages are produced by additional 1-L exposures.¹⁴ As shown in Fig. 2, we cannot resolve all the atomic transitions in our loss spectra because of broadening as occurs in the condensed phase.¹⁵ However, the observed features correspond well to the manifold of atomic transitions, blue shifted by ~ 0.1 – 0.2 eV. Contrary to earlier optical results,¹⁻³ it is clear that broadened atomlike excitations exist over a wide range of cov-

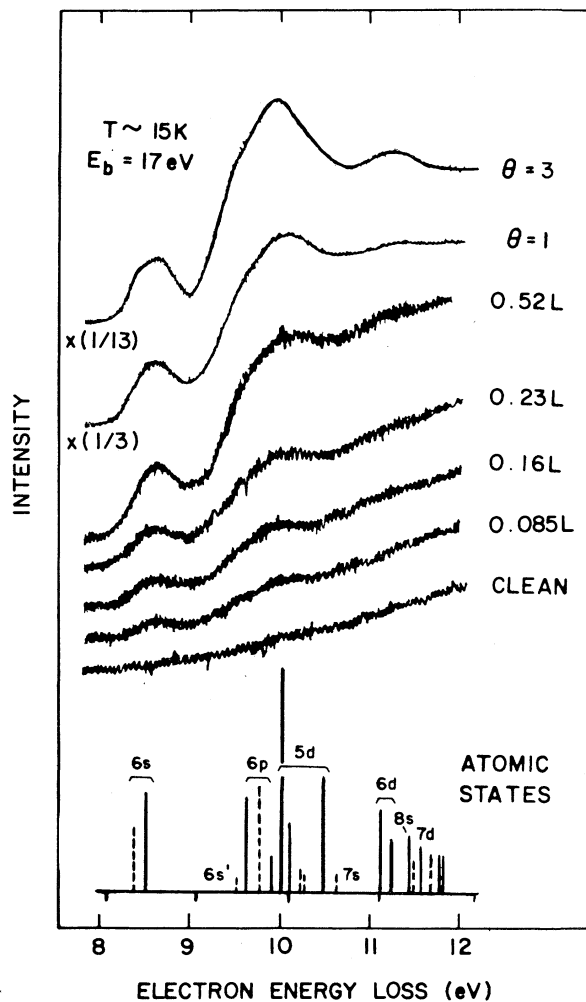


FIG. 2. Electron energy-loss spectra as a function of xenon coverage on gold. A schematic of the atomic spectra (Ref. 13) taken under similar conditions ($E_B = 20$ eV and $\theta_s = 130^\circ$) is shown for comparison with the final-state designations given and the optically allowed transitions indicated by the solid lines.

erages—even in the submonolayer regime. Our results for all systems studied are qualitatively similar. We do not observe dramatic, coverage-dependent changes in peak shapes or positions as reported previously.¹⁻³

In order to further interpret our coverage-dependent spectra, we have analyzed the intensity and line shapes of the $np^6 \rightarrow np^5(n+1)s$ excitation for monolayer and multilayer coverages. Again our results for all systems studied are qualitatively similar and are summarized in Fig. 3 for Xe on Au. As shown in Fig. 3, the $5p^6 \rightarrow 5p^56s$ peak height is not linearly related to coverage but rises more steeply above monolayer coverages.

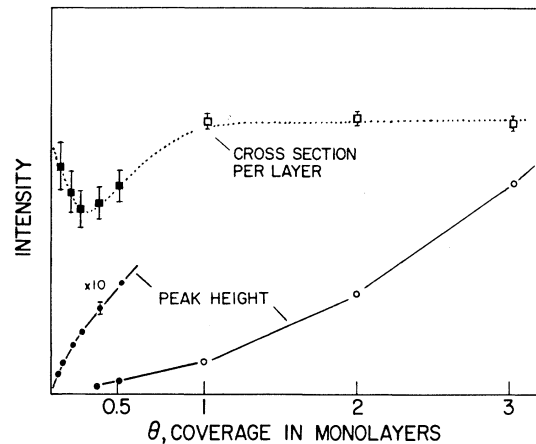


FIG. 3. Peak height of the $5p^6 \rightarrow 5p^56s$ loss feature of xenon on gold as a function of coverage, and the cross section per atom, per layer for different layers as described in the text.

To determine the relative cross section per atom in each layer we have used the clean surface background as a baseline and have integrated the area under the $5p^6 \rightarrow 5p^56s$ peak, up to the center of the peak. The cross section for the n th layer is taken as the difference in areas between the n and $n-1$ layers: for submonolayers we simply divide the area by the coverage. Within our experimental uncertainties, the cross section remains constant for the first three layers and tends to show some (system dependent) variations at intermediate submonolayer coverages.

The nearly constant cross section for each layer implies that the same $5p^6 \rightarrow 5p_{3/2}^56s$ ($J=2$ and $J=1$) transitions and ELS excitation mechanism(s) occur for multilayer and (sub)monolayer coverages. The coverage dependence of the peak height thereby arises from a broadening of the transition. Both homogeneous (lifetime) and inhomogeneous broadening can occur and be coverage dependent. From a line-shape analysis of the $np^6 \rightarrow np^5(n+1)s$ excitations for a monolayer of Ar or Xe on Au, Cu, and Al, we determine an upper limit to the lifetime-derived line broadening of $\sim 0.2 \pm 0.1$ eV.¹⁶ We find Ar to be lifetime broadened more than Xe and within these error bars both independent of the substrate. These values are significantly smaller than the ~ 1 eV broadening found theoretically for an isolated Xe or Ar atom on "Mg" and "Al"¹⁶ and may arise from limitations of the theoretical model. Alternatively, isolated rare-gas atoms may never occur experimentally as two-dimensional clustering of rare gases is

expected on low-temperature surfaces.¹⁷ Thus, the longer than calculated lifetime (weaker excited-state coupling to the surface) that we observe can be related to the nature of the excitations for the two-dimensional system. A similar level narrowing of excitation spectra has been observed for Xe impurities in Cs and K and has been attributed to a wave-function contraction due to excitation delocalization between pairs (or clusters) of impurity atoms.¹⁸ This apparent reduced coupling between rare-gas assemblies and our metal surfaces represents a potentially important phenomenon affecting energy and charge transfer to metal surfaces. It should be noted that we have found similar lifetime broadening for *molecular* monolayers on metals.¹⁹

In summary, we have observed weakly perturbed, atomlike excited states ($\Gamma \sim 0.2$ eV) of Ar and Xe on a variety of metals, and find no evidence to suggest any dramatic change in excited-state configuration with coverage or adsorbate. The strikingly different coverage dependences as well as strong shifts in atomic excitations observed in the previous optical studies¹⁻³ may arise from several factors we cannot unambiguously separate: uncertainties in analyzing optical reflectance measurements^{3,20} as well as local-field effects⁵ and unusual optical properties of adsorbates on *unannealed*, low-temperature evaporated films. However, we do not expect our ELS studies to be sensitive to local-field effects since our low-energy, large-momentum-transfer measurements favor nondipolar excitation mechanisms.

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¹J. E. Cunningham, D. Greenlaw, C. P. Flynn, and J. L. Erskine, Phys. Rev. Lett. 42, 328 (1979).

²J. E. Cunningham, D. Greenlaw, J. L. Erskine, R. P. Layton, and C. P. Flynn, J. Phys. F 7, L281 (1977).

³J. E. Cunningham, D. Greenlaw, and C. P. Flynn, Phys. Rev. B 22, 717 (1980).

⁴C. P. Flynn and Y. C. Chen, Phys. Rev. Lett. 46, 447 (1981).

⁵A. Bagchi, R. G. Barrera, and B. B. Dasgupta, Phys. Rev. Lett. 44, 1475 (1980).

⁶N. D. Lang, A. R. Williams, F. J. Himpsel, B. Reihl, and D. E. Eastman, Phys. Rev. B 26, 1728 (1982).

⁷J. E. Demuth, Surf. Sci. 69, 365 (1977).

⁸J. E. Demuth, K. Christmann, and P. N. Sanda, Chem. Phys. Lett. 76, 196 (1980).

⁹J. E. Demuth, D. Schmeisser, and Ph. Avouris, Phys. Rev. Lett. 47, 1166 (1981).

¹⁰Ion-gauge correction factors supplied with the Varian ion gauge.

¹¹G. Kaindl, T. C. Chang, D. E. Eastman, and F. J. Himpsel, Phys. Rev. Lett. 45, 1808 (1980); cf. J. W. Gadzuk, J. Vac. Sci. Technol. 12, 389 (1975).

¹²At low coverages these clusters can be dispersed by mild annealing or avoided by "indirect" gas exposures at lower pressures ($\sim 5 \times 10^{-9}$ Torr).

¹³W. Williams, S. Trajmar, and A. Kuppermann, J. Chem. Phys. 62, 3031 (1975).

¹⁴Our definition of monolayer coverage, $\theta = 1$, corresponds to a coverage which is $\sim 2 \times$ smaller than that defined in earlier studies (Refs. 1-3).

¹⁵G. Baldini, Phys. Rev. 128, 1562 (1962).

¹⁶Our analysis of the line shape involves convoluting the (ELS) spectral lines of the free atom with combinations of Gaussians and Lorentzians so as to produce the observed half-widths. We then determine the combinations which produce the best fit to the low-energy side of the $5p \rightarrow 6s$ peak. As a consistency check in this analysis we find the condensed-phase spectral line shapes are fitted well by a Gaussian distribution while the calculated resonances for an adatom (Ref. 6) are fitted well by a pure Lorentzian distribution.

¹⁷J. Unguris, L. W. Bruch, M. B. Webb, and J. M. Phillips, to be published.

¹⁸R. A. Tilton, D. J. Phelps, and C. P. Flynn, Phys. Rev. B 14, 5265 (1976).

¹⁹J. E. Demuth and Ph. Avouris, Phys. Rev. Lett. 47, 61 (1981), and J. Chem. Phys. 75, 4783 (1981).

²⁰J. D. E. McIntyre and D. E. Aspnes, Surf. Sci. 24, 417 (1971).