

Adsorbate Spectra on Metal and Oxide Surfaces

J. E. Cunningham, D. Greenlaw, and C. P. Flynn

Department of Physics and Materials Research Laboratory, University of Illinois at Urbana-Champaign, Urbana, Illinois 61801

and

J. L. Erskine

Department of Physics, University of Texas, Austin, Texas 78712

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Surface adsorbates on clean metal surfaces are being studied by vacuum-ultraviolet differential-reflectivity methods. Results for rear gases adsorbed on metals reveal ionic characteristics of the excited configurations and weak coupling to the host electron gas.

This Letter reports some newly observed characteristics of adsorbate excitation spectra on metal surfaces. The data reveal ionicity of the excited surface-impurity configuration in certain cases and a breakdown of impurity-host coupling in other cases. To obtain these results, we have developed an apparatus that extends the sensitive range of differential-reflection spectroscopy from the usual visible and ultraviolet (uv) region well into the synchrotron-radiation regime. The equipment is ultrahigh-vacuum compatible and operates normally beyond the LiF cutoff at $\hbar\omega \sim 12$ eV. It has been possible to detect adsorbates at coverages ~ 1 in 10^3 of surface atoms in favorable cases, using light from the University of Wisconsin storage ring. The sensitivity beyond $\hbar\omega = 9$ eV was more typically ~ 1 in 10^2 surface atoms, because of the limited photon flux. The data reported here are thus comparable in sensitivity with photoemission results.

Details of the experimental arrangement will be published elsewhere. The basic instrument contains a chopper that switches light between two channels, one containing a pure substrate and the other a substrate supporting a controlled coverage of adsorbed impurities.¹ The differential effect induced by the adsorbed species is observed by a single detector. This arrangement can eliminate both source and detector drift to leave the data limited only by the photon flux and chopper stability. Stabilities $\sim 10^{-5}$ appear possible with the present chopper system, and the effective use of photon fluxes $\sim 10^{10}$ photons/sec at the detector therefore appears accessible. We note that differential capabilities of this type are inevitably required to eliminate host effects and detector drift if new sources providing $\geq 10^8$ photons/sec at the detector are to be utilized effectively. The present experiments employ reflec-

tion methods (in both *s* and *p* polarizations), but transmission measurements appear equally feasible. Similar sensitivities to those achieved in the present work have previously been obtained by photoemission methods.^{2,3} The two techniques provide complementary information. Some sharp absorption spectra from rare-gas surfaces have also previously been reported.⁴

Metal substrates were prepared by evaporation in bell-jar vacuums typically in the low 10^{-10} -Torr range. A cryotip maintained the samples near He temperature, and the pressure in the cooled can was sufficiently low that no substrate deterioration could be detected over extended periods of time. Oxides were prepared by oxidation of the metal films at room temperature, when needed. One half of the freshly prepared surface was exposed for a chosen time interval, by means of cold movable shutters, to a molecular beam of the impurity gas originating from a gas leak. The leak was carefully calibrated using quartz crystals by methods described elsewhere.⁵ Experience with these systems has established that the impurity surface density can be controlled with absolute accuracy better than 10%, and a relative uncertainty of only a few percent between samples.

Figure 1 illustrates the sensitivity available with *p*-polarized light for Xe on 220 Å of MgO covering a Au substrate. Apparatus asymmetries $\sim 1\%$ were eliminated from the data by background scans conducted prior to the introduction of impurities on one substrate half. The first Xe excitation is observed at a noise figure $\sim 40:1$ for the most dilute Xe coverage of 0.026 monolayers, which gives a maximum reflectivity change $\sim \frac{1}{2}\%$. Also shown is the signal for Xe on 130 Å of MgO on a Au substrate. The same features are observed, but distorted by the substrate dielectric

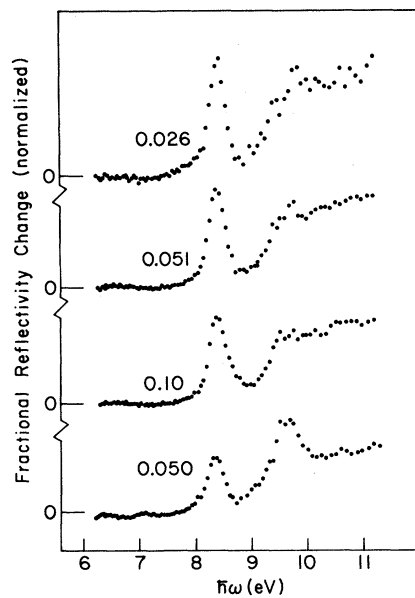


FIG. 1. Fractional reflectivity changes observed for Xe on MgO substrates with p -polarized light (coverages indicated in monolayers). The data are normalized to show the effect per adsorbed atom. The lowest curve is for 130 Å of MgO on Au and the remainder are for 220 Å of MgO on Au. The sensitivity is photon limited beyond 9 eV with the filter, grating, and source used.

properties. We hope to understand such distortions quantitatively by detailed modeling of the substrate dielectric behavior.⁶ The data in Fig. 1 are intended to show the sensitivity available below $\hbar\omega = 9$ eV and the deterioration in noise figure caused by the limited photon flux available at the Stoughton ring for $\hbar\omega \geq 9$ eV.

The remainder of this Letter concerns metal substrates where qualitative features of the results for $\hbar\omega \geq 10$ eV provide new information concerning the local excited configurations of the impurities. Our initial work has employed Xe, Kr, Ar, H₂, and CO on Au, Ti, Mg, and Al surfaces. Examples of these results are presented in what follows.

Spectra for various Kr coverages on clean Au surfaces are given in Fig. 2. The atomiclike excitation lines visible near 10 eV at high coverages *disappear completely* when the surface density is reduced to ≤ 0.2 monolayers. Apparently the oscillator strength is blue shifted above the shoulder at 13.5 eV, approximately coincident with the Kr ionization limit (this presumably appears negative because of substrate properties in this region). Similar effects are observed for Xe on Au, where the exciton near 8.4 eV is replaced

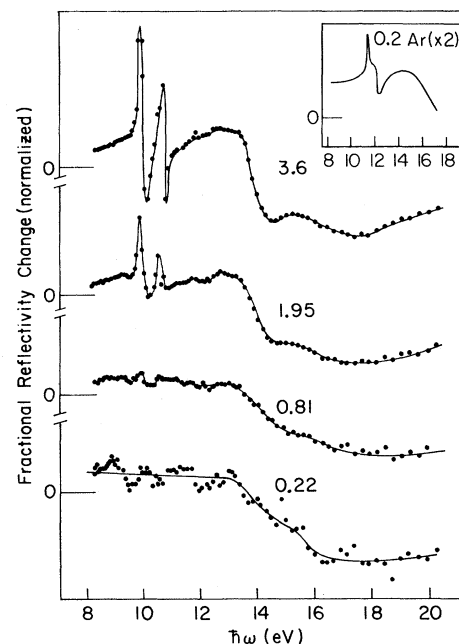


FIG. 2. Fractional reflectivity changes in p polarization for Kr on Au at the coverages indicated (data normalized as in Fig. 1). Analogous data for Ar on Au are shown in the inset, twice enlarged.

by a shoulder at 10.3 eV. For Ar on Au substrates, however, a small feature persists near the Ar exciton energy, even at low coverages (inset in Fig. 2). These experiments are consistent with the observation by Cunningham *et al.*⁷ that no Xe or Kr effects on Au or Ti could be detected in the energy range expected for atomic-like excitations.

Threshold effects with a more pronounced character are observed for rare-gas atoms adsorbed on Al and Mg. Spectra for Kr on Al are presented in Fig. 3 for comparison with the data for Au substrates in Fig. 2. At high coverages the atomic excitations again dominate the spectrum near 10 eV. These sharp lines and the broad peak near 14 eV both decrease in amplitude with reduced coverage and are almost eliminated at a coverage of 0.2 monolayers. They leave behind a broad, but well-defined threshold peak near 10 eV that is evidently characteristic of Kr in intimate contact with Al metal. Ar exhibits a large threshold peak on Al (inset in Fig. 3), and a weak peaking of oscillator strength is observed near the Xe exciton lines when Xe is adsorbed on Al at low coverages. Even Xe has a large threshold on Mg (Fig. 3, inset).

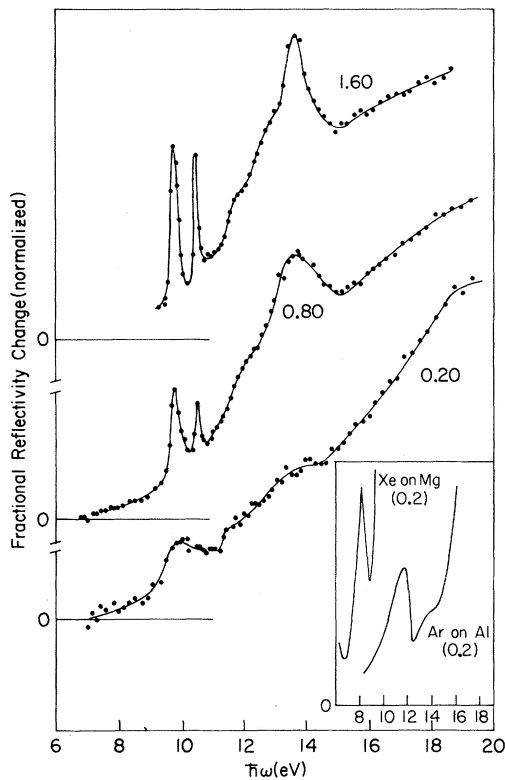


FIG. 3. Fractional reflectivity changes in p polarization for Kr on Al at the coverages indicated (data normalized as in Fig. 1). Data for Ar on Al and Xe on Mg are shown in the inset on the same vertical scale.

Our interpretation of these observations will not involve details of the host band structure but, rather, the chemical properties of the surface and excited foreign atom. For the main part, the data reveal charge-transfer effects in the excited configuration of the metal-impurity complex. Rare-gas atoms in their ground states physisorb on all these substrates at He temperatures, and the bonding has only a minor (~ 0.2 eV) effect on the energy of the composite system. However, rare-gas atoms in p^5s excited configurations greatly resemble their alkali-atom neighbors in the periodic table, and are therefore highly reactive.⁸ The $(p^5)^+$ rare-gas core differs from the $(p^6)^+$ alkali core only by a pseudopotential correction derived from the extra nuclear charge and core electron of the alkali. In effect, therefore, the rare-gas spectra reveal the properties of *alkali atoms* adsorbed on these metal substrates.

In the dilute limit, the excitation lines of heavy rare gases on Au (and presumably Ti also) disap-

pear because the alkalilike excited configuration is ionic. A positive alkali core is screened by electrons drawn to the crystal surface, and this negative charge shifts an alkali s orbital above the one-electron levels of the Au band. The Kr oscillator strength near 10 eV is therefore zero; the transitions are shifted to higher energies where propagating states can enter the rare-gas cell. The data show that the Kr^* ionic state, with the electron in the Au substrate, is bound more strongly by 3.6 eV than the atomic p^5s rare-gas configuration with the s electron in the Kr cell. Other data, to be reported elsewhere, show that the analogous shift is about 2 eV for Xe on Au. The Ar data, inset in Fig. 2, have a shift similar to that of Kr, but with a residual unshifted peak. The occurrence of "nonionic" excitation components for the lighter rare gases is consistent with the large ionization potentials of lighter alkali metals.

Ionic effects of the type discussed here have long been recognized⁹ for alkali atoms on transition-metal substrates, and were first discussed in a comprehensive way by Gadzuk.¹⁰ The effects are readily apparent in the work function, although careful work on Au is lacking. The present optical data provide an interesting comparison with photoemission results for Xe on W.³ Photoemission presumably ionizes the rare gas directly, and therefore produces a sharp line near the ionization potential, characteristic of the core width and its coupling to the substrate.

It appears that the excited rare gases are much less ionic on Mg and Al. So much is the case that the residual Kr peak at dilution on Al contains an oscillator strength per atom comparable with that in the sharp lines it replaces. Au has a larger atomic affinity (2.1 eV) than Al (0.52 eV) or Mg (-0.32 eV), so this trend falls naturally into the present interpretation. In all, a comparison of the alkali binding energy (Cs, 3.89 eV; Rb, 4.18 eV; K, 4.34 eV) with the substrate work function (Au, 4.3 eV; Al, 4.2 eV; Mg, 3.8 eV) seems to indicate the probable size of "nonionic" excitation components in a surprisingly effective way (cf. Figs. 2 and 3).

Persistent optical excitations coupled to an electron gas normally appear as threshold shoulders with extended high-energy tails.¹¹ This happens because the local excited configuration exposes conduction states to a changed local potential that deforms all band states. Electron-hole pairs are created when the band orbitals of the ground configuration project into the deformed

states, and this extra energy absorption causes the tail.¹² Theories of these effects have excited much interest and have been widely discussed, although some aspects remain imperfectly understood.¹³ It is expected that similar effects occur for adsorbed atoms that couple strongly to a metal substrate in one or both configurations connected by the optical transition.^{14,15}

The notable feature of the residual Ar peaks in Figs. 2 and 3 is that they lack substantial high-energy tails. One therefore needs to explain the absence of observable electron-hole pair creation in these surface excitation processes.

Two possible causes for effects of this type can be cited. First, transitions to a *magnetic* excited state yield a δ -function excitation spectrum lacking a high-energy tail.¹⁴ Second, theories predicting the tail are based on Δ SCF¹⁴ arguments that use one-electron orbitals extending through both the metal and excited center; this need not be correct if the metal-impurity coupling is so weak that Coulomb correlations isolate even the excited impurity state from the band¹⁴ in the manner of a Mott transition. Both these possibilities pertain to weak metal-impurity coupling. Magnetic and nonmetallic configurations should occur successively as the coupling is decreased.¹⁴ Adatoms are certainly expected to couple to the host band more weakly than atoms in the bulk metal. The observed effects suggest that the reduction in coupling strength may be a significant factor in the adatom excitation spectrum.

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⁶See J. D. E. McIntyre and D. E. Aspnes, *Surface Sci.* **24**, 417 (1971).

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⁸This is discussed in Ref. 5.

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