

Persistent optical excitation to Rydberg states: Xe on Au

W. Eberhardt* and A. Zangwill†

Brookhaven National Laboratory, Upton, New York 11973

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Auger-electron-yield measurements of a monolayer of Xe adsorbed onto a polycrystalline Au film are presented which show transitions from the Xe $4d$ levels to Rydberg-derived final states with essentially their gas-phase oscillator strength. These results are contrary to a charge-transfer instability model used to explain the lack of corresponding excitation strength from the Xe $5p$ subshell to similar final states. Both experimental observations are rationalized using a dielectric response model.

I. INTRODUCTION

Rare-gas atoms physisorbed on metal surfaces are among the simplest of adsorption systems. The nature of the ground-state electronic structure has been extensively studied both experimentally^{1,2} and theoretically.³ However, the excited-state configurations have only recently come under investigation, with very surprising results. Cunningham *et al.*⁴ have reported the results of differential reflectivity measurements for various rare-gas-metal-substrate combinations as a function of coverage. For high coverage (>1 monolayer), low-energy [(8–15)-eV] excitations from the outermost p shell into Rydberg final states are clearly visible and resemble comparable excitations observed in absorption for both vapor phase and condensed rare gases. However, for monolayer (or less) adsorption of Xe on Al, Ti, and Au, and Kr on Au, the normalized excitation strength per atom into these transitions is virtually eliminated. At similar low coverages for the other adsorbate-substrate combinations these excitations persist only slightly altered from their second-layer (or bulk) manifestation. The systematics of the observed behavior⁴ of the spectra is summarized in Table I. An empirical correlation between the persistence-extinction phenomenon and the difference between the substrate work function and the ionization energy of the free-atom excited state I^* lead the authors⁴ to propose a “charge-transfer instability” for rare-gas-metal-substrate systems. Briefly, if I^* exceeds ϕ , the final-state adsorbate configuration is presumed neutral with the Rydberg electron localized on the excited atom [Fig. 1(a)]. Conversely, if I^* is less than ϕ , the excited electron is imagined to ionize, hop into the metal, and localize in the surface region to screen the ion [Fig. 1(b)]. The implication relevant to the reflectivity measurements is that the optical matrix element connecting the ground state to the excited state is very much

smaller for the ionic configuration than for the neutral configuration. Hence, the persistence or absence of valence-level excitations to Rydberg states is seen as an optical monitor of the ionization state of the adsorbate.

The foregoing interpretation of the optical data has been criticized recently by Lang and co-workers.⁵ They point out that the ionization of the excited electron in an $I^*-\phi$ model would be governed by an effective ionization energy I^*_{screened} which takes account of metallic screening, rather than the bare atomic value I^* . As may be inferred directly from experiment,⁵ ϕ always exceeds I^*_{screened} (for the cases studied in the reflectivity experiments) so that the ionic final-state configuration would *always* be expected. In fact, the configuration mixing of the two suggested final states where the excited electron is either localized on the atom or delocalized in the solid is simply a one-body quantum-mechanical overlap phenomenon which leads to the familiar resonant-level picture extensively studied for atoms on jellium by local-density-functional methods.⁶ The appropriate excited atom-on-jellium calculations have been performed by Lang *et al.*⁵ and indeed a broad (1-eV) s -like final-state resonance above the Fermi level is found for all the cases of interest. Although no optical matrix elements were explicitly calculated, the resulting densities of states suggest that one-electron transitions should occur with appreciable oscillator strength per atom into these final-state resonances. Hence, this analysis predicts persistent excitations with ionization of the excited electron in all cases.

The purpose of the present work is to provide new experimental information for a particular rare-gas-metal-substrate system and to suggest an explanation which rationalizes all of the available results. We have studied excitations from the $4d$ core level of Xe to Rydberg-derived final states for monolayer coverage on Au. For these high-energy

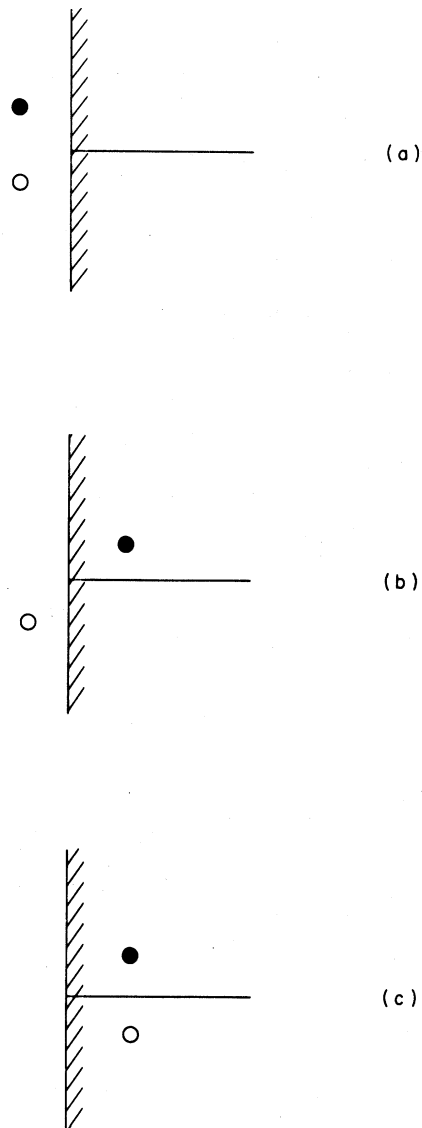


FIG. 1. Three possible excited-state configurations for the combined adatom-metal system. The adatom is to the left of the metal surface. Horizontal line denotes the metal Fermi level.

[(65–70)-eV] transitions to resonance states well above the Fermi level the oscillator strength per atom is found to be nearly identical to comparable transitions in gas-phase and condensed Xe. This result establishes experimentally that the position of the final state relative to the Fermi level is not necessarily relevant to the question of dipole transition strength. Our findings agree with the predictions of Lang *et al.*⁵ and indeed are consistent with similar studies for adsorbed molecules⁷ where even final-state shape resonances are known to persist

barely changed upon adsorption on a metallic substrate. For the Xe-on-Au system, the persistence of high-energy Rydberg transitions, the unusual extinction of low-energy Rydberg transitions, and the failure of one-electron theory to describe the latter suggests that a many-body effect may be responsible. We propose that a proper description of the frequency-dependent dielectric response of the coupled adsorbate-substrate system can rationalize not only our own results but also the systematics reported by Cunningham *et al.*⁴ Section II of this paper is devoted to a description of the experiment, and the method of analysis and results. In Sec. III, the theoretical issues are examined and the dielectric response model discussed. Section IV summarizes our conclusions.

II. EXPERIMENT

In this work we use Auger-yield spectroscopy to monitor intra-atomic photoabsorption from the $4d$ near core level to Rydberg and continuum final states of xenon adsorbed to one-monolayer coverage on Au. Thus we study transitions to the same type of final states (with the exception of a different angular momentum) as Cunningham *et al.*⁴ at the coverage where the valence-level excitations were extrapolated to vanishing oscillator strength. In particular, we measure the intensity of photoelectrons emitted in the Auger decay of the Xe $4d$ hole following photoabsorption. If the initial excitation is to continuum final states, the frequency dependence of the Auger yield is directly proportional to the absorption cross section $\sigma_{4d}(\omega)$. For the free atom, when the photon energy is lowered so that discrete Rydberg final states are probed, the emitted Auger electrons correspond to a resonant shakeup process and $\sigma_{\text{Auger}}(\omega)$ can reflect additional frequency dependence besides $\sigma_{4d}(\omega)$.^{8,9} However, in the present adsorption case, we shall find that the Rydberg final-state resonance decays into the bulk before the Auger process occurs so that $\sigma_{\text{Auger}}(\omega)$ and $\sigma_{4d}(\omega)$ are again simply proportional.

The photoemission experiments were performed at the Synchrotron Radiation Center of the University of Wisconsin using a toroidal grating monochromator.¹⁰ The experimental chamber was equipped with a double-pass cylindrical-mirror analyzer (CMA) and a liquid-helium- or liquid-nitrogen-cooled cryostat. Au was evaporated directly onto the Cu body of the cryostat and a surface temperature of about 70 K was achieved by pumping on the liquid N₂. At this temperature, saturation coverage of Xe corresponds to exactly one monolayer, as in similar studies with Ag substrates.¹¹ In the Xe $4d$ excitation energy range (60–80 eV) the Au

absorption is quite smooth and our use of partial electron-yield measurements ensures high surface sensitivity.

Figure 2 shows a photoelectron energy distribution curve (EDC) for one monolayer of Xe adsorbed on a polycrystalline Au substrate. The lowest energy structures are the well-resolved spin-orbit-split Xe 4*d* levels. The absence of further splitting due to distance-dependent relaxation shifts¹ is additional evidence that all the xenon atoms are in contact with the metal. At higher kinetic energy the Xe 4*d* Auger-electron peaks are found. This latter structure may be analyzed in detail to obtain information about the spin-orbit coupling of the Xe 5*p* shell in the Auger final state.¹² Finally, the smoothly varying background is due to inelastically scattered photoelectrons from the Au valence band and the Xe 5*s* and 5*p* levels. In the present work we simply monitor the Auger intensity as a function of incident photon energy. Indeed, the 20% Auger-electron signal-to-background ratio near 39 eV illustrates one of the advantages of the photoelectron-yield technique. This may be compared to the differential reflectivity measurements⁴ of the valence-level excitations where the true changes upon adsorption are of the order of 10⁻⁴ so that phase-sensitive detection is required.

We have directly integrated the total Auger intensities from energy distribution curves taken at several photon energies. Taking account of the incoming photon flux, these data points are plotted in Fig. 3 along with the measured solid and vapor phase absorption curves.¹³ The Auger intensities are normalized to the absorption data at a single point (83.5 eV) using the known absolute cross sections of the Xe 5*s* and 5*p* valence levels.¹⁴ It is important to note that the complete Auger spectrum obtained at

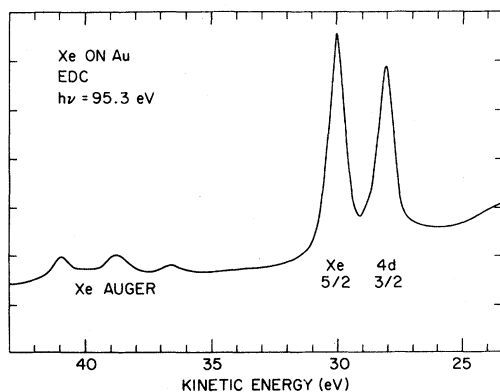


FIG. 2. Partial EDC of a monolayer of Xe adsorbed onto a polycrystalline Au film showing the Xe 4*d* emission lines and Xe Auger-electron emission resulting from the decay of the 4*d* hole.

the lowest photon energy (Rydberg region) is *not* shifted in kinetic energy relative to the Auger electrons collected at the highest excitation energies (continuum region). Therefore, we do not have the resonant shakeup situation where such a shift is expected^{9,15} and direct comparison with $\sigma_{4d}(\omega)$ is appropriate.

Since the collection of many EDC's over the entire photon energy range shown in Fig. 3 is impractical we have measured instead the total yield of photoelectrons within a kinetic energy window of (39 ± 2) eV as a function of photon energy. This yield spectrum is shown in Fig. 4 for the clean Au film (solid curve) and for one-monolayer adsorption of Xe at 70 K (dashed curve). Again, the only normalization is with respect to the storage-ring beam current. The monochromator output was measured with a W diode in parallel with the yield spectra. The difference curve (dash-dotted curve) contains the information of interest.

In principle, $\sigma_{4d}(\omega)$ can be extracted from the difference curve by fitting to the functional form:

$$I_{\text{diff}}(\omega) = A[\sigma_{4d}(\omega) + B\sigma_{5s+5p}(\omega) + \Delta\sigma_{\text{Au}}(\omega)] . \quad (1)$$

$\sigma_{4d}(\omega)$ is given directly by the Auger yield. The second term describes the Xe 5*s* and 5*p* electrons scattered into the kinetic energy window while $\Delta\sigma_{\text{Au}}$ takes account of the change in Au absorption upon Xe adsorption. Since we expect the frequency dependence of these background terms to be rather weak, we have, for simplicity, replaced them by a constant, equal to the yield at 60 eV excitation energy where the Xe 4*d* cross section is zero. The constant A is determined, as before, by normalization to the gas-phase absorption spectrum at 83.5 eV. The resulting curve for monolayer adsorption of Xe on Au (Fig. 3) nicely mirrors the absorption data of Haensel *et al.*¹³ over the entire frequency range. The small deviations of the normalized difference curve from our absolute Auger data points reflect the small frequency dependence neglected in (1).

The broad structure between 65 and 69 eV corresponds to the 4*d* to Rydberg transitions for the monolayer. The integrated oscillator strength is roughly the same as for gaseous or even solid Xe. As noted in the Introduction, upon adsorption, these final-state levels become broadened into resonances with a calculated width⁵ of about 1 eV. The convolution of this width with the sharp features in the gas-phase spectrum clearly reproduces our results and confirms the identification of the absorption bump with transitions to Rydberg-derived final states. Additionally, we note that the energies of the transitions are not more than 0.5 eV blue-shifted

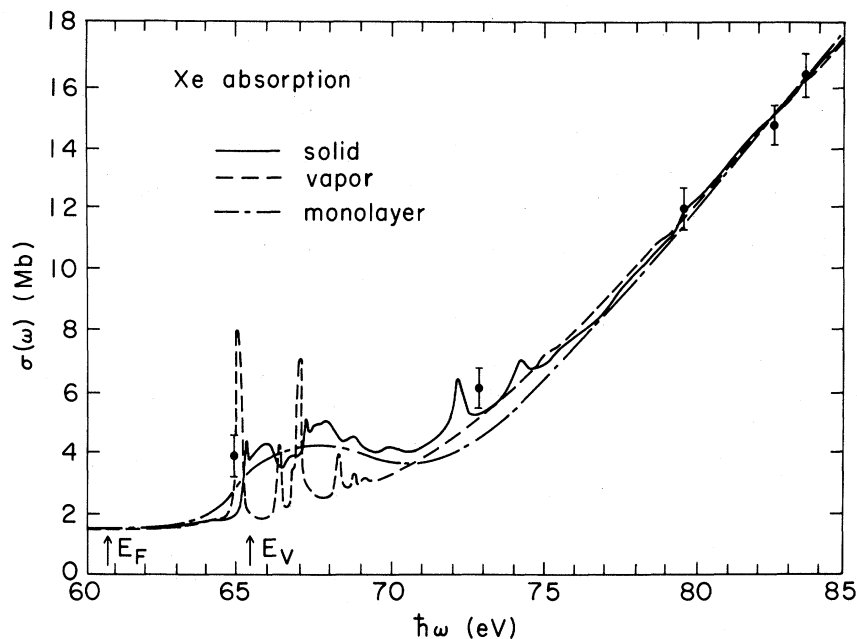


FIG. 3. Photoabsorption cross section for xenon solid, vapor, and monolayer adsorption on gold. See text for normalization and discussion. E_F and E_V denote the Fermi level and the vacuum level of the adsorption system referenced to the Xe $4d$ level.

from, if not identical to, the gas-phase values, keeping in mind the inherent final-state widths. This confirms recent theoretical results¹⁶ which show that both the $4d$ and $6p$ levels are shifted upward by relaxation effects by the same amount. These shifts

naturally cancel in the bound-to-bound transition.

In summary, we have observed $4d$ to Rydberg transitions in a monolayer of Xe adsorbed onto an Au substrate with oscillator strength and transition energy almost identical to gas-phase Xe. This pro-

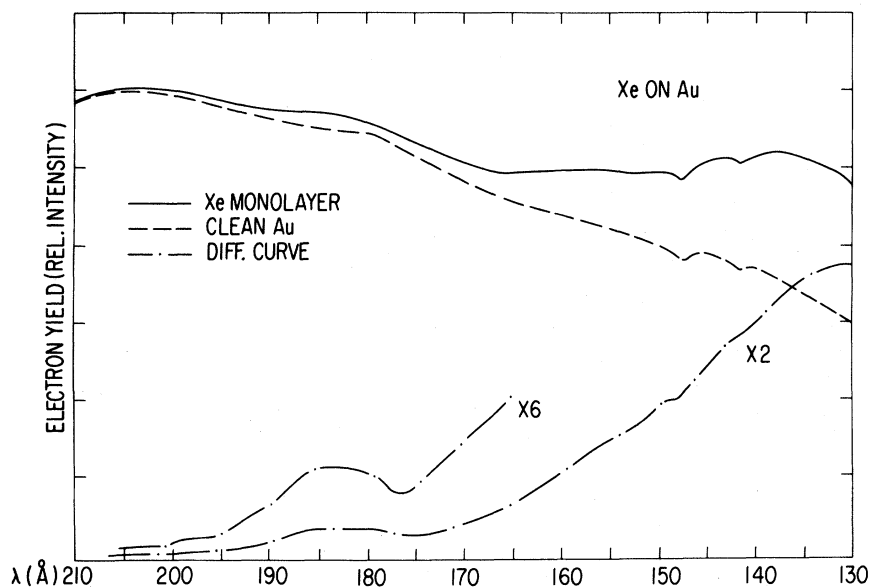


FIG. 4. Partial-yield spectra of a monolayer of Xe adsorbed onto Au. The electron analyzer was set at a final-state energy of (39 ± 2) eV in the center of the Xe Auger emission to enhance the sensitivity.

vides an experimental counter example to the $I^*-\phi$ model of an optical-absorption "switch" advocated by Cunningham *et al.*⁴ to explain their valence-level-excitation data. However, we agree with these authors that the excited electron quickly leaves the vicinity of the adatom and tunnels into the metallic substrate.

III. DISCUSSION

In order to facilitate a systematic discussion of both the core-level- and valence-level-excitation spectra of Xe on Au we shall consider the optical absorption process from a rather general point of view. In the long-wavelength limit, the exact eigenstates of the adsorbate-substrate system can be used in a golden-rule expression for the optical absorption cross section:

$$\sigma(\omega) = 4\pi^2 \alpha \hbar \omega \sum_F |\langle F | U^{\text{ext}} | 0 \rangle|^2 \times \delta(\hbar\omega - E_F + E_0). \quad (2)$$

Here α is the fine-structure constant and U^{ext} is the dipole operator. Typically, an independent particle approximation to (1) is made which takes the form

$$\sigma(\omega) = 4\pi^2 \alpha \hbar \omega \sum_{i,f} |\langle f | U^{\text{ext}} | i \rangle|^2 \times \delta(\hbar\omega - \epsilon_f + \epsilon_i). \quad (3)$$

The one-particle wave functions and energy levels in this expression would come from, for example, a Lang-Williams atom-on-jellium calculation⁶ or from a full semi-infinite monolayer adsorbate-substrate band-structure calculation.¹⁷ Often the further approximation of ignoring matrix-element effects is adequate. This density-of-states approximation is evidently sufficient to describe our Xe on Au near core-level absorption results since, as noted, the calculated⁵ 1-eV broadening of the final states convoluted with the gas-phase adsorption spectrum in Fig. 4 adequately reproduces our monolayer results.

In order to understand the apparent extinction of valence-level transitions to Rydberg states observed by Cunningham *et al.*⁴ for the same Xe on Au system we seek an additional broadening or shifting mechanism which either differentiates the initial states ($5p$ vs $4d$), the final states ($6s$ vs $6p$), or depends explicitly on the excitation energy. The former, a dramatic difference in the respective hole lifetimes, seems unlikely considering the similar widths obtained from the energy distribution curves for photoemission to the free continuum. Similarly, the final-state resonance width is not expected to differ greatly in the two cases. Therefore, a decay channel

directly related to the entire excitation process is required. The most likely candidate is nonradiative excitation of particle-hole pairs (and plasmons) in the metal substrate.¹⁸ That is, one mixes in an additional final-state configuration [Fig. 1(c)] to the two considered previously. It is now necessary to treat the excitation process as a many-body problem and the simple independent particle expression (2) will no longer be adequate. The type of frequency-dependent configuration interaction described above amounts to the inclusion of the nonlocal dielectric response of the coupled adsorbate-substrate system.

For the present purposes it will be sufficient to introduce the dielectric response at the level of the random-phase approximation (RPA). Within this scheme it is possible to build all the desired effects of electron correlation into an effective, complex, frequency-dependent driving field $U^{\text{eff}}(x | \omega)$, which simply replaces the external-field dipole operator in the golden-rule formula (3).¹⁹ For a nontranslationally invariant system, this effective field is determined by solution of an integral equation in position space. To date, realistic solutions for the optical cross section have only been obtained for semi-infinite jellium²⁰ and free atoms.¹⁹ Nonetheless, the essential features of the exact solution for the problem of interest in this paper can be written down simply if the one-body resonant-level widths of the initial and final states in the Rydberg transition are ignored. In that case one finds²¹

$$U^{\text{eff}}(x | \omega) = U_1(x | \omega) + U_2(x | \omega) \times \frac{\langle f | U_1(\omega) | i \rangle}{\omega - (\omega_f - \omega_1) - \langle f | U_2(\omega) | i \rangle}. \quad (4)$$

In this expression, the auxiliary fields $U_1(x | \omega)$ and $U_2(x | \omega)$ have particularly clear physical interpretations. $U_1(x | \omega)$ reflects the screening of the *external field* by the dielectric response of the entire adsorbate plus metal system which we may express in terms of an effective local dielectric function as

$$U_1(x | \omega) = \frac{U^{\text{ext}}(x)}{\epsilon(x | \omega)}. \quad (5)$$

Of course, $U_1(x | \omega)$ is obtained by considering the full *nonlocal* response by solution of the aforementioned integral equation. Similarly, $U_2(x | \omega)$ represents the screening of the *Coulomb field* created by the overlap charge density of the transition of interest; that is

$$U_2(x | \omega) = \frac{U_{fi}(x)}{\epsilon(x | \omega)}, \quad (6)$$

where

$$U_{fi}(x) = \int dx' \frac{\psi_f^*(x') \psi_i(x')}{|x - x'|}. \quad (7)$$

The absorption cross section is found by simply inserting (3) in place of U^{ext} in the golden rule. One can easily verify²¹ that the result is a modified Fano formula where the complex number $\langle f | U_2(\omega) | i \rangle$ determines the frequency-dependent resonance energy shift and autoionization width. The reintroduction of the one-body widths to the “discrete” states does not alter the essential physics.

As noted, the exact RPA solution of the true adsorbate-substrate problem does not appear to be at hand. Nonetheless, various model calculations have appeared which seek to capture the main features implicit in (4). Most of these ventures have addressed the damping of vibrational excitations of adsorbed molecules¹⁸ so that the goal is to obtain an estimate of $\langle f | U_2(\omega) | i \rangle$. From (6) and (7) we see that $U_2(x | \omega)$ is the response of the polarizable electronic system to a driving Coulomb field centered at the adsorbate. For the Xe $5p \rightarrow 6s$ transition this field is purely dipolar (for the $4d \rightarrow 6p$ transition higher multipoles are also present). Hence, a common approximation replaces the entire system by a classical point dipole situated a distance d above a mirror characterized by a local dielectric function $\epsilon(\omega)$. This classical image model predicts

$$\langle f | U_2(\omega_{fi}) | i \rangle \sim \tau_{fi}^{-1} (\lambda/d)^3 \frac{\epsilon(\omega_{fi}) - 1}{\epsilon(\omega_{fi}) + 1}, \quad (8)$$

where τ_{fi}^{-1} is the free-atom dipole transition rate. Bagchi *et al.*²² have considered a two-dimensional array of such dipoles and their images in an attempt to understand some of the results of Cunningham *et al.* although the disappearance of oscillator strength per atom was not directly addressed. In the context of this paper we use measured optical data²³ for Au and calculated transition rates for Xe (Ref. 24) in (8) to obtain

$$\frac{\text{Im} \langle 6s | U_2 | 5p \rangle}{\text{Im} \langle 6p | U_2 | 4d \rangle} \sim 10^2. \quad (9)$$

This result indicates the type of effect we believe can rationalize both the valence-level and core-level Rydberg excitation linewidths. However, this estimate cannot be taken quantitatively seriously since it is known that the classical formula overestimates damping rates for vibrational and electronic excitations of adsorbed molecules.²⁵ Minimally, the higher-order—multipole fields present in the core-level excitation will decrease this estimate. Nevertheless, recent theoretical work on the point-dipole—jellium model which includes nonlocal dielectric response and realistic surface barriers²⁶

continue to show damping rates which are strongly frequency dependent. In particular, low-energy excitations couple to the plasmons and electron-hole pairs in the substrate more efficiently than high-energy excitations. Future calculations approaching the proper RPA solution (including the electronic structure of the adsorbate and the bond, for example) should be carried out over a wide spectral range to test the ideas suggested here.

Other aspects of a dielectric response model relevant to the original reflectivity measurements do not require detailed calculations. The shifting and broadening of the oscillator strength distribution depends critically on particle-hole pair production in the substrate. Hence, the observed persistence of $5p$ excitations to Rydberg states for Xe adsorbed on insulating substrates⁴ is not surprising in this view. In addition, the dielectric coupling of the adsorbate to the substrate is expected to scale with the polarizability of the adatom. For the rare gases, the low-frequency polarizability triples passing from argon to xenon.¹⁹ Therefore, the Ar $3p$ excitations should be most persistent, Xe excitations least so, and Kr $4p$ excitations somewhat intermediate, a trend noted in the original study (see Table I). Finally, let us consider the nature of the final state implicit in such a dielectric response picture. As discussed earlier, the intuitive view represented by any one of the configurations in Fig. 1 is probably inadequate. If the many-body effects discussed above in terms of $U^{\text{eff}}(x | \omega)$ were instead projected onto the final-state wave function, the result would be a rather complicated superposition of particle-hole pairs in the adatom, the metal substrate, and the bond region. The real space decomposition of this state could then be used to interpret the optical absorption in terms of overlap with the initial state.

IV. CONCLUSION

This study was motivated by the unusual observations reported by Cunningham *et al.*⁴ of the apparent disappearance of strong spectral features associated with valence to Rydberg transitions for submonolayer coverage of Xe on Au as well as other rare-gas—metal combinations. In that study it was

TABLE I. Crosses denote rare-gas—metal-substrate systems where $np \rightarrow (n+1)s$ valence oscillator strength per atom decreases dramatically as coverage is reduced through one monolayer (from Ref. 4).

	Mg	Al	Au
Ar			
Kr			×
Xe		×	×

suggested that the lack of a sharp line in reflectivity was the result of the ionization and transfer to the metal of an electron excited to a Rydberg state above the metallic Fermi level. In this work we have tested this claim by studying excitations to very similar Rydberg states from deeper-lying states of the adatom. In particular, we have monitored the Auger filling of the Xe 4d near core hole created by photoabsorption to Rydberg states and have demonstrated that these transitions persist for monolayer coverage on Au with oscillator strength essentially unchanged from their gas-phase or condensed-phase counterparts. This situation is found despite the fact that the final states lie well above the Au Fermi level. Nevertheless, the Auger spectrum itself strongly suggests that the excited electron does indeed quickly tunnel from the Rydberg states into extended states in the metal. Hence, the simple persistence or extinction of spectral oscillator strength into these excitations does not appear to be a reliable optical monitor of the adatom ionization state.

The strong frequency dependence of the transition strength to the Rydberg final states (extinction at low energy from 5p initial states, persistence at high

energy from 4d initial states) suggests that the dielectric response of the complete electronic system may explain this phenomenon. In particular, nonradiative energy transfer to plasmons and particle-hole pairs can be very efficient at low energies and thereby produce a considerable autoionization width to the 5p-6s Fano spectral profile. This mechanism is less important at higher energies. Although further theoretical and experimental work is needed, the dielectric response model seems capable of rationalizing the systematics of the available optical data.

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*Present address: Exxon Corporate Research Lab, P. O. Box 45, Linden, NJ 07036.

† Present address: Department of Physics, Polytechnic Institute of New York, Brooklyn, NY 11201.

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