

Evolution of the Pt conduction band in a solid Xe layer

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A photoemission study of the growth of Pt clusters in a solid Xe layer condensed onto a metallic substrate is presented. The evolution of the Pt conduction band is monitored in great detail. Simultaneously, the Xe emission is recorded and changes are correlated with the growth of the Pt band. It is argued that the energy position of the dilute-limit Pt emission tracks the change in substrate work function, which shows that the Pt is referenced to the local vacuum level in the atomic limit. Finally, effects of interactions between Pt clusters and substrates are found to depend on the work function and band structure of the substrate employed.

Clusters of metals can often be conveniently studied in rare-gas matrices.^{1,2} This is because the interaction between metal atoms is much larger than the metal-matrix interaction, and thus the latter can be neglected for many purposes. We report here a photoelectron spectroscopic study of Pt clusters embedded in a layer of Xe. The growth of the conduction band is studied in great detail, from the atomic photoemission peaks to the fully developed conduction band. This work is performed in a method similar to that of Colbert, Zangwill, Strongin, and Krummacher,¹ in which the evolution of Pd clusters was studied, and we will draw comparisons to that work throughout this report. Whereas the 4*d* shell for the Pd atom is completely filled, the 5*d* shell of the Pt atom contains a hole, which may very well be of considerable importance for interactions between the small metallic cluster and the metallic substrate beneath the solid Xe layer. These interactions and the effects of change of the substrate work function are addressed later in this report. We will show that changing the substrate work function changes the positions of the atomic Pt levels in these measurements, which implies that the clusters at very dilute concentrations in Xe are referenced to the substrate vacuum level. This is in contrast to studies of larger clusters on carbon, where equilibration of Fermi levels³ provides the reference level.

This experiment was performed using a liquid-helium cryostat that enabled us to reach temperatures down to about 20 K at the Ta substrate. The Ta substrate was a recrystallized foil of thickness 0.001 in., cleaned by flash heating to above 2000°C. Xe was condensed on this substrate at low temperatures from the gas phase using a microchannel plate doser. The thickness of the Xe layer was estimated to be 30–50 Å by monitoring the attenuation of the substrate conduction states. Pt was evaporated from a filament that was thoroughly outgassed prior to the experiment. The photoelectrons were excited by the He I line at 21.2 eV, and the spectra were recorded in the angle-integrated mode using a double-pass cylindrical mirror analyzer from Physical Electronics.

In Fig. 1 is shown the photoelectron spectrum corresponding to the most dilute Pt concentration, i.e., the atomic limit. The top curve in the right-hand part of Fig. 1 shows the atomic 5*d* emission from Pt after a magnification of 80. The spin-orbit splitting between the $J = \frac{5}{2}$ (lower binding energy) and $J = \frac{3}{2}$ components is measured to be

1.2 eV. The Xe 5*p* emission is characteristic of a multilayer coverage. The Pt concentration is estimated from similar evaporation rates on the bare metallic substrate to be of the order of 0.1–0.2 of an "equivalent" monolayer. The actual concentration is expected to be more dilute due to a dispersion of Pt atoms in the top few monolayers of the solid Xe. The ionization potentials of Pt and Pd are 9.0 and 8.3 eV,⁴ respectively. Therefore, the binding energies of the Pt 5*d* levels would be expected to be larger than those of the Pd 4*d* levels. However, the opposite is seen experimentally for Pt (this work) and Pd (the work of Colbert *et al.*¹) clusters embedded in a solid Xe matrix. Consistent energies for the Pd 4*d* levels in the dilute limit were obtained by Unwin and Bradshaw,⁵ using a carbon substrate. We take this as possible evidence that the isolated Pt atoms in Xe are in the d^{10} and not in the atomic d^9s^1 configuration. If we assume the d^{10} configuration, the ionization energies of the Pt 5*d* levels

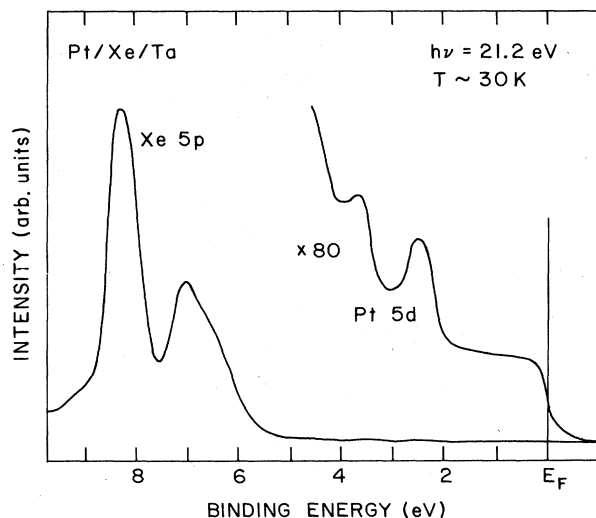


FIG. 1. Photoemission in the region of the Xe 5*p* and the Pt 5*d* levels from a Xe layer of a thickness about 30–50 Å with submonolayer coverage of Pt (0.1–0.2 equivalent monolayer). The top curve represents a magnification by a factor of 80, and shows the atomic-like Pt 5*d* emission.

can be lowered on the order of 2 eV (from Moore's atomic energy level tables, Ref. 4), and could thus explain the observed results. A local-density calculation⁶ shows that the Pt 6s level is within 0.2 eV of the 5d orbitals. It is conceivable that any small interaction between the s level and the Xe matrix pushes the s level above the d states, and a d^{10} configuration is therefore observed. Note that about 1 eV of screening from the Xe matrix is needed to agree with the free-atom values.

The evolution of the Pt conduction band is shown in Fig. 2. The bottom curve *a* is the same as in Fig. 1, except that the photoemission spectrum from the bare Xe layer has been subtracted out. We note that the two atomiclike peaks persist even after states start to build up at the Fermi level. The top curve *g* corresponds to a few equivalent monolayers of Pt coverage, and considerable weight is, at this point, built up near the Fermi level. This spectrum quite closely resembles the photoemission from a thick evaporated Pt layer. Presumably, the buildup of states at the Fermi level occurs when the affinity level of the clusters drops below the substrate Fermi level and equilibrium can occur between the cluster and the substrate, i.e., the Fermi levels align. The most prominent features of the spectra in Fig. 2, apart from the continuing presence of the dilute-limit, atomic Pt 5d components, are the development of the shoulders at binding energies of about 4.1 and 1.5 eV. Simultaneously, weight is being transferred in the direction of the Fermi level in a seemingly continuous fashion. Finally, at large Pt concentrations, curve *g*, only the high-binding-energy shoulder (about 4 eV) can be readily resolved. The changes

of the Xe 5p emission with coverage are displayed in Fig. 3. The bottom curve *a* corresponds to the clean Xe layer, and the top curve *f* shows the same high Pt exposure as curve *g*, Fig. 2. At first the Xe peaks shift slightly to lower binding energies, curves *a*–*d*, which reflects the increasing work function of the system. Then, at higher Pt concentrations, curves *e* and *f*, the shifts become larger. This is at the point where the photoemission of the Pt clusters builds up weight at the Fermi level, and the shift in the Xe peaks reflects an increase in the screening from the larger Pt clusters. This latter shift is due to final-state relaxation effects, whereas the smaller shifts at lower Pt levels are caused by changes in the local electrostatic potential (work function) and therefore are initial-state effects. We note that Xe constitutes a highly polarizable medium,⁷ which presumably tends to diminish electrostatic effects. The overall shape of the Xe 5p emission stays pretty much the same, which is different from the observations made in the work of Colbert *et al.*¹ on Pd/Xe, where they saw distinct changes in both the $J = \frac{3}{2}$ and $\frac{1}{2}$ components of the Xe 5p emission. The very small changes in the shape of the Xe 5p emission with Pt deposition are indicative of a uniform distribution of Pt clusters of almost the same size throughout the top few monolayers of the Xe layer. Also, the absence of a relaxation shift in the Xe peaks may indicate that very few Pt atoms have reached the Ta substrate, which in turn may suggest that the diffusion of Pt in Xe is less than that of Pd in Xe. However, the differences from the work of Colbert *et al.*¹ could be explained if the Xe layer was thicker in this present work.

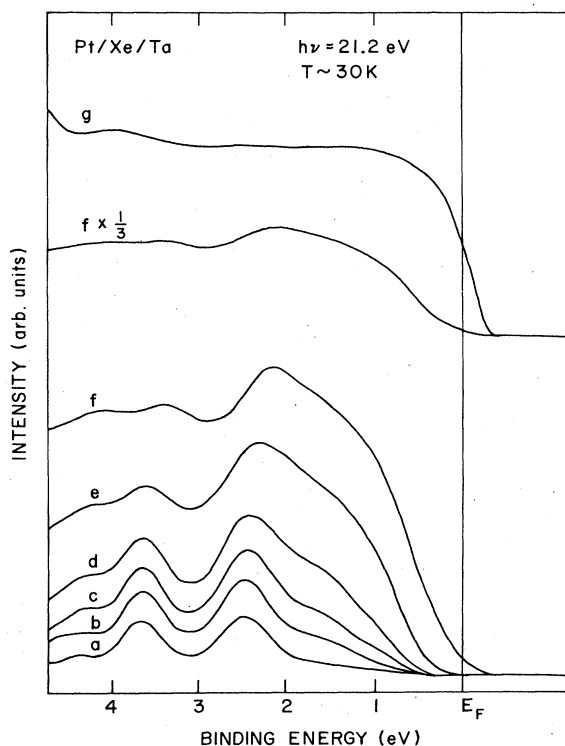


FIG. 2. Photoemission spectra showing the evolution of the Pt conduction band with Pt deposition, from submonolayer to a few monolayers coverage; see text.

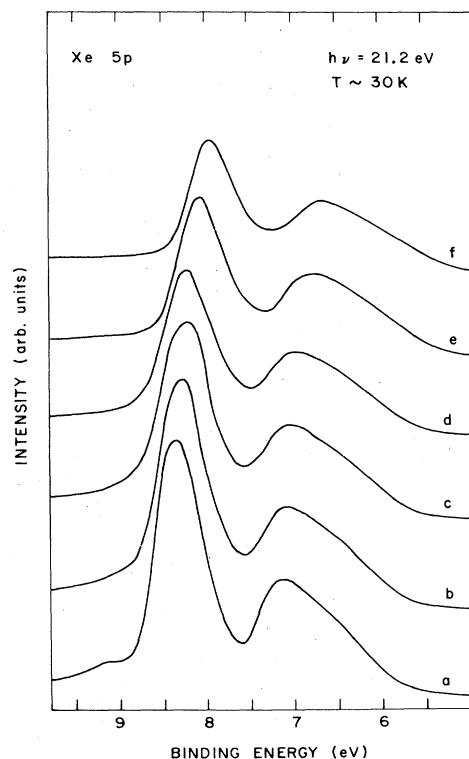


FIG. 3. Dependence of the Xe 5p photoemission with Pt deposition; see Fig. 2.

In order to investigate the effects of changing the substrate, we repeated the experiment, evaporating a thick layer of Pt on the Ta substrate, thereby in effect having a Pt substrate. The atomiclike Pt 5d levels could also now be seen at the most dilute Pt concentration (Fig. 4, curve *a*); however, the levels were shifted about 1 eV to lower binding energies. In addition, the Xe 5p levels were shifted the same amount, which also is near the difference in work functions between Ta and Pt.^{8,9} It has previously been concluded that the rare gases are referenced to the vacuum level^{10,11} because of their incapability of transferring charge to the metallic substrate. Our work shows also that the small Pt clusters are referenced to the vacuum level, since their shifts are the same as the change in the work function of the substrate. This observation was also made in the work of Colbert *et al.*,¹ in which they used a substrated Nb and Pd which have a work-function difference of about 1 eV.

The development of the Pt conduction band was observed to be quite different on the Pt substrate compared to on the Ta substrate (Fig. 4), and while this is not completely understood, we argue tentatively that the explanation comes from the differences in band structure and energy-level positions of the substrate. One of the most prominent changes is the very small intensity of the Pt emission. Even though we can resolve the atomiclike Pt 5d peaks at the dilute limit, the intensity is considerably smaller than it was when Ta was used as a substrate. The great dilemma in this explanation is that we basically assume a vanishing substrate interaction when the levels are aligned with the vacuum level. We note that in Fig. 2 (Ta substrate) the Pt 5d levels shift to lower binding energy as the clusters grow, whereas in Fig. 4 (Pt substrate) they shift to higher binding energy as the clusters grow. We emphasize that these shifts are due to initial-state alignment as the cluster size changes. As cluster size decreases, final-state effects always shift the cluster levels to higher binding energy by the Coulomb term $e^2/2r$.³ There is little evidence for this term in the large cluster regime here, presumably because the charge transfer from the metal substrate is more substantial than for clusters of carbon.

In summary, we have monitored the evolution of the Pt conduction band in a solid Xe layer. Atomiclike Pt 5d levels are seen in the dilute limit, and they are argued to be referenced to the vacuum level, based on the shift in peak positions using substrates with different work functions. The Pt

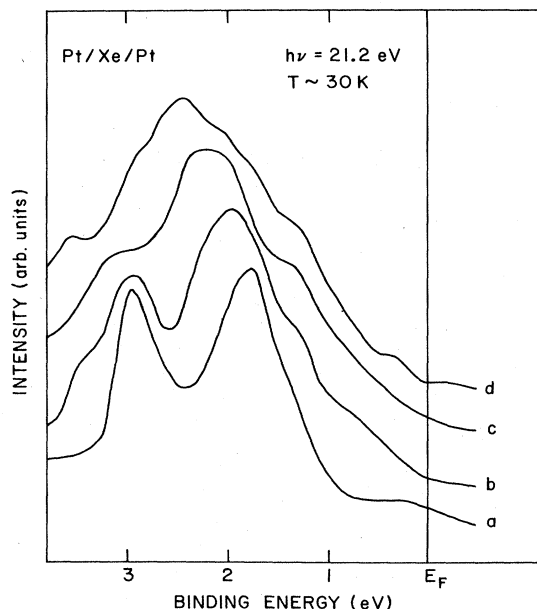


FIG. 4. Pt 5d photoemission with increasing Pt coverage, *a*–*d*, on a Xe layer on a Pt substrate. Differences from Fig. 2 reflect substrate effects; see text.

levels were seen to shift towards higher binding energies with increasing cluster size when the Xe layer was condensed on a Pt substrate. This unusual effect is attributed to initial-state reconfiguration of the Pt energy levels as the clusters grow. Effects of interactions between the Pt clusters and the underlying metallic substrate (across the Xe layer) were observed, but still remain to be fully understood.

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