

Photoemission from Mass-Selected Monodispersed Pt Clusters

W. Eberhardt, P. Fayet,^(a) D. M. Cox, Z. Fu,^(b) A. Kaldor, R. Sherwood, and D. Sondericker

Exxon Research and Engineering Co., Route 22E, Annandale, New Jersey 08801

(Received 15 September 1989)

We report measurements of the valence- and core-level photoemission spectra of mass-selected monodispersed Pt clusters. For individual samples consisting of the platinum atom through the six-atom cluster deposited onto a silica substrate, we have followed the development of the individual valence-band electronic structure and the Pt 4*f* core-electron binding energy, and conclude that such small metal clusters do not yet exhibit metallic character.

PACS numbers: 79.60.Cn, 36.40.+d, 73.20.Dx

The development of the electronic structure as single atoms are put together to form a solid has been an intriguing subject of research over the past decades.¹⁻³ There are very fundamental questions to be answered about the onset of metallic behavior in small metal clusters^{4,5} or the influence of quantum size effects on the electronic structure of small particles. Apart from these fundamental aspects small clusters also represent new materials to the extent that their physical or chemical properties are different from those of the bulk materials.⁶ As such, small metal particles deposited onto various substrates are widely used as catalysts and have been shown to exhibit different catalytic properties depending on cluster size.^{7,8}

Most of the previous experimental studies of the electronic structure of deposited (supported) small metal clusters were carried out on evaporated or sputtered thin films^{1-3,9,10} or samples prepared by decomposition of organometallic precursors,^{11,12} where the average particle-size distribution was inferred from different observations. Here we present the first valence- and core-level photoemission data of mass-selected, monodispersed, Pt clusters deposited onto a Si wafer which was covered by a thin layer of natural oxide. We have chosen Pt since small Pt clusters supported by various semiconducting or insulating substrates are widely used in catalysis. The thin native-oxide layer of the Si substrate has a band gap of more than 9 eV,¹³ which largely eliminates charge transfer to or from the clusters in the ground state. In the language of catalysis the SiO₂ substrate is classified as exhibiting no, or only a very weak, metal-support interaction.^{7,8}

Pt cluster ions are produced by rare-gas (Xe⁺) ion sputtering of a Pt target.¹⁴⁻¹⁷ As described elsewhere,¹⁶⁻¹⁸ the cluster ions are energy and mass selected with a quadrupole mass filter and then deposited at room temperature onto a silicon wafer. The Pt cluster energy is 10 ± 5 eV. In order to limit the nucleation of the deposited clusters on the Si wafer surface, the cluster coverage is kept below 1×10^{14} cm⁻² as determined by measurement of the total charge deposited.

After deposition the samples are transported in a small

UHV vacuum system (10^{-8} Torr) to the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory and inserted into the UHV photoemission setup (10^{-10} Torr) at the U1 beam line.¹⁹ The electrons are analyzed by a commercial hemispherical electron-energy analyzer (Microscience HA 100). The Si 2*p* core levels of the substrate, taken simultaneously with the Pt 4*f* core levels, serve as an internal standard for the photon energy, and to verify that no charging or band bending occurs.

The Pt 4*f* core-level photoemission spectra for clusters containing from one to six Pt atoms are shown in Fig. 1. Clearly the binding energy of the Pt 4*f* levels, measured relative to the Fermi level, changes with cluster size. The binding energy of the Pt 4*f*_{7/2} line for the deposited atom is about 2 eV larger than bulk Pt metal (71.2 eV). The solid curves are the result of a curve fit, where after subtraction of a linear background function, each 4*f* line is approximated by a Lorentzian folded into a Gaussian of 0.6 eV FWHM, which represents the combined resolution function of the monochromator and electron spectrometer. The binding energies and the Lorentzian widths (FWHM) of the 4*f*_{7/2} levels are plotted in Fig. 2(a) for Pt₁ through Pt₆. The 4*f* binding energies of the deposited atom (and clusters) reported here are significantly larger than any previous value for the lowest-coverage deposits produced by evaporation,^{1,3,7,9} supporting the assumption that the atoms and clusters remain well dispersed, and the fact that each sample exhibits a different width and shift is evidence that (a) most clusters remain intact upon deposition, and (b) do not aggregate after deposition.

This raises the question as to the oxidation state of the Pt clusters, i.e., whether part of the observed binding energy shift is due to a chemisorption-induced shift. From a surface-science point of view the deposition and transport conditions are not ideal. Nevertheless, we feel that we can argue against contamination of the clusters, except possibly by hydrogen, for the following reasons:

(1) The chemical shifts for various Pt oxides and hydroxides are well known,^{20,21} typically being about 3 eV for the stoichiometric compounds, significantly larger

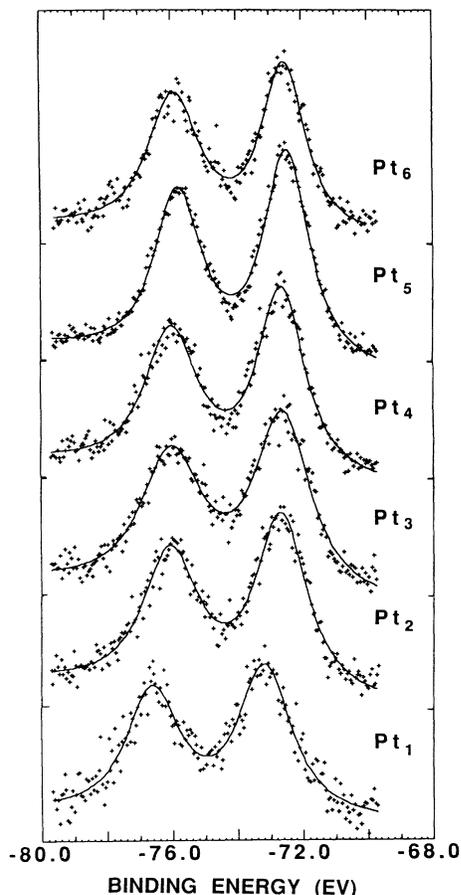


FIG. 1. Pt $4f$ core-level photoemission for monosize clusters deposited onto an oxidized Si(100) wafer. The spectra were taken at a photon energy of 280 eV with an overall resolution of 0.6 eV. The cluster size is indicated next to each curve and the binding energy is referenced to the substrate Fermi level. The binding energy of the $4f_{7/2}$ level of bulk Pt metal is 71.2 eV.

than the maximum shift measured here (2 eV for Pt atom). Moreover the $4f$ lines of a cluster, for example, Pt₅, might be expected to exhibit a multiple-peak substructure or significant broadening since it is not likely that only the stoichiometric compound will be formed in all cases.

(2) X-ray photoemission spectroscopy (XPS) studies of commercial Pt catalysts, which consist of large (> 100 atoms) Pt particles highly dispersed on a support, exhibit an oxide core-level shift of about 2 eV which disappears upon H reduction of the catalyst.²² Our largest cluster contains only six atoms and exhibits a core-level shift of only 1.3 eV, indicating that it is not oxidized.

(3) No features are observed in the valence-band spectra discussed below suggesting the presence of molecular adsorbates such as CO.

The values for the $4f$ binding energies of Pt₁ through Pt₆ clusters decrease with increasing cluster size, in con-

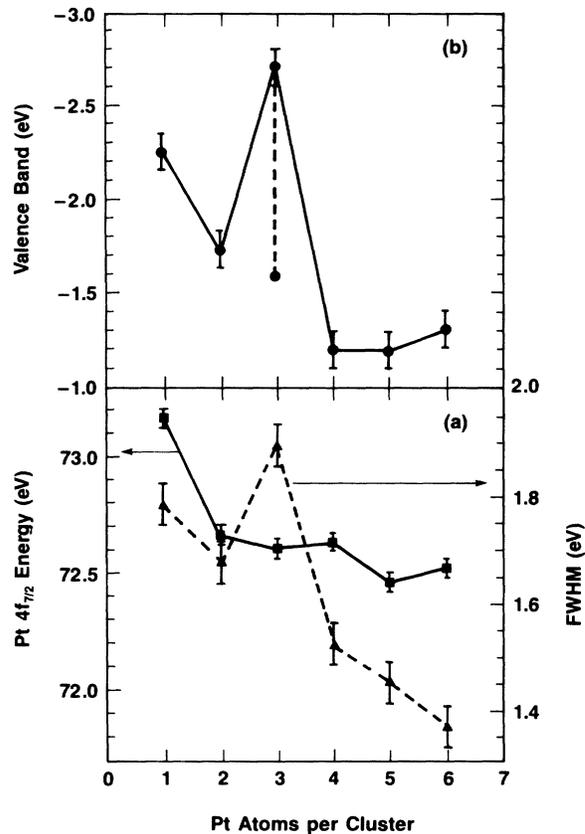


FIG. 2. (a) Energy position and width (FWHM) of the Pt $4f_{7/2}$ peaks of the deposited clusters as a function of cluster size. For comparison the binding energy of bulk Pt is 71.2 eV and the width less than 0.5 eV. (b) Top of the cluster valence band measured relative to the substrate Fermi level (5.1 eV) as a function of cluster size. To obtain the electron binding energy of the clusters the magnitude of the numbers should be increased by 5.1 eV. See text for discussion of the two values shown for Pt₃.

trast to earlier results where a constant energy was reported for the lower coverages of deposited metal,^{1,2,9,10} but consistent with observations on larger gold clusters deposited on carbon.⁵ Such shifts might possibly be explained by purely a change in the final-state relaxation, but based on photoemission results alone, we cannot unambiguously differentiate between initial- and final-state effects. The observation that the core-level shift differs from the valence-band energy shift for most clusters (see Fig. 2) rules against core-level shifts being caused by a change in "reference level" or work function of the clusters, as was previously suggested for Pt particles embedded in SiO₂.³ Finally, as expected, we note that the spin-orbit splitting of the $4f$ levels for all the clusters remains near 3.35 eV as in bulk Pt metal.

Note that except for Pt₃, which will be discussed below, both the core binding energies and the linewidths decrease with increasing cluster size in agreement with earlier results.^{1,2,5,9} We attribute this fairly large ob-

served linewidth to phonon broadening in addition to broadening induced by inhomogeneities in the sample. As the cluster size increases, the phonon coupling to the Si-oxide layer becomes weaker and the linewidth approaches the value of bulk Pt. In addition, the $4f$ core levels do not exhibit the characteristic asymmetry observed for bulk metals, indicating that the clusters are not yet metallic. The nonmetallic character is also confirmed by the valence-band results discussed below.

On the SiO_2 substrates the cluster valence electron states show up in an energy range where substrate emission is nearly absent. Figure 3 shows the valence-band photoemission spectra of the various cluster samples taken at 40 eV. The solid curves result from cluster samples deposited on the Si wafer, whereas the dashed curves are results from a piece of the same Si wafer without any clusters. For the samples containing clusters additional emission is observed at binding energies less than the top of the Si-oxide valence-band emission, which is 4.9 eV below the Fermi level.¹³ This "new" emission is entirely due to the photoemission from the valence states of the deposited clusters as is more clearly seen in the difference curves shown on the right-hand side of Fig. 3.

Since the interpretation of difference curves becomes uncertain in a region where there is a strong emission from the Si wafer, we discuss only states with a binding energy less than 5 eV below E_F . The top region of the density of states does not exhibit the characteristic modified step function of the metallic Fermi level (within our overall resolution we expect a Fermi-level width of about 0.3 eV), nor is it close in energy to the Fermi-level position. Whereas hole localization might account for a shift in energy,^{2,10} the missing step-function change is rather conclusive evidence of the nonmetallic character of these small clusters. Therefore we determine the location of the highest filled cluster valence states by linear extrapolation as conventionally done for semiconductors. These values are plotted in Fig. 2(b) and show a strongly size-dependent IP as observed previously in studies of gas-phase transition-metal clusters.²³ In the determination of IP's we had to take into account that the Pt $6s$ -derived states located at the top of the valence band become clearly discernible only at higher photon energy (e.g., 120 eV) due to relative changes in the cross section.²⁴

The Pt atom has an IP of 8.98 eV and a ground-state valence electronic configuration of $5d^96s$, where the $5d^{10}$ configuration is about 0.75 eV higher in energy.²⁵ The extrapolated valence-band edge of the deposited atom is located at 2.25 eV below the Fermi level of the substrate. Adding the work function of the substrate [5.1 eV (Ref. 13)] to this value, the IP of the deposited atom is 7.35 eV. Similarly the IP of the deposited dimer is 6.9 eV compared to 8.68 eV for the gas-phase dimer.²⁶ Thus we conclude that the substrate contributes about 1.6–1.8 eV of extra atomic screening energy. Substrate screening also lowers the core-level energies by a similar amount.

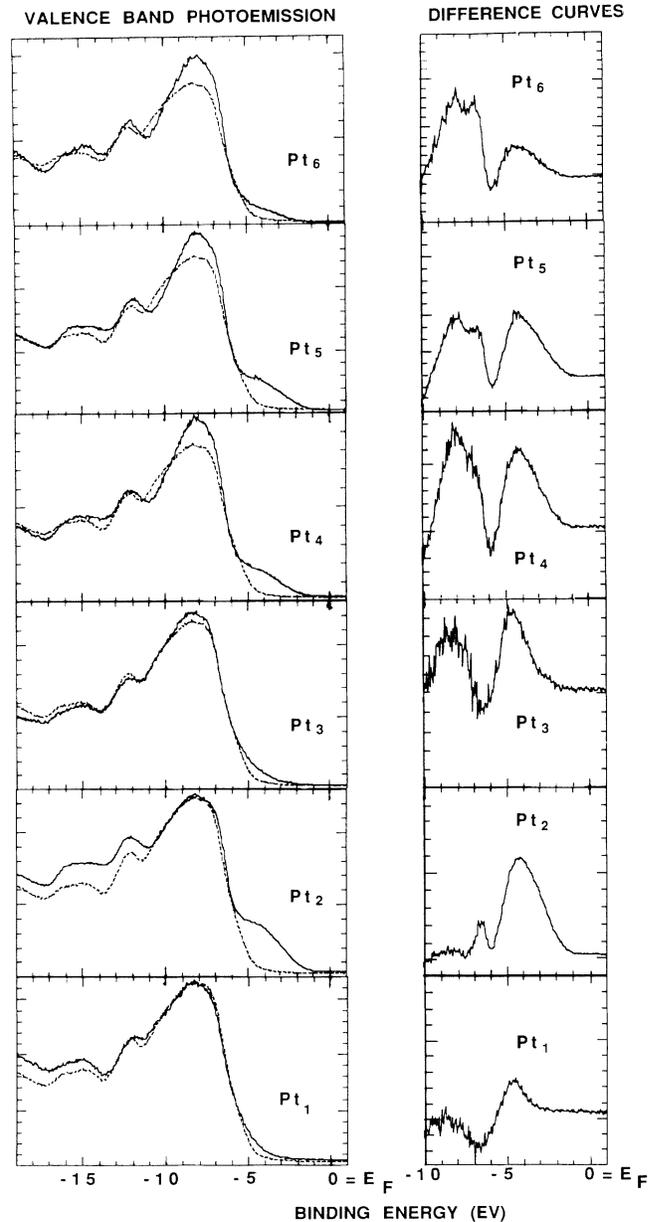


FIG. 3. Valence-band spectra of the deposited clusters taken at a photon energy of 40 eV and overall resolution of 0.25 eV. The dashed curves show the emission of the same kind of substrate, taken under similar conditions. The difference curves are shown on the right-hand side.

Previous estimates of the screening contribution to the core-level energies were 1 eV (Ref. 7) to 1.2 eV (Ref. 1).

The Pt_3 valence-electron-emission spectrum shows an onset at 1.6 eV followed by a second rise at 2.7 eV below E_F . These features do not exhibit any relative cross-section variation with photon energy. Thus we propose that two Pt_3 isomeric configurations are present, possibly one triangular and one linear, or two different bent structures. This assignment is also supported by the unusually large width observed for the $4f$ levels of Pt_3 (see Fig.

2), where superposition of both sets of core levels would, if unresolved, result in an apparent broadening of the lines. In addition, we note that the J -averaged d^8s^2 and d^9s^1 atomic configurations differ little in energy. This suggests that the linear and triangular structures may be nearly isoenergetic, similar to theoretical predictions for the nickel trimer.²⁷

In summary, photoemission studies of Pt₁ through Pt₆ deposited on SiO₂ exhibit individual, discrete electronic-structure features characterized by unique valence-band energies and Pt 4*f* core-level binding energies and widths. This confirms that we are able to prepare supported metal cluster systems with individually selected cluster sizes. Since each size cluster may exhibit unique materials and chemical properties, we now plan to characterize such species by probing not only their electronic and structural properties, but also their chemical activity as a function of cluster size and support material.

The photoemission measurements were carried out at the U1 beam line at NSLS, Brookhaven National Laboratory. The NSLS is supported by the U.S. DOE, Office of Basic Energy Sciences.

^(a)Present address: Ecole Polytechnique Federale de Lausanne, CH-1015 Lausanne, Switzerland.

^(b)Permanent address: Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian, People's Republic of China.

¹M. G. Mason, Phys. Rev. B **27**, 748 (1983), and references therein.

²S. B. DiCenzo and G. K. Wertheim, Comments Solid State Phys. **11**, 203 (1985), and references therein.

³V. Murgai, S. Raaen, M. Strongin, and R. F. Garrett, Phys. Rev. B **33**, 4345 (1986); S. Raaen and M. Strongin, Phys. Rev. B **32**, 4289 (1985).

⁴C. Brechignac, M. Broyer, Ph. Cahuzac, G. Delacretaz, P. Labastie, J. P. Wolf, and L. Woste, Phys. Rev. Lett. **60**, 275 (1988).

⁵S. B. DiCenzo, S. D. Berry, and E. H. Hartford, Jr., Phys. Rev. B **38**, 8465 (1988).

⁶A. Kaldor, D. M. Cox, and M. R. Zakin, in *Advances in*

Chemical Physics, Vol. 70, edited by I. Prigogine and Stuart A. Rice (Wiley, New York, 1987), p. 211, and references therein.

⁷A. Masson, B. Bellamy, Y. Hadj Romdhane, M. Che, H. Roulet, and G. Dufour, Surf. Sci. **173**, 479 (1986).

⁸For a recent review, see, R. Burch, *Catalysis* (The Royal Society of Chemistry, London, 1985), Vol. 7, p. 149, and references therein.

⁹T. T. P. Cheung, Surf. Sci. **127**, L129 (1983); **140**, 151 (1984).

¹⁰G. K. Wertheim and S. B. DiCenzo, Phys. Rev. B **37**, 844 (1988).

¹¹E. W. Plummer, W. R. Salaneck, and J. S. Miller, Phys. Rev. B **18**, 1673 (1978).

¹²P. Legare, Y. Sakisake, C. F. Brucker, and T. N. Rhodin, Surf. Sci. **139**, 316 (1984).

¹³F. J. Himpsel, F. R. McFeely, A. Taleb Ibrahimi, J. A. Yarmoff, and G. Hollinger, Phys. Rev. B **38**, 6084 (1988).

¹⁴G. Hortig and M. Miller, Z. Phys. **221**, 119 (1969).

¹⁵F. M. Devienne and J. C. Roustan, Org. Mass. Spectrom. **17**, 173 (1982).

¹⁶P. Fayet and L. Woste, Spectrosc. Int. J. **3**, 91 (1984); Surf. Sci. **156**, 134 (1984); Z. Phys. D **3**, 177 (1986).

¹⁷W. Begemann, S. Dreihöfer, K. H. Meiwes-Broer, and H. O. Lutz, Z. Phys. D **3**, 83 (1986).

¹⁸P. Fayet, D. M. Cox, and A. Kaldor (to be published).

¹⁹M. Sansone, R. Hewitt, W. Eberhardt, and D. Sonnericker, Nucl. Instrum. Methods Phys. Res., Sect. A **266**, 422 (1988).

²⁰M. Peuckert and H. P. Bonzel, Surf. Sci. **145**, 239 (1984).

²¹K. Duckers, K. C. Prince, H. P. Bonzel, V. Chab, and K. Horn, Phys. Rev. B **36**, 6292 (1987).

²²W. Hoffmann, M. Graetzl, and J. Kiwi, J. Mol. Catal. **43**, 183 (1987).

²³R. L. Whetten, D. Cox, D. J. Trevor, and A. Kaldor, Phys. Rev. Lett. **54**, 1494 (1985).

²⁴J. J. Yeh and I. Lindau, At. Data Nucl. Data Tables **32**, 1 (1985).

²⁵C. E. Moore, in *Atomic Energy Levels*, edited by C. C. Keiths, NBS Circular No. 467 (U.S. GPO, Washington, DC, 1971).

²⁶S. Taylor, C. W. Lemire, Y. M. Hamrick, Z. Fu, and M. D. Morse, J. Chem. Phys. **89**, 5517 (1988).

²⁷S. P. Walch, J. Chem. Phys. **86**, 5082 (1987). Although similar calculations have not yet been performed for Pt, Walch found the linear and triangular structures for nickel trimers to differ in energy by only 0.1 eV.