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TECHNICAL COMMENTS

Metal-Metal Bonds in Bimetallic Surfaces

J. A. Rodriguez and D. W. Goodman show (1) an interesting correlation between core-electron binding-energy shifts and desorption temperatures for monolayer metal adsorbates on transition metal substrates. From the shift they deduce a charge transfer that turns out to be "completely contrary to that observed in bulk alloys." This deduction is most unexpected and warrants further discussion. We used a Born-Haber cycle to clarify the origin of the observed correlation of binding-energy shift with desorption temperature and point out that there are other important contributions to the shift, not mentioned in the article, that preclude a simple connection with charge transfer.

The correlation between binding energy and desorption temperature has a well-known theoretical basis. It arises because the desorption temperature provides a measure of the adsorption enthalpy. A simple expression for the core-electron binding-energy shift from the bulk metal to the adsorbed monolayer, each measured relative to its own Fermi level, is readily obtained from the corresponding Born-Haber cycles (2):

$$\Delta E_{\text{ads}}^{\text{B}} = (E_{\text{ads}}^{\text{Z}} - E_{\text{ads}}^{\text{Z}+1}) - (E_{\text{coh}}^{\text{Z}} - E_{\text{coh}}^{\text{Z}+1}) + \Delta E_{\text{imp}}^{\text{Z}+1 \rightarrow \text{Z}} \quad (1)$$

In this formulation the E_{ads} are adsorption enthalpies, the E_{coh} are bulk cohesive energies, and the superscripts Z and Z + 1 denote the adsorbate element and the element with next high atomic number. The Z + 1 term enters the equation through an equivalent-cores argument (2). The cohesive energy terms are properties of the bulk metals and are independent of the substrate. The last term is the difference between the monolayer and bulk implantation energies (2). These are the energies obtained when a Z + 1 atom is moved from an environment of Z + 1 atoms to one of Z atoms. This term should be small, but it is important if quantitative results are required. Thermodynamically sound Born-

Haber expressions of this type provide good estimates of core-electron binding energies in metals (2) as well as of binding-energy shifts of adsorbates (3). The important point is that the Z and Z + 1 adsorption enthalpies enter the equation on equal terms but with opposite signs. The simple correlations shown in the figures of the article by Rodriguez and Goodman tell only half the story. One should not conclude that such correlations are typical of all adsorbate systems, because even the sign of the shift will change if the Z + 1 atom is more strongly adsorbed than the Z atom. It would be interesting to compare the data in the article (1) with the predictions of Eq. 1.

Unfortunately, the Born-Haber treatment gives no clue about the charge transfer between adsorbate and substrate. However, binding-energy shifts in metals and alloys depend not only on charge transfer, but also on changes in reference level, hybridization, and final-state screening (4). The fact that charge transfer alone cannot explain the observations became inescapable when it was found experimentally in many noble and transition metal alloy systems that the core-electron binding-energy shift of both components has the same sign. This demonstrates that some of the other terms can be as large or larger than the charge-transfer contribution. Changes in screening and hybridization are likely to make large contributions for alloys with Ni and Pd. Changes in reference level are important when metals with different work functions are combined. Correlations between differences in work function and core-electron binding energy demonstrate the importance of the reference-level term. These additional terms are equally relevant to adsorbate layers. There is no more justification for using the core-electron binding-energy shift as a simple indicator of charge transfer in bimetallic systems than there is for using it in alloys. When the charge transfer in these systems is properly evaluated, the disagreement with the behavior of

bulk alloys is likely to vanish.

There are cases in which charge transfer is the major source of core-electron binding-energy shifts (5), for example, in molecular systems and insulating solids. In these systems the charge transfer is between well-defined, localized electronic orbitals; while in bimetallic systems the charge flow is between delocalized conduction band states that may contain contributions from both substrate and overlayer orbitals, making it difficult even to define the charge transfer (5).

For the adsorbate systems discussed in the article by Rodriguez and Goodman (1), it would be of great interest to measure not only the core-electron binding-energy shift of the adsorbate but also the effect of the adsorbate on the surface layer of the substrate. This should present no difficulty because the signal from the first atomic layer of the substrate is readily resolved in photoemission (6) for some of the metals discussed in the article. Such data could add an important new dimension to this study and might lead to a better understanding of the interaction between substrate and adsorbate.

G. K. Wertheim

J. E. Rowe

AT&T Bell Laboratories,
Murray Hill, NJ 07974

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Response: The conclusions in our article were based not only on a correlation between core-level binding-energy (CLBE) shifts and desorption temperatures of metal adsorbates but also on correlations between CLBE shifts and results of work function measurements, ultraviolet photoemission spectroscopy (UPS), CO thermal desorption mass spectroscopy (CO-TDS), CO Fourier transform infrared spectroscopy (CO-FTIR), and CO high-resolution electron energy loss spectroscopy (CO-HREELS). As pointed out by Wertheim and Rowe, CLBE shifts may "depend not only on charge transfer, but also on changes in reference level, hybridization, and final-state screening. . . ." Taking this into consideration, we compared the charge-transfer

predictions of x-ray photoelectron (XPS) binding energy with the predictions of other experimental techniques and found general agreement (1, 2). For example, in the case of Pd/Ta(110), the direction of charge transfer predicted by XPS agrees with results of work function measurements, UPS, CO-FTIR, CO-HREELS, and CO-TDS (1, 2). In a similar way, XPS and all the other techniques indicate that Pd transfers more charge to W(110) than to Ru(0001) (1, 2). We cannot rule out that orbital rehybridization and final state effects contribute to the core-level shifts of the metal adlayers. Nevertheless, all the experimental data discussed in our article indicate that the CLBE shifts of Cu, Ni, and Pd overlayers are dominated by charge-transfer effects.

To the best of our knowledge, figures 2, 3, and 4 in our article represent the first systematic study showing a correlation between experimental values for core-level binding energies and desorption temperatures of metal adlayers. It is not clear that equation 1 of the comment by Wertheim and Rowe can reproduce the numerical values or explain the experimental trends reported in our article. The derivation of this equation involves several approximations (3), and the $\Delta E_{\text{imp}}^{Z+1 \rightarrow Z}$ term is difficult to evaluate in a precise way (3, 4). Thus, for most systems a real quantitative test of equation 1 is not possible. If the term $\Delta E_{\text{imp}}^{Z+1 \rightarrow Z}$ is approximately consistent, then any trend in the difference in CLBE between the bulk metal and an adsorbed monolayer supported in a series of substrates should be given by $E_{\text{ads}}^Z - E_{\text{ads}}^{Z+1}$, with the adsorption energies of the Z and Z+1 species varying from one substrate to another. The difference between the adsorption energies of Pd and Ag on Ru(0001), about 1.1 eV (1, 2, 5), is larger than the corresponding difference on W(100), about 0.8 eV (6, 7). According to equation 1, the CLBE shift for supported Pd should be about 0.3 eV larger on Ru(0001) than on W(110). This is not observed in the experimental measurements, which show a CLBE shift for Pd/W(110) that is about 0.5 eV larger

than that of Pd/Ru(0001) (1, 2). Similar discrepancies appear when one compares the predictions of equation 1 and the experimental data for Ni and Cu adlayers. It may be argued that the variations in the $\Delta E_{\text{imp}}^{Z+1 \rightarrow Z}$ term from one substrate to another will bring the predictions of equation 1 and the experimental results into better agreement, but it is difficult to imagine how this term will cancel the error in all cases, especially when one takes into consideration that the absolute sign of the error may change from one system to the other. The results for Cu/Pt(111) (8) show CLBE shifts, calculated with the use of a Born-Haber cycle and the Z+1 approximation, that are about 38% larger than the experimental values. The equivalent core approximation, a priori, may not be valid for the bimetallic systems discussed in our article for several reasons (9), including differences in the effective size of the atoms and charge transfer effects.

Wertheim and Rowe propose that a measurement of the shift induced by the admetal on the core levels of the metal substrate should give additional information about the properties of the metal-metal bond. This is an excellent idea, provided the shift in the core levels of the metal substrate are analyzed in a proper way. Previous studies indicate that shifts induced by an adsorbate on the core levels of a metal surface are sensitive to changes in the coordination number of the metal atoms, orbital rehybridization, and final-state effects (10). Any conclusion about charge transfer will require comparison with the results from other experimental techniques, as we did for the CLBE shifts of the metal adlayers.

Our model for metal-metal bonding on surfaces is based on general trends observed for Cu, Ni, and Pd films supported on several metal substrates. It explains the experimental data in a simple and clear way. The results of several techniques indicate that the direction of charge transfer in a bimetallic surface can be opposite to that predicted by bulk electronegativities and observed in bulk alloys. The phenomena

responsible for this difference in behavior are not well defined; a possible cause is a variation in the coordination number or in the geometrical arrangement of the metal atoms (11). The bimetallic systems discussed in our article contain elements with similar electron donor-electron acceptor properties. It is likely that the bonds in these systems are mainly covalent with a small, yet important, degree of ionic character. For this type of system, a change in the number of neighbors or in the structural geometry could alter the bonding capabilities of a metal atom, modifying the subtle balance that determines the flow of charge within the metal-metal bond.

José A. Rodriguez

Department of Chemistry,
Brookhaven National Laboratory,
Upton, NY 11973

D. Wayne Goodman

Department of Chemistry,
Texas A&M University,
College Station, TX 77843

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