

**Riffe, Wertheim, and Citrin Reply:** In the above Comment, Bagus and Pacchioni [1] show that the effect of a screened, bare, external positive charge on the core-electron binding energy of surface atoms in a Cu cluster is much smaller than the shift obtained with the cluster orbitals kept frozen. For a unit positive charge, which is meant to represent an adsorbed alkali ion, their calculations give a net shift of  $-120$  meV, but with an estimated uncertainty of  $\sim 100$  meV.

The cluster calculations with a bare external charge, representing a hypothetical, fully ionized alkali adatom are applicable only in the limit of low coverage, because even at moderate coverage, a partially occupied alkali  $s$  band is known to form [2]. Accordingly, the comparison with experimental data must be based not on substrate surface-atom binding energy shifts measured at saturation coverage, but on those at very low coverage. In our Letter [3], such energy shifts were quoted only for  $\frac{1}{3}$  monolayer and saturation alkali adatom coverages. Additional results are shown in Fig. 1. Note that the W  $4f$  binding energy shifts at low coverage are positive for all three alkali metals, i.e., opposite in sign to that obtained from the cluster calculation. Experimental shifts that can be compared to those calculated in Ref. [1] are obtained by extrapolating the initial slope to saturation coverage, yielding  $+5$ ,  $+22$ , and  $+8$  meV for Na, K, and Cs, respectively, compared to a calculated shift of  $-120$  meV. Changes in final state screening cannot be responsible for this discrepancy, since the improved screening due to the additional charge density in the substrate conduction band would make the calculated binding energy even more negative.

The observed crossover to negative shift in Fig. 1 is associated with the decrease in dipole moment per adsorbate atom where the alkali atoms begin to form a partially occupied metallic  $s$  band [2], enhancing the screening of the W surface-atom core hole. In the ionic model, back donation would make the shift deviate in a positive direction, contrary to the data. The total excursion of the binding energy in Fig. 1 is  $\leq 30$  meV for all three alkalis. Thus, not only are the extrapolated low-coverage shifts of opposite sign from those calculated [1], but they as well as the excursion of the shifts over the full range of coverage are small compared to the calculated ionic value whose large uncertainty precludes meaningful comparison with experimental data.

It is argued [1] that the key feature of the calculations is to show that even for a fully ionized adatom the shifts are small. However, they are small only relative to the shifts of several eV obtained by keeping all the atomic orbitals around the core hole frozen, shifts which are theoretical constructs that have no relevance to physical reality. A more relevant comparison can be made with experimental surface-atom shifts for the clean metal surface, where charge flow is small, and with those due to adsorbed O [3] or H [4], where the shifts are approximately an order of magnitude larger than those due to

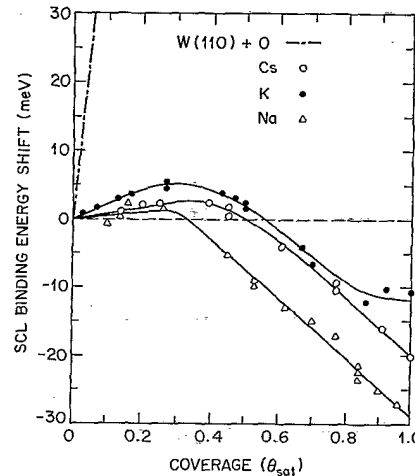


FIG. 1. Change in W  $4f$  surface-atom core-level binding energy produced by various adsorbates on W(110), plotted vs the fractional saturation coverage.

the alkalis.

The relatively large negative shift obtained for a positive test charge [1] is most likely due to the unrealistic nature of the model, which forces the screening charge to be in substrate conduction band states. A more realistic calculation would place charge in a hybridized orbital [5], resulting in a shift in better agreement with the data. We maintain that the observed small, positive shifts at low coverage are indicative of covalent bonding, in line with the conclusion drawn not only in our work, but in the majority of subsequent alkali adsorption experiments [6-10].

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