Abstract: Orbital shifts associated with chemical bonding of organic molecules on ZnO nonpolar surfaces*

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Several recent experiments on transition-metal surfaces have demonstrated the value of uv photoemission spectroscopy (UPS) for understanding the chemisorption of molecular adsorbates on solid surfaces. In these experiments adsorption-induced changes in the binding energy of molecular orbitals from their free-molecule values were observed. These shifts involve two effects of comparable size: (i) extramolecular relaxation/polarization shifts present for all orbitals and (ii) chemical bonding shifts of those orbitals directly involved in chemisorption bonding of the molecule to the surface. Since for all orbitals of a particular adsorbed molecule the relaxation/polarization shifts appeared to be essentially the same, the orbitals forming the chemical bond to the surface could be identified.

We have used UPS at $h\nu = 40.8$ eV to observe the position of valence orbitals of a wide variety of organic molecules adsorbed on atomically clean ZnO (1100) nonpolar surfaces in ultrahigh vacuum at 120 and 300 K. ZnO is at the same time a metal oxide known to be catalytically active and also a wide-gap tetrahedral semiconductor (wurtzite structure). Of particular interest is the behavior of organic molecules containing $\pi$ and lone-pair electron orbitals. These orbitals should be active in chemisorption bonding because they are energetically highly lying (weakly bound) and because they protrude significantly from the molecule.

A number of molecules (e.g., $\text{C}_6\text{H}_6$, $\text{H}_2$, $\text{O}_2$, CO) produce no significant changes in the ZnO UPS spectrum at either 300 or 120 K, except for small band-bending changes which rigidly shift the entire spectrum in energy by $\approx 0.1$–0.3 eV. At 300 K, strong changes in the shape of the spectrum are found only for adsorbates which decompose on the surface (e.g., HCOOH). At 120 K, many molecules adsorb to produce marked spectral changes in the UPS spectrum. Compared to their gas-phase counterparts, the adsorbate orbitals appearing in the difference spectrum are in each case shifted upward (to smaller binding energies) by an increment $\Delta E_p$ which in many cases (e.g., $\text{O}_2$, $\text{C}_6\text{H}_6$) is essentially constant for all orbitals. In nearly all of the remaining cases, the highest-lying orbital(s) (at smallest binding energy) deviate from this pattern. We associate the upward shift of all orbitals with extramolecular relaxation/polarization effects. Since these shifts are uniform for most of the orbitals, as in the case of hydrocarbons on transition metals, similarly useful conclusions can be made from the UPS spectra of such semiconductor surfaces as ZnO about the nature of the chemisorption bond. With the assumption of a uniform relaxation/polarization shift for all orbitals, we then attribute the additional shift of high-lying orbitals to chemical bonding to the surface via those orbitals.

As in the case of Ni(111), benzene ($\text{C}_6\text{H}_6$) exhibits a dominant bonding shift ($\Delta E_B \approx 0.6$ eV on ZnO) for the highest-lying, doubly degenerate $\pi$ orbital. We observe an additional bonding shift $\Delta E_B \approx 0.3$ eV for two orbitals (from $\sigma$ and $\pi$) at larger binding energy. It is interesting to note that while both $\text{C}_2\text{H}_2$ and $\text{C}_2\text{H}_4$ chemisorb readily on Ni(111) with significant bonding shifts, $\text{C}_2\text{H}_4$ does not adsorb appreciably on ZnO(1100), and $\text{C}_2\text{H}_4$ displays only relaxation/polarization effects (without any additional chemical bonding shifts) and thus seems to be simply physisorbed.

Ethylene oxide ($\text{C}_2\text{H}_4\text{O}$), methanol ($\text{CH}_3\text{OH}$), and acetone ($\text{CH}_3\text{CO}$) display bonding shifts $\Delta E_B \approx 0.4$ and 0.7 eV, respectively, for their highest-lying, oxygen lone-pair orbitals. In dimethyl sulfoxide ($\text{CH}_3\text{SO}$) the highest-lying orbital undergoes a bonding shift $\Delta E_B \approx 1.2$ eV. One low-lying orbital of (CH$_3$)$_2$SO exhibits a shift on adsorption which is significantly different (~1 eV) from the uniform relaxation/polarization shift of all other low-lying orbitals. Adsorbed CO, produced by $\text{H}_2$+CO coadsorption at 120 K or by formic acid (HCOOH) decomposition at 300 K, reveals bonding shifts $\Delta E_B \approx 1.0$ and 0.6 eV for both its highest-lying 5$\sigma$ (carbon lone-pair) and 1$\pi$ orbitals, respectively. This multiple-bonding behavior for CO may be a consequence of the open atomic structure and directed-bond character of the partially covalent ZnO surface.

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