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INITIAL STATE SHIFT OF THE C2S LEVELS OF CHEMISORBED HYDROCARBO--ETC(U)
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**INITIAL STATE SHIFT OF THE C_{2s} LEVELS OF CHEMISORBED
HYDROCARBONS ON Ni**

by

J. E. Demuth

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IBM Thomas J. Watson Research Center
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Initial State Shift of the Carbon 2s Levels of Chemisorbed Hydrocarbons on Nickel†

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Typed by: W. L. Wilson

Abstract: UV photoemission results using filtered $h\nu = 40.8$ eV radiation show strong shifts in the low-lying C 2s-derived levels of chemisorbed hydrocarbons on Ni relative to the higher-lying σ -levels. These differential shifts provide evidence for initial state potential and/or rehybridization effects which are important in interpreting high-lying valence orbital shifts and the bonding of chemisorbed species.

† This work was partially supported by the Office of Naval Research

Here, we present filtered $h\nu = 40.8$ eV photoemission results for chemisorbed hydrocarbons on Ni which show a new type of chemisorption-induced shift in the low-lying C 2s-derived states that has not been detected for other chemisorption systems. Namely, we find that the ionization levels of the low-lying C 2s-derived σ -states are shifted by ~ 1 eV to larger electron binding energies and broadened relative to the ionization levels of the σ_{CC} and σ_{CH} -derived states - a similar effect as observed for the π -orbitals¹. These low-lying C 2s-derived valence states for chemisorbed hydrocarbons have not been observed previously nor have they been explicitly considered theoretically despite numerous recent calculations to better understand the bonding and energy level shifts of chemisorbed hydrocarbons².

We present evidence that these differential σ -level shifts arise in the initial state and are the result of either the asymmetry of the potential at the surface or surface-induced molecular rehybridization. Such effects are not only important in understanding the bonding of hydrocarbons to surfaces but may also be present in other systems. Thus, these results are of general importance for interpreting and relating high-lying valence orbital shifts of chemisorbed species to chemical bonding^{1,3,4}.

The experimental system is the same as that described elsewhere⁵ while the procedures used to prepare and clean the Ni(111), (100) and (110) samples have also been described previously^{1,5}. We note that the higher reactivity of the (100) and (110) surfaces requires the study of chemisorption on these surfaces at low temperatures ($T \sim 100$ K). Purified reagent grade hydrocarbons or ultra-high purity gases were used and checked for impurities by mass spectroscopy. The photoemission measurements were performed with a new high-intensity dc resonance lamp equipped with a 200-300Å carbon filter which completely suppressed the He I ($h\nu = 21.2$ eV) radiation so as to obtain essentially pure He II ($h\nu = 40.8$ eV) radiation as done in gas phase studies^(6,7). Typical count rates from the Ni d-bands for our filtered He II angle-integrated studies with a cylindrical mirror analyser were 50,000 counts per second for 0.25 eV resolution. The light source-sample analyser geometry is also identical to that described elsewhere⁵. Finally, we believe that our results are characteristic of angle-

integrated spectra as we see insignificant energy shifts in the adsorbate ionization levels for rotation and/or tilting of the sample relative to the light beam and energy analyzer which are both fixed.

Experimental Results: We present results here for chemisorption on the Ni(100) surface which are qualitatively similar to our results for the (111) and (110) Ni surfaces. In Fig. 1a we show a composite of the filtered He II N(E) spectra for a near saturation exposure of benzene ($\Delta\phi = -1.2$ eV) to Ni(100) at $T \sim 100$ K. In Fig. 1b, we show the difference in emission $\Delta N(E)$ after chemisorption as determined from direct subtraction of the N(E) spectra of the clean and benzene covered surface. For comparison we also show the $\Delta N(E)$ and N(E) spectra in Fig. 1c for a thick layer of condensed benzene (obtained under identical conditions) and two gas phase spectra. The first gaseous spectrum (solid line) was obtained with a similar energy analyzer, energy resolution and light beam/analyzer geometry as used here⁸. The second spectrum (dashed line) was obtained under different conditions in a higher resolution spectrometer⁷.

In order to facilitate comparison of the levels of chemisorbed benzene to gaseous and condensed benzene and to roughly account for initial state screening and final state relaxation effects^{1,9}, we have shifted the latter spectra toward smaller binding energies so as to arbitrarily align the high-lying σ_{CC} and σ_{CH} -derived levels. We also indicate in Fig. 1 the principle orbital character(s) of the benzene levels in the high resolution gas phase spectra as determined from ground state calculations we have made using an ab-initio SCF Hartree-Fock LCAO method (Gaussian-70¹⁰) with a 4-31G basis set. Here, the molecular orbitals derived primarily from C 2s atomic orbitals are denoted as ss-orbitals.

From the relative level positions in Fig. 1, we observe that chemisorption has caused significant orbital-dependent shifts in the low lying ionization levels of the free benzene molecule which were not observed in previous studies¹. Namely, in addition to a 1.2 eV shift of the π -level of chemisorbed benzene, the ss-levels are also shifted by 0.7, 0.6, and 0.3 eV, respectively, relative to the more uniformly shifted σ_{CC} and σ_{CH} levels. Designating the xy

plane as the molecular plane, we note that the levels derived from either the C $2p_z$ atomic orbitals (π -levels) or the C 2s atomic orbitals (ss-levels) are shifted relative to those derived from the C $2p_{x,y}$ atomic orbitals (σ_{CC} and σ_{CH} levels). Molecular orbitals having both C 2s and C $2p_{x,y}$ atomic components appear to be shifted according to the degree of admixture as seen for the four lowest lying valence levels of benzene (fig. 1) which have decreasing C 2s character and increasing C $2p_{x,y}$ character with decreasing binding energy. We also find additional level broadening (~ 0.3 eV) for the lowest lying ss-level.

We observe similar shifts in the valence levels of other unsaturated hydrocarbons chemisorbed on Ni, but not for the saturated hydrocarbons which only physically adsorb on Ni at low temperatures. Specifically, in Fig. 2, we show the ionization spectra of gaseous and chemisorbed C_2 hydrocarbons on Ni(100). Again, the ionization levels of the π and C 2s-derived levels are shifted to larger binding energies relative to the σ_{CC} and σ_{CH} -derived ionization features. Here, the ss^* -levels of acetylene and ethylene have less C 2s character and more C $2p_{x,y}$ character, and are less strongly shifted than the ss-levels. The preferential level broadening of the ss levels of acetylene and ethylene (~ 0.7 and 0.3 eV, respectively) are more clearly observed here than for benzene.

Discussion: A variety of initial and final state effects can occur together so as to shift molecular ionization levels upon adsorption^{1,9}. However, the differential shifts observed here for the C 2s-derived levels relative to the C $2p_{x,y}$ -derived levels are characteristic of rather specific initial state effects which for these cases appear to be larger than, for example, orbital-dependent relaxation effects.

Neither orbital-dependent extra-molecular relaxation effects for the C 2s versus the C 2p-derived states nor chemisorption-induced geometry changes are consistent with the observed differential level shifts. Namely, greater extra-molecular relaxation for the lower-lying, more core-like states - as observed for the C 2s-derived orbitals of certain organic molecules on ZnO^3 , as well as predicted for the more core-like orbitals of CO on Ni¹¹ and found for CO on Pt(111)¹² - is expected to shift the C 2s-derived states in an opposite sense

to that observed here. An opposite shift would also occur for orbital-dependent relaxation effects arising within either of two screening models: an image charge screening model¹³ where the molecule lies flat on the surface; or a molecular-like screening model¹⁴. Finally, our comparisons of calculated molecular orbital eigenvalues for free and distorted molecules show that the large shifts in the lowest lying C 2s-derived levels are not consistent with any likely geometry of benzene or the geometry of ethylene as deduced from the higher-lying σ_{CC} and σ_{CH} -derived levels. We note that vibrational loss spectroscopy for benzene chemisorbed on Ni(100) also suggests only small geometry changes upon chemisorption¹⁵.

The observed differential level shifts for these low-lying C 2s-derived states are consistent with an orbital-dependent initial state potential shift. The initial state potential is known to shift the core levels of implanted rare gas atoms by 2-3 eV to larger binding energies¹⁶. At a surface the asymmetry of the potential, i.e. the surface barrier, can cause orbital-dependent valence level shifts of 1-2 eV as theoretically found for the 3s, 3p_z and 3p_{x,y} orbitals of Si¹⁷. For a molecule on a surface, we also expect similar differential shifts which would depend upon the orientation of the molecule and its orbitals on the surface. Assuming the likely case that the hydrocarbon molecule lies parallel to the surface in the xy plane, the orbitals derived from C 2p_z and C 2s atomic components will be shifted to larger binding energies relative to those derived from C 2p_{x,y} atomic components. The relative magnitudes as well as the orbital character dependence of the observed differential level shifts for the C 2s-derived levels, e.g., the four ss-levels of benzene, are well explained by this type of initial state effect. We also expect a potential shift for the π -levels comparable to or greater than that for the purest C 2s-derived states. Finally, the observed broadening of the shifted C 2s-derived levels may arise from more efficient Auger neutralization, i.e., shorter lifetimes, for these photo-ionized states than those derived from the higher-lying valence states.

The relative shift of the C 2s-derived levels can also arise from the rehybridization of the C 2s and C 2p_z atomic orbitals during bonding - driven by the surface potential¹⁸ and/or covalent bonding. Such an effect is found to occur in our SCF Hartree-Fock LCAO calcula-

tions (Gaussian -70^{10}) of acetylene and ethylene bonded in a variety of geometries on 1 to 4 atom Be clusters. Here, rehybridization in conjunction with charge rearrangement, shifts the π - and ss -levels to larger binding energies relative to the σ -levels. Such rehybridization would imply that the C 2s atomic orbitals play an important role in bonding. Clearly, more detailed theoretical calculations are necessary to fully understand the C 2s shifts observed here and discriminate between these two possible effects.

Conclusions: In summary, new results are presented which show unusual differential level shifts and broadening of the low-lying C 2s-derived states of chemisorbed hydrocarbons on Ni. We provide evidence that these differential shifts arise in the ground state from an initial state potential effect and/or a rehybridization effect associated with a new mode of bonding. Such effects may occur in other chemisorption systems and are important in interpreting valence orbital energy level shifts and the nature of bonding from photoemission measurements. For example, the π -level shifts for chemisorbed hydrocarbons (or the 5σ level shift of CO) can occur independent of the bonding mechanism via potential shifts and/or rehybridization effects. Such non-chemically specific effects would explain why similar high-lying orbital "bonding" shifts are observed for adsorbates on different substrates, such as Cu or Ni, despite expected differences in the nature and/or strength of the chemisorption bonding interaction⁴.

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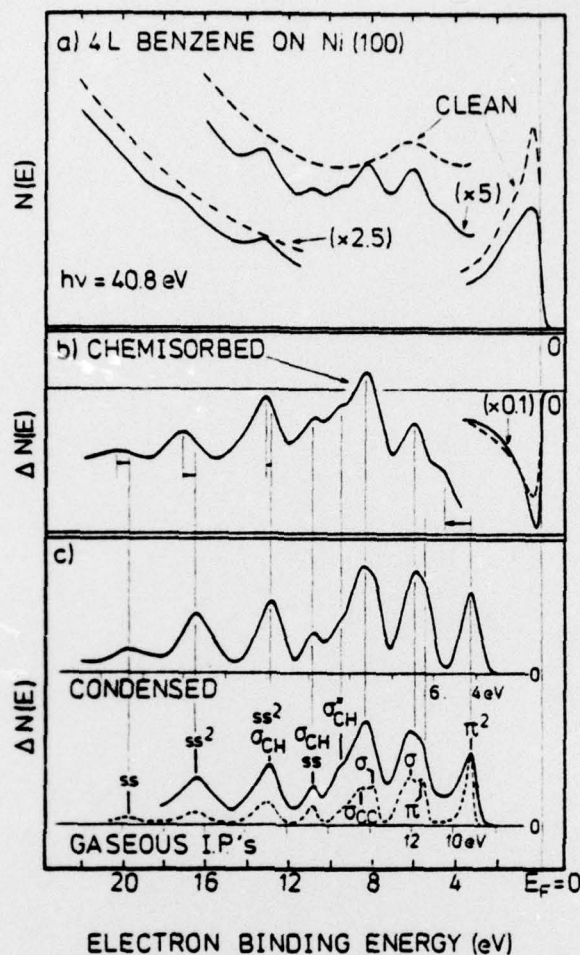


Figure Captions

Fig. 1. Photoemission spectrum $N(E)$ at $h\nu = 40.8$ eV for (a) clean Ni(100) ($\phi = 5.2$ eV) and for chemisorbed benzene on Ni(100) formed after a 4×10^{-6} Torr-second exposure of benzene to Ni(100) at $T \sim 100$ K ($\Delta\phi = -1.2$ eV). Comparison of the relative level positions of the $\Delta N(E)$ spectrum for chemisorbed benzene (b) are made with those of condensed and gaseous benzene (c)^{7,8} where we have labeled the principal orbital character of the ionization levels. (Here σ denotes equal σ_{CH} and σ_{CC} character). We note that we have reversed the ordering of the two levels at 11.6 and 12.2 eV (IP) from that calculated since the 11.6 eV levels appear to shift upon chemisorption - an effect which identifies the π -orbitals of several chemisorbed hydrocarbons on a variety of metals^{1,4,5}.

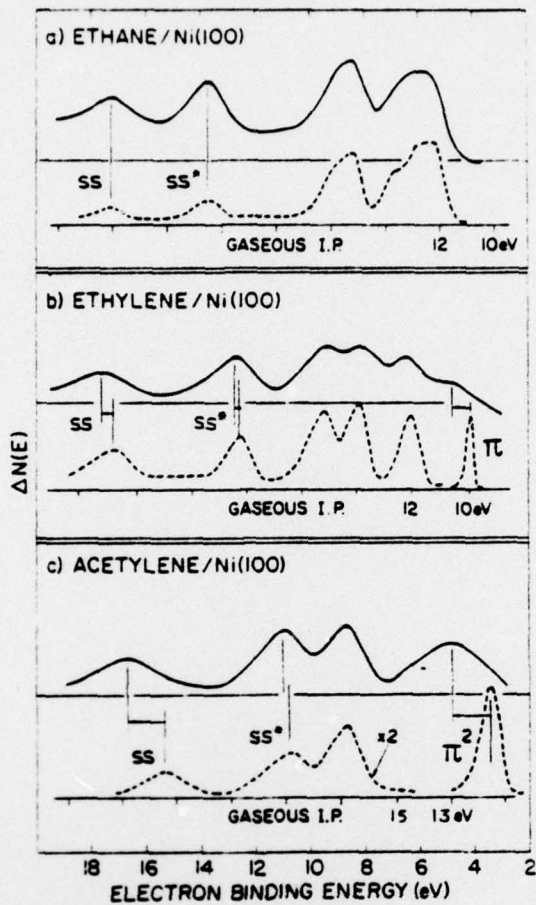


Fig. 2 Comparison of the photoemission difference spectra $N(E)$ for near saturation coverages (4×10^{-6} Torr-seconds exposure) at $T \sim 100$ K of (a) physisorbed ethane, (b) chemisorbed ethylene and (c) chemisorbed acetylene to their respective gas phase ionization spectra. The gas phase spectra for ethylene and acetylene were obtained in a gas phase spectrometer of similar geometry and resolution as ours⁸ while that for ethane was obtained in a higher resolution spectrometer⁶.

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