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P. C. Stair, and G. A. Somorjai

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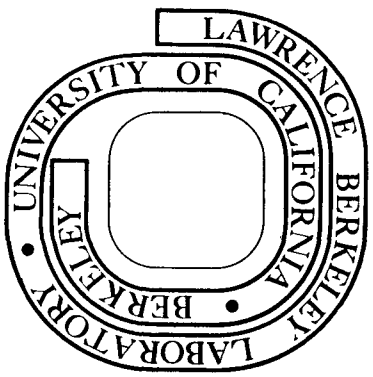

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ULTRAVIOLET PHOTOEMISSION STUDIES OF ACETYLENE AND ETHYLENE ADSORPTIONS ON THE Pt(111) SURFACE: CORRELATIONS WITH LEED STUDIES

by

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Abstract

The chemisorption of acetylene and ethylene on platinum (111) surfaces for $T \geq 300$ K has been studied with ultraviolet photoelectron spectroscopy (UPS) at 21.2 eV. An activated metastable-stable acetylene transition observed recently in low-energy electron diffraction (LEED) intensity-energy profiles has been seen with the UPS spectra. The upper-lying electronic levels of the metastable acetylene state are related to a shifted gas-phase acetylene spectrum. The stable acetylene state appears to involve a stronger molecule-surface interaction and probable rehybridization, consistent with the LEED analysis showing the molecule to be situated in a triangular position at covalent Pt-C distances. Ethylene is found to dehydrogenate at room temperature to the stable acetylene species on Pt(111) surfaces.

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The chemisorption of acetylene (C_2H_2) on the Pt(111) single crystal surface has been studied using low-energy electron diffraction (LEED) by several authors.[1-4] It has been well established under conditions of low acetylene exposure (3 Langmuirs) to the clean metal surface in ultra-high vacuum that the adsorbed acetylene forms a well-ordered overlayer structure with a diffraction pattern characteristic of a (2x2) unit mesh. By measuring the diffraction beam intensities from this system as a function of electron energy, Stair and Somorjai[3] found the adsorption took place in two steps: first, acetylene adsorbed at 300 K into a metastable state followed by the chemical conversion into another more stable state upon heating to 350 K. Both structures showed the characteristic (2x2) diffraction patterns which could be distinguished only through changes in the diffraction beam intensity profiles (I vs eV curves). By adsorbing ethylene (C_2H_4) on the same Pt(111) crystal at 300 K followed by low-energy (100 eV) electron beam exposure, they found that the initially disordered adsorbate yielded the same (2x2) diffraction pattern with the I vs eV curves identical to those of the more stable acetylene structure. Whether the disordered adsorbate is ethylene or acetylene prior to ordering with the aid of the electron beam could not be ascertained by LEED studies.

Recent dynamical LEED calculations by Kesmodel[4] et al. have shown that the bonding of the molecule in the more stable acetylene state occurs at a triangular site 1.95 Å above the plane of Pt atoms, the carbon atoms coordinating at covalent bonding distances to three surface platinum atoms. Analysis of the metastable acetylene structure is at present incomplete, but preliminary evidence indicates the molecule is farther away from the

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surface in this state and hence less strongly bound.

In the past few years ultraviolet photoelectron spectroscopy (UPS) has been quite successfully used to study the chemisorption state of adsorbed molecules on the transition metal surfaces.[5] It is of importance to apply UPS to investigate the chemical bonding of adsorbate systems that have also been studied by LEED. In this way the structure and bonding of the surface species can be established more completely and with greater certainty. For this reason, we have undertaken the investigation of the UPS spectra of chemisorbed acetylene on the Pt(111) surface employing experimental conditions that are identical to those utilized in the LEED studies.[3] Further, by comparing the room temperature chemisorbed ethylene photoemission spectrum with that of the more stable acetylene structure, we can identify the chemical state of the adsorbed ethylene molecule as well on the Pt(111) surface.

All the experiments were performed in a ultrahigh vacuum chamber ($P \sim 1 \times 10^{-10}$ torr) equipped with HeI($h\nu$ = 21.2 eV) discharge lamp, double-pass cylindrical mirror analyzer (CMA) with internal coaxial gun, LEED optics and quadrupole mass spectrometer. The Pt(111) single crystal surfaces were cleaned by argon ion sputtering and heating (1000 K) in oxygen atmosphere. Surface characterization was performed by LEED, Auger electron spectroscopy (AES) and UPS. The energy of the photoemitted electron was analyzed with a double-pass (angle-integrating) cylindrical analyzer operated in a constant retarding mode so as to have a resolution of 0.15 eV. The angle of incidence of the photons on the sample was 75° from the axis of CMA. Two orientations of the sample have been used with sample normal direction either 75 or 67.5 degrees from the incident

photon beam. The same results were obtained independent of these two orientations. In order to remove the acetone (CH_3COCH_3) invariably present in small concentrations in research grade cylinders of acetylene, a molecular-sieve trap held at dry-ice temperature (195 K) was introduced between the gas cylinder and the gas-manifold of the system.

In Fig. 1a, we show the photoemission difference spectrum $\Delta N(E)$ for Pt(111) after exposure to 3L(1L = 1×10^{-6} torr-second) acetylene for $h\nu$ = 21.2 eV with a sample temperature of 300 K. The energy scale was measured from the Fermi energy E_F. We observed two acetylene-derived emissions at -3.8 eV and -8.2 eV of approximately equal intensities. The accompanying work function change measured by the changes of the low-energy cut-offs of the photoelectron spectra was -0.4 eV. In agreement with the results of Stair and Somorjai, a distinct (2x2) pattern could be seen by LEED. After heating this chemisorbed C_2H_2 surface structure to 350 K for one hour and cooling it down to room temperature, we found a different more stable chemisorbed acetylene state characterized by a new photoemission difference spectrum that is shown as $\Delta N(E)$ in Fig. 1b. A new emission peak appeared at -5.5 eV and the relative intensities and positions of the peaks characteristic of the metastable surface structure have changed. from -8.2 eV to -7.8 eV while the lower binding energy peak shifted The higher binding energy peak shifted/from -3.8 eV to -4.0 eV. The ratio of these two emission intensities was about 3 to 1 as seen from Figure 1b. The LEED pattern showed the same (2x2) ordered overlayer structure except that the spot intensities changed, consistent with the findings of the previous LEED analysis.[3] After saturating the Pt(111) surface with 10^3L acetylene exposure, the UPS spectra remained unchanged. However, the long range (2x2) ordering was destroyed, and the work function change was

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higher (-1.0 eV) for this saturated condition.

Fig. 2 shows the difference spectrum $\Delta N(E)$ for chemisorbed ethylene at 300 K with 3L exposure on Pt(111) surfaces. The adsorbate was disordered as seen by LEED and gave a very similar photoemission spectrum to that of Fig. 1b. When exposed to the 100 eV electron beam for 100 seconds, we observed by LEED a (2x2) pattern gradually developing across the whole surface. The photoemission spectrum for this (2x2) structure was identical to that in Fig. 2 or Fig. 1b. The accompanying work function change $\Delta\phi$ was -0.5 eV. All the experiments have been repeated using two different Pt(111) single crystal surfaces. The results obtained and reported here were all reproducible.

We find there is a very close correlation between the changes in the UPS spectra and structural transitions detectable by LEED from chemisorbed acetylene on the Pt(111) surface. Both techniques reveal that chemisorbed acetylene on Pt(111) surfaces at room temperature (300 K) is in a metastable state. It can be converted into a more stable state by a gentle heating for an hour and this transformation is observed by marked changes in the UPS spectra. In addition, we find that at room temperature ethylene dehydrogenates to acetylene which is still in a disordered state on the Pt(111) surface. The incident electron beam merely orders the already dehydrogenated species. This information could not be obtained by LEED analysis alone since LEED studies are insensitive to the properties of adsorbates that do not exhibit long-range order.

By comparison with the gas phase spectrum of acetylene molecules,[6] we can associate the C_2H_2 induced emission at -3.8 eV and -8.2 eV (Fig. 1a) to the acetylene $1\pi_u$ and $3\sigma_g$ molecular orbitals. Assuming uniform

relaxation shifts,[5] there is a 0.6 eV chemical bond shift for π-orbitals due to the bonding between acetylene π-orbitals and Pt atoms on the surface in this metastable chemisorbed state. With thermally activated conversion into the stable chemisorbed state the acetylene undergoes an apparent rehybridization, i.e., the electrons originally populated in the degenerate π levels redistribute themselves into new levels. This is reflected by the reduction in emission of the -4.0 eV peak and the appearance of the -5.5 eV peak. The lower state which is associated with the $3\sigma_g$ orbital shifts from -8.2 eV to -7.8 eV. This may arise from either an increased relaxation effect due to decreasing distance from the surface[5] or the increase of carbon-carbon distance within the acetylene molecule.[7] The nature and degree of the indicated rehybridization in terms of surface-induced CC bond elongation and CCH angle bending cannot be ascertained from the limited data available to us with the 21.2 eV HeI line.

We note that a transformation very similar to the one reported herein but at a lower temperature has been studied by UPS in detail on Pd(111) by Demuth.[8]

We are grateful to Dr. J. E. Demuth for stimulating discussions and for providing us with a copy of his recent work (Ref. 8) prior to publication. This work was carried out under the auspices of the U. S. Energy Research and Development Administration.

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Figure Captions

Fig. 1 Photoemission difference curves $\Delta N(E)$ relative to E_F for (a) metastable acetylene state after exposure 3L acetylene (C_2H_2) on Pt(111) surfaces at room temperature (~300 K). Preliminary identification with the molecular orbitals of gas phase acetylene is indicated; (b) the stable acetylene state after heating the acetylene adsorbed Pt(111) surface to 350 K for an hour. Work function change $\Delta\phi$ in (a) and (b) is -0.4 eV.

Fig. 2 Photoemission difference curve $\Delta N(E)$ for chemisorption of ethylene (C_2H_4) on Pt(111) surface at room temperature. Work function change $\Delta\phi$ is -0.5 eV.

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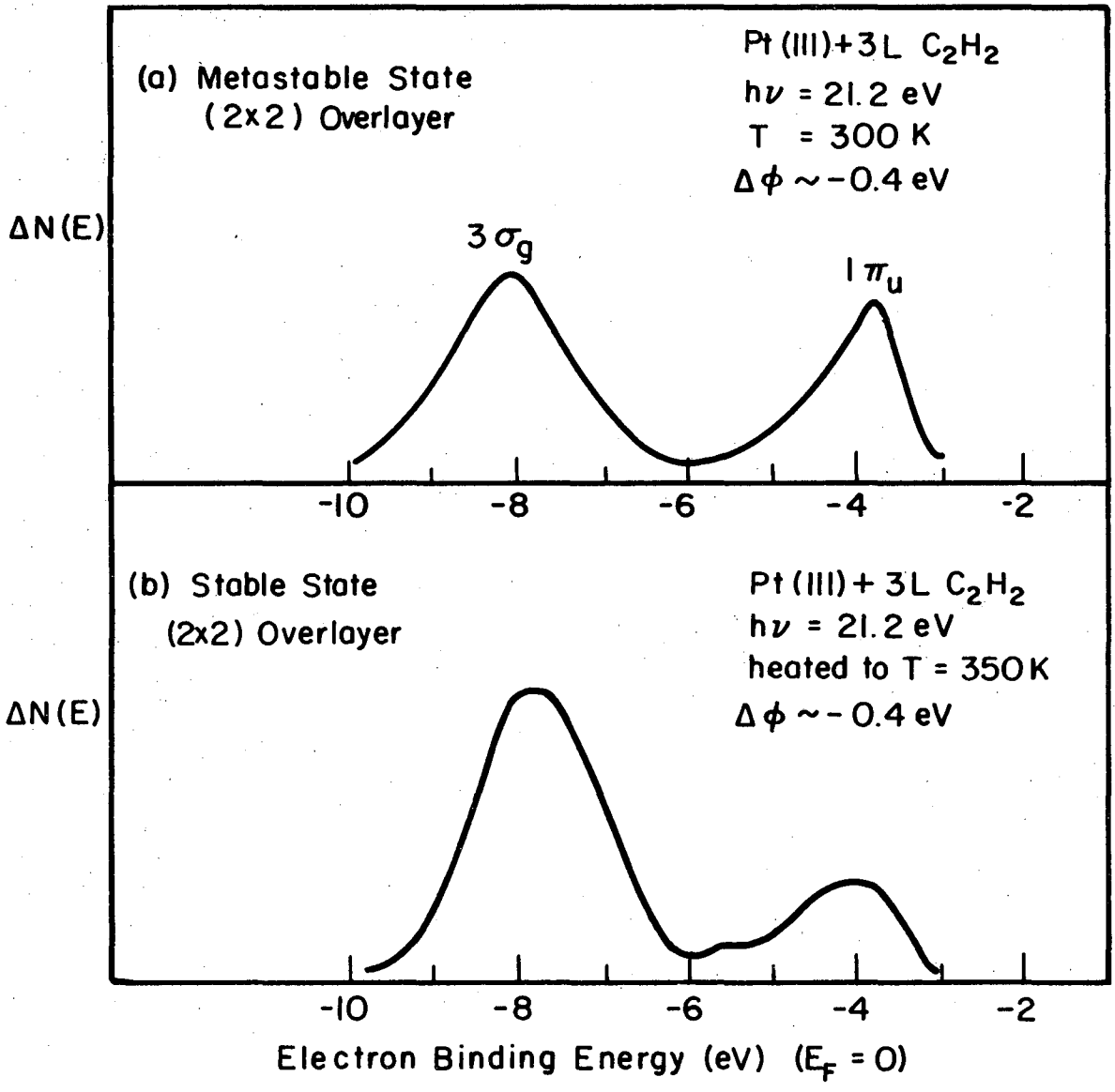

Fig. 1

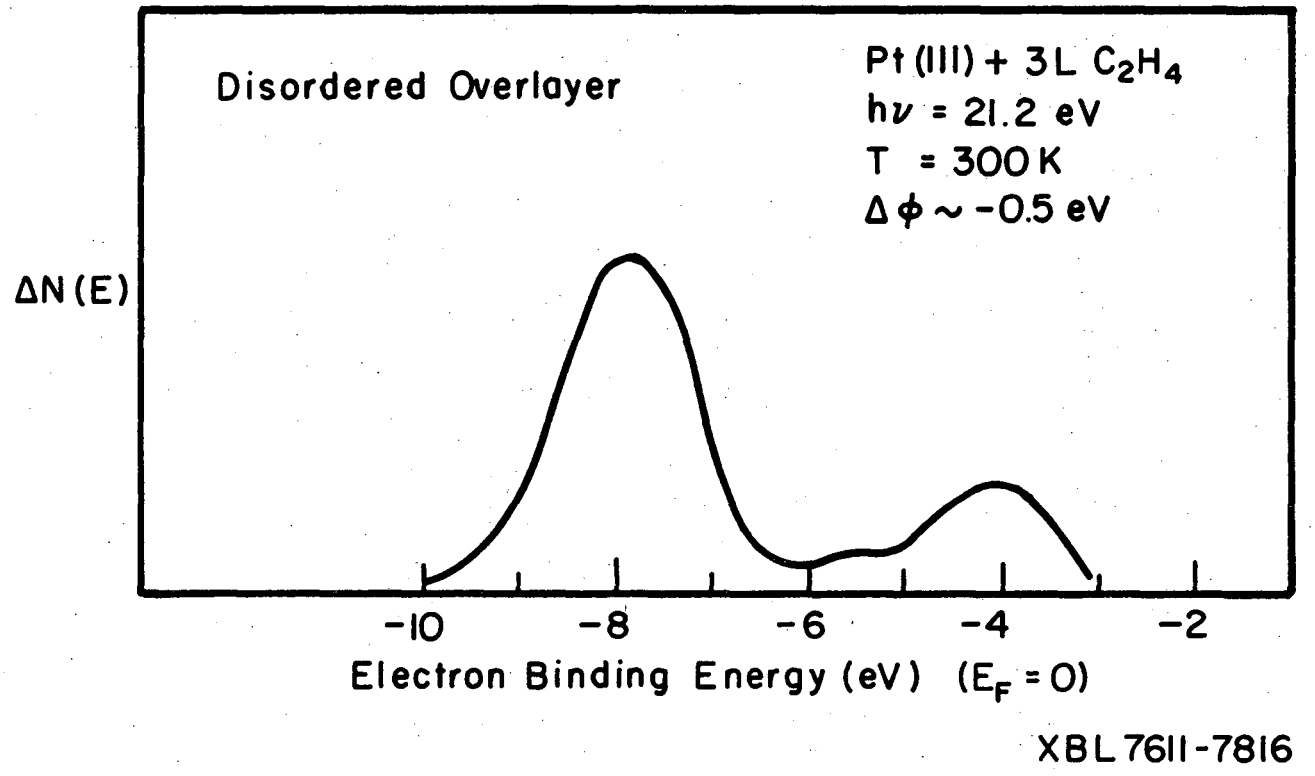
Disordered Overlayer
Pt(111) + 3L C_2H_4
$h\nu$ = 21.2 eV
T = 300 K
$\Delta\phi \sim -0.5$ eV
$\Delta N(E)$
-10
-8
-6
-4
-2
Electron Binding Energy (eV) ($E_F = 0$)
XBL 7611-7816

Fig. 2

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