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LETTER TO THE EDITOR

Following the changes in local geometry associated with a surface reaction: the dehydrogenation of adsorbed ethylene

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Abstract. Using scanned-energy-mode photoelectron diffraction we have determined the local adsorption geometry of the reactant and product molecules in a model heterogeneous reaction on a Ni(111) surface in which ethylene (C_2H_4) is dehydrogenated to acetylene (C_2H_2). Although the C–C axis remains essentially parallel to the surface, a change in adsorption site occurs, indicating that for the case of a concerted reaction mechanism only two distinct pathways are possible. Precise structural information on a model system of this kind has hitherto been unavailable.

Almost twenty years ago Demuth and Eastman [1] showed with the aid of UV photoemission that adsorbed ethylene dehydrogenates to acetylene on Ni(111), thereby demonstrating for the first time how a spectroscopic technique can be used to identify reactants and products in a simple heterogeneous reaction on a single-crystal surface. In their experiment ethylene adsorbed at 100 K was found to give the photoemission spectrum corresponding to that of adsorbed acetylene when the crystal was warmed to 230 K. Later measurements [2–4] confirmed this result and, in particular, showed that the vibrational spectrum of the surface after the reaction corresponds exactly to that obtained by co-adsorbing acetylene and hydrogen [3]. Apart from being a result of intrinsic importance (the corresponding gas phase reaction would be endergonic), it also engendered the hope that surface science would soon be in a position to deliver detailed information on the mechanism of such reactions. The experience of recent years has, however, been rather disappointing in this respect. In fact, not even for one of the simplest and most studied surface reactions, namely for CO oxidation, is this information available. Although the Langmuir–Hinshelwood mechanism [5] pertains in this case (i.e. an adsorbed CO molecule reacts with an adsorbed O atom), nothing is known on the atomic scale about the reaction pathway leading to CO_2 formation. In this work we described the successful application of photoelectron diffraction to the model heterogeneous reaction originally reported by Demuth and Eastman. We determine the local adsorption geometries of the ethylene molecule before the reaction and of the acetylene molecule after the reaction, which then enables us to speculate as to the possible reaction pathways.

It has recently been shown by us [6–9] and others [10] that the technique of scanned-energy-mode photoelectron diffraction [11] is particularly useful for determining the structural parameters of adsorbed molecules. In essence, the intensity of a core-level photoemission peak from an atom of the adsorbate is measured at a particular emission

angle as a function of photon energy, and thus of photoelectron kinetic energy. As a result of interference between the primary photoelectron wave and the secondary waves scattered by the substrate atoms, modulations appear in the diffraction spectrum, i.e. in the plot of core-level photoelectron intensity against energy. These modulations provide information on the scattering path lengths and thus on the local bonding geometry, i.e. the surface site and the distance to the nearest-neighbour substrate atoms. The structural information is extracted by comparing the experimental diffraction spectra with calculated ones using a multiple-scattering approach. In order to reduce the volume of parameter space to be explored in such theory/experiment comparisons we have recently developed two direct methods [12, 13] that allow the adsorption site to be rapidly determined and also give approximate structural parameters that may then be refined with the full trial-and-error procedure. Other direct method schemes have also recently been reported [14]. (The recent interest in direct methods for experiments of this kind was initiated by the concept of photoelectron holography [15]. However, this approach has yet to be used for adsorbate site determination with real experimental data.) The advantage of scanned-energy-mode photoelectron diffraction is that, unlike conventional low-energy electron diffraction (LEED), the method does not rely on the presence of long-range order: many adsorbed molecular systems do not form ordered arrays, particularly when they result as products in heterogeneous reactions.

The experiments were performed in a purpose-built ultra-high-vacuum system on the HE-TGM 1 monochromator [16] at the Berlin synchrotron radiation source BESSY. The Ni(111) sample was cleaned and characterized with standard techniques. A 152 mm mean radius 150° electrostatic deflection analyser (VG Scientific) was used to measure the C 1s photoelectron signal at a fixed angle of 60° relative to the direction of the incident radiation. The initial layer was prepared by exposing the surface to 2×10^{-6} mbar s ethylene at 120 K, which produces a (2×2) phase [4], and annealing to 200 K to induce the conversion to adsorbed acetylene and hydrogen. The resulting layer does not show long-range order, although pure acetylene adsorption does produce three ordered structures [4]. The conversion process causes the C 1s photoelectron peak to shift from 284.0 ($\pm$ 0.2) eV to 283.3 ($\pm$ 0.2) eV binding energy; adsorption of acetylene at temperatures up to 300 K on the clean surface produced a C 1s peak at the same binding energy with identical line shape. C 1s photoelectron diffraction spectra were measured at four emission angles for ethylene and acetylene, respectively, in each of the $[2\bar{1}\bar{1}]$, $[11\bar{2}]$ and $[01\bar{1}]$ azimuths. The acetylene spectra obtained after dehydrogenaton of adsorbed ethylene and after direct adsorption of acetylene were identical. Using standard data analysis procedures, modulation functions were derived and compared with those obtained from multiple-scattering calculations [17] with the aid of reliablity (or R-) factors, as in our previous studies [8–11]. After preliminary adsorption site determination with both direct methods, the surface coordinates of the two C atoms in each molecule were determined more accurately using multi-spectrum R-factors. (The multi-spectrum R-factor is equivalent to the multi-beam R-factor LEED.)

The application of the direct methods [12, 13] immediately demonstrates that the local adsorption geometries are different for the two molecules. The basic physics behind these techniques lies in the high scattering factor for photoelectrons backscattered at or near 180° at low to intermediate electron energies. Figure 1 shows the images obtained from the approach described by Hofmann and Schindler [13], in which several experimentally determined modulation functions are projected onto calculated single-scattering modulation functions that would be given by substrate atoms situated in a Cartesian coordinate frame below the emitter. The coefficient $C(x, y, z)$ from this procedure, which is some measure of the probability of finding a substrate atom below the emitter, is plotted in a plane parallel to

the surface at distances below the emitter of 1.94 Å and 1.37 Å for ethylene and acetylene in figure 1(a) and 1(b), respectively. Use is made of the rotational symmetry of the substrate in order to extend the data set before the reconstruction of the image. Whereas the ethylene results indicate that a substrate atom is located directly beneath each of the C atoms, the sixfold symmetry of the acetylene pattern shows that the atoms in this case occupy both sorts of threefold hollow site, as in the case of acetylene adsorbed on Cu(111) [9]. The images in the projection method have a plate-like form corresponding to the loci of constant path-length difference which are parabolic in form [14]. This is also seen in planes perpendicular to the surface for ethylene (not shown for reasons of space), where the image of the substrate atom is streaked, in the same way as those for acetylene parallel to the surface in figure 1(b). If the C atoms of the ethylene molecule are above, or nearly above, Ni atoms, only the so-called aligned bridge configuration with the C–C axis aligned in the (110) set of directions can give a plausible C–C bond length. Identical adsorption site assignments are obtained with the other, Fourier-transform method [12].
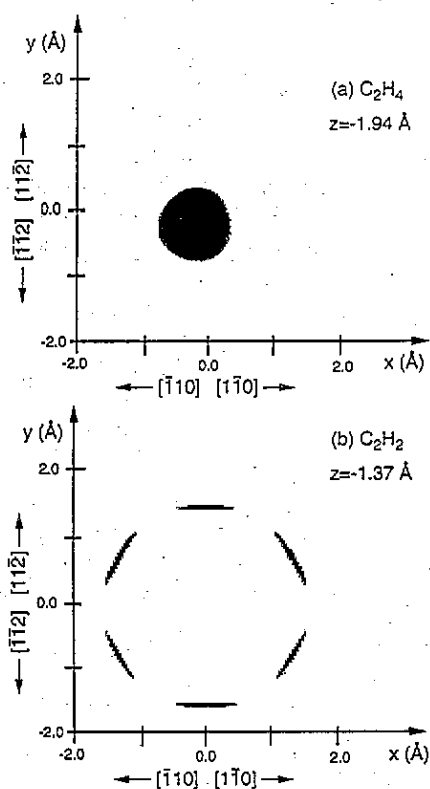

Figure 1. Intensity plot of the coefficient $C(x, y, z)$ from the direct projection method [13] in a plane parallel to the surface (xy) at distances of (a) 1.94 Å for ethylene and (b) 1.37 Å for acetylene below the emitting carbon atom.
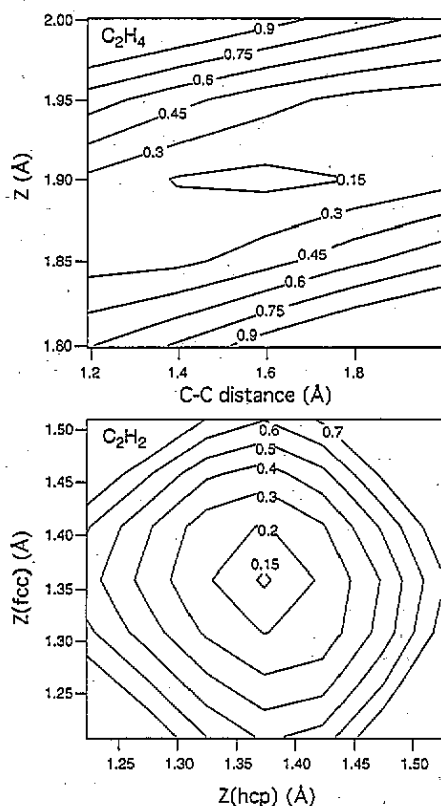
Figure 2. Contour plots of the reliability factor, R_m [7]. Above: height of the ethylene molecule z above the outermost Ni layer against C–C distance. Below: height of the C atom above the outermost Ni layer in the FCC threefold hollow site, z, against the height of the C atom above the outermost layer in the HCP threefold hollow site, z (HCP).

These preliminary conclusions are supported by the results of subsequent multiple-

scattering calculations in which a five- or six-spectrum R-factor was used. For ethylene the emission directions used were $O°$ in the $[2\bar{1}\bar{1}]$, $[11\bar{2}]$ and $[11\bar{1}]$ azimuths as well as $20°$ in the $[11\bar{2}]$ and $[01\bar{1}]$ azimuths; for acetylene they were $0°$ and $40°$ in the $[2\bar{1}\bar{1}]$, $[11\bar{2}]$ and $[01\bar{1}]$ azimuths. Three structural parameters, namely, the height of each C atom above the outermost Ni layer and the C–C separation, were varied in each case. Some of the results are shown in the form of contour plots for the reliability factor R_m [7] in figure 2; the resulting final structures are shown at the bottom of figure 3. (This particular R-factor is based on a simple normalized square-deviation function; as in the case of the Pendry R-factor frequently encountered in LEED [18], it is defined such that the value of zero corresponds to perfect agreement, a value of unity to uncorrelated data and a value of two to anticorrelated data.) For ethylene the minimum in R_m corresponds to a geometry in which the C–C axis is parallel to the surface, the two C atoms are almost atop Ni atoms, $z = 1.90$ (± 0.02) Å and d(C–C) = 1.60 (± 0.18) Å. In addition, there is a Ni first-layer/second-layer expansion of $0.15(\pm 0.10)$ Å The upper contour plot of figure 2 demonstrates that the R-factor is more sensitive to z than to the C–C distance, hence the larger error bars on the latter. Other possible geometries were also checked with the full-scale calculations, but were only found to correspond at most to shallow local minima in the R-factor. For acetylene the minimum in R_m corresponds to a geometry in which, as noted above, the C–C axis is aligned in the other principal azimuth, i.e. one of the set $\langle 211 \rangle$, such that neighbouring, inequivalent threefold hollow sites are occupied. However, as the lower contour plot in figure 2 shows, the minimum in the R-factor corresponds to a small difference in the z distance for the two carbon atoms. For the C atom over the 'FCC' site (Ni atom underneath in the third layer) $z = 1.36$ (± 0.04) Å and for that over the 'HCP' site (Ni atom underneath in the second layer) $z = 1.37$ (± 0.04) Å; the effect may be connected with filled-orbital overlap repulsion. In addition, there is a contraction of the Ni first/second-layer separation of 0.01 (± 0.06) Å. This adsorption geometry for acetylene is very similar to that obtained in an early LEED study [19] of the (2×2) phase which may be obtained by adsorbing at low temperature and annealing. The C–C distances of 1.60 Å and 1.44 Å for the ethylene and acetylene, respectively, may be compared with 1.34 Å and 1.21 Å for the free molecules. This degree of bond stretching is consistent with vibrational spectra which show in both cases a considerable lowering of the C–C stretching frequency [20].

As figure 3 shows, there appear to be two possibilities for the surface reaction pathway: (a) a rotation of the C–C axis by $90°$ and a reduction in the height of the molecule above the surface by 0.50 Å which accompany the loss at the two H atoms, or (b) a rotation of the C–C axis $30°$ with a concomitant *translation* which also occur at the same time as the change in z distance and the loss of hydrogen. Note that only a very small change in C–C separation takes place. On the basis of the investigations reported here, these two alternatives cannot be distinguished nor, indeed, can it be ascertained whether the individual events form a concerted process, as implied by these descriptions. However, mechanism (a) represents a very plausible scenario: the C–H bonds on opposite sides of the ethylene molecule (in a so-called *trans* configuration) could dissociate, allowing the H atoms to become bonded to the neighbouring threefold hollow sites, as the molecule rotates. Since the C–H bonds of the adsorbed acetylene molecule are probably bent upwards by as much as $60°$ [21], there would be little steric hindrance between the products. Further, hydrogen is known also to adsorb in both sorts of threefold hollow site on Ni(111) [22]. On the other hand, addition reactions to multiple bonds in homogeneous catalysis (essentially the reverse situation) normally occur via a *cis* mechanism, although these are unlikely to be concerted processes and occur under quite different conditions [23].

In summary, we have been able using scanned-energy-mode photoelectron diffraction to
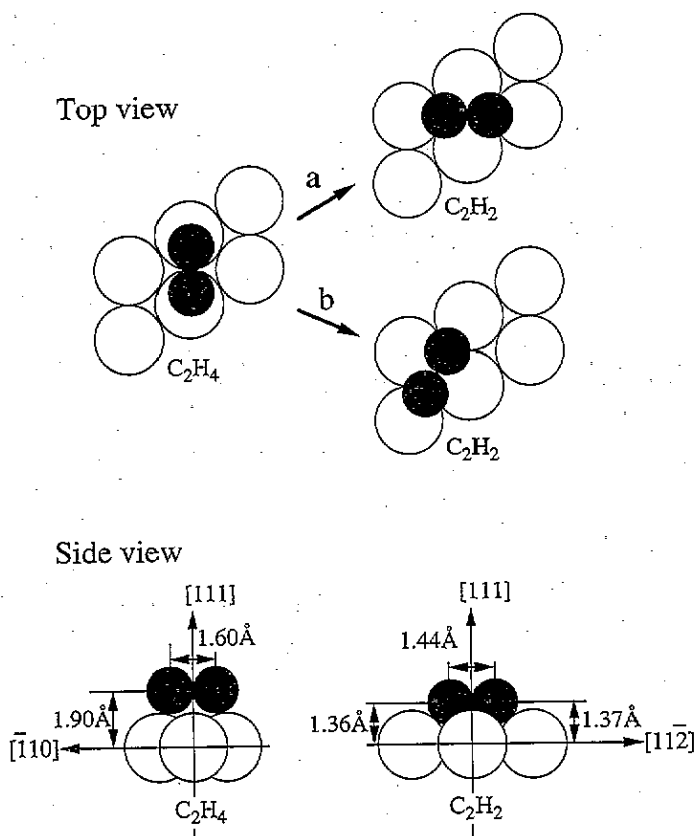
Top view

Side view

Figure 3. Above: the two possible reaction pathways for ethylene dehydrogenation on a Ni(111) surface. Below: local adsorption geometries (side view) for ethylene and acetylene on Ni(111).

determine the local adsorption geometries of ethylene on Ni(111), and its product, acetylene, in a simple heterogeneous reaction. Assuming a concerted reaction mechanism, there are then only two possibilities for the surface reaction pathway. Precise structural information of this kind is likely to provide a stimulus for better quantum mechanical description of surface reaction mechanisms.

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