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On the orientation of low temperature π-bonded ethylene on Pt(111)

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The adsorption of ethylene on Pt(111) has been followed, using UPS and detection at the normal and off-normal, at temperatures low enough to allow multilayer growth. The absence of an orbital, at the normal, during the first stages of adsorption and its presence from the beginning, off-normal, allowed us to conclude that the first (π-bonded) monolayer is oriented flat and parallel to the surface.

1. Introduction

The adsorption of ethylene on Pt(111), at temperatures below 52 K, leads to the formation of multilayers [1]. The first layer is almost undistorted, compared to the gas phase molecule, as seen by the spacings between the molecular orbitals (UPS) [1] and the positions of the σ^* resonances in the first layer and the multilayer [2]. During the adsorption process, the work function decreases (-1.40 ± 0.05 eV) before levelling off to a constant value. Simultaneously, UPS shows a shift of the molecular orbitals towards higher binding energies (~ 0.8 eV) and a change between their relative intensities. The shift is consistent with work-function variations sampled by a loosely bonded molecule, taking into account the initial state [3], or final state screening changes [4], while modifications of the intensities may be connected to changes of the molecular orientation during the growth process. In contrast to the di-σ species, parallel to the surface, observed by HREELS [5], UPS [6] and NEXAFS [7], the low-temperature phase has been called a π-bonded species [1]. Indeed, strong modifications of the d-band of platinum, especially near the Fermi edge, appear during the first adsorption stages. However, in the first layer, the position of the π orbital is possibly obscured by the d-band of platinum and the difference in spacing expected for such a bonding between the two low-lying orbitals in the adsorbed state and the gas phase was not measured [1]. Contrary to what was written in ref. [1], due to a wrong potential applied to the retarding lenses and the use of a slit instead of a hole, all orbitals were previously detected off-normal, as seen from the strong platinum orbital near the Fermi edge. π-bonded species have also been obtained on Ag(100) [8] and Pd(111) at higher temperatures (below 160 K [8] and at about 95 K [9,10], respectively). The two low-lying orbitals (π and π'_{CH_2} [11]) are spaced apart more than in the gas phase for ethylene/Pd(111). These π-bonded species have also been shown to be parallel to the surface by using the polarization of the light in NEXAFS experiments [8,10] or changing the orientation of the incident light (He I) and the angle of detection while collecting UV spectra [9]. Indeed, the molecular orientation may be determined using various methods: HREELS, NEXAFS, polarized UV light or unpolarized light. However, one of the striking results obtained in the ethylene/Pd(111) work [9]

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is that the π'_{CH_2} orbital was not detected in the normal direction, whatever was the incidence angle of the unpolarized UV light but appeared at other angles of detection. This simple method has been used here to bring additional information on the orientation of the first low temperature layer of ethylene on Pt(111) and will be discussed hereafter.

2. Experimental

The experiments have been performed in an ultrahigh vacuum chamber (base pressure in the low 10^{-10} mbar range after baking), pumped using a turbomolecular pump. A Pt(111) sample (6 mm) attached through isolated tantalum leads to a cold head (APD Cryogenics) could be cooled down below 52 K (about 45 K) and heated resistively above 1000 K (temperatures were measured with a chromel–alumel thermocouple). After the cleaning procedure (oxygen treatment at 1000 K, neon ion bombardment and annealing to 1000 K), the cleanliness of the sample was checked using XPS (Kratos DS800 – spherical analyzer with preretarding lenses – angle of collection = 5°). The sample was located at the center of the UHV chamber and could be rotated axially, while being irradiated by the UV light (He I – VG He lamp). The angle of incidence of the light was 55°, with the analyzer axis normal to the sample and 65° when the sample was rotated to detect the photoelectrons at 33° off-normal. UV spectra (He I) were obtained with the sample biased at −90 V and medium resolution of the analyzer (pass energy = 40 eV, resolution = 400 meV) to allow fast collection of the data with a reasonable signal-to-noise ratio. Ethylene (deuterated ethylene was made by MSD Isotopes, isotope purity: 99 at.% D) was dosed without further purification through a pinhole (2 μm) followed by a long stainless steel tube (7 cm). In order to record spectra while dosing, the doser end was located at 20 mm from the sample. The ethylene pressure before the pinhole was also adjusted to a value low enough to avoid appreciable increase of ethylene coverage during the recording time of a full spectrum (30 s). Corrections have been applied to take into account changes in exposure with the orientation of the sample. Work function variations were monitored from the onset of the UV spectra. The gas-phase composition and the desorbing species during TPD were monitored by a UTI 100C quadrupole mass spectrometer.

3. Results and discussion

After long exposures and formation of ethylene multilayers (at about 45 K), the UV spectra (at normal and off-normal) resemble the one obtained previously at 37 K [1]. However, while the spacings between the orbitals are identical, some discrepancy exists in their absolute positions (within 0.3–0.4 eV). Steinrück [12] has recently studied ethylene adsorption on Ni(110). He has shown, using ARUPS that the c(2 × 4) layer exhibits significant dispersion (up to ~ 1 eV) for the molecular levels. The possible existence of a 2D band structure may explain the variations in absolute positions of the orbitals, with the angle of detection. However, the observed orbital spacings (independent on the detection angle) are characteristic of undistorted ethylene molecules with preserved C=C double bond.

Further transformation with temperature was also studied in our apparatus, for comparison, using UPS and TDS. A temperature increase to 52–60 K leads to desorption of the multilayer and the UV spectrum becomes characteristic of the di-σ ethylene species with a work-function decrease, compared to the clean surface, equal to −1.05 eV, in good agreement with previous results [1]. Further heating above 250 K leads to ethylidyne formation, exhibiting another clear UV spectrum. TPD agreed also with our previous results [1]. Partial ethylene desorption occurs at about 280 K and a strong hydrogen desorption peak is observed near 310 K, close to the temperature of formation of ethylidyne. The smaller hydrogen peaks at higher temperatures corresponded to the decomposition of ethylidyne.

At 45 K, during the early stages of adsorption and formation of the first layer, several orbitals appear, but their number depends on the detection angle (see below). The development of π'_{CH_2}

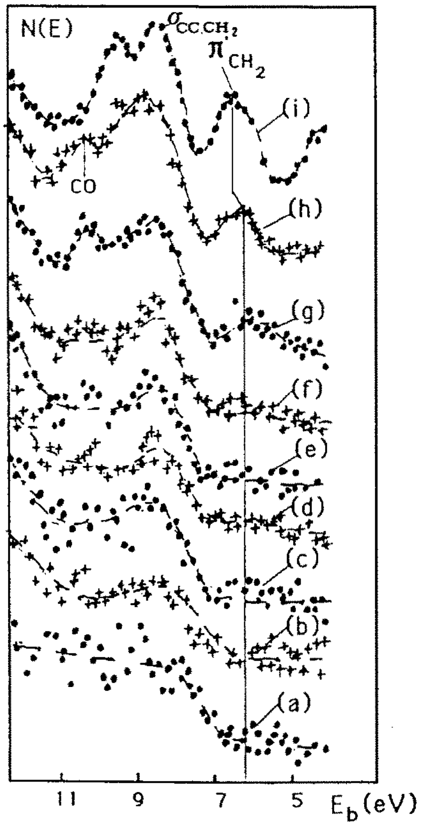

Fig. 1. UV spectra (He I) of adsorbed ethylene on Pt(111) with photoelectron detection at the normal. Energies are referred to the Fermi level. Each curve has its own scale in arbitrary units. Exposure times: (a) 154 s; (b) 264 s; (c) 354 s; (d) 444 s; (e) 534 s; (f) 624 s; (g) 804 s; (h) 1164 s; (i) 2064 s.

and σ_{CC,CH_2} orbitals is shown in figs. 1 and 2 with time (proportional to exposure). Quite clearly, they both appear immediately when detecting off-normal while the first orbital becomes detectable only after a significant exposure, when detecting at the normal. The intensity of π'_{CH_2} orbital is reported in both cases in fig. 3. It confirms the preceding qualitative results and shows that the π'_{CH_2} orbital is only visible, in the normal direction, after 550 s exposure time. The fact that π'_{CH_2} orbital can be detected off-normal, at any stage of the adsorption process, indicates that its absence, at the normal, is not connected to a low cross section but to a specific orientation of the molecule, as discussed below. The work-function variations were determined fron the onset of the same UV spectra

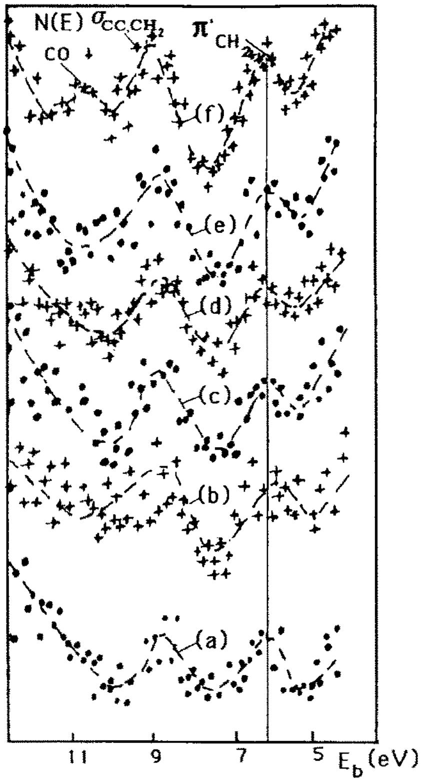

Fig. 2. UV spectra (He I) of adsorbed ethylene on Pt(111) with off-normal photoelectron detection (33°). Energies are referred to the Fermi level. Each curve has its own scale in arbitrary units. Exposure times: (a) 154 s; (b) 264 s; (c) 354 s; (d) 444 s; (e) 534 s; (f) 714 s.

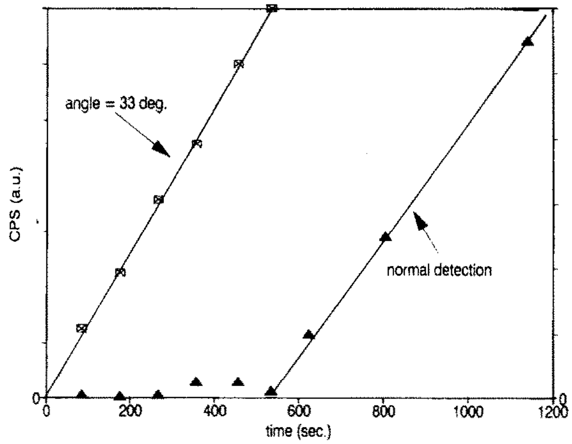

Fig. 3. Intensities of the π'_{CH_2} orbital with exposure (expressed in time) with detection at the normal and off-normal (33°).

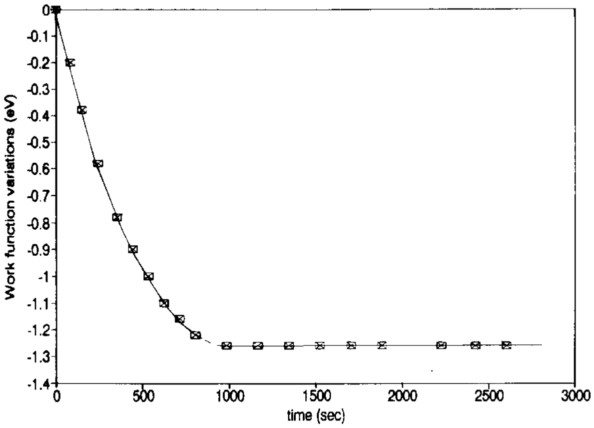

Fig. 4. Work-function variations during ethylene adsorption versus time (the scale is the same as in fig. 3).

used to monitor the orbital intensities. They are shown in fig. 4. The work function of the covered surface levels off at about −1.25 eV, slightly later than the appearance of the π'_{CH_2} orbital at normal detection. The absolute work-function variations (−1.40 eV ± 0.05 eV [1] and −1.25 ± 0.05 eV [this work]) are in acceptable agreement. With exposure, there is a fast decrease of the work function followed by a levelling-off to an almost constant value during the multilayer growth.

In the previous results, the completion of the first monolayer was set when the work function was not changing anymore [1]. For hydrocarbons, at temperatures where a single layer may be formed, a steep and nearly linear decrease of the work function is generally observed as a function of exposure with saturation values between −1.0 and −1.8 eV for different adsorbates [13–16]. However, in the case of benzene on Ru(001) [16], depolarization effects and changes in sticking coefficient are responsible for reaching a minimum work function value at only 85% of the saturation coverage. At lower temperatures, when multilayer formation is possible, the sticking coefficient is expected to stay constant over a wider monolayer coverage range [17] before reaching a value corresponding to the multilayers and the work function is expected to level off closer to the completion of the first monolayer. Moreover, the second layer may participate slightly in work function variations, particularly if the first layer is not dense. As a consequence, the saturation of the first layer cannot be deduced accurately from the work-function variations. In any case, the initial steep linear decrease of the work function has to be attributed to the first layer and it has been shown from figs. 1 and 3 that π'_{CH_2} is absent during its formation, with detection at the normal.

Selection rules and polarization effects in photoemission have been extensively discussed (ref. [18] and references therein).

The free ethylene molecule belongs to the point group D_{2h}. Adsorbing it on a hypothetical structureless surface as a π-bonded complex (molecule lying flat and parallel to the surface) results in a reduction of symmetry to C_{2v}. In this group, the π'_{CH_2} orbital is a_2. During a photoemission experiment, information on the initial state can be derived by placing constraints on the final state. For normal emission, the final state wave function must belong to the totally symmetric representation of the C_{2v} group (a_1). Transitions are allowed only when the symmetries of the electric vector and of the initial state are the same. Since for non-polarized light, the projections of the electric vector along x- (C–C bond), y- and z-axis (perpendicular to the molecular plane) belong to the representations b_1, b_2 and a_1, respectively, the final states become b_2, b_1 and a_2 in the x-, y-, and z-directions. It is therefore not possible to obtain emission at the normal from the π'_{CH_2} orbital with this symmetric representation (see table 1, reproduced from ref. [18]. It is only allowed off-normal.

With unpolarized light, lowering the symmetry allows emission from all orbitals in all directions, including the direction of the normal, as also shown in table 1. The C_2 situation (with a totally symmetric a orbital replacing a_2) corresponds to a twist about the C–C bond while the two C_s configurations correspond to a plane of the ethylene molecule no longer parallel to the surface. Even in the case of a random azimuthal orientations of the (molecular) mirror planes, "boths s and p light will excite both a′ and a″ in normal emission" [18].

From the selection rules, it becomes therefore clear that the only configuration of ethylene which has no normal emission of the π'_{CH_2} orbital is one

Table 1
Correlation table for the molecular orbitals of adsorbed ethylene

D_{2h}	C_{2v} flat	C_2 twisted	C_s (σ_{xz}) end tilted	C_s (σ_{yz}) side tilted
$1b_{1u}$ (π)	a_1	a	a′	a′
$1b_{1g}$ (π'_{CH_2})	a_2	a	a″	a″
$3a_g$ (σ_{CC,CH_2})	a_1	a	a′	a′
$1b_{2u}$ (π'_{CH_2})	b_2	b	a″	a′

where the molecule lies flat and parallel to the surface.

Experimentally, it has been proved that ethylene is π-bonded in the chemisorbed layer on Pd(111) using UPS [9,10]. In order to determine the orientation of the molecule [18], Tysoe et al. [9] have changed the angle of incidence of the light and the angle of detection of photoelectrons. Their results agree with a flat, parallel-to-the-surface geometry. The parallel orientation of the C–C bond has been confirmed by NEXAFS results [10]. They give in their paper a table (table IV, analogous to table III in ref. [18]), which also shows that with such an orientation, no detection is allowed at the normal for the π'_{CH_2} orbital. They also mention that "the peak at 6 eV below E_F appears only for $\theta \neq 0°$". Clearly, this simple experimental result, along with the selection rules [18], determines the orientation and the absence of distortion of the adsorbed ethylene molecule in the chemisorbed layer, as indicated above.

Contrary to the ethylene/Pd(111) system, π-bonded ethylene can only be observed on Pt(111) at a temperature where multilayer formation develops. Indeed, above 52 K, transformation into di-σ bonded ethylene occurs [1]. The completion of the first layer is not accurately determined (see discussion above). However, the appearance of the π'_{CH_2} orbital in an exposure range where the work function does not vary much (see figs. 3 and 4) indicates that the molecular orientation is probably lost near saturation of the first layer. We suppose that the first layer is more strongly bonded that the following ones (of almost the same adsorption energy) and therefore that all orientations compared to the substrate become possible after monolayer completion. In the case of benzene on Ru(0001) [19], the first physisorbed layer (on top of the chemisorbed layer) is more strongly bonded than the bulk and it remains parallel to the surface. "This can be due to a residual π-interaction with the metal through the chemisorbed layer or to electrostatic influences of the polarized chemisorbed layer (-1.82 eV)" [19]. These effects are negligible for ethylene; it is less strongly interacting with Pt(111) even in the first layer. The lower adsorption energy of π-bonded ethylene on metals, compared to benzene, is supported by the final changes of the work function, and a desorption temperature of about 160 K on Ag(100) [8], 200 K on Pd [9], compared to a desorption temperature of 360 K for benzene from Ru(001) [16].

In conclusion, as a consequence of this discussion, we believe that our experimental results show conclusively that at low temperature (52 K), where π-bonded ethylene is formed on Pt(111), at least the first layer lies flat and parallel to the surface. The molecular orientation is lost during the subsequent growth. This (not surprising) result agrees with a negligible change of the C–C length in the monolayer range, compared to the multilayer [2] and spacings of the molecular orbitals comparable to those of the gas phase [1].

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References

[1] M.B. Hugenschmidt, P. Dolle, J. Jupille and A. Cassuto, J. Vac. Sci. Technol. A 7 (1989) 3312.

[2] A. Cassuto, Mane Mane and J. Jupille, Surf. 249 (1991) 8.
[3] K. Wandelt, J. Vac. Sci. Technol. A 2 (1984) 802.
[4] T.C. Chiang, G. Kaindl and T. Mandel, Phys. Rev. B 33 (1986) 695.
[5] H. Steininger, H. Ibach and S. Lehwald, Surf. Sci. 117 (1982) 685.
[6] M.R. Albert, L.G. Sneddon, W. Eberhardt, F. Greuter, T. Gustaffson and E.W. Plummer, Surf. Sci. 120 (1982) L17.
[7] J.A. Horseley, J. Stöhr and R.J. Koestner, J. Chem. Phys. 83 (1985) 3146.
[8] D. Arvanitis, K. Baberschke, L. Wenzel and U. Döbler, Phys. Rev. Lett. 57 (1986) 3177.
[9] W.L. Tysoe, G.L. Nyberg and R.M. Lambert, J. Phys. Chem. 88 (1984) 1960.
[10] L.P. Wang, W.T. Nysoe, R.M. Ormerod, R.M. Lambert, H. Hoffman and F. Zaera, J. Phys. Chem. 94 (1990) 4236.
[11] J.W.L. Jorgensen and L. Salem, The Organic Chemist's Book of Orbitals (Academic Press, New York, 1973).
[12] H.P. Steinrück, 3S'91, Symposium on Surface Science, Obertraun, Austria, February 10–16, 1991, Eds. P. Varga and G. Betz, p. 67.
[13] J.C. Bertolini and J. Rousseau, Surf. Sci. 89 (1979) 467.
[14] M. Abon, J.C. Bertolini, J. Billy, B. Tardy, T.M. Tri, J. Massardier and P. Gallezot, Bull. Soc. Chim. 3 (1985) 321.
[15] M. Abon, J. Billy and J.C. Bertolini, Surf. Sci. 171 (1986) L387.
[16] P. Jakob and D. Menzel, Surf. Sci. 201 (1988) 503.
[17] A. Cassuto and D.A. King, Surf. Sci. 102 (1981) 388.
[18] N.V. Richardson and A.M. Bradshaw, in: Electron Spectroscopy, Theory, Techniques and Applications, Vol. 4, Eds. C.R. Brundle and A.D. Baker (Academic Press, New York, 1981) p. 153.
[19] P. Jakob and D. Menzel, Surf. Sci. 220 (1989) 70.