Identification of a laterally mobile state during CO adsorption

A Beutler, A J Jaworowski, M Wiklund, A Sandell, R Nyholm, S Gray and
J N Andersen

Department of Synchrotron Radiation Research, Institute of Physics, Lund University Box 118,
S-221 00 Lund, Sweden

Abstract.   We have investigated CO adsorption at 300 K on ∼1.5 atomic layer thick Pd films on
a Mo(110) surface by high-resolution core level photoemission. We describe how high-resolution
core level spectroscopy may be utilized to study the influence of laterally mobile states on the
sticking probability of molecules on such a laterally heterogeneous surface. The present Pd films
are laterally heterogeneous in the sense that the additional ∼0.5 atomic Pd layer forms mesoscopic
one-layer thick islands on top of the first Pd layer. At 300 K, CO chemisorbs on these two-layer
thick islands but not on the one-layer parts of the film. The rate at which these two-layer islands
are filled by CO molecules as the surface is exposed to CO is found to be consistent with a picture
where CO molecules that initially impinge on the one-layer parts of the surface enter a laterally
mobile state and diffuse to the two-layer islands and adsorb there. This mobile state is in many
respects similar to a classical precursor state.

1. Introduction

A fundamental property of the interaction between a gas and a surface is the sticking probability,
that is, the probability that a gas molecule that hits the surface ends up in an adsorbed state on
the surface. In many adsorption systems, the sticking probability remains almost constant over
a large coverage range. This behaviour of the sticking probability led to the introduction of
so-called mobile precursor states (see e.g. [1, 2]), that is, transitory states which the molecules
enter upon arrival from the gas-phase and which allow the molecules to move laterally across
the surface and search for vacant sites where they can adsorb. In addition to being important for
adsorption on homogeneous surfaces, any mobile state which a molecule enters upon arrival
at the surface may also significantly influence adsorption on laterally heterogeneous surfaces
since these states enable adsorbing molecules to search for the parts of the surface with the
higher adsorption energy and adsorb there. This may influence the adsorption probability on
one part of a heterogeneous surface, such as, for example, small metal particles dispersed on an
inert support. The existence of such mobile and possibly short-lived states could therefore be
of paramount interest for understanding the adsorption properties of heterogeneous surfaces.

In the present contribution we describe how high-resolution core level photoemission
applied to a laterally heterogeneous surface may be used for investigating if adsorbing
molecules enter a short-lived and mobile state. Assume that the molecules under investigation
do not adsorb on the investigated surface at the given sample temperature. Assume also that the
surface contains localized areas, which we will designate as 'traps', on which the molecules
do adsorb at the given temperature. If a molecule encounters such a trap during its diffusion,
it will adsorb on it. The rate at which these traps are filled will depend on whether or not the

adsorbing molecules enter a mobile state. If the molecules do *not* enter such a mobile state, the only molecular flux incident on the traps is due to molecules that hit these areas directly upon arrival from the gas-phase. This flux is proportional to the area of the traps. Therefore, if no mobile state exists, the total number of trapped molecules after a given exposure is proportional to the area of the traps and the coverage of molecules on the traps (i.e. the number of molecules per trap area) is independent of the relative area of the surface covered by the traps. The contribution to the coverage on the traps from molecules hitting these directly from gas-phase may be determined experimentally by noting that it equals the measured coverage in the case where the traps cover the whole surface. If, on the other hand, a mobile state does exist on the surface parts between the traps, the laterally diffusing molecules in this state will contribute an additional incident flux on the traps. In this case, the total number of molecules adsorbed on the trap areas is higher than that which would result from the gas-phase flux directly hitting the trap areas. Specifically, if a mobile state exists, the total number of trapped molecules will no longer be proportional to the trap area and the coverage of molecules on the traps will depend on the relative surface area covered by the traps.

2. Results

The necessary traps may, for example, be created experimentally by growing two-dimensional islands of a metal on the surface under investigation. If the adsorption energy of the molecules is much higher on these islands than on the bare surface, the islands will act as traps for the molecules. In the present study, we have accomplished such a situation for adsorption of CO by growing ∼1.5-layer thick Pd overlayers on a Mo(110) surface. Experimental conditions and procedures for sample cleaning and deposition of the Pd films are as previously described in [3]. As shown by the scanning tunnelling microscopy (STM) picture in figure 1, such a Pd deposition results in a one atomic layer thick Pd film with half of its area covered by islands of an additional Pd layer (i.e. with a total thickness of two atomic layers). From STM measurements we find that these second layer (the layers are counted starting from the Mo(110) surface) islands typically have diameters between 20 and 150 Å, see figure 1. One- and two-layer thick Pd films, respectively, behave quite differently concerning CO adsorption. On one layer of Pd on Mo(110), CO shows only weak chemisorption and at a sample temperature of 300 K no CO adsorbs [3, 4]. In passing we note that at lower temperature, where CO does adsorb on one-layer Pd films, the molecules are known to adsorb in on-top sites at least up to a coverage of 0.33 monolayers [3, 4]. On two Pd layers, CO adsorbs more strongly and high CO coverages can be obtained even at 300 K [4]. Thus, for CO adsorption at 300 K there is no stable chemisorbed state for CO on the one-layer parts of the surface, whereas the two-layer Pd islands will behave as the above-mentioned traps for the CO molecules.

We use high resolution core level photoemission (with a total energy resolution of ∼0.3 eV) for monitoring the CO adsorption on the surface. The simplest way of doing this is to monitor the C 1s intensity as a function of CO exposure since this intensity is proportional to the total number of adsorbed molecules. At 300 K we find no C 1s intensity even after extensive exposure of a one-layer Pd film showing that no CO adsorbs on such a one-layer film at 300 K. It therefore seems justified to assume that if a 1.5-layer Pd film is exposed to CO at 300 K, all of the C 1s intensity is due to CO molecules on two-layer islands, i.e. on the traps.

An alternative method of deriving the CO occupation of the two-layer islands is to monitor the Pd $3d_{5/2}$ core level. As described in detail below, a simple analysis of high-resolution core level spectra of the Pd $3d_{5/2}$ level allows us to determine the CO coverages separately on the one- and two-layer parts of the surface. In agreement with the above assumption, such an analysis shows that at 300 K no CO adsorbs on the one-layer parts of the surface for a 1.5-layer film.
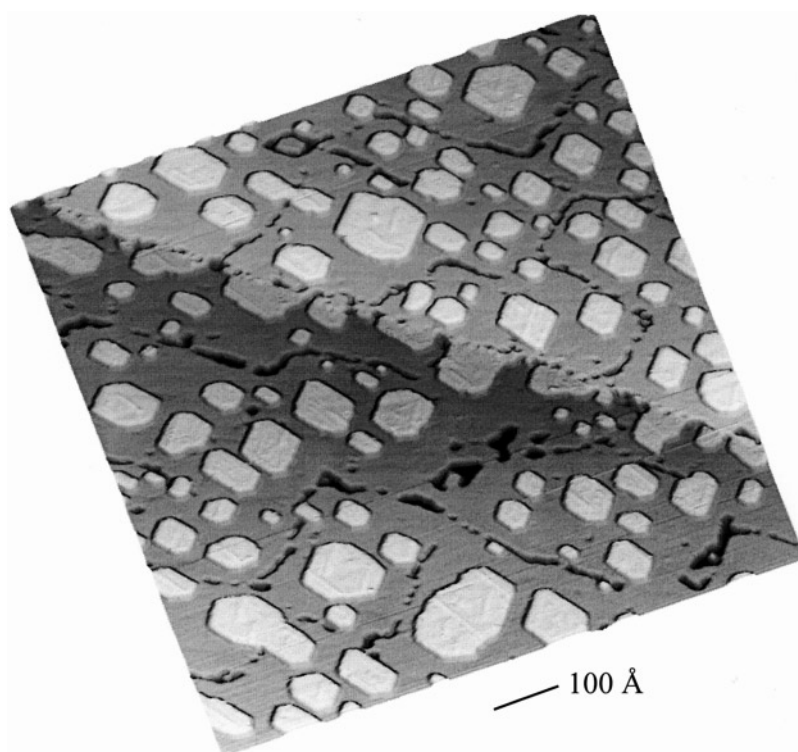
Figure 1. STM topograph of second-layer Pd islands on one layer of Pd on Mo(110).

Before continuing to describe our results we will briefly comment on the possibility of using the C 1s spectra for determining on what parts of the surface the CO molecules have adsorbed. The C 1s binding energy for CO adsorbed on a two-layer Pd film varies from ∼285.7 eV at low coverage to just below 286 eV for saturation coverages of CO. On the one-layer films (where CO chemisorbs weakly at lower temperatures) the C 1s binding energy is ∼286.3 eV [3] and the C1s emission contains a strong shake-up close to the main line [3]. Because of the different C 1s binding energies for adsorption on one- and two-layer Pd films, C 1s spectra can be used to decide on what part of the surface the CO adsorbs. From C 1s spectra we find that all C 1s emission even after extensive CO exposure of a 1.5-layer Pd film at 300 K can be attributed to CO adsorbed on the two-layer islands. This confirms the above assumption that no CO adsorbs on the one-layer parts of the surface for a 1.5-layer Pd film.

Figure 2 shows the C 1s intensity versus CO exposure for a 1.5- and a two-layer Pd film at 300 K, where CO does not adsorb on a one-layer film. The C 1s intensity is seen to be similar for the two films for CO exposures up to about 0.75 Langmuir (L, 1 L = 10^{-6} Torr s^{-1}). That is, the total amount of adsorbed CO is about the same for the two films even though the area of the two-layer Pd islands for the 1.5-layer film is only half of that for the two-layer film. Thus, the total number of CO molecules on the traps is not proportional to the trap area. As mentioned above, this behaviour shows that a laterally mobile state exists for CO molecules that adsorb on one layer of Pd on Mo(110). The similar total number of CO molecules on the 1.5- and two-layer films after a given CO exposure (for CO exposures below 0.75 L) furthermore shows that the capture of adsorbing CO molecules into this mobile state and the subsequent lateral diffusion of the molecules is very efficient in the sense that nearly all of the CO molecules
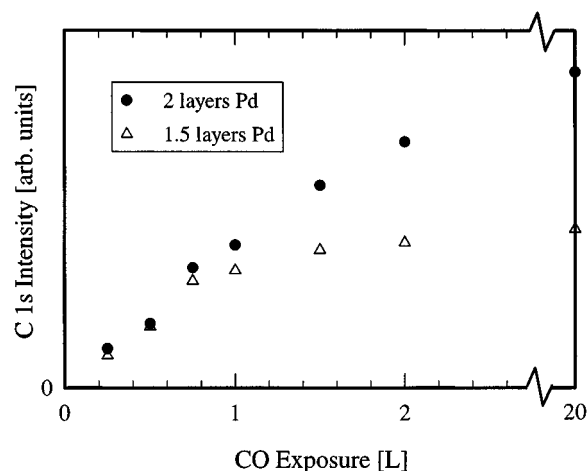
Figure 2. The integrated C 1s intensity versus CO exposure at 300 K for 1.5- and two-layer Pd films, respectively, on Mo(110).

make it to the islands. Finally, at higher CO exposures, the C 1s intensity increase levels off as the traps become saturated with CO. After a 20 L exposure, which corresponds to saturation, the C 1s peak from the two-layer film is about twice as intense as from the 1.5-layer film reflecting the twice as large second layer area for the two-layer film.

The above conclusions may also be obtained through analysis of the Pd $3d_{5/2}$ spectra. Figure 3 shows Pd $3d_{5/2}$ core level spectra from one-, 1.5- and two-layer Pd films on Mo(110) before and after an exposure to 1 L of CO at 130 K, at which temperature CO also adsorbs on a one-layer Pd film. The clean one-layer Pd film shows a single Pd $3d_{5/2}$ component at a binding energy (BE) of 335.5 eV. The clean two-layer Pd film shows two Pd $3d_{5/2}$ components, one at 335.7 eV BE due to the inner Pd layer in direct contact with the Mo surface, and one at 334.7 eV BE due to the outermost Pd surface layer. The spectrum from the 1.5-layer film is a superposition of the one- and two-layer spectra with an intensity of the low BE component that is proportional to the surface area covered by two Pd layers.

As CO is adsorbed on any of these films, the Pd $3d_{5/2}$ level of the Pd atoms bonding to CO molecules shows a large shift towards higher BE. For the one-layer Pd film, the CO-induced Pd $3d_{5/2}$ peak ends up at a BE energy above 336 eV. No other peaks are present in this range. Thus it is easy to detect CO adsorption on the one-layer parts of the surface. For the second layer Pd atoms, the CO induced Pd $3d_{5/2}$ peak ends up at a BE just above 335.5 eV. This is close to the BE of the first clean Pd layer, which makes it more difficult to detect the CO-induced Pd $3d_{5/2}$ emission. However, CO adsorption on the second Pd layer is still easily detected by the reduction of the clean second layer peak at 334.7 eV BE. This low BE component disappears at the particular CO coverage where all second-layer Pd atoms are influenced by CO. Thus, the minimum CO exposure needed to reach this particular CO coverage can be determined in a straightforward way. More quantitative information may be obtained by decomposing the Pd $3d_{5/2}$ spectra into components corresponding to the various kinds of Pd present. We use the following parameter values for the Pd $3d_{5/2}$ lineshapes. First layers, Lorentzian width $L = 0.39$ eV, Gaussian width $G = 0.30$ eV, asymmetry index $\alpha = 0.02$, second layer: $L = 0.39$ eV, $G = 0.28$ eV, $\alpha = 0.14$. All widths are given as full width half maximum (FWHM). For instance, we use three components for the CO exposed two-layer Pd film: one for the first Pd layer, one for the Pd atoms in the second layer not influenced by CO, and one
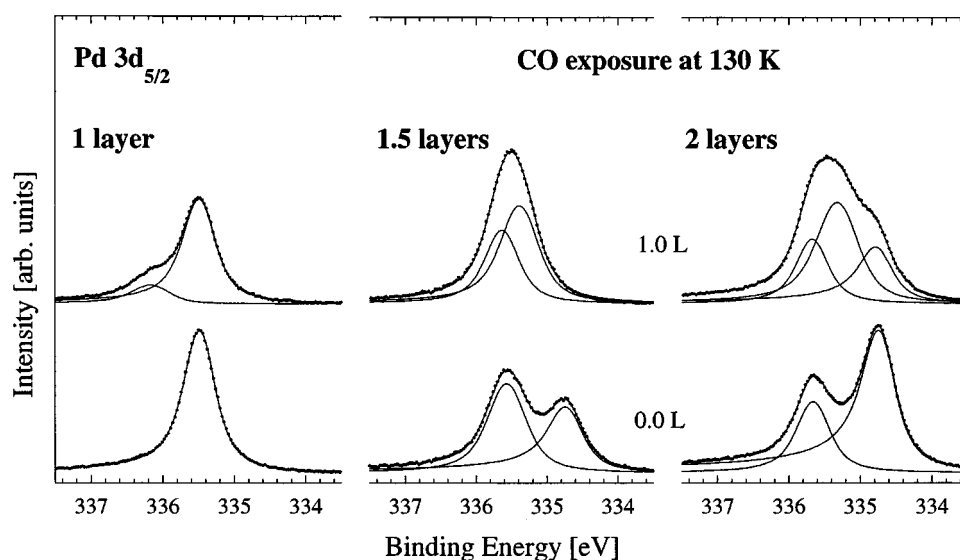
Figure 3. Pd $3d_{5/2}$ spectra of one-, 1.5- and two-layer Pd films, respectively, on Mo(110) before and after exposure to 1 L of CO at 130 K. Note that at 130 K CO *does* adsorb on the first Pd layer [4, 5]. Photon energy was 400 eV.

for the CO influenced Pd atoms in the second layer. Note that we use only one component for the first-layer Pd, also in the 1.5-layer situation, although the first Pd layer in that situation contains two kinds of Pd atoms; those covered by a second Pd layer and those not. The BE shift between the two kinds of Pd atoms is, however, quite small and the two peaks may be satisfactorily described by one slightly broadened Pd $3d_{5/2}$ peak. Examples of decompositions are included in figure 3. The intensity of the CO-induced peak divided by the total intensity from the second-layer Pd atoms is equal to the fraction of second-layer Pd atoms influenced by CO. Thus, from these decompositions we can determine the CO exposure needed to influence the same fraction of Pd atoms for the 1.5- and two-layer films, i.e. to obtain the same CO coverage on the second layer areas of the two films. The quantitative relationship between the intensity of the CO-induced Pd $3d_{5/2}$ peak and the CO coverage of course depends on the CO adsorption site as different numbers of Pd atoms are influenced for different CO adsorption sites. However, the CO adsorption sites are expected to be the same for a 1.5- and a two-layer Pd film for a given local CO coverage. Therefore, the quantitative relationship between CO coverage and the relative intensity of the CO-induced Pd $3d_{5/2}$ peak should be the same for these two films.

Figure 4 shows Pd $3d_{5/2}$ spectra for a 1.5- and a two-layer Pd film versus CO exposure at 300 K, where CO does not adsorb on the one-layer thick Pd film. These spectra show that an exposure between 0.75 and 1 L is sufficient to remove all of the low BE intensity for a 1.5-layer film, whereas between 1.5 and 2 L is needed for a two-layer film. That is, only about half the exposure is needed for a 1.5-layer film in order to reach a coverage where all second-layer Pd atoms are influenced by CO. This shows that CO molecules impinging on the one-layer parts of the surface enter a laterally mobile state and migrate to the two-layer islands. A more detailed analysis based on decompositions of the Pd spectra shows, for all CO coverages, that a 1.5-layer film needs only about half the CO exposure of a two-layer film in order to reach the same CO coverage. This, in agreement with the C 1s results above,
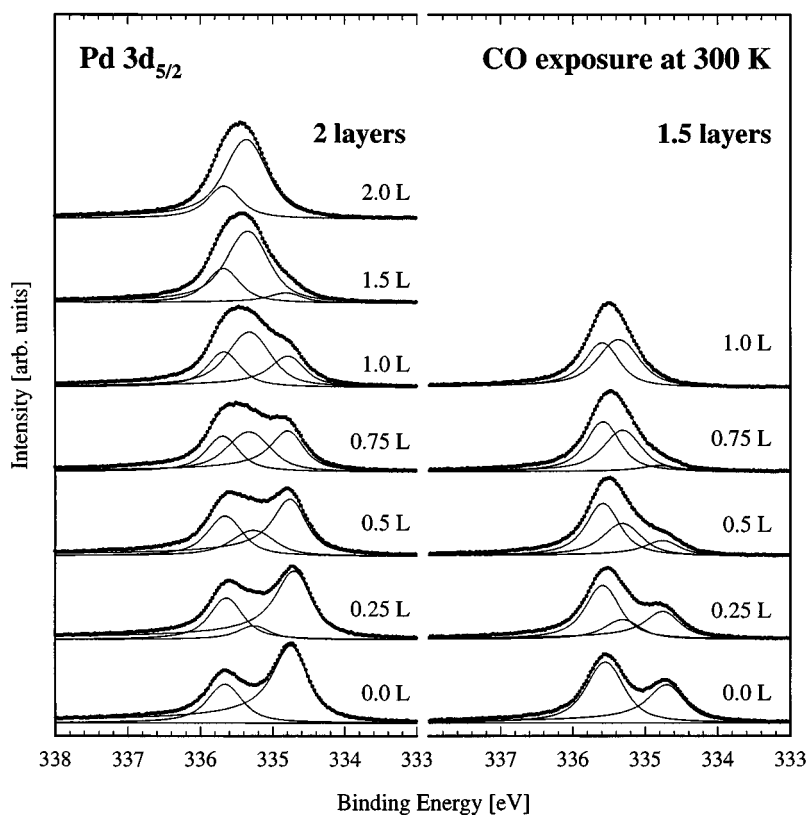
Figure 4. Pd $3d_{5/2}$ spectra for 1.5- and two-layer Pd films, respectively, on Mo(110) after the indicated CO exposures at 300 K. Photon energy was 400 eV.

demonstrates that the capture and subsequent migration of the CO molecules are very efficient processes. Furthermore, we find no Pd $3d_{5/2}$ components which can be attributed to first-layer Pd atoms influenced by CO even after extensive CO exposure at 300 K, which verifies that no CO chemisorption occurs on the one-layer parts of the Pd film at 300 K.

Returning to figure 3 it may be noted that no CO-induced first-layer Pd component is present for the 1.5-layer film despite the facts that CO actually has a stable chemisorption state on a one-layer Pd film at 130 K and that the exposure of 1.5 L is actually larger than that needed for influencing all second-layer Pd atoms. The reason for this is that 1.5 L is too low an exposure to saturate the second-layer islands and, even though this necessitates a compression of the CO overlayer on the islands, the CO molecules still prefer to diffuse to the islands and adsorb there as opposed to adsorbing on the one-layer parts of the surface. This behaviour is very similar to the one we have earlier reported [5, 6] for the adsorption of CO on laterally heterogeneous Pd films on Rh(111).

3. Discussion

Whereas the present measurements clearly show that CO molecules enter a laterally mobile state when adsorbing on one layer of Pd on Mo(110) they are not conclusive when it comes to the exact nature of this state. One possible interpretation of these results is that the CO

molecules enter a chemisorbed state on the one-layer Pd film and stay in that state for a finite time before they desorb back to gas-phase at 300 K. While chemisorbed, the molecules may diffuse on the surface and reach the second-layer islands. This is the interpretation we have previously given for CO adsorption and migration on heterogeneous surfaces consisting of Pd islands on Rh(111) [5, 6]. For those systems (and for the present system at 130 K, see [3, 4]), CO has a stable chemisorption state on all parts of the surface at the investigated temperatures, i.e. the residence time of the CO molecules on the surface may be regarded as infinite, making it natural to think in terms of such states. The difference to the present case at 300 K is that here the residence time for the molecules on the surface is finite. A description in terms of chemisorbed molecules which diffuse on the surface seems, however, still meaningful if the time a molecule needs in order to diffuse a distance comparable to the typical distance between the second-layer islands is much shorter than the average residence time of the CO molecules on the surface. The weakly chemisorbed state of CO on one layer of Pd on Mo(110) has previously [3, 4] been found to involve only CO molecules adsorbed on top of the Pd atoms for CO coverages below 0.33 ML. It therefore seems likely that, if the above interpretation in terms of diffusion in a chemisorbed state is correct, the laterally mobile state of the CO molecules on the one-layer parts of the surface involves CO molecules in on-top sites. Another possible interpretation of the laterally mobile state is that it is a loosely bound transitory state which adsorbing molecules enter when approaching the surface and from which they may jump, possibly having to surmount a barrier, to a chemisorbed state (or desorb back to gas-phase). Such a state could be due to a physisorption well at larger distances from the surface than the chemisorption well. The state could also simply be due to those molecules which have given up their momentum normal to the surface, tumble around on the surface while giving up their rotational energy as well as their momentum parallel to the surface.

4. Summary

In summary, we believe that the above results unambiguously show that CO molecules enter a laterally mobile state when adsorbing on a one-layer Pd film on a Mo(110) surface at 300 K and at 130 K. The measurements demonstrate that this state is highly efficient when it comes to capturing incoming CO molecules and allowing them to move to areas on the surface where they can adsorb. The existence of this state has a strong impact on the adsorption properties of CO on one-layer Pd films on Mo(110). The consequences of the state are in many respects similar to those expected for a classical (intrinsic) precursor state [1, 2], e.g. due to this state we would expect that the sticking probability of CO versus coverage would stay close to constant over a large coverage range. The present measurements do not allow us to determine the exact nature of this mobile state. Irrespective of the exact nature, the existence of such a laterally mobile state for adsorbing molecules will have a major influence on the adsorption on laterally heterogeneous systems, such as small metal clusters dispersed on a support surface. In fact, results from molecular beam scattering experiments [7] on supported Pd clusters have previously been interpreted in terms of CO diffusion occurring from the supporting oxide to the Pd particles. Such diffusion processes may have a significant influence on the turnover rate for reactions catalysed by small supported metal particles.

References

[1] Kisliuk P J 1957 *J. Phys. Chem. Solids* **3** 95
     Kisliuk P J 1958 *J. Phys. Chem. Solids* **5** 78
[2] King D A and Wells M G 1972 *Surf. Sci.* **29** 454
     Casuto A and King D A 1981 *Surf. Sci.* **102** 388
[3] Sandell A *et al* 1998 *Phys. Rev.* B **57** 13 199
[4] Xu C and Goodman D W 1996 *Surf. Sci.* **360** 249
[5] Beutler A, Sandell A, Jaworowski A J, Nyholm R, Wiklund M and Andersen J N 1998 *Surf. Sci.* **411** 111
[6] Beutler A, Sandell A, Jaworowski A J, Wiklund M, Nyholm R and Andersen J N 1998 *Surf. Sci.* **418** 457
[7] Matolin V and Gillet E 1986 *Surf. Sci.* **166** L115
     Matolin V and Stará I 1998 *Surf. Sci.* **398** 117
     Henry C R, Chapon C and Duriez C 1991 *J. Chem. Phys.* **95** 700