

Hydrogen-induced CO displacement from the Pt(111) surface: an isothermal kinetic study

Deborah Holmes Parker ¹

Department of Chemistry and Biochemistry and Cooperative Institute for Research in Environmental Sciences, University of Colorado, Boulder, CO 80309-0216, USA

Daniel A. Fischer

Exxon PRT, NSLS, Brookhaven National Laboratory, Upton, NY 11973, USA

Jeff Colbert

Instrumentation Division, Brookhaven National Laboratory, Upton, NY 11973, USA

Bruce E. Koel ²

Department of Chemistry and Biochemistry and Cooperative Institute for Research in Environmental Sciences, University of Colorado, Boulder, CO 80309-0216, USA

and

John L. Gland

Department of Chemistry, University of Michigan, Ann Arbor, MI 48109-1055, USA

Received 5 February 1991; accepted for publication 2 May 1991

Chemisorbed CO can be completely removed from the Pt(111) surface in the temperature range 318 to 348 K for hydrogen pressures above 2×10^{-2} Torr. Thermal desorption of CO in this temperature range in the absence of hydrogen removes only a fraction of the adsorbed CO. A series of in situ isothermal kinetic experiments are presented in this paper which show that CO displacement in the presence of 0.2 Torr of hydrogen is a first-order process in CO coverage with an activation energy of 10.9 kcal/mol. We propose that the origin of this effect is that repulsive interactions between coadsorbed atomic hydrogen and carbon monoxide induce high desorption rates of CO characteristic of high CO coverages, presumably due to lower values of the desorption activation energy. The importance of these results is to show that high coverages of coadsorbed hydrogen resulting from substantial overpressures of H₂ may substantially modify desorption activation energies, and thus the coverages and kinetic pathways available, even for strongly chemisorbed species. These phenomena may play an important role in surface reactions which occur at high pressure.

¹ Present address: Institute for Surface and Interface Science and Department of Chemistry, University of California, Irvine, CA 92717, USA.

² Present address: Department of Chemistry, University of Southern California, Los Angeles CA, 90089-0482, USA.

1. Introduction

There have been many studies focussed on chemisorption of CO and H₂ on transition metal

surfaces because of the widespread use of these adsorbates to characterize metal catalysts and because these molecules are the primary reactants for Fischer–Tropsch synthesis of hydrocarbons. Chemisorption of hydrogen on platinum surfaces has been investigated in detail [1–3]. Hydrogen adsorbs dissociatively on Pt(111) with an initial sticking coefficient of 0.1 at 150 K which decreases with increasing coverage [2]. The saturation coverage of hydrogen on clean Pt(111) is 0.80 ML [2]. In the limit of zero coverage, the activation energy for H₂ desorption from Pt(111) is 19 kcal/mol [1]. CO adsorption on Pt(111) has also been studied extensively [4–8]. CO is adsorbed molecularly on Pt(111) with an adsorption energy of 31 kcal/mol at low coverage [4–7]. The desorption activation energy decreases sharply above $\theta_{\text{CO}} = 0.50$ ML where compression of the adlayer begins and repulsive interactions become important [4]. The activation energy for desorption continues to decrease as θ_{CO} increases, approaching the heat of sublimation as the CO adlayer becomes closest-packed.

Studies of the coadsorption of CO and H₂ reveal repulsive interactions between these adsorbed species and a tendency for these coadsorbed species to form islands [9]. On a Pt(111) surface precovered with $\theta_{\text{CO}} = 0.22$ ML, Bernasek et al. [10] performed thermal energy atom scattering (TEAS) experiments which showed that CO forms islands with a local density of $\theta_{\text{CO}} = 0.50$ ML on the hydrogen saturated surface at 180 K. The CO islanding induced by coadsorbed hydrogen has also been studied by infrared reflection absorption spectroscopy (IRAS) [11]. These IRAS studies confirm the results of Bernasek et al. [10] and suggest an optimum temperature of 150 K for the growth of large islands. Evidence has also been presented for a weak direct interaction between these coadsorbed species [11].

These coadsorption experiments performed in UHV have provided a great deal of useful information on the interactions of these adsorbed species, yet some processes and intermediates may dominate only under high pressures of the reactant gases. Several experiments have been performed recently to investigate the interaction between CO and hydrogen on transition metal

surfaces under high pressures of hydrogen. It is helpful to summarize the results briefly here. The displacement of CO on Ni(100) has been studied with transient fluorescence yield near-edge spectroscopy experiments [12] similar to the experiments reported in this paper. On the Ni(100) surface, in situ isothermal displacement experiments in the 278 to 330 K temperature range indicate that CO is rapidly displaced by hydrogen pressures above 1.0×10^{-3} Torr. The displacement rate can be fit by two sequential first order processes with activation energies of 7 kcal/mol for high CO coverages and 10 kcal/mol for lower CO coverages. These in situ transient results were verified by a series of ex situ temperature-programmed Desorption (TPD) experiments [13,14]. Recently, a new low-temperature displacement mechanism for CO on the Pt(111) surface was observed in the presence of high pressures of hydrogen (0.001 to 0.1 Torr H₂) [15]. Temperature-programmed fluorescence yield near-edge spectroscopy (TPFYNES) was used to continuously monitor the CO coverage as a function of temperature both in the presence and absence of hydrogen. For hydrogen pressures above 0.01 Torr, removal of CO began at 130 K ($E_{\text{d}} = 10.6$ kcal/mol) instead of near the desorption temperature of 400 K ($E_{\text{d}} = 26$ kcal/mol) in the absence of hydrogen. The large decrease in CO desorption energy appears to be caused by substantial repulsive interactions in the compressed monolayer induced by coadsorbed hydrogen.

In the in situ experiments, reported in this paper, fluorescence yield near-edge spectroscopy FYNES was used in isothermal kinetic studies to continuously monitor the CO coverage at constant temperature both in the presence and absence of hydrogen on Pt(111). FYNES is a photon-in/photon-out method which allows near-edge X-ray absorption fine structure (NEXAFS) spectra to be obtained in situ under high pressures of reactive gases [16]. The in situ capability of FYNES to monitor the π^* resonance of chemisorbed CO as a function of time at various crystal temperatures and pressures of hydrogen was used in order to obtain the surface CO concentration as a function of time in the presence of substantial hydrogen overpressures.

2. Experimental

These experiments were performed at the National Synchrotron Light Source at Brookhaven National Laboratory on the U1 beamline. The details of the experimental apparatus have been described in greater detail previously [13,16,17]. The experimental apparatus consists of a multi-level UHV analysis chamber with a reaction chamber which can be isolated from the main chamber by using a gate-valve. The Pt(111) crystal was given a saturation exposure of CO at $T < 100$ K in the main chamber and then raised into position in the reaction chamber where the FYNES spectrum was recorded at normal incidence in order to locate the energy position of the π^* resonance. The photon energies were calibrated using the strong carbon absorption feature at 291 eV in the incoming beam due to carbon deposited on the beam line optics. The CO π^* resonance was measured at 288.9 eV. Uptake experiments for CO on Pt(111) (vide infra) show that the intensity of the CO π^* resonance is linearly dependent on surface CO coverage. The experimental arrangement precluded measurement of absolute dosing pressures when the sample was in the FYNES position. Therefore absolute sticking coefficients could not be determined. Control experiments were performed to ensure that the energy position of the CO π^* resonance was invariant with coverage and temperature. FYNES spectra were recorded periodically to verify that the energy position of the π^* resonance had not drifted due to instrumental instabilities.

A typical transient FYNES desorption experiment involved dosing the Pt crystal with a saturation exposure of CO at low temperature (< 100 K). The monochromator was then positioned to provide an incident photon energy of 288.9 eV, the energy of the CO π^* resonance for chemisorbed CO on Pt(111). The temperature was then adjusted to the reaction temperature after the desired H_2 pressure was established. The fluorescence yield intensity resulting from the CO π^* resonance transition, i.e., the concentration of adsorbed CO, was measured as a function of time at constant temperature in the presence of flowing hydrogen and in vacuum. Special precautions were

taken to ensure that the hydrogen was free of impurities [13].

CO uptake experiments were performed by positioning the monochromator at 288.9 eV and placing the clean Pt crystal in the reaction chamber. With the gate-valve open, the CO pressure was adjusted with the gas doser in the main chamber. The CO π^* resonance was monitored as a function of time to record the adsorption of CO on the Pt(111) surface.

3. Results and discussion

Fig. 1 shows the uptake for CO on Pt(111) performed at several different temperatures. These uptake experiments were performed in order to verify that the CO π^* resonance intensity is linearly proportional to CO coverage. The initial slope for all of the curves is linear, indicating that the intensity of the π^* resonance is indeed linearly proportional to CO coverage. Absolute sticking coefficient measurements could not be made because the experimental arrangement precluded absolute pressure measurements. The inset shows a typical FYNES spectrum for a saturation coverage of CO on Pt(111) showing the CO π^* resonance at 288.9 eV. The two higher temperature uptake curves (233 and 313 K) show only a weak dependence of S_0 on T , as has been observed previously [18], and lower saturation values than for 153 K.

Fig. 2 shows a typical isothermal transient experiment for both vacuum and 0.2 Torr hydrogen performed at 338 K. First the Pt(111) surface was given a saturation exposure to CO at 100 K, and the intensity of the CO π^* resonance was monitored for about 100 s to calibrate the signal at saturation coverage. At this point the hydrogen flow was initiated while the crystal was at 100 K. In agreement with previous work [15], fig. 2 shows that no CO displacement occurs at this temperature and H_2 pressure. After the hydrogen pressure was stabilized, the temperature was ramped to the desired reaction temperature. Reaction temperature was reached in about 40 to 60 s and this point defines the zero of the time axis. Once the signal had decayed to a constant value, the temperature

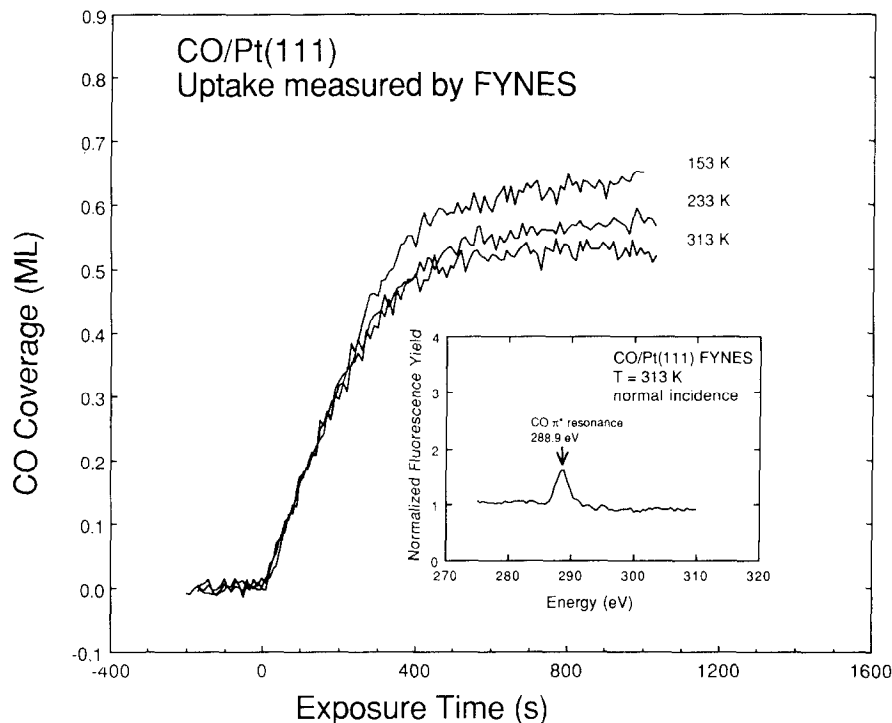


Fig. 1. Uptake of CO on Pt(111) measured at three different temperatures. The inset shows a typical FYNES spectrum of a saturation coverage of CO on Pt(111) taken at normal incidence showing the CO π^* resonance at 288.9 eV.

of the crystal was flashed to 650 K in order to desorb any remaining CO so that a calibration point for zero coverage could be established. From our earlier work on this system [15], we know that removal of the compressed layer of CO (0.64 down to 0.5 ML) occurs at very low temperatures (beginning at 130 K). Fig. 2 clearly shows that the desorption rate is higher in the presence of hydrogen than in vacuum and that a much larger amount of CO is desorbed in the presence of hydrogen. In vacuum, at 338 K, the coverage decays to a constant value of 0.28 ML, while in the presence of 0.2 Torr H_2 , the CO coverage decays to 0.03 ML.

Fig. 3 shows a summary of our results for isothermal desorption of CO in hydrogen and in vacuum. The results for all temperatures show that the rate of desorption is greater in the presence of hydrogen than in vacuum and that the equilibrium coverage of CO is less in the presence of hydrogen than in vacuum at a given temperature. Fig. 3 also shows the fit of each curve to a single exponential function of the form $\theta(t) = c + \nu_1^* \exp(-kt)$, the

integrated rate expression for a first-order reaction. The value of c was fixed at 0.03 ML (the CO coverage remaining at infinite time measured from the experiments performed in the presence of hydrogen) for all displacement experiments. The data for the hydrogen experiments is fit nicely by this integrated rate equation. The poor fit for the vacuum data to a single exponential decay is due to the fact that the activation energy for vacuum desorption of CO from Pt(111) is increasing as the CO coverage decreases [4]. The good fit in the presence of hydrogen indicates that there is little coverage dependence of the activation energy for CO desorption.

Fig. 4 shows an Arrhenius plot for the rate constants for the isothermal displacement of CO by 0.2 Torr hydrogen determined from the exponential fits shown in fig. 3. This plot gives an activation energy of 10.9 kcal/mol. This is in excellent agreement with the value of 10.6 kcal/mol we obtained from TPFYNES experiments [15].

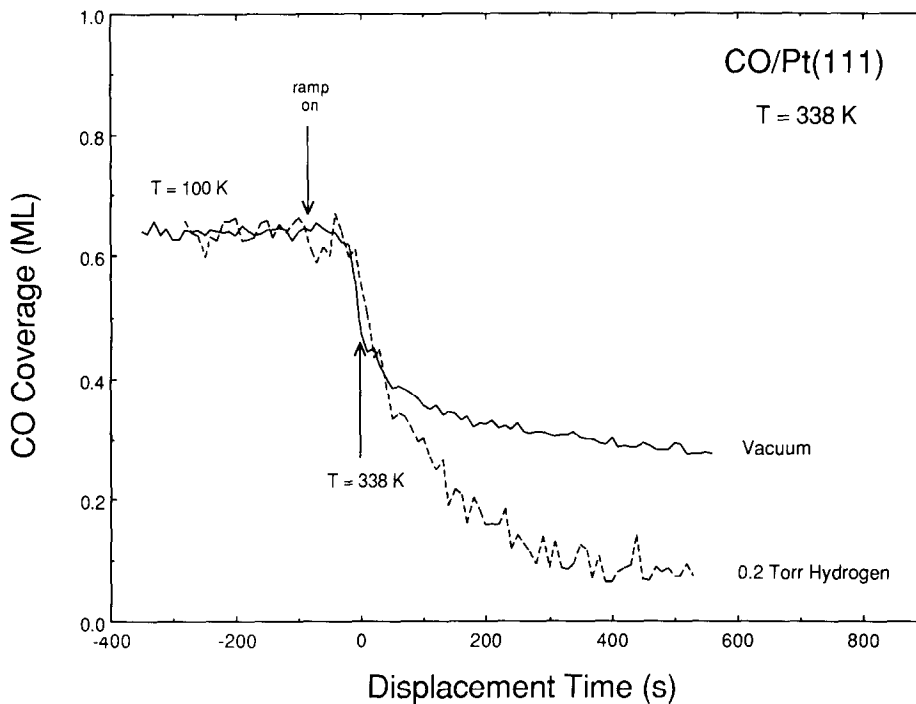


Fig. 2. A typical isothermal transient experiment performed in vacuum and in 0.2 Torr hydrogen. The arrows show when the temperature ramp was initiated and when the reaction temperature was reached.

Hydrogen-induced displacement of carbon monoxide from the Pt(111) surface is consistent with simple energetic arguments. The heat of de-

sorption of CO is strongly dependent on the coverage for $\theta_{\text{CO}} > 0.5$ ML, causing E_d to decrease from 26 kcal/mol at $\theta_{\text{CO}} = 0.5$ ML to less

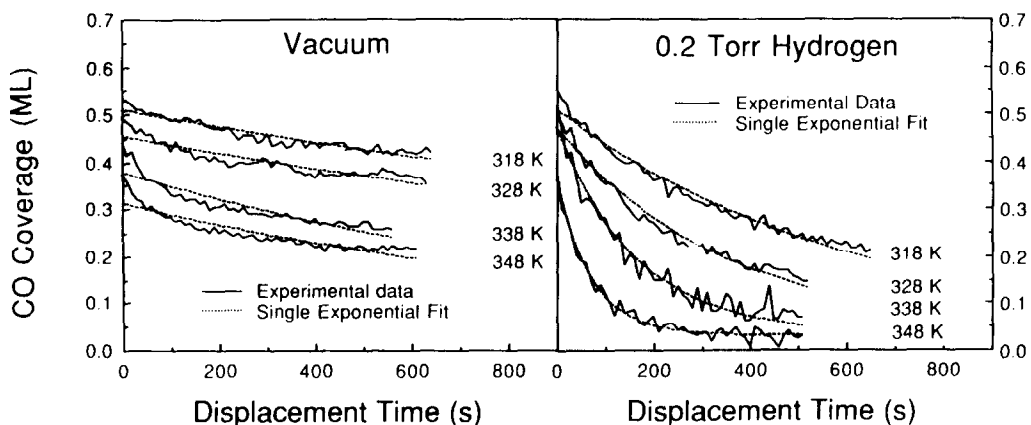


Fig. 3. Transient isothermal kinetic experiments performed on Pt(111) at 318, 328, 338 and 348 K. The left panel shows isothermal CO desorption measurements in vacuum. The right panel shows isothermal desorption (displacement) of CO in the presence of 0.2 Torr hydrogen. The dotted lines in both panels are single exponential fits of the form $\theta(t) = c + \nu_1 \exp(-kt)$.

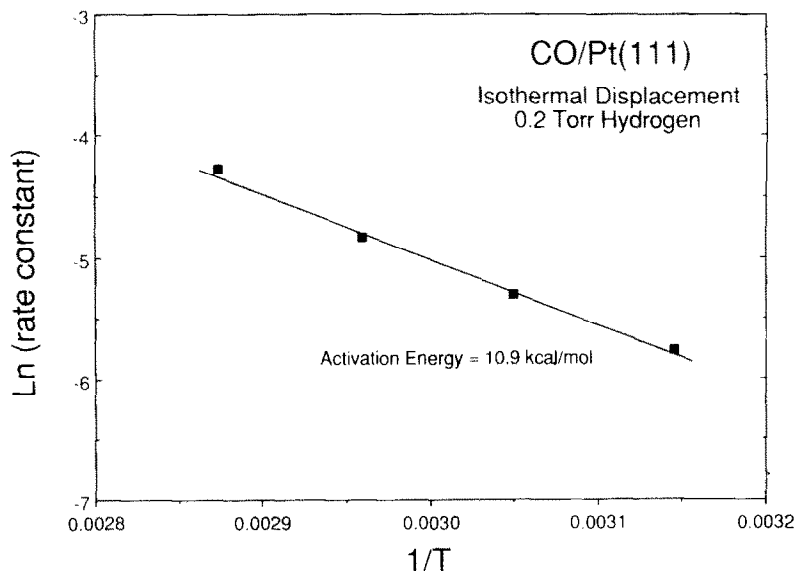


Fig. 4. An Arrhenius plot for the rate constants determined from the exponential fits shown in fig. 2 for $P_{\text{H}_2} = 0.2$ Torr. The slope gives an activation energy of 10.9 kcal/mol.

than 10 kcal/mol at saturation [4]. Hydrogen will displace more weakly bound CO under conditions where repulsive interactions in the adsorbed layer (CO(a)–CO(a), CO(a)–H(a)) reduce the desorption energy for CO to a value smaller than the heat of adsorption for hydrogen. Based on the predominance of nearest neighbor interactions, and using the 6–8 kcal/mol value for the CO–H repulsion energy estimated by Bernasek et al. [10], the lowering of the activation energy for desorption (displacement) from 26 to 11 kcal/mol suggests that two to three hydrogen atoms are involved in the displacement of each CO molecule. We propose that under isothermal conditions, hydrogen overpressures are inducing formation of CO islands with local coverages near the saturation value of 0.64 ML because of repulsive interactions in the coadsorbed overlayer. Thus as displacement proceeds, the coverage of hydrogen increases to maintain the densely packed CO islands which contain CO molecules with a heat of adsorption of about 11 kcal/mol. In the absence of hydrogen, desorption of a small amount of CO increases the heat of adsorption of the remaining CO molecules, causing a decrease in the desorption rate.

Selected experiments were also performed with 0.02 Torr hydrogen flowing through the reaction chamber. These experiments give similar results since this lower pressure is still sufficient to generate high enough surface hydrogen coverages to induce the formation of islands of CO having high local coverage.

4. Conclusions

Chemisorbed CO can be removed in the presence of hydrogen in the range of 2×10^{-2} to 2×10^{-1} Torr at temperatures that remove only a small fraction of adsorbed CO in the absence of hydrogen. In situ isothermal displacement experiments indicate that CO displacement is a first-order process with an activation energy of 10.9 kcal/mol in the presence of hydrogen pressures above 0.2 Torr in the temperature range 318 to 348 K. In the absence of hydrogen, isothermal desorption is not well-described by a simple first-order process, reflecting the increase of desorption activation energy with decreasing coverage. Substantial repulsive interactions occur between coadsorbed CO and hydrogen which induce for-

mation of CO islands with local coverages near the saturation value of 0.64 ML. Extensive CO desorption occurs at low temperatures characteristic of $E_d = 11$ since the coverage of hydrogen increases as displacement proceeds to maintain the densely packed CO islands which contain CO molecules with a heat of adsorption of about 11 kcal/mol. These experiments emphasize the importance of understanding the chemistry of coadsorbed overlayers in the presence of reactive atmospheres in order to develop a realistic model of high-pressure catalytic reactions.

Acknowledgements

We gratefully acknowledge the assistance of Judah Levine at the Joint Institute for Laboratory Astrophysics in Boulder with transferring the data to personal computer format. D.H.P. acknowledges support in the form of an Exxon Fellowship from the Exxon Educational Foundation. BEK acknowledges support from the US Department of Energy, Office of Basic Energy Sciences, Chemical Sciences Division.

References

- [1] B. Poelsema, G. Mechtterscheimer and G. Comsa, Surf. Sci. 111 (1981) 519.
- [2] K. Christmann, G. Ertl and T. Pignet, Surf. Sci. 54 (1976) 365.
- [3] P.R. Norton and P.J. Richards, Surf. Sci. 44 (1974) 129.
- [4] G. Ertl, M. Neumann and K.M. Streit, Surf. Sci. 64 (1977) 393.
- [5] H.J. Krebs and H. Luth, Appl. Phys. 13 (1977) 147.
- [6] R.W. McCabe and L.D. Schmidt, Surf. Sci. 66 (1977) 101.
- [7] B. Poelsema, R. Palmer and G. Comsa, Surf. Sci. 136 (1984) 1.
- [8] P.R. Norton, J.W. Goodale and E.B. Selkirk, Surf. Sci. 83 (1979) 189.
- [9] K.A. Thrush and J.M. White, Appl. Surf. Sci. 24 (1985) 157.
- [10] S.L. Bernasek, K. Lenz, B. Poelsema and G. Comsa, Surf. Sci. 183 (1987) L319.
- [11] D. Hoge, M. Tüshaus and A.M. Bradshaw, Surf. Sci. 207 (1988) L935.
- [12] J.L. Gland, Surface Kinetics with Near-Edge X-ray Absorption Fine Structure, Chemistry and Physics of Solid Surfaces VII, Eds. R. Vanselow and R.F. Howe, Vol. 10 of Springer Series in Surface Sciences (Springer, Berlin, 1988) pp. 221–242.
- [13] S. Shen, F. Zaera, D.A. Fischer and J.L. Gland, J. Chem. Phys. 89 (1988) 590.
- [14] J.L. Gland, S. Shen, F. Zaera and D.A. Fischer, J. Vac. Sci. Technol. A 6 (1988) 2426.
- [15] D.H. Parker, D.A. Fischer, J. Colbert, B.E. Koel and J.L. Gland, Surf. Sci. Lett. 236 (1990) L372.
- [16] F. Zaera, D.A. Fischer, S. Shen, and J.L. Gland, Surf. Sci. 194 (1988) 205.
- [17] D.A. Fischer, J. Colbert and J.L. Gland, Rev. Sci. Instrum. 60 (1989) 1596.
- [18] C.T. Campbell, G. Ertl, H. Kuipers and J. Segner, Surf. Sci. 107 (1981) 207.