

**Experiment title:**

Surface structural investigations of CO adsorption, CO/K and CO/Cs co-adsorption on the Rh(111) surface.

Experiment number: SI 247**Beamline:****Date of experiment:**

from: 97/02/1 1

to: 97/02/17

Date of report:

24047

Shifts:**Local contact(s):** E. Lundgren

2

Received at ESRF:

9 AUG 1997

Names and affiliations of applicants (* indicates experimentalists):

J. N. Andersen

A. Beutler

H. Over

S. Ferrer

J. Alvarez

E. Lundgren

Report: Surface structural investigations of CO adsorption, CO/K and CO/Cs co-adsorption on the Rh(111) surface

The goal of our experiment was twofold; first to study the geometrical structure of the high coverage CO-(2x2)-Rh(111) adsorption structure, secondly to study the influence of co-adsorbed alkali metals on the CO internal bondlength and on the bond of the CO molecule to the Rh(111) surface. Due to several experimental problems, such as problems with the sample holder and sample preparation, we were only able to investigate the structure of the high coverage CO-(2x2)-Rh(111) adsorption structure, and this investigation took place during the last three days of the experimental time given. The results from this investigation, as presented below, demonstrate the feasibility of studying CO induced and related reconstructions on metals at ID3.

The investigation was performed due to a disagreement concerning the adsorption sites of the CO for high coverage CO-(2x2)-Rh(111) adsorption structure. Previous LEED measurements assigned two CO molecules to on top sites and one CO molecule to a bridge site [1] (hereafter bridge model), while recent core level measurements [2] strongly support one CO molecule in an ontop site and two molecules in threefold hollow sites (hereafter hollow model). A recent reanalysis of the LEED data [3] however confirmed the core level measurements. The results presented in this report confirm these findings.

A total of 284 structure factor data F_{hk} were collected resulting in a total of 141 symmetry in-equivalent structure factor data. The average agreement factor, estimated from 79 measurements of equivalent reflections, due to sample misalignment, sample quality, diffractometer imperfections, etc. was found to be 11.2 %.

28 fractional order structure factor data were collected in-plane, $L=0.2$, resulting in 10 symmetry equivalent reflections with an agreement factor of 5.5 %. The peak counting rate from the strongest fractional order beams induced by the CO adsorption at this L was found to be 4500 cts/sec. From the inplane data, via a pair-correlation function, it could be concluded that there is three CO molecules, in a hexagonal structure, per 2x2 unit cell. However, no additional information whether the favored model is the hollow model or the bridge model was obtained.

In order to gain information on the adsorption sites of the CO molecules one has to turn to out-of plan measurements of the Crystal Truncation Rods (CTR:s). These are sensitive to the CO registry with respect to the substrate [4]. In Figure 1a are shown the integral order rods (1,1,L) and (2,2, L) (agreement factor between symmetry equivalent rods 4.5 %). In the figure are also shown the optimized fits for the hollow model (full line) and the bridge model (dot-dashed line). It may directly be seen from the figure that the hollow model is the preferred model. It should be noted that the major difference between the two models is observed in the (1, 1, L) rod as a larger magnitude of the structure factor in the minimum of the CTR for the bridge model, while in the case of the (2, 2, L) rod the difference is insignificant, the magnitude of the structure factor in the minimum in this case is the same for the two models. This indicates that the structure factor in the minimum of the CTR decays more rapidly, for higher parallel momentum transfer, for the bridge model as compared with the hollow model, the reason being the higher registry between the CO and the Rh substrate for the hollow model as compared to the bridge model.

Having established the adsorption sites of the CO molecules, we turn to the more detailed geometry of the structure. In Figure 1 b are shown the (1/2, 1/2, L), (3/2, 0, L) and the (1/2, 0, L) fractional order rods (agreement factor 16 %). The optimized fits for the hollow model (full line) and the bridge model (dot-dashed line) are included in the figure. The optimum geometry, at this time, for CO adsorbed as in the hollow model is detailed in Table. The χ^2 , as defined in ref [5], obtained for the hollow model was found to be 1.24 as compared with 2.17 for the bridge model. In Table 1 is also included the result from the recent reanalyses [3] of the earlier obtained LEED data. It may be seen from Table 1 that the agreement between the LEED results and the present results is reasonably good.

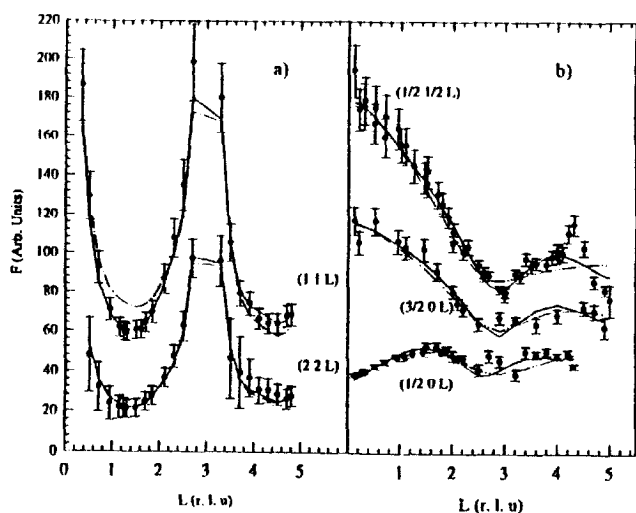


Fig 1 .a) Experimental (filled circles) and calculated structure factors for the hollow (full line) and the bridge (dot-dashed line) for the (1 1 L) and the (2 2 L) CTR's. b) Experimental (filled circles) and calculated structure factors for the hollow (full line) and the bridge (dot-dashed line) for the (1 1 L) and the (2 2 L) CTR's

Atom	SXRD	LEED
1 O (CO on top)	0	0
2 C (CO on top)	-1.15	-1.15
3 O (CO hcp)	-0.39	-0.33
4 C (CO hcp)	-1.55	-1.51
5 O (CO fcc)	-0.46	-0.33
6 C (CO fcc)	-1.59	-1.49
7 Rh	-3.02	-2.98
8 Rh	-3.01	-2.98
8 Rh	-3.01	-2.98
8 Rh	-3.01	-2.98
9 Rh	-5.23	-5.24
9 Rh	-5.23	-5.24
9 Rh	-5.23	-5.24
9 Rh	-5.23	-5.24
10 Rh	-7.42	-7.43
10 Rh	-7.42	-7.43
10 Rh	-7.42	-7.43
10 Rh	-7.42	-7.43

Table 1. structural parameters as obtained for the present investigations and with LEED [3].

[1] M. A. van Hove, R. J. Koestner, and G. A. Somorjai, Phys. Rev. Lett. 50 903 (1983).
 [2] A. Beutler, E. Lundgren, R. Nyholm, J. N. Andersen, B. Setlik, and D. Heskett. Surf. Sci. 371 (1997) 38 1.
 [3] M. Gierer, A. Barbieri, M. A. Van Hove, and G.A. Somorjai, Surf. Sci. submitted.
 [4] I. K. Robinson, S. Ferrer, X. Torrelles, J. Alvarez, R. van Silfhout, R. Schuster, K. Kuhnke, and K. Kern. Europhys. Lett, 32, 37 (1995).
 [5] X. Torelles, H. A. van der Vegt, V. H. Etgens, P. Fajardo, J. Alvarez, S. Ferrer, Surf. Sci. 364 (1996) 242