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CONTRIBUTIONS

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Adsorption of small molecules on oxide surfaces: Cr$_2$O$_3$(111)/Cr(110)[1]

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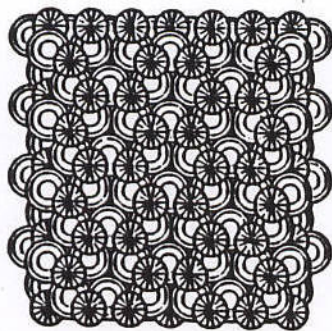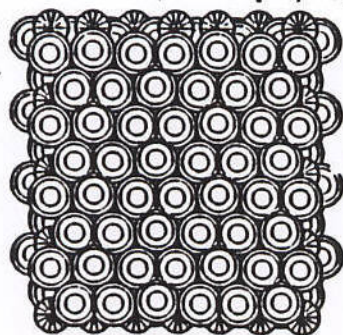Fig.1a: LEED pattern of Cr$_2$O$_3$(111)

Fig.1b: Cr-terminated surface

Fig.1c: O-terminated surface

Oxidation of Cr(110) under controlled, i.e. UHV conditions, leads to the formation of a thin epitaxial Cr$_2$O$_3$ oxide layer with (111) surface orientation. The hexagonal LEED pattern is shown in Fig.1a. This LEED pattern has been reported before[2], and there is general agreement that it is due to a (111) surface of rhombohedral Cr$_2$O$_3$ with lattice parameters very similar to the chromium oxide bulk. Starting from bulk Cr$_2$O$_3$ there are two possible terminations, i.e. Cr-termination and O-termination as schematically shown in Fig.1b in the right and left panel, respectively. ELS in the electronic regime indicates that the surface contains Cr and O terminated areas. The ELS spectra (Fig.2a) exhibit d-d excitations which are due to Cr^{3+} and Cr^{2+} ions. The Cr^{2+} ions are located in the surface as indicated by their attenuation upon adsorption of additional oxygen (Fig.2f). Before the oxide surface is saturated with oxygen it is chemically rather reactive. Several molecules have been adsorbed on the surface, some of which show pronounced reactivity even at very low surface temperature. For example CO$_2$ and NO$_2$ dissociatively adsorb on the surface close to 100 K concomitantly forming adsorbed oxygen and CO and NO. At the same time the diatomics CO and NO adsorb associatively. The dissociation of the triatomics is documented by the disappear-
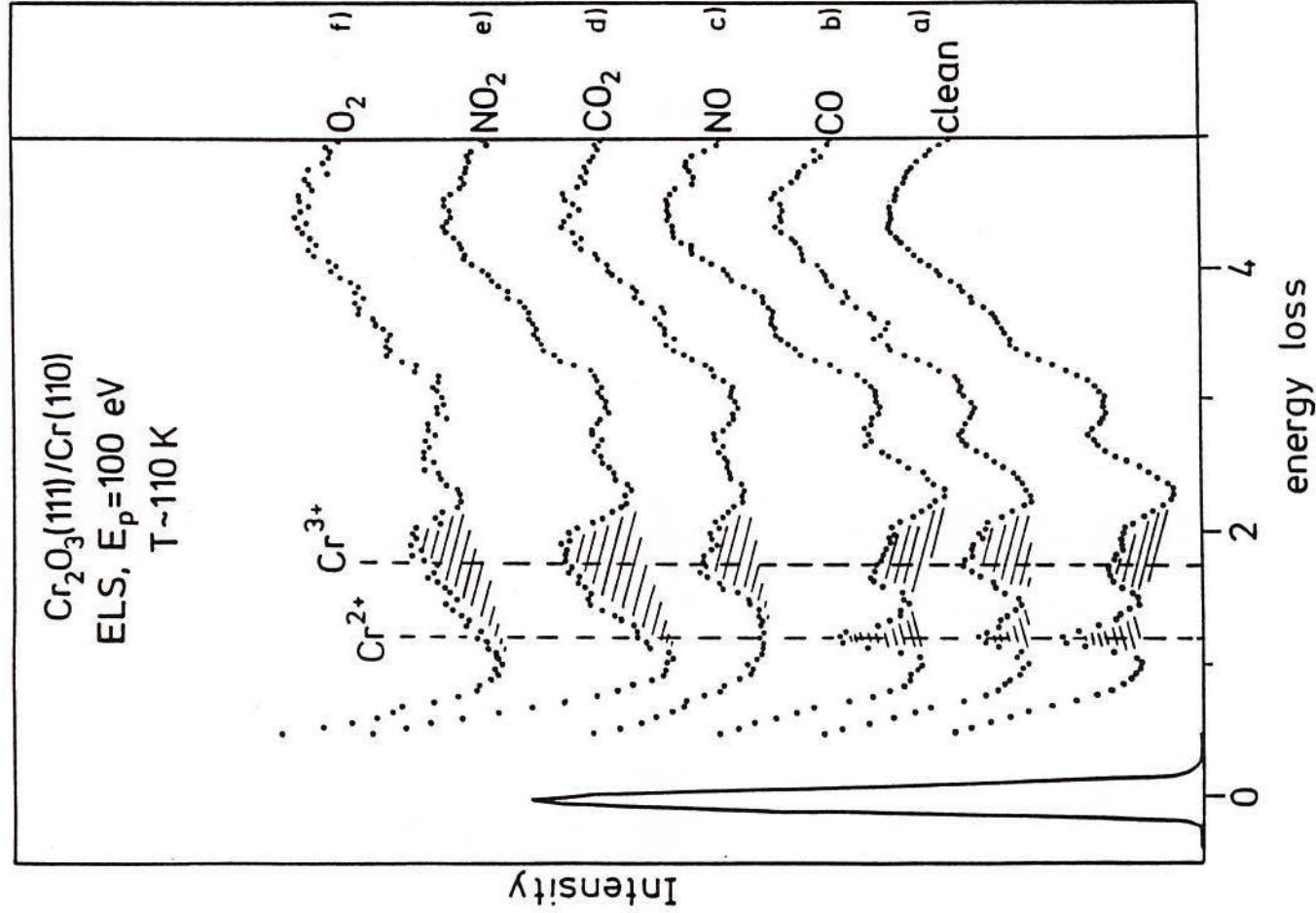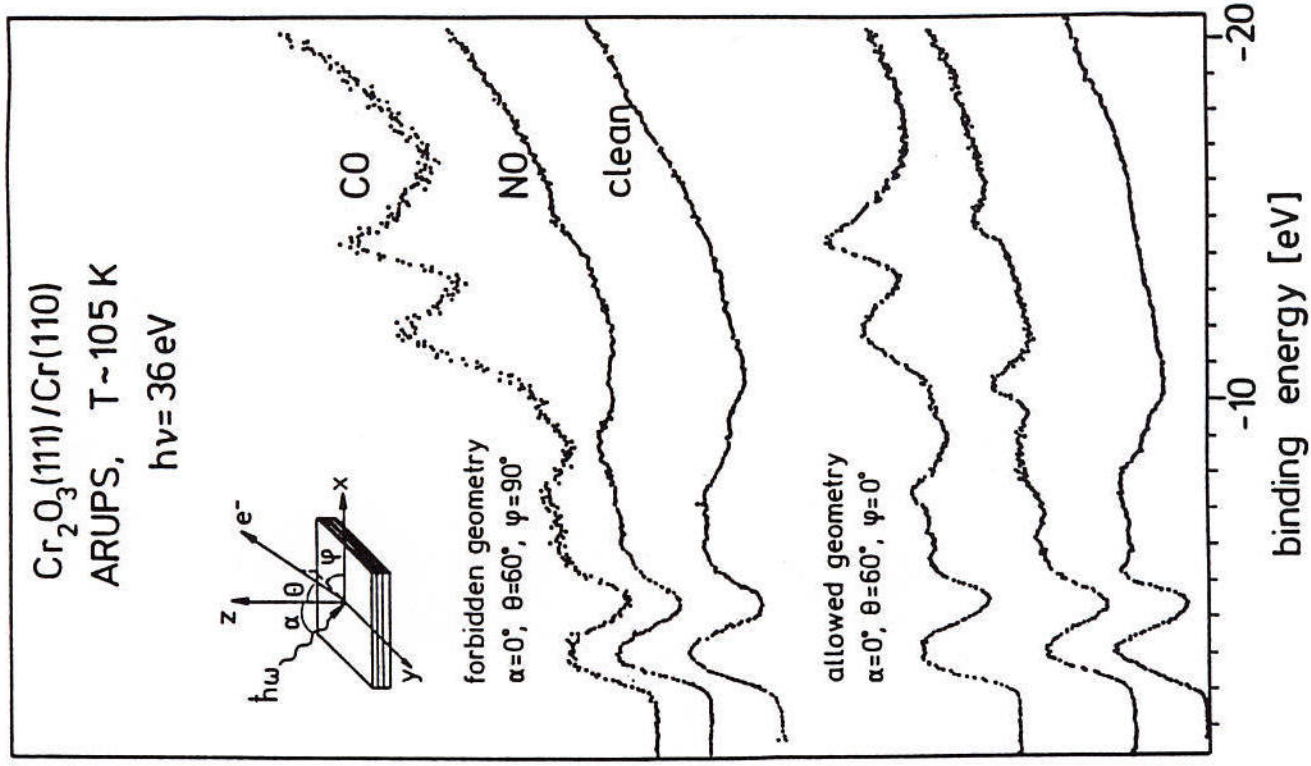
343

Cr$_2$O$_3$(111)/Cr(110)
ARUPS, T~105 K
hν= 36 eV

CO

NO

clean

forbidden geometry
α=0°, θ=60°, φ=90°

allowed geometry
α=0°, θ=60°, φ=0°

binding energy [eV]

-20

-10

Fig. 3

342

Cr$_2$O$_3$(111)/Cr(110)
ELS, E$_p$=100 eV
T~110 K

f)   O$_2$

e)   NO$_2$

d)   CO$_2$

c)   NO

b)   CO

a)   clean

Cr^{2+} Cr^{3+}

energy loss

0   2   4

Intensity

Fig. 2

ence of the Cr^{2+} features in the ELS spectra (Fig.2d and Fig.2e) indicating the oxidation of the surface via the oxygen atoms. Adsorption of CO and NO on the other hand attenuate the Cr^{2+} peaks but do not cause complete suppression as in the case of the triatomics (Fig.2b and Fig.2c).

CO and NO desorb at 175 K and 350 K respectively indicating weak chemisorption in the former and strong chemisorption in the latter case. It is interesting to note that CO forms an ordered $(\sqrt{3}x\sqrt{3})R30^0$ overlayer as revealed by LEED while for NO adsorption no ordered pattern has been observed. The same is true for CO_2 and NO_2. Angle resolved photoemission (ARUPS) as well as near edge x-ray absorption fine structure has been used to get further information about the bonding geometry of the molecules on the surface. Fig.3 shows photoelectron spectra in the so called allowed (upper three traces) and forbidden (lower three traces) collection geometry[3]. If the molecule is oriented with its molecular axis perpendicular to the surface plane ion states of the adsorbed molecule with σ-symmetry are intense. In the forbidden geometry they are attenuated and ion states of π-symmetry are intense. If the molecular axis is oriented parallel to the surface at random azimuthal distribution allowed and forbidden geometry cannot be differentiated and we expect σ-emission in both cases. Fig.3 indicates that we are dealing with the latter situation for CO on the present surface. This also is supported by an investigation of the σ-shape resonance which is observed to peak at large off-normal emission angles. We are able to choose an electron emission geometry where we mainly observe emission of ion states of π-symmetry, i.e. grazing incidence light and near normal electron detection. The experimental results in this geometry show that the 1π-emission is not situated energetically close to the 5σ-emission but rather close to the 4σ emission. This is a very unusual observation if we compare with the situation found on metal surfaces[3]. The observed high binding energies of the CO induced features are another unusual result. A reasonable explanation for these findings is to assume a bonding geometry where the CO molecules are bound to the positively charged Cr ions. This interaction induces a chemical shift of the ion states of CO towards higher binding energies. Considering the observed orientation parallel to the surface and the lateral ordering in a $(\sqrt{3}x\sqrt{3})R30^0$ structure suggests a structure of the adsorbate as shown in Fig.4. CO-metal complexes are known[4-6] where CO bridges two metal atoms establishing both carbon-metal and oxygen-metal contacts.

For NO, however, there are differences of the intensities of the NO induced features in Fig.3. The 4σ-emission, for example, is attenuated in forbidden geometry but it is not completely suppressed as we would expect for perfect perpendicular orientation. A more quantitative analysis shows that we expect a tilt angle of the molecular axis of about 30^0 with respect to the surface normal. This conclusion is supported by the NEXAFS results which are not shown here.
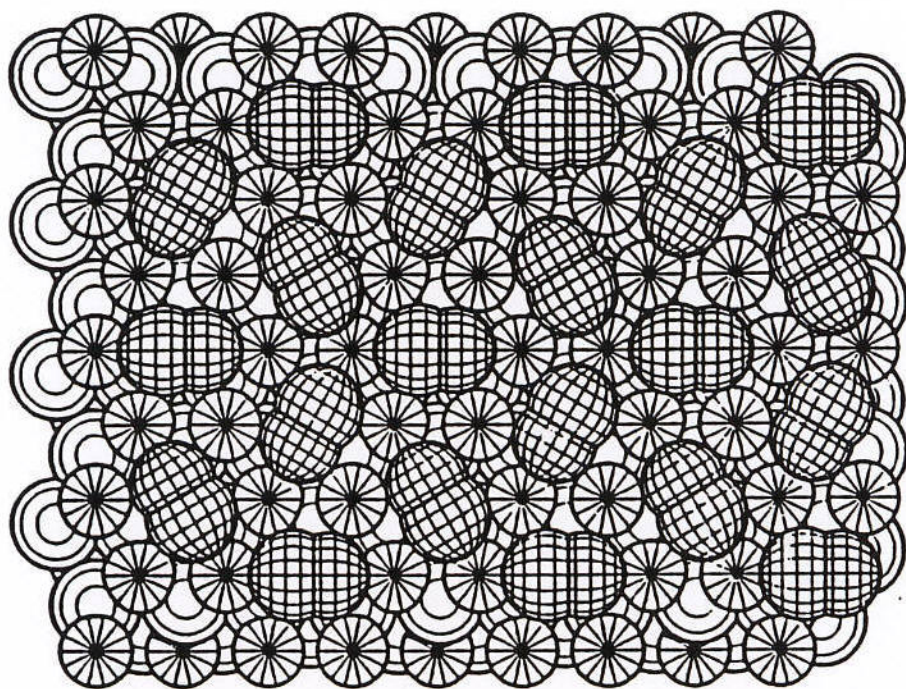
Fig.4 Schematic representation of the CO adsorbate on Cr_2O_3

A sample of our NEXAFS results is shown in Fig.5 where we have plotted NEXAFS spectra of adsorbed CO in comparison with those NEXAFS data after CO_2 adsorption at various temperatures. The features seen in the spectra of the clean substrate are due to photoemission peaks, i.e. due to the O2s and a valence band satellite emission of Cr_2O_3. CO_2 shows up as an intense feature at low temperature. The small extra feature at lower photonenergy has not been assigned yet. At 170 K the dissociation product CO is clearly identified by comparison with the pure CO adsorbate. The second feature at higher binding energy is due to carbonate (CO_3) and not to CO_2, which is only revealed by a more detailed inspection.

Summarizing we find that the $Cr_2O_3(111)/Cr(110)$ surface is rather reactive and shows a different behaviour as compared with other oxide surfaces such as $NIO(100)$[7,8] and $Al_2O_3(0001)$[9] which are much more inactive towards chemisorption of molecules from the gas phase.

/1/   C. Xu, Thesis, Ruhr-Universität Bochum, in preparation.
/2/   P. Michel, Ch. Jardin, Surf. Sci. **36**, 478 (1973).
/3/   H.-J. Freund, M. Neumann, Appl.Phys. **A47**, 3 (1988).
/4/   C.J. Commons, B.F. Hoskins, Austr. J. Chem. **28**, 1663 (1975).
/5/   W.A. Herrmann, H. Biersack, M.L. Ziegler, K. Weidenhammer, R. Siegel,
      D. Rehder, J. Amer. Chem. Soc. **103**, 1692 (1981).
/6/   M. Manassero, M. Sansoni, G. Longoni, J. Chem. Soc. Chem. Comm. 919 (1976).
/7/   H. Kuhlenbeck, G. Odörfer, R.M. Jaeger, G. Illing, M. Menges, Th. Mull,
      H.-J. Freund, M. Pöhlchen, V. Staemmler, S. Witzel, C. Scharfschwerdt,
      K. Wennemann, T. Liedke, M. Neumann, Phys. Rev. **B**, in press.
/8/   M. Bäumer, D. Cappus, H. Kuhlenbeck, H.-J. Freund, G. Wilhelmi, A. Brodde,
      H. Neddermeyer, Surf. Sci., to be published.
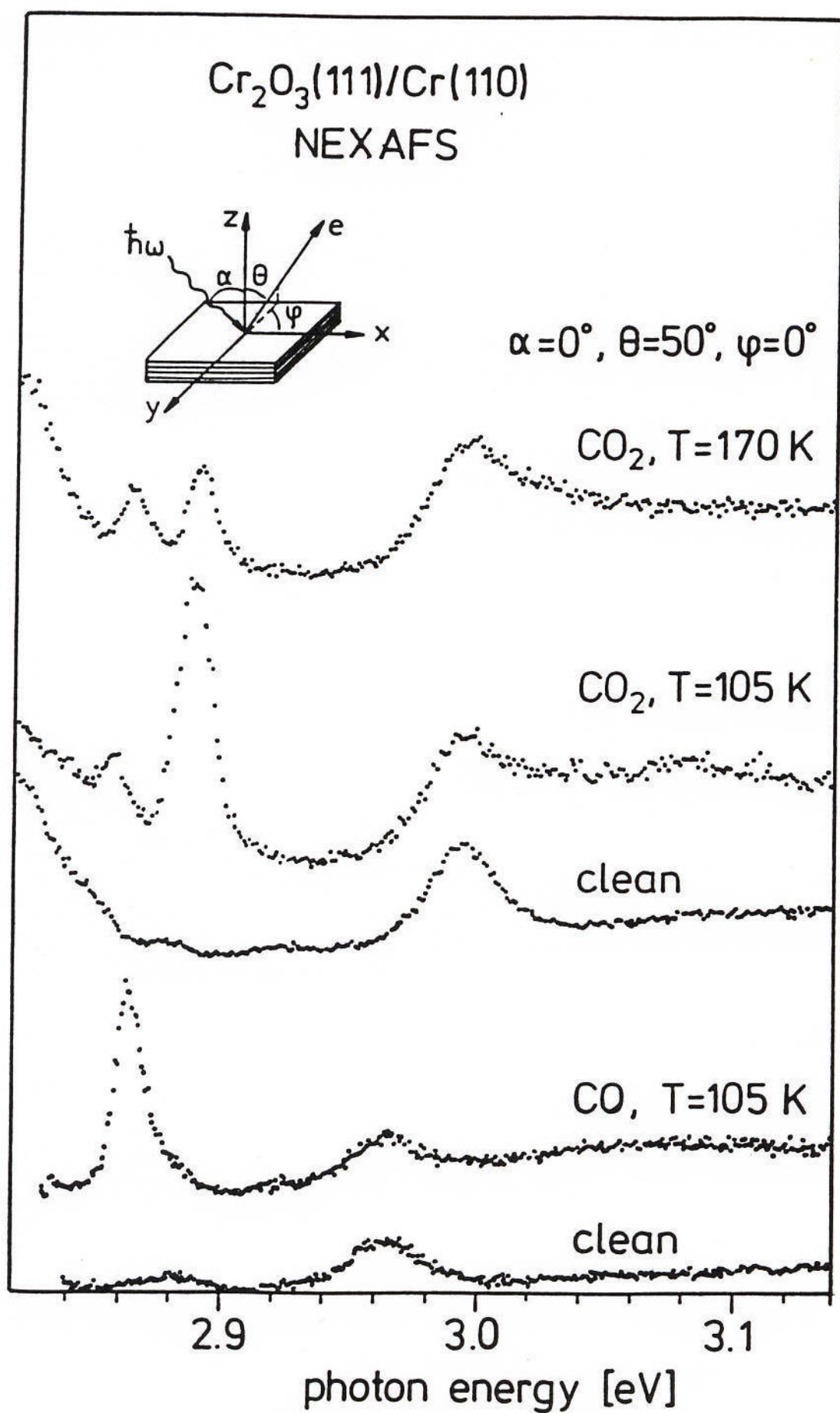/9/   M. Wuttig, W. Hoffmann, R.M. Jaeger, H. Kuhlenbeck, H.-J. Freund,

Fig. 5