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# Interaction of CO and NO with WC(0001)

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## Abstract

The results of angular resolved photoemission and thermal desorption spectroscopy investigations of the adsorption of CO and NO on a WC(0001) single crystal surface are reported. Both molecules are stable only at low temperature. Similar to the case of adsorption on many transition metals, CO is co-ordinated to the surface via its carbon end, standing upright on the surface. Upon warming up, complete dissociation takes place at temperatures of ca 270 K for CO and 160 K for NO. A part of the CO molecules also desorbs between 200 and 250 K, whereas no molecular desorption is found for NO. Recombinative/reactive desorption is observed in the temperature range between 700 and 1200 K. © 1998 Elsevier Science B.V.

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## 1. Introduction

Tungsten carbide is a refractory material with important technical applications. Due to its hardness, it is often used as a coating, for instance for drills. Its small thermal expansion coefficient gave rise to applications as a material for pointers in electric instruments in the past. But it also has catalytic properties. For instance, it has been shown to be active for hydrogenation and dehydrogenation reactions [1–5]. The type of active sites is not known yet. To date there have not been many studies reported on tungsten carbide single crystal surfaces; probably due to the limited availability of single crystals. The electronic structure was probed using photoemission by Johansson et al. [6] and some adsorption data (CO, O<sub>2</sub>) were reported in Refs [7,8]. An overview of the available

data for transition metal carbides, including thin films and some data for powder samples may be found in Refs [9–11]. In this work, the adsorption behaviour of NO and CO on single crystalline WC(0001) as studied with angular resolved photoemission (ARUPS) of the valence band and thermal desorption spectroscopy (TDS) is discussed. With CO the influence of preadsorbed oxygen was also investigated.

## 2. Experimental procedures

The experiments were performed in a ultra-high vacuum (UHV) system containing facilities for angular resolved photoelectron spectroscopy (ARUPS) with light from the TGM3 monochromator at the BESSY Synchrotron Radiation Center in Berlin, Auger electron spectroscopy (AES), thermal desorption spectroscopy (TDS) using a differentially pumped quadrupole mass

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spectrometer equipped with a so-called Feulner cup [12] and facilities for sample preparation. The sample was attached to two tantalum wires (0.25 mm thickness) which were spot-welded to two tungsten rods (1 mm thickness). These were plugged into a sapphire block connected to a liquid nitrogen reservoir so that the sample could be cooled down to  $T=90$  K. Heating was achieved either by electron impact or by heat radiation from a filament mounted behind the backside of the crystal. With this setup temperatures of  $>2000$  K could be reached. The sample temperature was determined with a W–Re 5%/W–Re 26% thermocouple spotwelded to one of the tantalum wires at a point where the latter was in direct contact with the crystal.

The WC(0001) sample was cut from a tungsten carbide block after orientation with Laue backscattering. Due to the way the carbide block was manufactured the sample contained a considerable amount of iron which was removed by annealing at  $T \geq 2000$  K. Thereafter the sample was polished using standard procedures. One special problem was the stoichiometry of the surface which was adjusted by oxidation with  $O_2$  if there was too much carbon on the surface or by glowing in methane or ethene in case the surface was carbon deficient. Sometimes also sputtering was employed to remove thick graphite overlayers or other impurities. Annealing at  $T \geq 2000$  K could be used to remove impurities like oxygen or sulfur from the surface. Another problem was that the carbon on the surface was sometimes graphitic instead of carbidic. In order to change its chemical state annealing at  $T=1600$  K for typically several hours was employed. Both the stoichiometry and the chemical state of the carbon were checked with AES. Carbidity carbon is characterized by an Auger spectrum with two well defined satellites at kinetic energies somewhat less than that of the main peak. These states are missing for graphitic carbon (see Fig. 1). It was noted that it was always possible to reach a state with an AES spectrum similar to the one shown in Fig. 1 (upper panel) although this could need several days of preparation. Most of the ARUPS spectra presented in the following have been recorded with the analyser set to detect electrons emitted normal to the surface plane. The

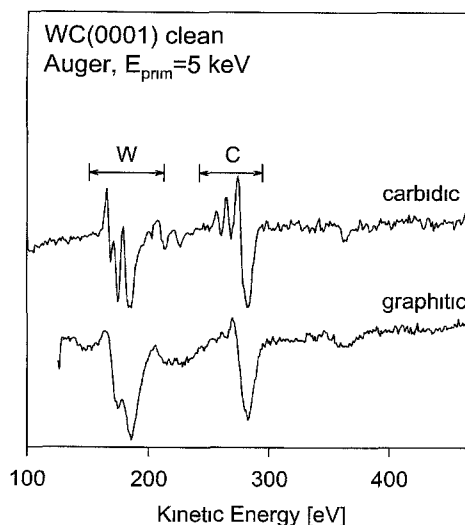


Fig. 1 Auger spectra of WC(0001) with carbidity and graphitic carbon on the surface. The carbidity surface was obtained after prolonged annealing at  $T=1600$  K.

meaning of the angles given in some of the figures is explained in Fig. 2.

### 3. Results and discussion

#### 3.1. Clean surface

In Fig. 3 the structure of the WC(0001) surface [13] is schematically depicted assuming that the surface is not reconstructed. As is obvious from this figure the surface may be terminated by carbon or by tungsten in case the arrangement of atoms at the surface is like that in the bulk. Also a mixed termination as proposed in Ref. [7] and, of course,

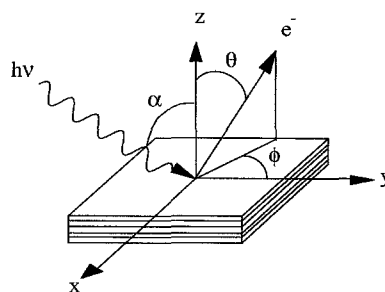


Fig. 2 Experimental geometry of the ARUPS experiments.

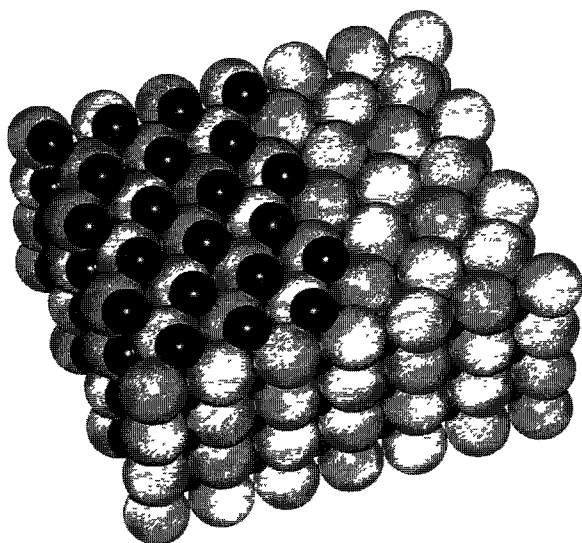


Fig 3 Structural model of WC(0001) [13] assuming that the surface is partly carbon (left side) and partly tungsten (right side) terminated. The real surface structure is not known yet.



Fig 4. LEED pattern of stoichiometric WC(0001)  $E_{kin} = 130$  eV

a reconstructed surface is conceivable. The ideal bulk-truncated surface is a polar one demanding for some type of stabilization. However, since tungsten carbide is not very ionic it may be the case that small charge transfers between the surface atoms suffice to stabilize it. The structure of WC is hexagonal with a carbon and a tungsten atom in the unit cell. Therefore with low energy electron diffraction (LEED) a hexagonal pattern is observed for the stoichiometric surface as shown in Fig. 4.

### 3.2. CO adsorption

The reactivity of the WC(0001) surface is documented by its strong interaction with carbon and nitrogen monoxide. A set of photoelectron spectra of CO/WC(0001) taken as a function of temperature is shown in Fig. 5. In the temperature range from 100 K to about room temperature the two well-known CO derived valence band ionizations, that is, a  $5\sigma/1\pi$  derived feature at ca 8.5 eV and the  $4\sigma$  state at ca 11.5 eV are clearly visible. Upon raising the temperature to above room temperature these peaks disappear. This is not due to desorption (at least not fully) since the spectra of the

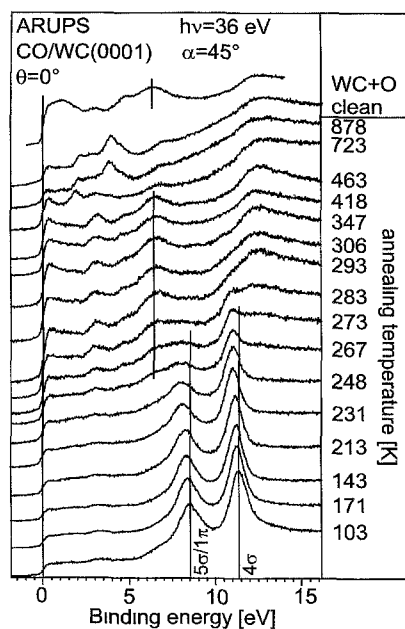


Fig 5 Valence band spectra of CO/WC(0001) taken after annealing the sample at different temperatures

surface taken after disappearance of the CO peaks differ considerably from those of the clean surface (see Fig. 5). Comparison with the spectrum of the

oxygen covered surface (top of Fig. 5) reveals that the marked features between 3 and 6.5 eV which rise up when the emission due to molecular CO vanish may be due to atomic oxygen which would be one of the dissociation products of CO. This indicates that CO dissociates on WC(0001) at about room temperature. After heating the surface to  $T=878$  K the spectrum of the clean surface is recovered. Therefore the dissociation products of CO must have recombined and desorbed at this temperature.

The dissociation of CO on WC(0001) is also obvious from TDS data. The spectrum exhibited in Fig. 6 shows a strong feature at  $T=720$  K. This temperature fits well to the data shown in Fig. 5 according to which recombination occurs in the temperature range between 723 and 878 K. In Fig. 6 two additional peaks are visible in the temperature range between 200 and 250 K indicating that part of the CO desorbs before dissociation occurs. This may also be the reason for the shift of the molecular ionizations as observed in Fig. 5. Whether these two TDS signals are due to desorption from different adsorption sites or to phase transitions within the adsorbate layer is not known yet and demands further studies.

The orientation of the molecular axes of the adsorbed CO molecules may be determined exploiting the dipole selection rules valid for the photoionization process. According to these the intensities of the  $4\sigma$  and  $5\sigma$  ionizations should

vanish in a plane containing the surface normal and being perpendicular to the plane spanned up by the surface normal and the electrical field vector (the so-called light incidence plane) when the molecular axes of the CO molecules are oriented perpendicular to the surface plane and the light is incident parallel to the surface normal ( $\alpha=0^\circ$ ,  $\phi=90^\circ$ ) [14,15]. This is called the “forbidden geometry”. Detection is “allowed geometry”, that is along a direction contained in the light incidence plane ( $\alpha=0^\circ$ ,  $\phi=0^\circ$ ) should lead to strong intensities, again under the assumption that the molecular axes are oriented parallel to the surface normal. Spectra taken in the allowed and forbidden geometries are depicted in Fig. 7. Obviously there is no remaining intensity of the  $4\sigma$  level in the forbidden geometry whereas some intensity remains in the region of the  $5\sigma/1\pi$  ionizations. The latter intensity may be attributed to the  $1\pi$  level which is not forced by symmetry to vanish in the forbidden geometry. Therefore it is concluded that the axes of the CO molecules are oriented parallel to the surface normal. However, this gives no hint as to whether the molecules are bonded to the surface via their carbon or their oxygen ends. This question may be answered by monitoring the intensity of the  $4\sigma$  and  $5\sigma$  valence ionizations as a function of the photon energy. Both levels exhibit an intensity resonance at  $h\nu=35$  eV due to the presence of the  $\sigma$  shape resonance. The resonant intensity is concentrated along the molecular axis in both cases

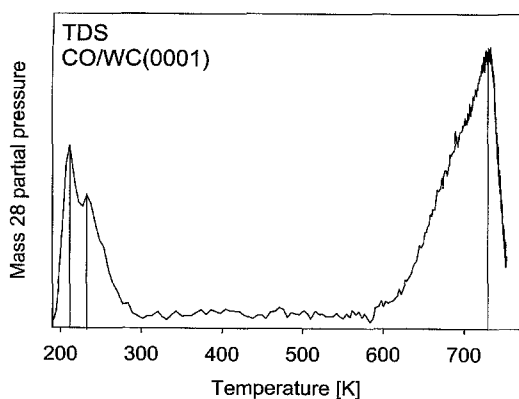


Fig. 6 Thermal desorption spectrum of CO on WC(0001). The quadrupole mass spectrometer was set to mass 28 during the scan.

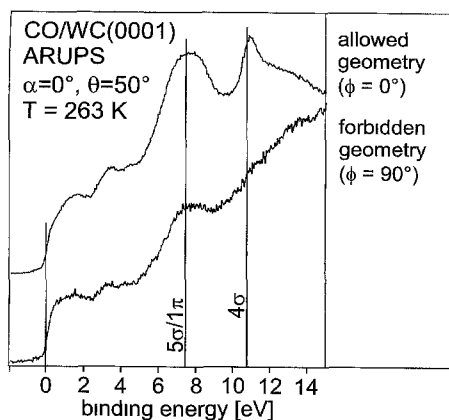


Fig. 7 ARUPS spectra of CO on WC(0001) taken in the so-called allowed and forbidden geometries.

but for the  $5\sigma$  level it is highest in the  $O \rightarrow C$  direction whereas for the  $4\sigma$  it is peaked in the opposite direction [16]. A set of data taken in normal electron emission is shown in Fig. 8 exhibiting well defined intensity resonances for the  $\sigma$  levels at  $h\nu = 36$  eV. The intensities of the  $\sigma$  levels as a function of photon energy are depicted in the inset of Fig. 8. Both levels exhibit a resonance at ca 36 eV. The one of the  $4\sigma$  level is somewhat more intense than that of the  $5\sigma$  state. This is in line with observations made for CO adsorbates on several transition metal surfaces where the CO molecules bond via their C-ends to the substrate. The observed intensity resonance of the  $5\sigma$  level may be explained by the reduced symmetry of the adsorbate as compared to free CO which allows for hybridizations not present for gaseous CO. Thus the observed intensities are fully in line with CO molecules co-ordinated via their carbon ends to the tungsten carbide.

Oxygen pre-adsorption strongly suppresses CO adsorption as indicated by Fig. 9 where ARUPS spectra of CO on oxygen precovered surfaces are shown. Moderate oxygen precoverages of up to 8 L ( $1 \text{ L} = 10^{-6} \text{ Torr s}^{-1}$ ) do not notably influence

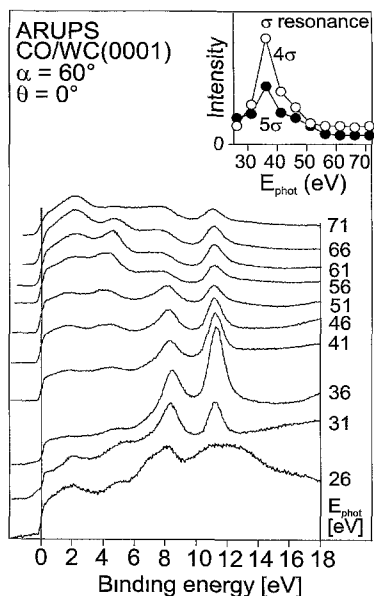


Fig. 8 ARUPS spectra of CO/WC(0001) taken as a function of the photon energy

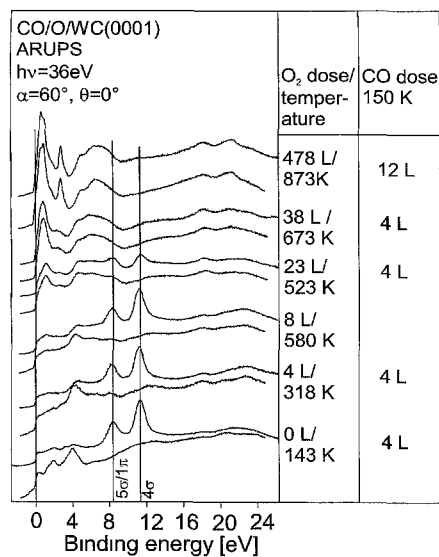


Fig. 9. ARUPS spectra of CO dosed at  $T = 150$  K onto an oxygen precovered surface for different preparation conditions. For comparison always a spectrum of the surface before CO dosage is shown below the spectrum taken of the CO covered surface.

the CO uptake. At higher doses  $WC_xO_y$  and  $WO$  form on the surface as is obvious from the increased intensity near to the Fermi edge [6–8,17]. As soon as this happens, the number of adsorbed CO molecules is reduced considerably. On strongly oxidized surfaces CO does not adsorb at  $T = 150$  K indicating that  $WC_xO_y$  and  $WO$  interact weaker with CO than stoichiometric tungsten carbide does. This is as expected since oxide surfaces tend to form weak bonds to CO via electrostatic interactions [18] as compared to the strong (most likely covalent) interaction of CO with the WC(0001) surface.

### 3.3. NO adsorption

NO behaves similar to CO in that it also dissociates on WC(0001). This is obvious from Fig. 10 which shows that the NO induced  $5\sigma/1\pi$  and  $4\sigma$  levels at ca 8.8 and 13.7 eV disappear at  $T = 160$  K. This is again due to dissociation as revealed by the difference of the spectra recorded before NO dosage and after disappearance of the NO molecular states and by the appearance of intensity due

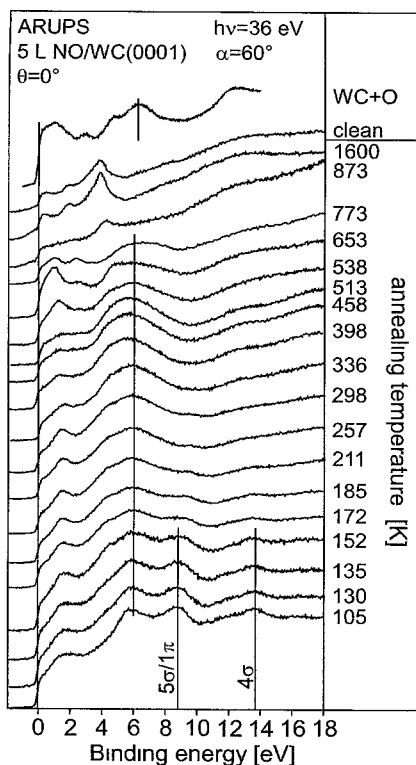


Fig. 10 ARUPS spectra of NO on WC(0001) taken as a function of the annealing temperature

to atomic N/O at ca 6 eV. The latter intensity is already observed at  $T=105$  K indicating that part of the NO molecules is already dissociated at this temperature. At temperatures above  $T=500$  K some features become visible in the valence band between 1 and 3 eV (marked in Fig. 10) that are characteristic of a surface covered with oxygen [6–8,17] as concluded from a comparison with the spectrum at the top of Fig. 9. A similar but less pronounced tendency is also observed for CO adsorption (Fig. 5).

However, contrary to the case of CO/WC(0001) there is no or very weak desorption of NO due to N–O recombination at higher temperature as concluded from TDS (data not shown here). This is not too surprising since CO and N<sub>2</sub> are the thermodynamically more stable products. A TDS spectrum of NO adsorbed on WC(0001) is exhibited in Fig. 11 in comparison with a spectrum of adsorbed oxygen. The mass spectrometer was set

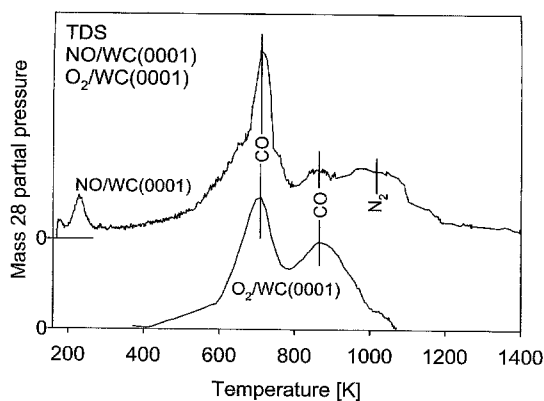


Fig. 11 TDS spectrum of NO on WC(0001) recorded with the quadrupole mass spectrometer set to mass 28 in comparison with a spectrum of an oxygen dosed surface

to  $m/e=28$ . At temperatures between 700 and 900 K oxygen reacts with the carbon on the surface and desorbs as CO. A comparison reveals that the high temperature peaks at 720 and 860 K in the spectrum of NO/WC(0001) are due to desorption of CO whereas desorption of N<sub>2</sub> occurs in the temperature regime between 900 and 1100 K. The low temperature peak in the upper curve of Fig. 11 is caused by CO impurities.

NO adsorbs mainly in an upright geometry on WC(0001) as indicated by the data shown in Fig. 12. There is only a weak intensity of the NO 4σ and 5σ levels in the forbidden geometry which may be due to the non-perfect polarization of the synchrotron radiation and possibly to some molecules not adsorbing in an upright geometry or to small inclinations of the molecules axes with respect to the surface normal.

#### 4. Summary and conclusions

Our studies show that from a chemical point of view WC(0001) is a rather unstable surface. The problems that have arisen during the preparation of a stoichiometric surface with carbon in a carbidic state show that only under special conditions such a surface may be formed. It is very easy to prepare a surface covered with graphitic carbon or an unstoichiometric surface. Also the dissociation products of CO and NO may modify the

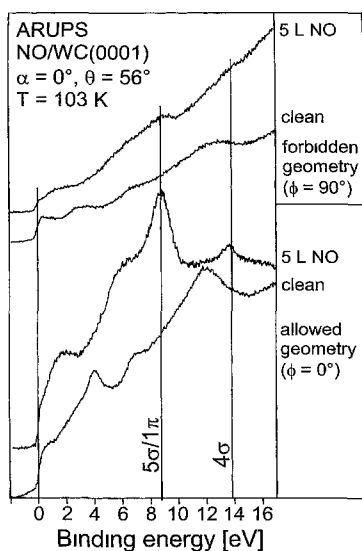


Fig. 12 ARUPS spectra of NO on WC(0001) taken in the allowed and forbidden geometries in comparison with spectra of the uncovered surfaces

surface composition. From a catalytic point of view this means that the activity of tungsten carbide may be related to a non-stoichiometric surface containing impurities like graphitic carbon, oxygen or chemisorbed nitrogen.

It has been argued that the chemical activity of the WC(0001) surface is similar to that of platinum due to a certain similarity of the electronic valence band structure [19]. This holds to a certain extent also for the data presented in this paper although platinum seems to be less reactive than tungsten carbide. However, it has been shown for small Pt clusters on oxidic surfaces that these are also able to dissociate CO at low temperature [20].

It was found that tungsten carbide reacts strongly with CO and NO. These molecules dissociate already at low temperature. At temperatures between 700 and 1100 K reactive/recombinative desorption takes place. No molecular desorption signal could be observed for NO whereas for CO part of the molecules desorbs at temperatures between 200 and 250 K. This fits well to results obtained for CO and NO adsorption on polycrystalline  $\beta$ -Mo<sub>2</sub>C films [21]. Similar to our results, CO dissociation at low temperature as well as recombinative CO desorption at high temperature

were found in this work. For NO only a tiny NO desorption signal could be observed by the authors. But it was possible to detect desorption of N<sub>2</sub>O, N<sub>2</sub> and CO.

As far as it concerns the bonding of CO and NO to the WC(0001) surface tungsten carbide behaves like a transition metal. This is not too surprising since its band structure is metal like [19]. There are good indications that the bonding of CO to the surface is to be described by the Blyholder model which is valid for transition metals. This means that there is a strong covalent CO-surface bond made up by a  $2\pi$  interaction with occupied substrate levels and an interaction of the  $5\sigma$  state with unoccupied substrate states resulting in a shift of the  $5\sigma$  state near to the  $1\pi$  level as observed in our data. For TiC(111) which may have a surface structure similar to that of WC(0001) extended Hückel calculations have shown that there is a considerable substrate  $\rightarrow 2\pi$  and a somewhat weaker  $5\sigma \rightarrow$  substrate donation [22] similar to what is observed for CO on many transition metal surfaces. It was also shown that the substrate  $\rightarrow 2\pi$  transfer decreases with an increasing number of carbon atoms present at the surface. Also typical for CO adsorption on transition metal surfaces is a general decrease of the ionization energies of the CO molecular levels as compared to the gas phase values due to the good screening of the molecular ion states provided by the substrate electrons. This was also found in our data. Finally it is noted that on transition metal surfaces the CO molecules are typically coordinated to the substrate via the carbon ends as was also indicated by our data for WC(0001) and has been concluded previously for CO on  $(5 \times 1)C/W(100)$  which was assumed to represent a model for the WC(0001) surface [23]. The adsorption site of the CO molecules is not yet known. It would not be too surprising if further studies showed that the molecules are bonded to the tungsten atoms but here structural investigations are needed.

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