

EVIDENCE FOR SUBSTRATE-MEDIATED INTERACTION BETWEEN C AND O UPON CHEMISORPTION OF CO ON Mo

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We present photoemission measurements on polycrystalline Mo which demonstrate the existence of an interaction between the C and O atoms of a CO molecule chemisorbed on Mo. However, this interaction is not necessarily a direct one but probably one mediated by the Mo surface. The spectra obtained from clean Mo show a structure that can be interpreted as being due to a surface state.

The photoemission spectra of clean polycrystalline Mo, and of CO and O₂ chemisorbed on Mo have been studied especially with regard to the nature of the CO room-temperature, low-coverage chemisorption state (β -state). Measurements on these particular types of system have earlier been reported by Atkinson et al. [1,2], who suggest a dissociative chemisorption state at room temperature. Broden et al. [3] have, more generally, discussed the chemisorption of CO to the transition metals and argued it to be likely that CO or Mo is dissociated. Our results indicate that this dissociation is not necessarily complete and that there still might exist an interaction between the C and O atoms in this state. Also, measurements on single crystals of Mo have been reported [4–7] where an attempt has been made to identify a surface state theoretically calculated to exist on the (100) surface [8–11]. Our results indicate that a certain part of the photoelectron spectrum from a polycrystalline sample may be related to this surface state.

The experiment was performed in an ultrahigh vacuum system reaching a base pressure of $\approx 1 \times 10^{-10}$ torr and equipped with a differentially pumped He-resonance lamp which produces useful photon intensities at energies 21.2 eV and 40.8 eV. With the lamp

operating, the pressure in the chamber increases to $\approx 1 \times 10^{-9}$ torr, the pressure change being entirely due to the He flow from the lamp.

The electron energy analyzer used is of a small hemispherical electrostatic type [12], operated in the constant resolving power mode, with $E/\Delta E \approx 100$. The sample was a mechanically polished 2 mm thick plate of molybdenum which was Ar-sputtered and annealed in situ. Four cycles of sputtering at 1 kV ($I_{\text{ion}} \approx 10 \mu\text{A}/\text{cm}^2$) and annealing at 750°C for 30 min were enough to produce a clean Mo surface as defined by the criterion that further cleaning would not change the electron energy distribution curve (EDC). Still, the EDC showed a minor peak at around -6 eV, structure E in fig. 1, which is believed to be due to contamination. A clear growth of this structure was observed within 3–4 h after the cleaning procedure. All spectra of the nonexposed surfaces were recorded within this time interval.

The EDC's for the clean Mo surface as obtained with photon energies 21.2 eV and 40.8 eV are shown in fig. 1. The main structures are labeled with capital letters from A to F. The shape of the 21.2 eV excited spectrum agrees well with that of the spectrum published by Atkinson et al. [1,2]. However, structure C at -2.6 eV is more pronounced in our spectrum. As can be seen from fig. 1 and table 1, there is also good agreement in peak positions between the two spectra

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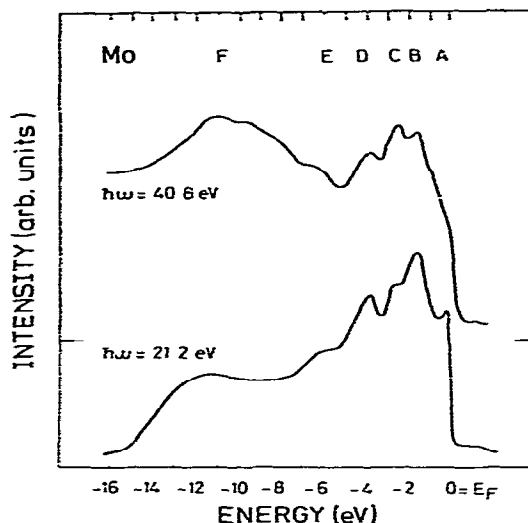


Fig. 1. FDC's from a clean Mo sample. Note the good agreement in peak positions of the two spectra. Structure F refers only to the 40.8 eV excited spectrum.

excited with different photon energies. Table I gives a comparison with the main peak positions obtained from a calculated density of states [13] and the experimental peak positions. The good agreement suggests an initial state origin of the peaks. The only large difference between the experimental spectra is the change of the intensity of the A and C structures. This could be due to the variation of the matrix element in the expression for the transition probability. From our data this does not seem very likely since the small

Table I

Initial energy of the main structures (± 0.1 eV) in the spectra from a clean Mo surface compared with the main peaks obtained from a calculated DOS [13]

	Energies of structures (eV)					
	A	B	C	D	E	F
He I	-0.3	-1.8	-2.6	-4.0	(-6.0)	
He II	-0.5	-1.8	-2.8	-4.0	-6.4	-11
DOS	9.0	-1.7	-3.0	-3.8, -4.3		
surface state [7]	-0.3					

changes of other structures indicate only a minor dependence on the final states in that energy region. It is, however, interesting to note that the more surface sensitive our probe is, the stronger is the C structure (the mean free path for 40 eV electrons is shorter than for 20 eV electrons [14]). This is also seen for $\hbar\omega = 21.2$ eV, where the intensity ratio of the C to B peaks grows from 0.84 to 0.93 when the emission angle from the surface normal (θ) is changed from $\theta = 0^\circ$ to $\theta = 60^\circ$. This change of angle corresponds to a small but finite change in the probe depth. It is also interesting to note that the sharp edge A seems to have the reverse behavior of the structure C. Structure A might represent the surface state as calculated to be present on the (100) face of Mo [8-11]. This explains the angular behavior of the structure since it has been shown by Gartland that the surface state is emitted only in a narrow core centered on the [100] direction [15]. Also, the lower intensity at the higher photon energy is explained since, according to Shang-Lin Weng et al., the intensity of the surface state should be considerably lower for $\hbar\omega = 40.8$ eV than for $\hbar\omega = 21.2$ eV [7].

Structure E is, as previously mentioned, due to the surface contamination. Compared with bulk emission, there is an increase in intensity with increasing emission angle of this structure.

Structure F in the 40.8 eV excited spectrum is believed to represent a loss peak which may be due either to the excitation of a surface plasmon or to a final density of states effect. The origin of the corresponding structure in the 21.2 eV excited spectrum is less clear and will not be further discussed since it interferes with the contribution from inelastically scattered electrons. The loss peak, F, decreases with oxygen exposure indicating a surface dependence. The surface plasmon energy, 11 eV, reported from electron loss experiments [16], seems somewhat large compared with our data since the energy separation between the valence band structure and the plasmon loss structure is ≈ 9 eV as measured between the points of highest intensity. This is, however, in agreement with the calculation of Ballu et al. [17], who locate the main surface plasmon loss peak around -9 eV.

Upon oxygen exposure two main changes occur in the 21.2 eV excited spectrum (see fig. 2). First, there is a large O 2p-induced structure growing up between -4 and -8 eV. From the difference spectrum obtained by subtracting the spectrum of a clean Mo-surface

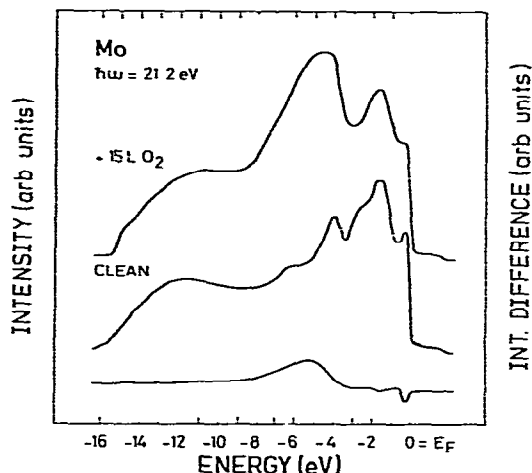


Fig. 2. Spectrum of O_2 -exposed Mo excited with $\hbar\omega = 21.2$ eV. The difference spectrum (which is reduced by a factor of 4) exaggerates the change just below E_F . This is probably due to a slight energy shift of the O_2 -exposed spectrum.

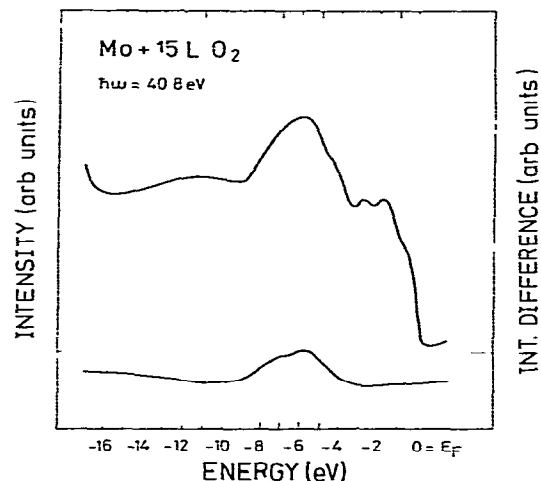


Fig. 3. Spectrum of O_2 -exposed Mo excited with $\hbar\omega = 40.8$ eV. The difference spectrum represents the difference divided by 2 between the above spectrum and the spectrum from a clean sample.

from that of an oxygen saturated (15 L) surface, it can be seen that this structure is asymmetric and is peaked at around -5.3 eV. Secondly, the sharp peak A just below the Fermi level evolves into a shoulder.

The 40.8 eV excited spectrum shows an approximately 5 eV wide O 2p structure peaked around -5.5 eV (fig. 3). Note that there is a difference in the peak energies for the two different photon energies. For both photon energies an increase of the emission angle causes the oxygen peak to grow in intensity. However, with 21.2 eV radiation the low energy part of the O 2p-derived peak is growing faster, giving a clear doublet structure at $\theta = 60^\circ$. The structural change in the case of 40.8 eV radiation, partly due to poorer resolution, is less clear.

Annealing for about 5 min at 650°C narrows the oxygen peak, that is, the high energy part of the doublet structure disappears while the low energy part is very much unaffected. The maximum peak intensity decreases by approximately 25%. Further annealing at this temperature has no important influence on the spectrum. Upon annealing, the secondary structure, F, is once again quite strong after being damped as a result of oxygen exposure. The sharpness of structure A is restored. Our belief is that upon annealing oxygen is incorporated into Mo since the spectral features

pertinent to the original Mo surface are restored. However, since there is only a slight decrease in the intensity of the O 2p structure, the oxygen atoms do not diffuse further into the bulk but remain close to the surface.

The clean Mo surface was also exposed to CO. After an initial exposure of about 3L, changes in the EDC on further exposures were very small. A spectrum for the highest exposure used, 15 L, is shown in fig. 4. Structures A, D and E as labeled in fig. 1 have grown in intensity relative to peak B. Structure C has become less pronounced. The difference spectrum in fig. 4 shows a broad doublet structure with a maximum intensity around -6 eV. Also here there is a difference in peak position depending on photon energy (see table 2 and fig. 5). No structures due to molecular orbitals of CO can be detected. After annealing for a few minutes at 650°C , the spectrum returns to its original shape, i.e. that of the original surface.

In our discussion we first dwell a moment on the energy shifts of the adsorption peaks. In the case of CO adsorption, one could imagine the adsorption-induced structure to consist of at least two energy separated structures (fig. 4) due to carbon and oxygen-related 2p orbitals, respectively. A variation with photon energy of the cross section for one or both of

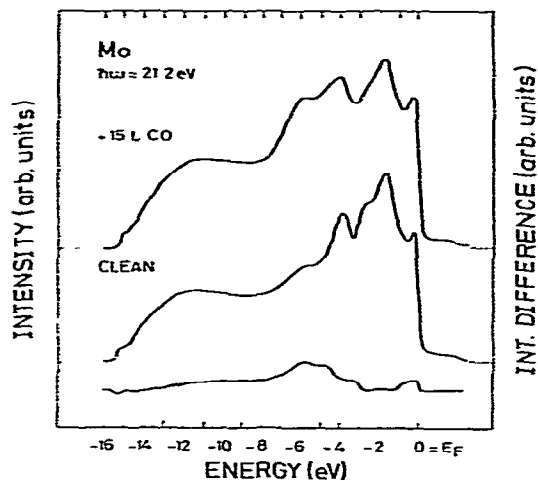


Fig. 4. EDC of Mo exposed to 15 L CO excited with $\hbar\omega = 21.2$ eV. The intensity of the structure just below E_F increases in intensity upon exposure. The difference spectrum is reduced by a factor of 2.

these orbitals would result in an energy shift of the total structure. Also, in the case of O adsorption, the total adsorption peak seems to consist of two energy separated parts, which is to be expected since the degeneracy of the 2p orbital should be broken by the interaction with the surface. This is manifested by the angular variation of the adsorption peak. Also here the shift in peak position can probably be explained by variations of the cross sections with photon energy depending on the orientation of the orbitals and their interaction with the surface.

Next, we conclude that there are large differences in the spectra obtained when exposing Mo to O_2 and CO, respectively. Firstly, there is the behavior of the structure A in the Mo spectrum. Upon CO exposure this structure will increase in strength (fig. 4) relative to the main peak (B), while for O_2 exposure it will

Table 2
Energy positions and widths of the adsorbate peaks

	Initial energy (eV)		Peak width (eV) He II
	He I	He II	
O_2	-5.3 ± 0.1	-5.5 ± 0.1	5.2 ± 0.3
CO	-6.0 ± 0.1	-6.3 ± 0.1	3.9 ± 0.3

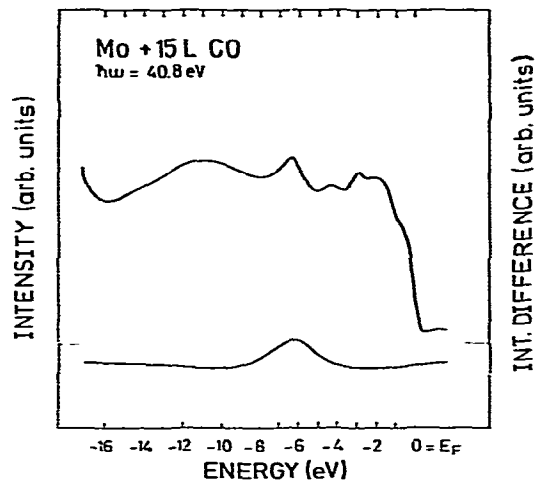


Fig. 5. EDC of Mo exposed to 15 L CO excited with $\hbar\omega = 40.8$ eV. Note the small intensity of the adsorbate peak compared with that of an O_2 -exposed sample (fig. 4).

get less sharp (fig. 2). The structure C seems to have a reversed behavior in the two cases of adsorption but not as distinct as that of the A structure.

We also want to stress the differences upon annealing. At higher temperatures oxygen seems to be incorporated in the surface layer, whereas in the case of CO an annealing will produce a clean sample due to desorption of C and O (or rather of CO).

It has been suggested that CO adsorbs dissociatively on Mo, that is, the C and O atoms are individually bonded to the surface and the direct bonding between the atoms is weak [1-3]. One of the reasons for this conclusion has been that no molecular orbitals have been observed in the photoemission spectra. However, we do not believe that the C and O atoms are *independently* bonded to the Mo surface. Rather, there exists an interaction between the C and O atoms, not necessarily a direct one but one mediated by the Mo surface [18]. The reasons for this assumption are the following:

(i) *The behavior of the O and C-O adsorbates upon annealing.* If the C and O atoms were independently bonded to the surface, annealing would change the oxygen-derived structures in more or less the same manner as in the case of the O_2 -exposed surface. This is not the case.

(ii) *The reverse behavior of peaks A and C upon O₂ and CO adsorption.* O₂ and CO seem to interact with the Mo substrate through the same electronic states of Mo but in drastically different ways. Therefore, C and O cannot be independently bonded to the surface.

(iii) *The widths of the adsorbate peaks.* The CO-induced peak width is considerably less than that of the O₂-induced structure (see table 2).

The absence of structure in the spectra due to CO molecular orbitals is thus explained. Even if there is some direct bonding between the C and O atoms, these orbitals would be drastically disturbed from that of the molecule since the CO molecule in this case probably lies flat down on the surface[‡]. Both the 1 π and 4 σ orbitals would, even though they are essentially nonbonding with respect to the metal [3], be expected to be much more affected than in, for instance, the case of Ni, where the CO molecule stands on the surface [20] and in which case the molecular orbitals are clearly resolved.

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[‡] Compare with CO on W [19].

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