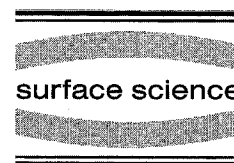




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HREELS study of O₂ molecular chemisorption on Ag(001)

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Abstract

O₂ adsorption on Ag(001) at 100 K has been investigated by HREELS. Contrary to previous reports we could resolve 4 oxygen related peaks, 3 of which are due to the internal stretching vibration as confirmed by isotope labelling. The lowest frequency mode at 63 meV is assigned to molecular oxygen chemisorbed at defect sites. The further two features are very close to each other in frequency, at 79 and 84 meV. We assign them to molecules chemisorbed in a peroxidic state in two different adsorption sites. Initially both sites are filled simultaneously while at higher coverage adsorption in the higher frequency site is favoured.

Keywords: Chemisorption; Electron energy loss spectroscopy; Low index single crystal surfaces; Oxygen; Silver; Vibrations of adsorbed molecules

1. Introduction

Adsorption of O₂ on Ag surfaces constitutes an important model system characterized by three wells, corresponding to physisorption, chemisorption and dissociative adsorption [1,2]. Most of the work published so far was addressed to Ag(110) and Ag(111), while only a few papers dealt with Ag(001) [3-7]. High resolution electron energy loss spectroscopy (HREELS) at 100 K showed, for the latter system and for the molecularly chemisorbed state [6], two main losses associated respectively with the Ag-O₂ vibration (at 30 meV) and with the internal stretching motion of the O₂ molecule, indicating that only one adsorption site is populated in analogy to the case of O₂-Ag(110) [1,8,9]. More recently a further loss was observed at about 63 meV, which was assigned

to the internal stretch of O₂ molecules chemisorbed at defect sites [5]. A recent theoretical work by Mehandru and Anderson [10] forecasted, however, that the O₂-Ag(001) system has at least three inequivalent sites with comparable binding energy, i.e. the fourfold hollow, the short bridge and the long bridge sites (see Fig. 1). In all cases the molecule should lie down with its axis parallel to the surface and be in a peroxidic state. The charge transfers from the substrate as well as the Mulliken overlap populations are predicted to be different for such species. To verify the prediction we performed a HREELS investigation with the highest possible resolution achievable with our HREELS spectrometer: $\Delta E=4$ meV. Indeed, in accord with theory and contrary to the case of O₂-Ag(110) [9], we find that the loss feature at 80 meV corresponds in reality to two peaks very close in frequency: at 79 and 84 meV. The two species are differently populated as a function of coverage.

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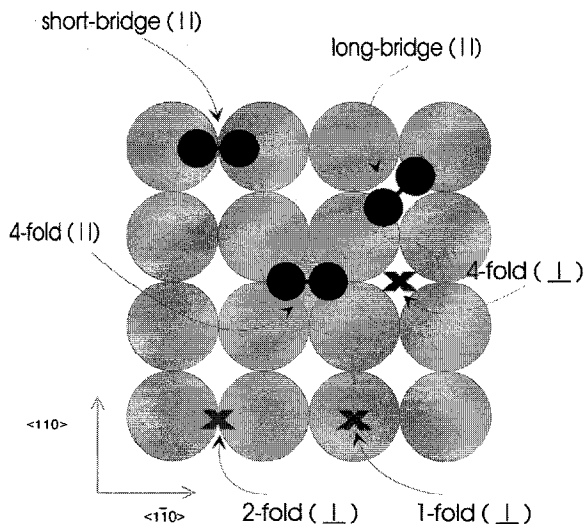


Fig. 1. Possible adsorption sites of O_2 on $Ag(001)$, considered by the theoretical paper by Mehandru and Anderson [10].

2. Experimental

The experiment was performed with the same apparatus utilized for our previous experiments [5,9], which was described elsewhere [11]. The sample, an $Ag(001)$ single crystal, was cleaned by Ar or Ne ion sputtering and annealing cycles, until no loss features were detected by electron energy loss spectroscopy (EELS). The crystal is kept at 100 K by flowing liquid nitrogen through a cryostat. In the present experiment, oxygen is dosed by a molecular beam thus reducing the possible background contamination: since the sticking probability increases strongly with increasing normal energy [12], a beam of O_2 seeded in He is used with the nozzle kept at room temperature. A cold trap is inserted on the gas line to prevent water and oil contamination. At 100 K only molecularly chemisorbed O_2 is present on the $Ag(001)$ surface [5]. The coverage was calibrated by comparing the area of the thermal desorption peak due to molecular oxygen with the intensity observed by a residual gas analyzer when an O_2 beam of known intensity enters the main chamber. The absolute intensity of the O_2 beam is measured by a spinning rotor gauge. The electron energy loss spectrometer was built [13] following Ibach's design [14] and is described elsewhere [15]. In the

present experiment the electron energy was set at 3.3 eV and spectra are recorded in specular at an incidence angle of 63° . Intensities of about 10^5 counts in the reflected beam at 4 meV resolution could be routinely obtained.

3. Results and discussion

Fig. 2 shows EEL spectra recorded in-specular after different exposures of the clean $Ag(001)$ surface to oxygen (impact energy, $E_{O_2} = 0.4$ eV). As one can see at very low coverage four peaks are observed: a small feature around 30 meV, a

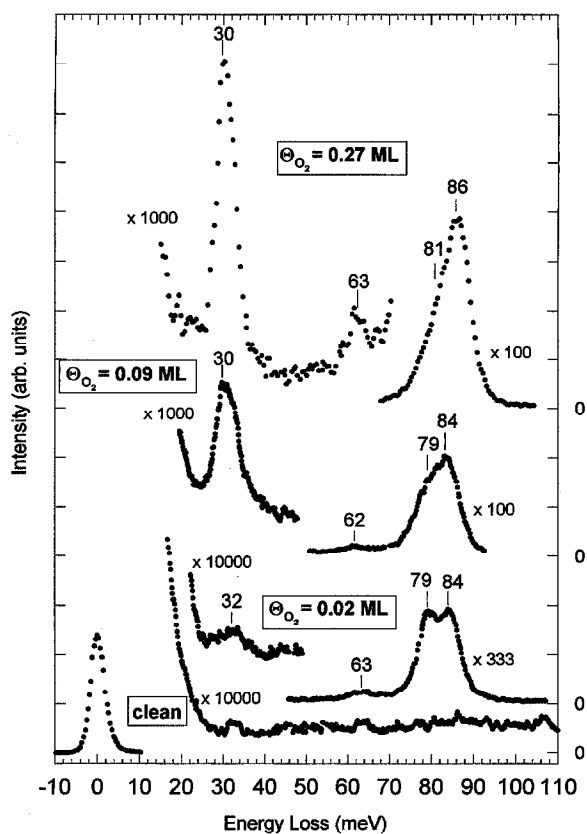


Fig. 2. HREELS spectra recorded in specular at an incidence angle of 63° and an electron energy $E_c = 3.3$ eV after different oxygen exposures performed at normal incidence and at 100 K, with the nozzle at room temperature ($E_{O_2} = 0.4$ eV). The coverage Θ_{O_2} is given in ML of chemisorbed O_2 . (1 ML = 1.18×10^{15} mol cm^{-2}).

weak loss at 63 meV and a doublet around 80 meV. With increasing oxygen coverage the intensities of the losses at 30, 79 and 84 meV increase while the intensity of the loss at 64 meV remains constant. Above 0.15 ML the feature at 84 meV increases more rapidly than the loss at 79 meV, eventually resulting in an intense loss centred around 84 meV with only a shoulder at lower frequency. The doublet nature of such a large peak could not be resolved in a previous study [6], due to insufficient energy resolution. All losses are due to adsorbed O_2 as demonstrated by isotope labelling using O_2^{18} . The loss at 30 meV shows thereby only a limited shift while the loss at 63 meV shifts to 61 meV and the doublet at 79 and 84 meV turns into a doublet at 75 and 80 meV. The coverage dependence of the integrated intensities of the losses of the doublet is shown in Fig. 3, together with the ratio of the normalized integrated intensities of these losses. As evident from Fig. 2, the losses at 84 and 79 meV have initially the same intensity until at $\theta_{O_2} > 0.15$ ML, the loss at 84 meV starts to prevail. We did not observe any ordered LEED pattern. The failure could, however, be

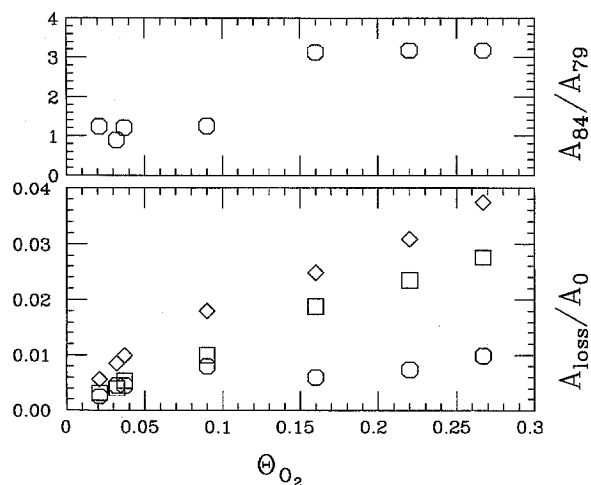


Fig. 3. Lower panel: integrated intensity of the losses (normalized to the area of the specular peak) at 79 meV (\circ), 84 meV (\square) and their sum (\diamond) reported as a function of total dioxygen coverage. Upper panel: ratio of the integrated intensities of the loss features at 79 and 84 meV vs total dioxygen coverage. As one can see the total intensity of the losses is approximately linear in the oxygen coverage for θ_{O_2} , their ratio depends however on θ_{O_2} .

connected to electron stimulated desorption. An ordered $p(2 \times 2)$ structure had indeed to be postulated for Ag(001) to reproduce the coverage dependence of the sticking coefficient [16], although no ordered structure is observed by LEED.

The assignment of the loss at 30 meV to the Ag– O_2 stretching is straight-forward as a similar frequency was reported for O_2 on Ag(110) [8,17]. As two different molecular species are present one could expect also two different oxygen–substrate vibrations. However, at high coverage this is not the case as a single peak at 30 meV is present. At $\theta_{O_2} \approx 0.09$ ML on the other hand a fit with two Gaussians yields a major contribution at $\hbar\omega_1 = 30.5$ meV and a minor contribution at 34.5 meV (approximately 1/7 of the intensity of the main peak). The weight of the peak at 34.5 meV diminishes at higher coverages and is not discernible any more above $\theta_{O_2} \approx 0.2$ ML. Our measurements unfortunately do not allow to be conclusive as the latter frequency coincides with the atomic O–surface vibration. The second peak could therefore be due either to O_2 –substrate vibration (probably associated to the lower frequency loss of the 80 meV doublet) or to a small fraction of dissociated oxygen.

The vibrational frequency is expected to change as the inverse square root of the reduced mass of the molecule (or atom)–surface complex [18] so that isotopic labelling provides a way to further substantiate vibrational assignments. The observed shift for the Ag– O_2 loss (≈ 0.5 meV) is actually slightly smaller than expected (1 meV), but such a discrepancy is at the limit of the experimental precision on the energy loss determination (0.5 meV).

The coverage dependence of the peak intensity of such loss is unusual being non-linear already at low coverage, contrary to expectation [19] and contrary to the behaviour of the internal vibrations. Non-linearities in EELS intensities with increasing coverage are usually attributed to depolarization effects; however this explanation seems not to be appropriate for a coverage as low as 0.1 ML. Moreover, depolarization limits the intensity of the loss at high coverage and it does not enhance it, as observed in the present case.

The loss at 64 meV has previously been assigned to the O–O stretching of molecules adsorbed at defect sites [5]. The vibrational frequency is even lower than that of the peroxide species, suggesting a larger charge transfer and a higher binding energy. In agreement with such a finding, the loss intensity almost immediately saturates, as expected for a species adsorbed on defects with a higher heat of adsorption. Its small intensity is, moreover, indicative of a low coverage, consistent with a low density of defects. The observed isotopic shift (3 meV) is of the expected magnitude and sign, thus further supporting this assignment.

The higher energy losses at 79 and 84 meV are assigned to O–O stretching of chemisorbed O₂ molecules at different adsorption sites. The frequency is close to the one observed for O₂–Ag(110) [8,17] and its value is indicative of a peroxide species, with substantial charge transfer. For comparison the superoxide should vibrate at 130 meV [20], a frequency much lower than for the physisorbed and gaseous O₂ (192 and 196 meV, respectively [21]). The similar frequency of the two components of the doublet suggests therefore to assign both of them to a peroxide form, the small frequency shift being due to a different adsorption site. The isotopic shift is comparable for both species and has the expected magnitude. The coverage dependence of the loss is weak in accord with the case of O₂–Ag(110) [22].

In a theoretical paper Mehandru and Anderson found side-on orientation to be energetically more stable than end-on orientation; moreover they considered 3 possible adsorption sites for the side-on orientation, namely short-bridge, long-bridge and four-fold [10] (see Fig. 1). Short-bridge and four-fold orientation have very similar binding energies (1.92 and 1.99 eV, respectively) while the long-bridge adsorption site is characterized by a smaller binding energy (1.58 eV). Such values are too large compared to the experimental value of ≈ 0.5 eV [16], but according to Mehandru and Anderson the trend in binding energy for the different sites should be correct. The strength of the O–O bond weakening can be inferred from the O–O Mulliken overlap population, with short and long bridge sites at very close values (0.4784

and 0.4593), while the four-fold site was found to have a lower overlap (0.3885).

The dynamical dipole moment was not evaluated, but it is reasonable to expect that species with similar binding energies and bond weakening have a similar dynamical dipole moment, too. Assuming it to be the same the ratio of the intensities corresponds to the ratio of the partial coverages of both species, at least as long as depolarization effects are negligible. As shown in Fig. 2 and Fig. 3, both sites are thus equally populated at low coverage, suggesting that they have a similar binding energy. In accord with this only one TDS peak is observed in such conditions [16]. Such a peak results therefore from the contribution of both moieties. At larger coverage repulsive interactions in the adlayer become important and the TDS spectra show that a low temperature shoulder develops [16]. Such a feature is mainly due to oxygen molecules in the adsorption site with higher frequency, whose population dominates at high coverage.

The discussion above, is consistent with recent experiments of Xe induced dissociation and desorption [23]. When the oxygen adlayer at 100 K is exposed to an energetic Xe beam, desorption and some dissociation of chemisorbed O₂ take place. The rates of decrease of the coverage of the two species are close to each other, again suggesting a similar binding energy. At intermediate exposures, when most dioxygen has been removed, HREELS spectra similar to those observed at low O₂ coverage are observed, with the only difference that a peak at 34 meV is now evident, due to dissociated oxygen. Energetic considerations favour, therefore, the assignment of the species to four-fold and short-bridge sites.

On the other hand the small difference in vibrational frequencies suggests a similar bond weakening for the two species thus supporting the assignment to short and long bridge sites. The highest energy loss must thereby correspond to the adsorption site with the highest Mulliken overlap population. On the other hand according to Mehandru and Anderson [10] the short bridge site and four-fold hollow site should have the highest binding energy.

4. Conclusions

In conclusion we have shown that O₂ on Ag(001) at 100 K is characterized by more than one chemisorption site in accord with the theoretical forecast by Mehandru and Andersson [10]. Such sites are characterized by a very similar binding energy as demonstrated by previous thermal desorption spectroscopy experiments [16], which show only one TDS peak at low coverage. The most probable candidates are therefore the four-fold hollow and the short bridge sites. At coverages larger than about 0.15 ML on the other hand the highest frequency mode, corresponding presumably to adsorption in the short bridge site, is favoured.

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