Simulating high-pressure surface reactions with molecular beams

Supplementary information

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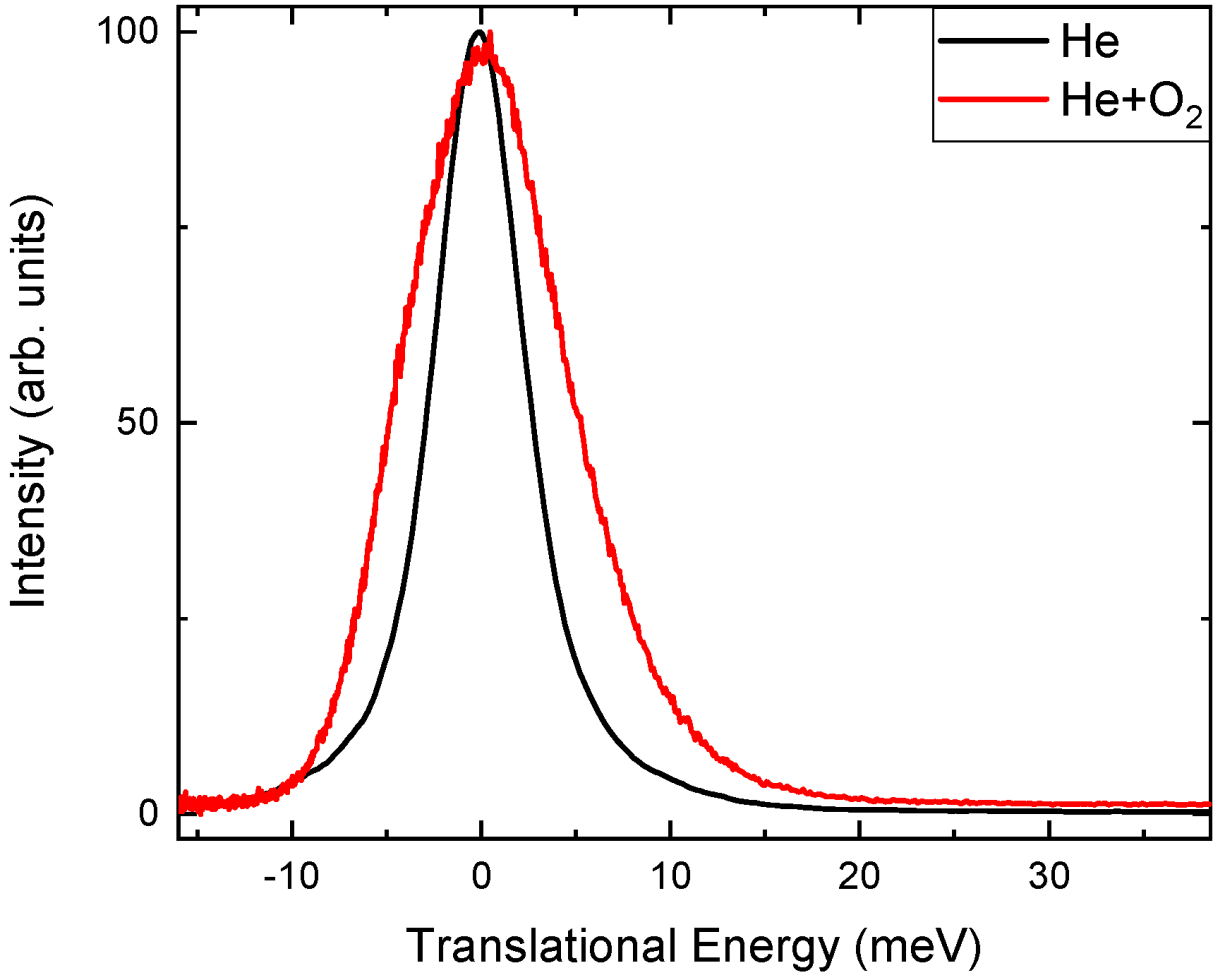
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Figure 1: **He/O$_2$ beam:** Kinetic energy distribution of the quasi-elastic peak of a pure He beam (black curve) and a seeded beam with 80%He-20%O$_2$ (red curve), measured with a nozzle temperature of 300 K. The corresponding mean energy of He atoms in the beam is 65 meV (black) and 30 meV (red) and the FWHM 10% and 33%, respectively.
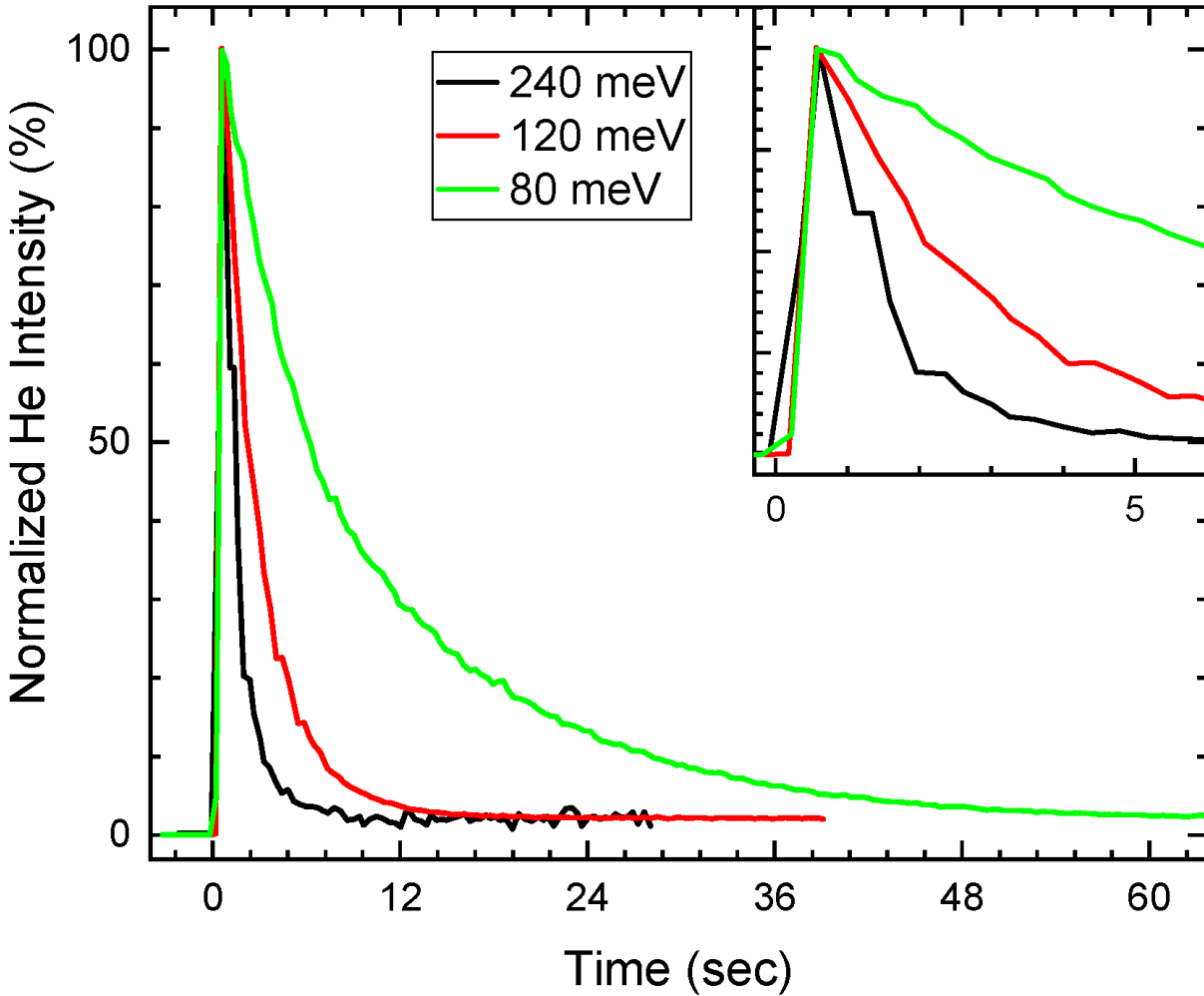
Figure 2: **He/O_2 beam:** Attenuation of He specular signal measured from Cu(111) at 300 K using a seeded beam with 80%He-20%O2 at an angle of incidence of 45° at three incident normal energies: 80 meV, 120 meV and 240 meV. The slope of such a reflectivity curve is proportional to the initial sticking probability of O_2 molecules.[1] The increase of ca. a factor of 10 when going from 80 meV (below the dissociation barrier) to 240 meV is consistent with sticking measurements reported by Zhang et al. for the same system.[2]

X-ray photoemission analysis

X-ray photoemission spectroscopy was carried out by illuminating the sample with Al K_{α} light ($h\nu = 1486.7eV$). The source was not monochromatized, therefore the resolution of the light is somehow broad. To estimate the resolution, the measured Fermi edge of the clean crystal at room temperature was fit by a Fermi-Dirac function resulting in a resolution 1.1 eV. For peak fits, Doniach-Sunjic lineshapes[3] have been employed together with a Shirley background[4] accounting for three peaks. The first peak at lowest energy associates with a Cu bonding configuration at the subsurface (bulk-like), the second one to O atoms at the very Cu surface, and a third peak for a possible hydroxide appearing at higher binding energy. In a first round, all approx. 20 spectra were fit without restrictions. This approach did not give useful results since peak asymmetries, width and background diverted too much. Nevertheless, it gave the predominant peak positions of the subsurface and surface O peaks at 529.6 eV and 530.1 eV, respectively. Furthermore, we observed that hydroxide peaks were only relevant in the long time exposures of the 0.24 eV beam. In a second fit round, the mentioned peaks were fixed, the width and asymmetry of the subsurface O peak was forced to coincide with the leading surface O peak. From this second round an average width and asymmetry of both peaks were extracted. These two values were then used in a third fitting round to fit all spectra. We noted that the spectra of the higher dosages in the 1 eV beam were not well fitted, therefore the peak position of the subsurface peak was no longer fixed. This loss of restriction leaded to the peak shift shown in Figs. **3** and **4**, characteristic of the transition to a bulk-like Cu_2O layer, and re-established the high-quality of the fit.
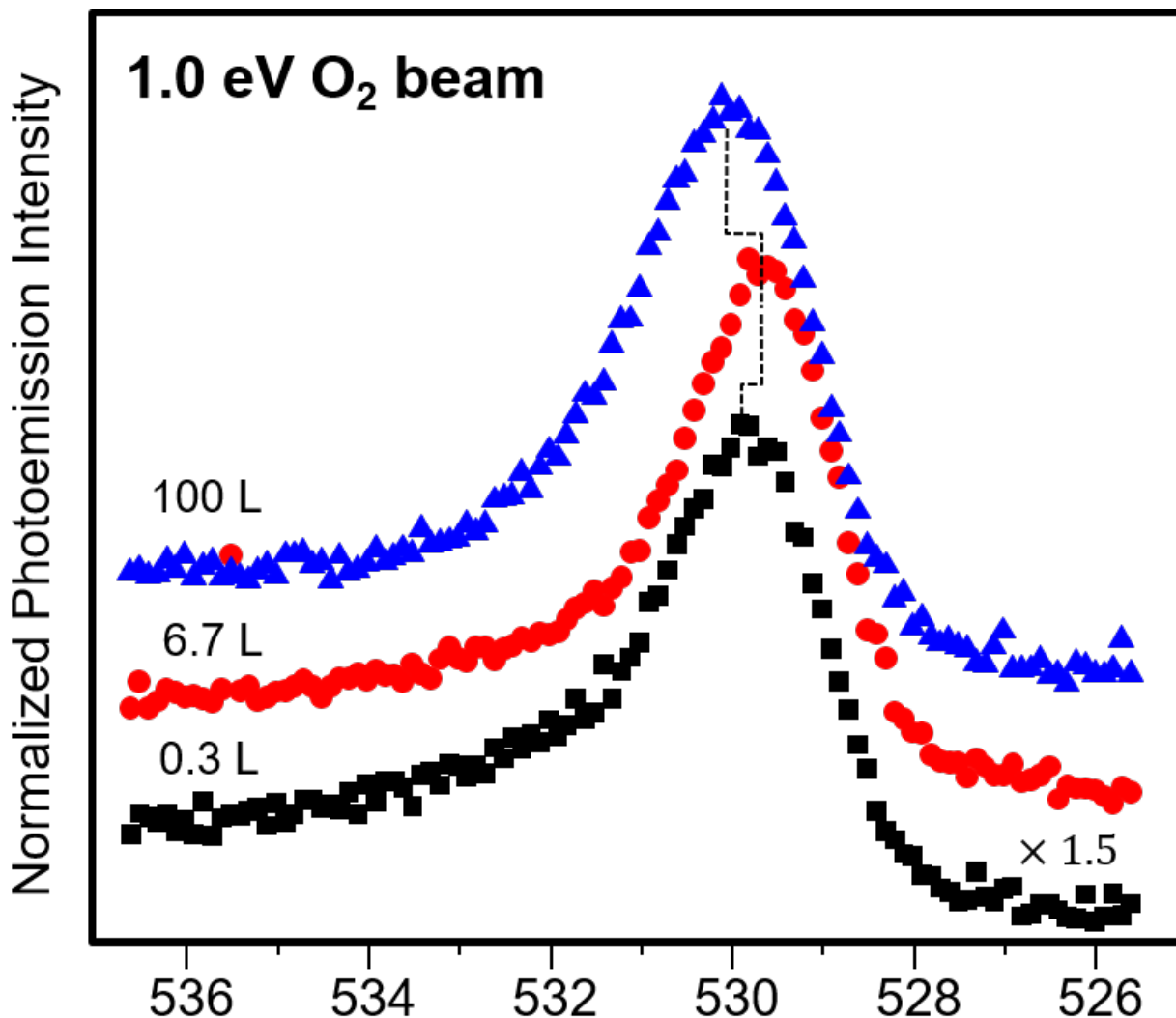
Figure 3: O 1s spectra at critical Cu oxidation steps: XPS O1s spectra acquired after exposing the Cu(111) to increasing doses of the E_{kin}= 1 eV O_2 beam. At the appropriate exposure and/or beam energy one can obtain the same successive oxidation steps as in a random O_2 gas experiment with exponentially larger doses.[5] Here we display the representative spectra for the subsurface-O-dominated regime (0.3 L), the complete surface Cu_2O layer, and the dominant bulk-like Cu_2O phase. Only surface Cu_2O has a sizeable presence of the lower-coordinated surface O atom, and hence the whole feature is shifted to the lowest binding energy (see the text). Changes in peak energies and width are in full agreement with earlier O_2 beam experiments[6,7] and recent random-gas oxidation data.[5]
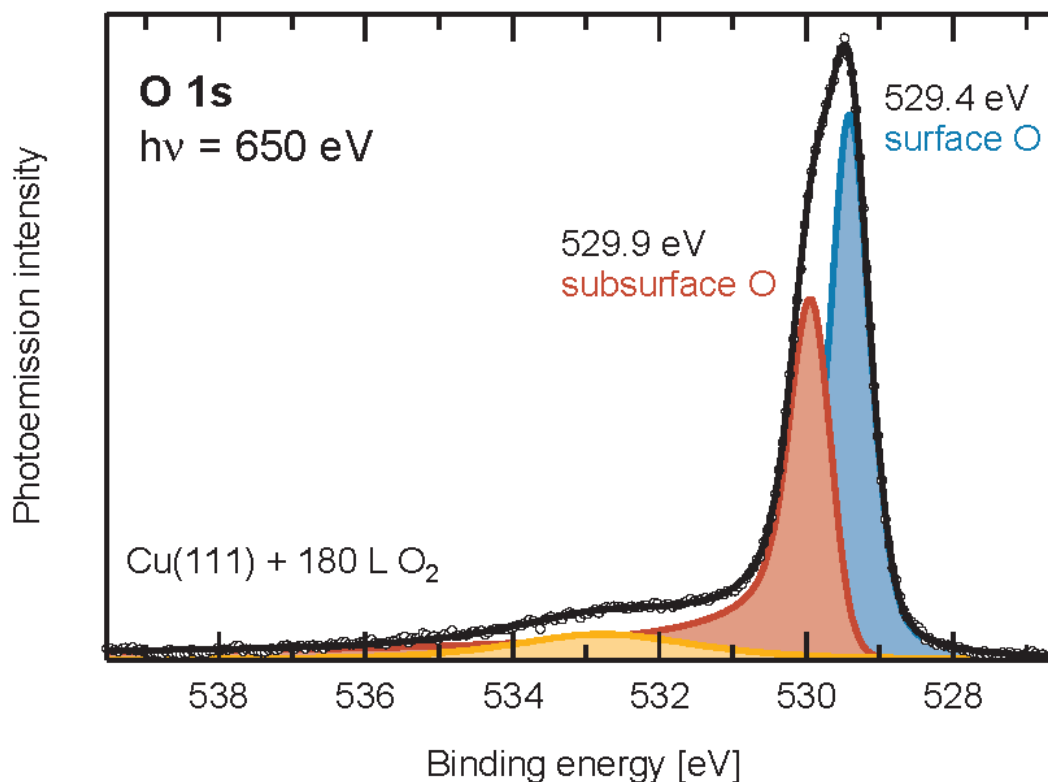
Figure 4: **High resolution surface Cu_2O spectrum:** O1s spectrum acquired after exposing the Cu(111) surface to 10^5 L at 300K. The data have been taken at the IOS beam line of the National Synchrotron Light Source (NSLS-II) in Brookhaven (USA). The excellent energy resolution allows a clear visualization of two different contributions to the spectrum, i.e., those from subsurface and surface O. The shift in the core level energy is readily explained by the high and low coordination of O with Cu atoms at the subsurface and the surface of the Cu_2O layer, respectively. Peak energies are in full agreement with the data presented in Fig. **S3** and the main text.

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