

## Probing the mechanism of facile water dissociation on oxygen covered Cu(111) by Reflection Absorption Infrared Spectroscopy (RAIRS)

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The presence of oxygen atoms on a Cu(111) surface strongly reduces the activation barrier for water dissociation, as compared to bare Cu(111). In this work, we present a direct experimental observation of the hydrogen abstraction mechanism for H<sub>2</sub>O dissociation on a O/Cu(111) surface using reflection absorption infrared spectroscopy (RAIRS). By dosing <sup>18</sup>O<sub>2</sub>(g) onto a Cu(111) single crystal, we create a partially oxidized <sup>18</sup>O/Cu(111) surface, which is subsequently exposed to a flux of H<sub>2</sub><sup>16</sup>O molecules, resulting in the detection of two RAIRS peaks assigned to <sup>18</sup>OH(ads) and <sup>16</sup>OH(ads). With continued H<sub>2</sub><sup>16</sup>O exposure, the <sup>18</sup>OH(ads) RAIRS signal decreases rapidly while the <sup>16</sup>OH(ads) signal continues to increase, indicating a disproportionation reaction of the adsorbed hydroxyl species, resulting in net desorption of H<sub>2</sub><sup>18</sup>O(g) and replacement of <sup>18</sup>O(ads) by <sup>16</sup>O(ads).

