Photochemistry of chemisorbed and physisorbed O\textsubscript{2} on reduced rutile TiO\textsubscript{2}(110)

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The ultraviolet (UV) photon-stimulated reactions of oxygen on TiO\textsubscript{2}(110) are studied. For chemisorbed O\textsubscript{2}, the photochemistry depends on the O\textsubscript{2} coverage. For small coverages, only \(~14\%\) desorbs while the rest either dissociates during UV irradiation, or remains molecularly adsorbed on the surface. For the maximum coverage of chemisorbed oxygen, the fraction of O\textsubscript{2} that photodesorbs is \(~40\%\). However when physisorbed O\textsubscript{2} is also present, \(~70\%\) of the initially chemisorbed O\textsubscript{2} photodesorbs. Experiments using O\textsubscript{2} isotopologues show that UV irradiation results in exchange of atoms between the chemisorbed and physisorbed oxygen. Annealing chemisorbed oxygen to 350 K maximizes these exchange reactions. The exchange products photodesorb in the plane perpendicular to the bridge-bonded oxygen rows at an angle of 45°. Remarkably, the chemisorbed species is stable under multiple cycles of UV irradiation with physisorbed O\textsubscript{2}, and the atoms in the chemisorbed species can be changed from \(^{18}\text{O}\) to \(^{16}\text{O}\) and then back to \(^{18}\text{O}\) via the exchange reactions. The results show that annealing oxygen adsorbed on TiO\textsubscript{2}(110) to \(~350\ K\) produces a stable chemical species with interesting photochemical properties. Possible forms for the photoactive species include O\textsubscript{2} adsorbed in a bridging oxygen vacancy or tetraoxygen.