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Photochemistry of chemisorbed and physisorbed O₂ on reduced rutile TiO₂(110)

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The ultraviolet (UV) photon-stimulated reactions of oxygen on TiO₂(110) are studied. For chemisorbed O₂, the photochemistry depends on the O₂ 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 O₂ that photodesorbs is ~40%. However when physisorbed O₂ is also present, ~70% of the initially chemisorbed O₂ photodesorbs. Experiments using O₂ 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 O₂, and the atoms in the chemisorbed species can be changed from ¹⁸O to ¹⁶O and then back to ¹⁸O via the exchange reactions. The results show that annealing oxygen adsorbed on TiO₂(110) to ~350 K produces a stable chemical species with interesting photochemical properties. Possible forms for the photoactive species include O₂ adsorbed in a bridging oxygen vacancy or tetraoxygen.