

**Probing the photochemistry of chemisorbed oxygen on TiO₂(110) with
Kr and other co-adsorbates**

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Supplementary Information

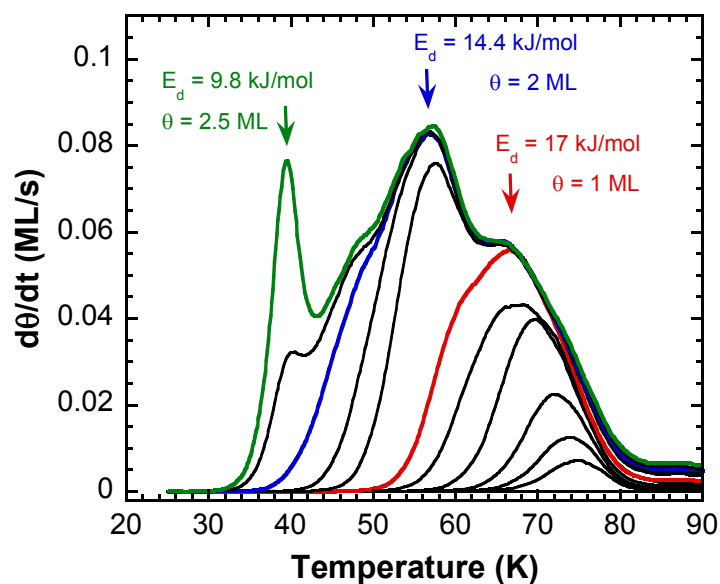


Figure S1. Kr TPD spectra on reduced $\text{TiO}_2(110)$. The Kr was adsorbed at ~ 30 K and the ramp rate was 1 K/s. Coverage-dependent activation energies for desorption are shown for the marked TPD peaks, as estimated from a Redhead analysis.¹

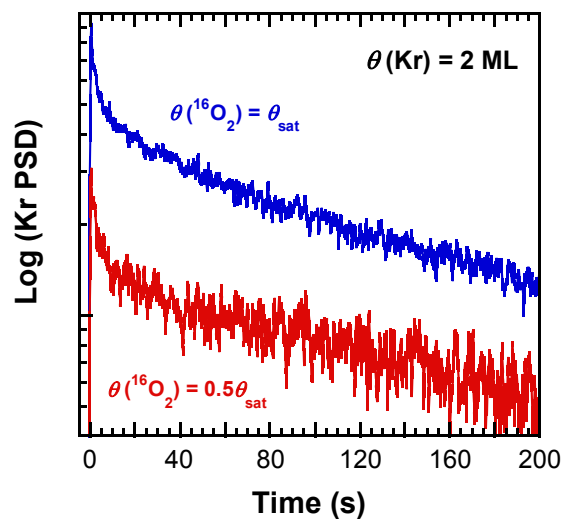


Figure S2. Semi-logarithmic plot of Kr PSD from 2 ML Kr dosed on $\text{TiO}_2(110)$ with $\theta(\text{O}_2) = 0.5\theta_{\text{sat}}$ (red line) and θ_{sat} (blue line).

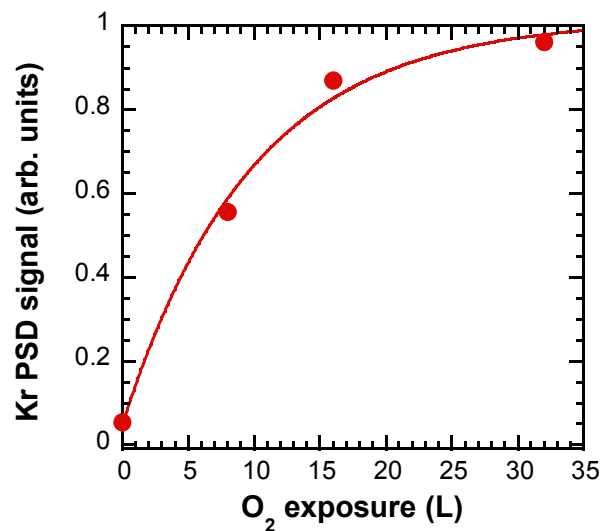


Figure S3. Integrated Kr PSD (for $\theta(\text{Kr}) = 2 \text{ ML}$) versus O₂ exposure. The TiO₂(110) sample was dosed with O₂ at 300 K, where it dissociatively adsorbs.

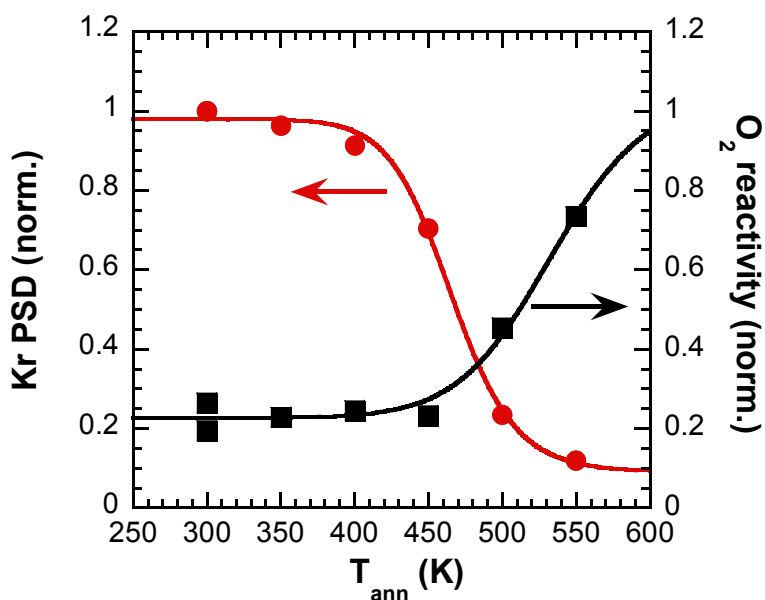


Figure S4. Integrated Kr PSD (red circles) versus annealing temperature. An oxidized TiO₂(110) surface was prepared by exposing the sample to 10 L O₂ at 300 K. The surface was then annealed to different temperatures, T_{ann}, for 60 s. The Kr PSD was then measured (for $\theta(\text{Kr}) = 1 \text{ ML}$). The amount of O₂ that could be chemisorbed on the surface after annealing, relative to θ_{sat} , was also measured (black squares).

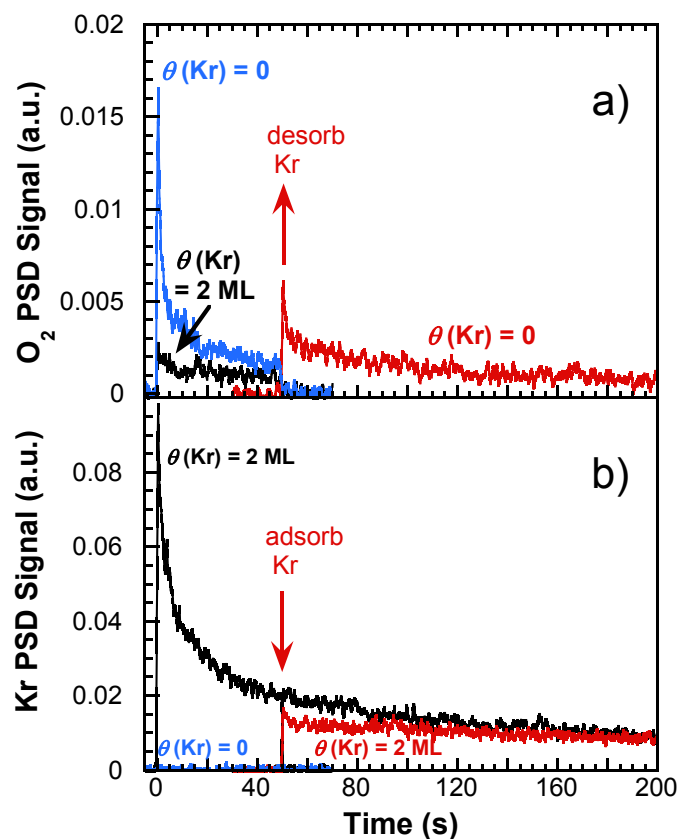


Figure S5. a) O_2 PSD for 0 – 50 s from 2 ML Kr dosed on the $TiO_2(110)$ surface predosed with $\theta(O_2) = \theta_{sat}$ (black). Next, the Kr was desorbed by briefly heating the sample to 100 K and the UV irradiation was resumed for 50 – 200 s. After desorbing the Kr and resuming the irradiation, the O_2 PSD increases (red line). This demonstrates that the co-adsorbed Kr decreases the rate of O_2 PSD. For comparison, the O_2 PSD for 0 – 50 s without co-adsorbed Kr is also shown (blue line). b) $TiO_2(110)$ with $\theta(O_2) = \theta_{sat}$ but no co-adsorbed Kr was irradiated for 50 s with UV light (blue line). Then, 2 ML of Kr was adsorbed at 30K and the UV irradiation was resumed (red line). For comparison, the Kr PSD for 0 – 50 s and 50 – 200 s from 2 ML Kr co-adsorbed with $\theta(O_2) = \theta_{sat}$ is shown in black. At $t = 50$ s, The Kr PSD signal is larger if Kr was co-adsorbed with the O_2 during the first 50 s of UV irradiation. This also shows that the oxygen photo-activity decreases more slowly when Kr is present.

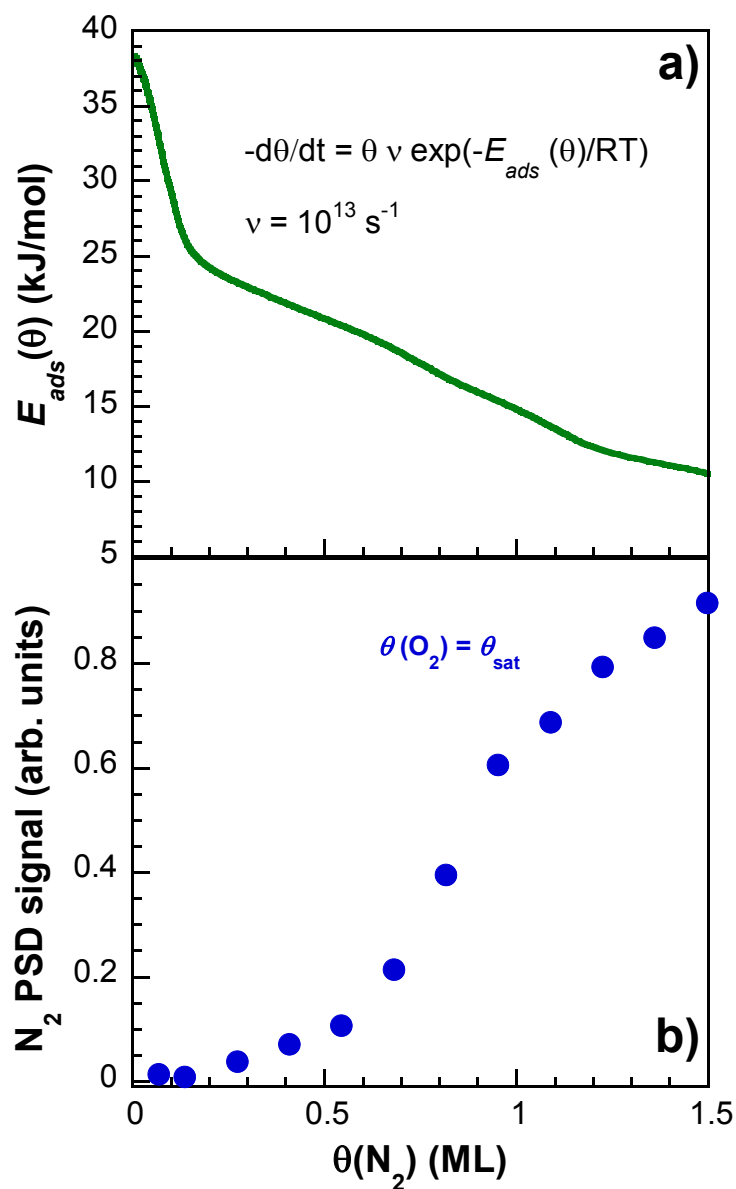


Figure S6. a) Coverage-dependent desorption energy, $E_{ads}(\theta)$, for N₂ versus $\theta(\text{N}_2)$. E_{ads} was obtained from inversion analysis^{2,3} of the N₂ TPD spectra on TiO₂(110) for $\theta(\text{N}_2) = 1.5$ ML (not shown). First-order desorption and a constant pre-exponential factor $1 \times 10^{13} \text{ s}^{-1}$ were used in the inversion procedure. b) Integrated N₂ PSD (0 – 5s) yield versus N₂ coverage on the TiO₂(110) with $\theta(\text{O}_2) = \theta_{sat}$.

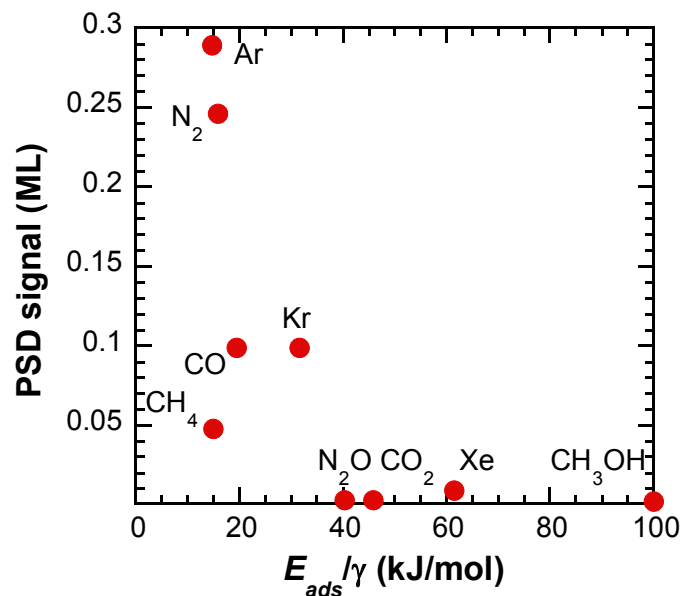


Figure S7. Integrated PSD (0 – 200s) yields for various co-adsorbates on TiO₂(110) versus E_{ads}/γ , where E_{ads} is adsorption energy for the co-adsorbate when its coverage is 1 ML, and γ is a kinematic factor governing energy transfer from an oxygen atom to the co-adsorbate. $\gamma = 4m_Y m_{Ox} / (m_Y + m_{Ox})^2$, where m_Y and m_{Ox} (= 16 amu) are the masses of the co-adsorbate and an oxygen atom.

References:

- (1) P. A. Redhead, *Vacuum*, 1962, **12**, 203-211.
- (2) Dohnálek, Z.; Kimmel, G. A.; Joyce, S. A.; Ayotte, P.; Smith, R. S.; Kay, B. D. J. *Phys. Chem. B* 2001, **105**, 3747.
- (3) Tait, S. L.; Dohnálek, Z.; Campbell, C. T.; Kay, B. D.; *J. Chem. Phys.*, 2005, **122**, 164707.