Supplementary Material for

Strong Influence of Coadsorbate Interaction on CO Desorption Dynamics Probed by Ultrafast X-ray Spectroscopy and Ab Initio Simulations


1. Materials and methods

Sample preparation

The clean Ru(0001) sample was prepared through cycles of 5 minutes of Ne ion sputtering followed by flashing the surface to ~1400 K under ultrahigh vacuum conditions. The (2O + CO)/Ru(0001) surface was initially prepared by exposing the clean Ru(0001) surface to an O₂ background pressure of 3 × 10⁻⁸ Torr at a temperature of 800 K. The surface was allowed to cool and at ~300 K, a CO background pressure of 2 × 10⁻⁸ Torr was introduced into the chamber. These conditions result in the (2O+CO)/Ru(0001) honeycomb surface structure, as shown in Figure S1 [1]. During experimental running conditions, the surface was further cooled using liquid nitrogen down to ~100 K while the background pressures of both CO and O remained constant at the pressures specified above. At 100 K, additional CO adsorbs onto the Ru surface.

Fig. S1 The (2O + CO) / Ru(0001) honeycomb structure. The O atoms occupy both fcc and hcp hollow sites. The CO molecules, each surrounded by six O atoms, adsorb at on-top sites.

Pump-probe setup

Optical pump, x-ray probe experiments were performed using the SSE endstation [2] at the soft x-ray (SXR) beam line [3] of the Linac Coherent Light Source (LCLS). The details of the methods and pump-probe setup are described in the supplementary online materials of ref. [4].

X-ray absorption spectra (XAS) were recorded in partial fluorescence yield mode. We
monitored the O Kα emission as a function of the photon energy using a grating spectrometer [2]. The photon energy was continuously scanned near the O K-edge absorption edge of 528.5 - 542.1 eV with coupled beamline monochromator energy and FEL electron energy scans. The x-ray pulses generated by the LCLS had a pulse length of less than 80 fs and were monochromatized using a 100 line/mm grating at an exit slit of 115 μm providing a resolving power of E/ΔE=3000 and a photon flux onto the sample of $1.3 \times 10^{10}$ photons/pulse [4].

Optical laser pulses at a wavelength of 400 nm and pulse length below 170 fs were used to drive the reaction. The pulse energy of the 400 nm laser was set to give a laser fluence below, but close to, the damage threshold of the Ru(0001) surface and the absorbed fluence was estimated to be around 140 J/m$^2$ (1/e$^2$). The 400 nm optical laser and x-ray laser were collinear with respect to each other and at 2° grazing incidence with respect to the sample surface.

To ensure that the x-ray beam was entirely overlapped by the 400 nm laser beam, the x-ray beam was focused to 50 μm at the position of the sample, whereas the 400 nm laser beam was set to a focus of 65 μm (FWHM). The x-ray laser was operated at 30 Hz, while the 400 nm laser was operated at 10 Hz to provide unpumped reference spectra between each pumped laser shot. The sample was scanned at a speed of 0.8 mm/s during experiments, separating the laser spots on the sample by 80 m, so that the laser continuously excited fresh spots on the sample. The time elapsed between consecutive 400 nm shots on any given spot on the sample was ~15 seconds. This was enough time for O and CO to re-adsorb back onto the surface from the background pressures of O$_2$ and CO.

The time-resolution of the pump-probe experiment is dependent on the inherent pulse width of the optical and free-electron laser pulses and the relative timing between these. Temporal overlap was determined using optical reflectivity of a Si$_3$N$_4$ sample [4,5]. The relative timing between the pulses was monitored for each shot using a non-destructive optical x-ray cross-correlator [6] and corrected for during data analysis. Based on the respective pulse lengths we estimate a time-resolution of 190 fs.

2. Density functional theory calculations
Density functional theory (DFT) calculations were performed using the real-space grid-based code GPAW [7]. The Ru(0001) surface was modeled as a (2×2) three-layer slab with 15 Å of vacuum separating slabs in the z-direction. A 6×6×1 Monkhorst-Pack k-point sampling [8] and a 0.18 Å grid spacing was used for all the calculations. A ¼ ML of CO (see Fig. S2 a-b) and a honeycomb surface structure (¼ ML CO and ½ ML O) (see Fig. S2 c-d) were set up to model the CO/Ru(0001) and oxygen-coadsorbed 2O-CO/Ru(0001) surface, respectively. Spin-polarization was not included in the calculations. To properly describe long-ranged van der Waals interactions, the BEEF exchange-correlation functional was used [9]. The finite temperature Fermi function ($k_B T=0.1$ eV) is utilized to facilitate the SCF convergence by smearing the band occupation around the Fermi level; the total energy of the system is, however, extrapolated back to $k_B T=0$ eV. For geometry optimization, the adsorbates and the top-two layers of Ru(0001) atoms were allowed to fully relax with converged forces less than 0.05 eV/Å.
3. Frozen-orbital calculations

The frozen orbital calculations were performed on cluster models of the surface with adsorbates using the StoBe-deMon (http://www.fhi-berlin.mpg.de/KHsoftware/StoBe/index.html) non-periodic DFT code. The cluster consisted of 21 Ru atoms from the top two layers described with a triple-ζ basis for the 14 valence electrons and a relativistic effective core potential for the 30 innermost electrons. Carbon and oxygen were described with a (6311/311/1) (s/p/d) basis set. The calculations of CO/Ru(0001) were done with a single CO adsorbing on-top while for 2O-CO/Ru(0001) the CO was surrounded by the six nearest oxygen atoms. The structures were taken from the optimized structures above.

The repulsion was obtained through a Constrained Space Orbital Variation (CSOV) [10] scheme with the initial orbitals defined for the separated systems, i.e. CO at large distance from the naked cluster or the cluster with adsorbed oxygen atoms. These orbitals were then orthogonalized but not allowed to relax when the CO was brought in to the different distances from the surface. The freezing was performed by simply setting to zero all off-diagonal matrix elements coupling occupied CO orbitals with occupied cluster orbitals in the Kohn-Sham matrix transformed to molecular orbital basis; all off-diagonal matrix elements coupling occupied and unoccupied orbitals were also set to zero. This procedure eliminates undesired orbital mixings in the subsequent diagonalization.

4. Ab Initio molecular dynamics

Ab Initio molecular dynamics (AIMD) simulations at 2000 K were carried out in the NVT ensemble using Langevin dynamics implemented in the Atomic Simulation Environment (ASE). The interatomic forces as a result of the potential energy surface were obtained on-the-fly from QUANTUM ESPRESSO [11] with 500 eV kinetic energy cutoff and the BEEF exchange-correlation functional [9]. In the Langevin equation [12,13], an electronic friction term against the velocity of atoms and a stochastic force via coupling to a heat bath are added into the equation of motion. The crucial parameter in this formalism is the electronic friction that governs the energy transfer. For the purpose of thermalization, the friction term is set to 0.002 a.u. without further effort to obtain ab initio friction from electron-phonon calculations.

To alleviate the size constraints on the dynamics due to concerted motion of surface species, a (2×4) three-layer Ru(0001) slab with 6×3×1 k-point sampling was used. Optimized structures of
CO/Ru(0001) and 2O-CO/Ru(0001) were read in as starting geometry. The velocity of the atoms was first initialized using the Maxwell-Boltzmann distribution at 3000 K. The system was then thermalized towards 2000 K for 1 ps. The trajectory during the thermalization process was discarded for any analysis. The simulations were then run up to 10 ps or until CO desorbs. A 2 fs time step was used for the integration of atomic motion.

5. Two-temperature model
Absorption of photons in the metallic substrate initially gives rise to a non-equilibrium distribution of electron-hole pairs. Due to electron-electron scattering in the metal the energetic electrons thermalize quickly resulting in a Fermi-Dirac distribution with a characteristic electronic temperature. The two-temperature model has been extensively used to describe energy relaxation of the hot electron gas [14]. It uses two coupled PDEs as shown in Eq. (1) to model the energy transfer among electron, phonon, the bulk as well as the energy source of a laser pulse, $S(z,t)$.

\[ C_{el} \frac{\partial}{\partial t} T_{el} = \frac{\partial}{\partial z} \left( k \frac{\partial}{\partial z} T_{el} \right) - g(T_{el} - T_{ph}) + S(z,t) \]
\[ C_{ph} \frac{\partial}{\partial t} T_{ph} = g(T_{el} - T_{ph}) \]  
Eq. (1)

In Eq. (1), $T_{el}$ and $T_{ph}$ are the electron and phonon temperature, respectively, and $k = k_0 T_{el} / T_{ph}$ is the thermal conductivity governing the energy dissipation into the bulk. The phonon temperature is linearly coupled to the electron temperature with the electron-phonon coupling coefficient, $g$, which has been measured and tabulated for many transition and noble metals [15]. The heat capacity of the electron system is estimated based on $C_{el} = \gamma T_{el}$ ($\gamma$ is the electron specific heat). The heat capacity of the phonon system, $C_{ph}$, can be calculated based on the Debye model,

\[ C_{ph} = 9 n k_B \left( \frac{T_{ph}}{\Theta_D} \right)^3 \int_0^{\Theta_D / T_{ph}} x^4 e^x dx / (x^3 - 1)^2 \]  
Eq. (2)

where $n$ is the atom density; $\Theta_D$ is the Debye temperature of metals. The time evolution of the phonon and electron temperature can be directly solved by imposing the time dependent source profile $S(z,t)$,

\[ S(z,t) = I(t) \lambda^{-1} e^{-z/\lambda} \]  
Eq. (3)

where $I(t)$ is the temporal profile of the source intensity taking into account the reflectivity of the metal and $\lambda$ is the penetration length of the light. $I(t)$ is written as a Gaussian distribution

\[ I(t) = F \exp \left( \frac{-t^2}{2 \sigma^2} \right) / \sqrt{2 \pi \sigma^2} \]  
where $\sigma = \Gamma / 2.355$ is the pulse duration and $\Gamma$ the full width at half maximum of the Gaussian distribution. $F$ is the absorbed fluence of the energy source. All the parameters relevant for this study are tabulated in Table S1.
Using the two-temperature model described above with the laser pulse profile of a Gaussian time-dependence with a full-width at half maximum of 170 fs and an absorbed fluence of 140 J/m², we computed the electron and phonon temperatures at the surface during the first 10 ps as shown in Fig. S3.

6. Potential of mean force

The potential of mean force (PMF) describes how the system’s free energy, $G(s)$, changes as a function of some specific reaction coordinate, $s$. At 0 K, it is simply the minimum energy potential, $V_0(s)$. For non-zero $T$, $G(s)$ can be calculated in Eq. (4) based on the interaction potential, $V(q,s)$, along all of the remaining coordinates orthogonal to $s$.

$$G(s) = V_0(s) - k_B T \sum_{q \neq s} \ln \int \exp[-V(q,s)/k_BT]dq$$  \hspace{1cm} Eq. (4)

In Eq. (4), $V(q,s)$ is the interaction potential for mode $q$ relative to $V_0(s)$ [16]. This approach essentially assumes that the potential energy is separable in the vibrational, translational and rotational degrees of freedom. To evaluate the free energy along the CO desorption path, we have explicitly calculated the interaction potential of three rotations (2 cartwheel modes and 1 helicopter mode) and 2 translations (in the x and y directions) of the CO molecule at each surface distance using the BEEF exchange-correlation functional [9]. The Ru-CO vibrational mode is the reaction coordinate for CO desorption and so is not included in Eq. (4). The C-O vibrational mode has a negligible contribution to the change of free energy and is not taken into account in this study. The interaction potential for each degree of freedom was then fitted to a polynomial function and inserted into Eq. (4) for an estimation of the free energy. Fig. S4 shows the potential of mean force (free energy surface) for CO desorption from CO/Ru(0001) and 2O-CO/Ru(0001) at varying
temperatures along the CO desorption path.

**Fig. S4** The free energy surface for CO desorption for (a) CO/Ru(0001) and (b) 2O-C0/Ru(0001) at 0 K, 500 K, 1500 K and 2000 K, respectively. The reaction path is defined as the distance between the center of mass of CO and the Ru surface plane.

### 7. Effects of disorder

At the start of the experiments, we have a (2x1) honeycomb structure. After the first laser pass and readsoption from the background pressure, the surface structure becomes less well defined. An indication of this is that the CO $\pi^*$ peak is broader in the LCLS experiments than in earlier synchrotron radiation studies with well-defined surface. We thus have to consider the possibility that we may have some type of mixed phase disordered structure. In Fig. S5 we show the computed potential energy surface (MEP) for a disordered phase significantly deviating in structure from the honeycomb phase investigated in the main manuscript. The resulting MEP shows a very similar enhanced long-range attraction for vertical CO compared to lying-down as for the honeycomb phase indicating the general validity of our conclusions.

**Fig. S5** The potential energy surface of a CO molecule perpendicular and parallel to Ru(0001) with
disordered oxygen surface structure (inset shows the model).

8. Effects of O adsorption

In view of our conclusion that the enhanced long-range attraction for vertical CO in the coadsorbed system is due to removal of charge from Ru by O, it becomes of interest to compare the charge density before and after O adsorption on Ru(0001), i.e. \( \rho(O/Ru(0001)) - [\rho(Ru(0001)) + \rho(O)] \). This charge density difference is shown in Fig. S6, which clearly shows the expected charge accumulation on the adsorbed atomic O and depletion of charge on the neighboring Ru to which CO will coordinate.

![Fig. S6 O adsorption-induced charge density difference on Ru(0001) without CO. The inset shows the direction cutting through the O and Ru atoms (blue represents electron accumulation and red represents electron depletion).](image)

References


