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Cite as: J. Chem. Phys. **157**, 164705 (2022); <https://doi.org/10.1063/5.0114399>

Submitted: 26 July 2022 • Accepted: 28 September 2022 • Accepted Manuscript Online: 29 September 2022 • Published Online: 25 October 2022

 Jerry LaRue,  Boyang Liu,  Gabriel L. S. Rodrigues, et al.

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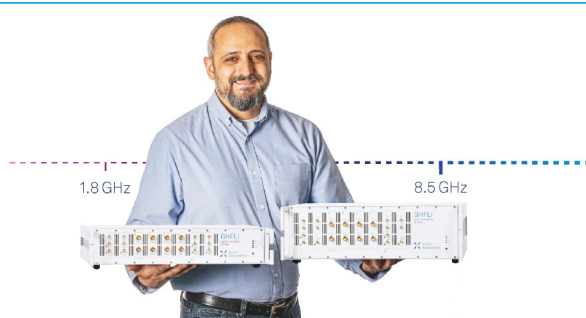
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Jerry LaRue,^{1,a)}  Boyang Liu,²  Gabriel L. S. Rodrigues,²  Chang Liu,² Jose Antonio Garrido Torres,³  Simon Schreck,² Elias Diesen,³  Matthew Weston,² Hirohito Ogasawara,⁵  Fivos Perakis,²  Martina Dell'Angela,⁶  Flavio Capotondi,⁷ Devon Ball,¹ Conner Carnahan,¹ Gary Zeri,¹ Luca Giannessi,⁷  Emanuele Pedersoli,⁷  Denys Naumenko,⁷  Peter Amann,⁸  Ivaylo Nikolov,⁷ Lorenzo Raimondi,⁷  Carlo Spezzani,⁷ Martin Beye,⁹  Johannes Voss,³  Hsin-Yi Wang,²  Filippo Cavalca,² Jörgen Gladh,³  Sergey Koroidov,² Frank Abild-Pedersen,³  Manuel Kolb,^{2,3} Piter S. Miedema,⁹  Roberto Costantini,^{6,10}  Tony F. Heinz,^{3,11}  Alan C. Luntz,³  Lars G. M. Pettersson,²  and Anders Nilsson²

AFFILIATIONS

¹Schmid College of Science and Technology, Chapman University, Orange, California 92866, USA

²Department of Physics, AlbaNova University Center, Stockholm University, SE-10691 Stockholm, Sweden

³SLAC National Accelerator Laboratory, SUNCAT Center for Interface Science and Catalysis, 2575 Sand Hill Road, Menlo Park, California 94025, USA

⁴Fritz-Haber Institute of the Max-Planck-Society, Faradayweg 4-6, D-14195 Berlin, Germany

⁵SLAC National Accelerator Laboratory, 2575 Sand Hill Road, Menlo Park, California 94025, USA

⁶CNR-IOM, SS 14-km 163.5, 34149 Basovizza, Trieste, Italy

⁷FERMI, Elettra-Sincrotrone Trieste, SS 14-km 163.5, 34149 Basovizza, Trieste, Italy

⁸Scienta Omicron AB, Danmarksgratan 22, 75323 Uppsala, Sweden

⁹Deutsches Elektronen-Synchrotron DESY, Notkestrasse 85, 22607 Hamburg, Germany

¹⁰Physics Department, University of Trieste, Via Valerio 2, 34127 Trieste, Italy

¹¹Department of Applied Physics, Stanford University, Stanford, California 94305, USA

^{a)} Author to whom correspondence should be addressed: larue@chapman.edu. Tel.: (714) 744-7660

ABSTRACT

We report on carbon monoxide desorption and oxidation induced by 400 nm femtosecond laser excitation on the O/Ru(0001) surface probed by time-resolved x-ray absorption spectroscopy (TR-XAS) at the carbon K-edge. The experiments were performed under constant background pressures of CO (6×10^{-8} Torr) and O₂ (3×10^{-8} Torr). Under these conditions, we detect two transient CO species with narrow $2\pi^*$ peaks, suggesting little $2\pi^*$ interaction with the surface. Based on polarization measurements, we find that these two species have opposing orientations: (1) CO favoring a more perpendicular orientation and (2) CO favoring a more parallel orientation with respect to the surface. We also directly detect gas-phase CO₂ using a mass spectrometer and observe weak signatures of bent adsorbed CO₂ at slightly higher x-ray energies than the $2\pi^*$ region. These results are compared to previously reported TR-XAS results at the O K-edge, where the CO background pressure was three times lower (2×10^{-8} Torr) while maintaining the same O₂ pressure. At the lower CO pressure, in the CO $2\pi^*$ region, we observed adsorbed CO and a distribution of OC–O bond lengths close to the CO oxidation transition state, with little indication of gas-like CO. The shift toward “gas-like” CO species may be explained by the higher CO exposure, which blocks O adsorption, decreasing O

coverage and increasing CO coverage. These effects decrease the CO desorption barrier through dipole–dipole interaction while simultaneously increasing the CO oxidation barrier.

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INTRODUCTION

The elementary processes that occur between molecules and metal surfaces are key to understanding heterogeneous catalytic reactions since they determine the available reaction pathways, selectivity, and kinetic rates. Insights into the details of the dynamics controlling these processes are important not only for describing catalytic reactions but also for predicting highly efficient and selective catalysts. It is of fundamental importance to examine how changing not only the catalytic surface but also the gas phase composition can affect these processes and, correspondingly, reaction pathways.

CO oxidation and desorption on metal surfaces have long been models for the study of reaction dynamics in catalysis.^{1–8,22} In this study, we investigate laser-induced CO desorption and oxidation on oxygen-covered Ru(0001) under CO-rich conditions at the C K-edge using symmetry-resolved time-resolved x-ray absorption spectroscopy (TR-XAS). We find two different CO species with different preferred orientations develop after laser excitation, each with narrow $2\pi^*$ gas-like peaks, suggesting little interaction between $2\pi^*$ and the surface. At higher x-ray energies, we find weak signals for bent CO₂, showing that the CO oxidation channel is still active. We compare our results to previous results not obtained under CO-rich conditions.

Optical pump/x-ray probe studies under CO-only conditions on Ru(0001) observed a transient intermediate gas-like precursor state of CO prior to desorption.¹¹ This state, which had long been theorized,^{23–26} traps CO in a physisorption well with little interaction with the surface and arises due to the increased rotational entropy of CO. When the experiments were repeated with oxygen-covered Ru(0001) under less CO-rich conditions than presented here, little evidence of this precursor state, or any CO gas-like states, was present.¹ Density functional theory (DFT) calculations showed that a long-range σ -driven interaction between the CO molecules and the surface due to the presence of O gives rise to a preferred perpendicular orientation of desorbing CO. This reduces the rotational entropy of CO and, consequently, destabilizes the associated precursor state. These results emphasize that not only is the catalytic surface a determinate of the reaction outcome but also the gas phase composition can critically control the final reaction paths.

EXPERIMENTAL

We employed pump–probe spectroscopy to access the ultrafast dynamics, with the pump being a 400 nm femtosecond laser pulse and the probe being a femtosecond x-ray free-electron laser (XFEL) pulse around the C K-edge. The experiments were performed using the DiProl endstation at the FERMI XFEL in Trieste, Italy. FERMI is a two-stage fully seeded soft x-ray free electron laser,²⁷ with access to x-ray energies in the range of the carbon $2\pi^*$ (~ 288 eV) feature. As

a seeded source, FERMI provides x-ray pulses with very little time jitter with respect to the optical pump pulses. The surface science endstation (Titan) was transported from Stockholm University to FERMI and installed downstream from the permanent DiProl endstation. The endstation is equipped with standard surface-science preparation tools, including an ion-sputtering gun, sample cooling, and sample heating by radiation and electron bombardment. Other tools include a four-axis sample manipulator to provide both full sample translation and sample rotation, a high-efficiency and large-solid-angle fluorescence yield (FY) detector, and beam monitors and timing tools that are used for the spatial and temporal overlapping of optical laser with the XFEL pulses.

During the pump–probe measurement, 400 nm optical laser pulses with a pulse duration of ~ 100 fs and laser fluence close to, but below the damage threshold for Ru(0001) induced the reaction. The subsequent temporal evolution was probed using the XFEL pulses. The optical laser and x-ray laser were collinear with respect to each other and at 3° grazing incidence with respect to the sample surface. The soft x-ray pulses were generated within the two-stage seeding scheme of the FERMI free-electron laser (FEL)^{27,28} and were of ~ 50 fs duration. Since the XFEL laser seed and optical pump pulses are generated from the same laser system, the optical laser pump and the XFEL probe are intrinsically synchronized very closely to one another although there is some thermal drift. This results in a time resolution of ~ 110 fs. A fluorescent phosphor screen was used to visualize the XFEL beam to spatially overlap the optical laser with the XFEL beam. To achieve temporal overlap, a two-step process was used. First, the tip of an in-vacuum SMA cable was moved into overlapped beams. The XFEL and optical laser pulses both create short electronic pulses on the SMA cable that can be measured and visualized using a GHz-bandwidth oscilloscope. By adjusting the delay between the optical laser and XFEL, both electronic pulses on the oscilloscope could be temporally overlapped to within a few picoseconds. In the second step, temporal overlap on the ~ 100 fs scale was established by monitoring the x-ray total fluorescence yield (TFY) XAS intensity from CO adsorbed on a Ru(0001) surface as a function of delay between the optical laser and FEL. The ultrafast x-ray response to laser-induced CO desorption in the CO/Ru(0001) system has been well studied.^{11,29} We monitored the XAS intensity at 289 eV, which is on the high-energy flank of the CO $2\pi^*$ resonance.

In our measurements, a well-established surface science method¹ was initially employed to produce a clean, well-ordered Ru(0001) surface. To this end, the ruthenium crystal was treated by repeated cycles of Ne⁺ sputtering and high-temperature flash annealing in an O₂ atmosphere at 1070 K. The molecular adlayer was then prepared in the following way: The sample was first dosed with 20 L [Langmuir (L) = 1×10^{-6} Torr for 1 s] of O₂ when the temperature dropped below 620 K. Subsequently, the sample was exposed to CO at a temperature of 170 K to reach CO saturation coverage. This procedure has been shown to give the well-known

(2O + CO)/Ru(0001) honeycomb surface structure, where the O atoms sit on hollow sites in a honeycomb structure and the CO molecules sit on the top sites at the center of each hexagon.³⁰ During the measurements, a background gas pressure of 6×10^{-8} Torr CO and 3×10^{-8} Torr O₂ was maintained, while the sample temperature remained at ~ 100 K. In order to have a newly prepared surface spot during the measurements, the sample was continuously scanned and each spot on the sample was revisited after a cycle period of 10–20 s to repopulate the spots that had been previously measured. Every 2–3 h, we cleaned the sample and prepared a fresh monolayer of CO and O using the procedure described above to ensure our sample was not contaminated.

We recorded the TR-XAS data using polarizations that were in-plane with respect to the Ru(0001) surface and out-of-plane with respect to the Ru(0001) surface at a repetition rate of 10 Hz. The central average XFEL photon energy was scanned over the desired range around the carbon K-edge resonance with a step of 0.3 or 0.5 eV depending on the resonance range (e.g., pre-edge or post-edge of the 1s to $2\pi^*$ resonance). The delay between the optical laser and the XFEL pulse was set to pre-defined values before recording 1000 XFEL shots for each photon energy and delay combination. At early timescales (-1.0 – 2.0 ps), data were recorded at 0.25 ps intervals. Extended time delays were recorded at 5.0 and 10.0 ps. We continuously measured laser-induced CO₂ desorption using a mass spectrometer to ensure that CO₂ production and, hence, surface conditions remained constant throughout the measurements (see the [supplementary material](#)).

The raw experimental recorded data were post-processed based on the data analyses of the FERMI online spectrometer on a shot-to-shot basis. For this analysis, we checked the spectral intensity distribution for each XFEL shot and obtained the central photon energies, bandwidth, and intensity of each shot. In the data processing, shots with low (close to zero) intensity and large FEL bandwidth (FWHM > 0.5 eV) were filtered out. We sorted all shots based on their central photon energy into bins of 0.1 eV width. For each bin, the TFY intensity was normalized by the incident intensity and the standard error was calculated based on Poisson statistics.

RESULTS

Figure 1 shows the C K-edge in-plane and out-of-plane TR-XAS spectra for the $2\pi^*$ region of CO. Selected time slices are

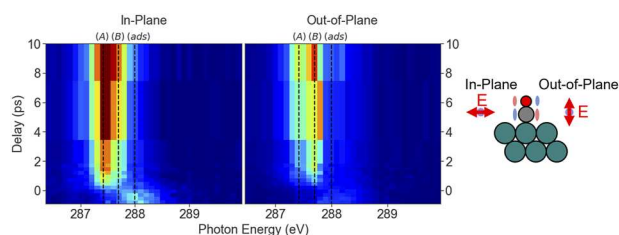


FIG. 1. False color plot of the CO $2\pi^*$ region TR-XAS spectra for (left) in-plane and (center) out-of-plane polarizations. Red indicates highest intensity, and blue indicates lowest intensity. The dashed lines represent the peak positions for CO_(A), CO_(B), and CO_(ads). Right: The geometry of the x-ray laser polarization with respect to the surface for in-plane and out-of-plane.

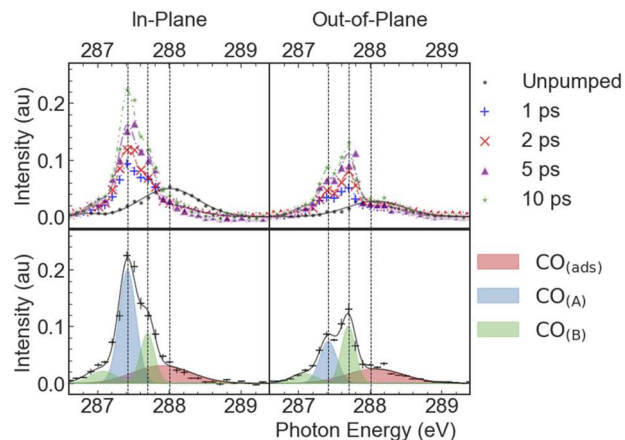


FIG. 2. Top: CO $2\pi^*$ region TR-XAS spectra showing (left) in-plane and (right) out-of-plane polarizations. The data are binned using 1.0 ps bins for better statistics. The dashed lines represent fits for the peaks using Gaussian profiles, as described in the text. Bottom: The corresponding TR-XAS spectra fits at 10 ps time delay. The dashed vertical lines indicate the center of the fitted peaks.

represented in Fig. 2, where data are averaged over 1.0 ps time bins for better statistics. Three features are evident in the data: (1) a broad peak near 288 eV representing adsorbed CO, referred to as CO_(ads); (2) a narrow peak centered at the CO gas phase value of 287.42 eV, referred to as CO_(A), both in the in-plane scan; and (3) a second narrow peak between the adsorbed and gas phase energies at 287.7 eV, referred to as CO_(B) in the out-of-plane scan. After femtosecond laser excitation, the CO_(ads) peak decreases in intensity and redshifts to lower energy. CO_(A) and CO_(B) peaks, without any initial intensity in the unpumped spectrum, continuously grow in strength over the 10 ps timeframe of the data. These trends can be seen in Fig. 3, where the unpumped signal has been subtracted from the data.

We fit each of the CO peaks with a Gaussian profile. The CO_(ads) feature is centered at 288.0 eV with a FWHM of 0.94 eV. CO_(A) is centered at 287.42 eV³¹ with a FWHM of 0.24 eV. CO_(B)

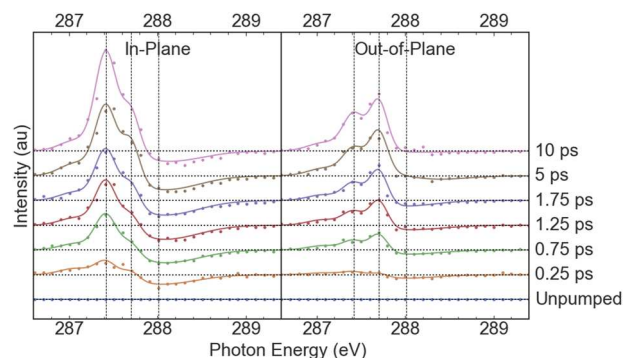


FIG. 3. Changes in the CO $2\pi^*$ region TR-XAS spectra relative to the unpumped system for (left) in-plane and (right) out-of-plane polarizations. The dashed vertical lines indicate the center of the fitted peaks.

consists of two peaks, one centered at 287.7 eV with a FWHM of 0.24 eV and a broader, lower-energy peak at 287.08 eV with a FWHM 0.42 eV. See the section titled “Discussion” for more details. The top panel of Fig. 4 shows the transient changes of the spectral features as a function of pump–probe delay for the three CO species. The $\text{CO}_{(\text{ads})}$ peak intensity decreases on the 0.45 ± 0.05 ps timescale, while the intensities of the $\text{CO}_{(\text{A})}$ and $\text{CO}_{(\text{B})}$ peaks rapidly increase over a 0.78 ± 0.04 ps timescale, as shown by the solid lines. The $\text{CO}_{(\text{A})}$ and $\text{CO}_{(\text{B})}$ peaks continue to increase in intensity over the 10 ps timescale, and their intensities are nearly identical to each other. The increase in intensity arises as adsorbed CO enters these gas-like states although quantitative estimates are not possible as gas-like CO absorbs more strongly than adsorbed CO. After 2 ps, the $\text{CO}_{(\text{ads})}$ peak starts to recover some of its original intensity but is still redshifted.

As the $\text{CO } 2\pi^*$ orbitals lie in the plane perpendicular to the CO molecular axis, excitation of these orbitals requires the polarization of the x rays to be perpendicular to the CO molecular axis. For CO molecules oriented perpendicular to the surface, only in-plane absorption intensity (I_{IP}), and no out-of-plane intensity (I_{OP}), would thus be observed. For CO molecules with their axis parallel to the surface, the out-of-plane intensity would be twice that of the in-plane intensity. We calculated the relative orientations of the three different CO spectral features by calculating the polarization anisotropy parameter ρ given by the difference between the intensities of the in-plane and out-of-plane fits compared to the sum of their intensities,

$$\rho = \frac{I_{\text{IP}} - I_{\text{OP}}}{I_{\text{IP}} + I_{\text{OP}}}.$$

If the CO molecule is perpendicular to the surface, $\rho = 1$ will result, while parallel CO will yield $\rho = -1/3$. The bottom panel of Fig. 4 shows the experimental value of ρ for the three different CO spectral features as a function of delay time. After laser excitation, $\text{CO}_{(\text{ads})}$ moves toward a more parallel orientation with respect to the surface, as indicated by the decreasing ρ value. Despite the similar peak intensities, $\text{CO}_{(\text{A})}$ favors a more perpendicular orientation to the surface than unpumped $\text{CO}_{(\text{ads})}$, while $\text{CO}_{(\text{B})}$ favors a more

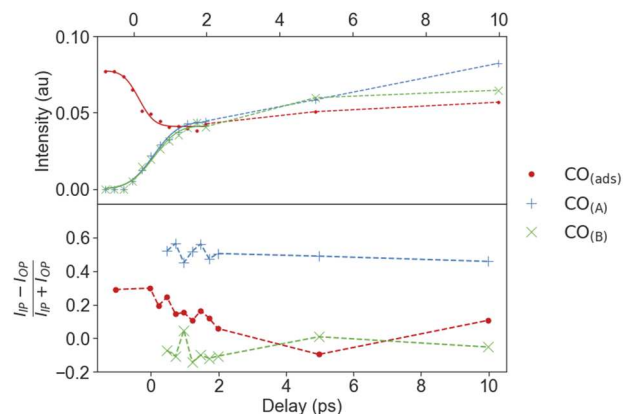


FIG. 4. Top: The time evolution of the TR-XAS features based on our fitting model. The in-plane and out-of-plane intensity are summed together for each CO species. Solid lines represent the evolution for each peak on the 2 ps timescale, and the dashed lines are added to aid the eye. Bottom: Polarization anisotropy parameter $\rho = (I_{\text{IP}} - I_{\text{OP}}) / (I_{\text{IP}} + I_{\text{OP}})$ resulting from the CO fits of the spectra for different x-ray polarizations as a function of pump–probe delay. Higher values of ρ represent CO in a more perpendicular orientation (maximum value of 1), and lower values represent CO in a more parallel orientation (minimum value of $-1/3$).

perpendicular orientation to the surface. The orientation differences highlight that these are distinct gas-like CO species.

We confirmed that gas-phase CO_2 is produced using mass spectrometry (see the [supplementary material](#)) and even see evidence that the resonant x-ray pulses enhance CO oxidation. This is likely due to the core-excited CO becoming vibrationally excited, promoting CO oxidation.³² Despite the confirmation of CO_2 formation, changes in the $\text{CO } 2\pi^*$ region are dominated by CO desorption dynamics, obscuring any observable CO oxidation dynamics. Bent CO_2 has been reported as an anionic precursor to CO and O and may form in the reverse process of CO oxidation.^{33–35} We recorded data at x-ray energies above the $\text{CO } 2\pi^*$ resonance, up to 295 eV, where we observe bent surface CO_2 on the surface. Figure 5 shows the TR-XAS bent CO_2 peak corresponding to a bent, weakly

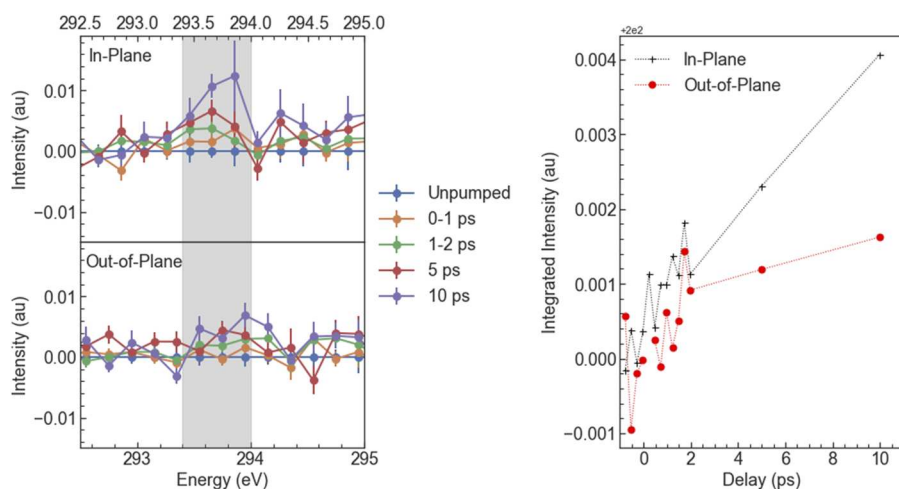


FIG. 5. Left: Difference spectra of the bent CO_2 region grouped with 1.0 ps time bins and 0.2 eV energy bins for better statistics. The unpumped data are subtracted from all time bins. Right: The change in integrated intensities from 293.4 to 294.0 eV using 0.25 ps time steps.

chemisorbed CO₂ species.¹ The integrated intensity between 293.4 and 294 eV is displayed on the right panel of Fig. 5. Due to the σ -bond character of this state, we see more intensity in the in-plane geometry, as expected. The intensity of the signal steadily rises over the course of 10 ps, implying that this is likely driven by thermal processes of the phonon bath heating up due to electron-phonon coupling.

DISCUSSION

In our measurements, we initially prepared the CO+O honeycomb structure; however, our experimental conditions required continuous background pressures of CO and O₂ at $\sim$ 100 K. Below 149 K, O forms a 2×1 structure and CO forms a disordered overlayer with a coverage of 0.36 monolayer (ML).²² Some of O that adsorbs to replace previously reacted O may adsorb in the $p(2 \times 1)$ phase. O₂ requires two nearby vacancies to dissociatively adsorb on the surface. Isolated O vacancies would likely remain as vacancies until a nearby vacancy develops to allow O₂ to dissociate as the diffusion barrier for O on Ru(0001) is relatively high, between 0.55 and 0.70 eV.³⁶ Adsorbed CO is known to block the adsorption of other species, including O₂, further increasing O vacancies. As a result, our surface likely has a lower O coverage and a higher CO coverage than the initially prepared CO+O honeycomb structure. Mass spectrometry data show that CO₂ desorption yields do not change over time, indicating that the surface has reached a steady state. See the [supplementary material](#).

Using the polarization dependence of the integrated intensities of the unpumped spectra, we calculate an average tilt angle of the initial state of the adsorbed CO to be $42^\circ \pm 3^\circ$ from the surface normal. See the [supplementary material](#) for details on the calculation. Previous studies have reported CO tilt angles on O/Ru(0001). On the $p(2 \times 2)$ (O+CO)/Ru(0001) surface (0.25 ML O), CO tilt angles of $12.6^\circ \pm 4.6^\circ$ were inferred from LEED data at 120 K, while on the $p(2 \times 2)$ (2O + CO)/Ru(0001) surface (0.50 ML O in honeycomb structure), no information on tilt angles was reported.^{30,37} The tilt angle of CO toward neighboring O atoms has been calculated to be up to 41° on the (2×2) (2CO+O)/Ru(0001) surface with less than a 0.03 eV barrier from the perpendicular position.³⁸ The coverage and structure of O on the surface impact the CO tilt angles, and the resulting overlayer structure from the experimental conditions seems to favor larger CO tilt angles than similar previous studies.

On the sub-picosecond timescale after laser excitation, the CO_(ads) $2\pi^*$ intensity redshifts and decreases in strength. Previous investigations of the dynamics induced by ultrafast laser pulses for CO + O on Ru(0001) have found that electron- and phonon-mediated processes both play a central role in CO oxidation and desorption.^{2,12} In laser-induced chemical reactivity on Ru(0001), the frustrated rotation of CO, the CO internal stretch, and the O–Ru surface vibration^{39,40} are excited on the sub-picosecond timescale by coupling to the electron bath.^{41,42} Excitation of the frustrated rotation of CO can lead to a small redshift in the $2\pi^*$ peak, and excitation of the internal stretch can cause a modest decrease in the XAS intensity.⁴² Prior studies of CO on Ni(100) have shown that there is a redshift and broadening of the CO $2\pi^*$ peak as CO shifts from the top-site to hollow-site.⁴³ The broadening of the adsorbed peak is due to stronger interaction with the surface. Due to the emergence

of other features overlapping with the adsorbed CO intensity, it is difficult to identify whether the CO $2\pi^*$ peak broadens although prior studies of CO on Ru(0001) and O/Ru(0001) have reported that CO does become more highly coordinated immediately after laser excitation.^{1,11}

The intensities of the CO_(A) and CO_(B) peaks continuously increase over the 10 ps timeframe that the data were recorded. These gradual increases in intensity suggest that hot phonon modes, which heat up on the picosecond timescale due to electron-phonon coupling, are required for CO desorption, consistent with prior studies.^{11,44,45} The narrowness of both peaks (FWHM of 0.24 eV) suggests that there is a strong reduction in the interaction of the CO $2\pi^*$ system with the surface, similar to the previously reported precursor state.^{11,22} This transient precursor state was experimentally observed on CO/Ru(0001) in pump-probe experiments by exciting with 400 nm femtosecond laser pulses and recording the time-resolved x-ray absorption spectroscopy (TR-XAS) signal for the O K-edge using an x-ray free electron laser (XFEL).¹¹ Subsequent pump-probe studies at the O K-edge found little evidence of this precursor state when O was coadsorbed on the Ru(0001) surface. The free energy surfaces for CO desorbing from CO/Ru(0001) and 2O–CO/Ru(0001) have been previously calculated using DFT.^{44,46–49} On Ru(0001), the 5σ state of CO exhibits a repulsive interaction with the surface due to Pauli repulsion,⁴⁴ while the CO π system facilitates bonding with the surface. The DFT results showed that when present, the O atoms pull electron density away from neighboring Ru atoms, reducing the σ -repulsion between CO and the metal surface,⁴⁴ giving rise to the long-range interaction. Since 5σ lies along the intermolecular axis, this CO–surface interaction only occurs in the perpendicular orientation, leading to a preferred perpendicular orientation of the desorbing CO. At such long distances, it is highly unlikely that the $2\pi^*$ system would be interacting with the surface, and we would expect to see CO gas-like behavior in the spectra. The gas-like behavior and favored perpendicular orientation to the surface are consistent with the behavior of CO_(A) although it is unclear whether the CO_(A) molecules are trapped in a physisorption state.

TD-DFT calculations were performed to simulate the polarization independent CO $2\pi^*$ C K-edge x-ray spectra as CO desorbs from the O/Ru(0001) surface in the parallel and perpendicular orientations (see the [supplementary material](#)). We examined three different oxygen coverages, motivated by the possibility that we have less surface oxygen than the prepared (2O + CO)/Ru(0001) honeycomb structure. The first is the honeycomb structure that arises from the saturated coadsorption of CO and O. In this structure, O has a 0.5 monolayer (ML) coverage, where 1 ML is defined as the ratio of the number of adsorbates to the number of surface metal atoms. Two modified structures were added to represent half the oxygen coverage of the honeycomb structure (0.25 ML), as illustrated in Fig. 6. Both modified structures gave rise to indistinguishable x-ray spectra. For perpendicular CO, $2\pi^*$ forms an antibonding orbital with the metal d_π states, which increases the $2\pi^*$ energy. When the CO tilts from the perpendicular position to parallel, the symmetry of $2\pi_x^*$ and $2\pi_y^*$ is broken as one orbital is pointed toward the surface and the other is parallel to it. In the parallel orientation, there is an increased interaction between $2\pi^*$ and the surface, making possible bonding contributions with the metal and lowering the $2\pi^*$ energy. These bonding contributions appear in the spectra below

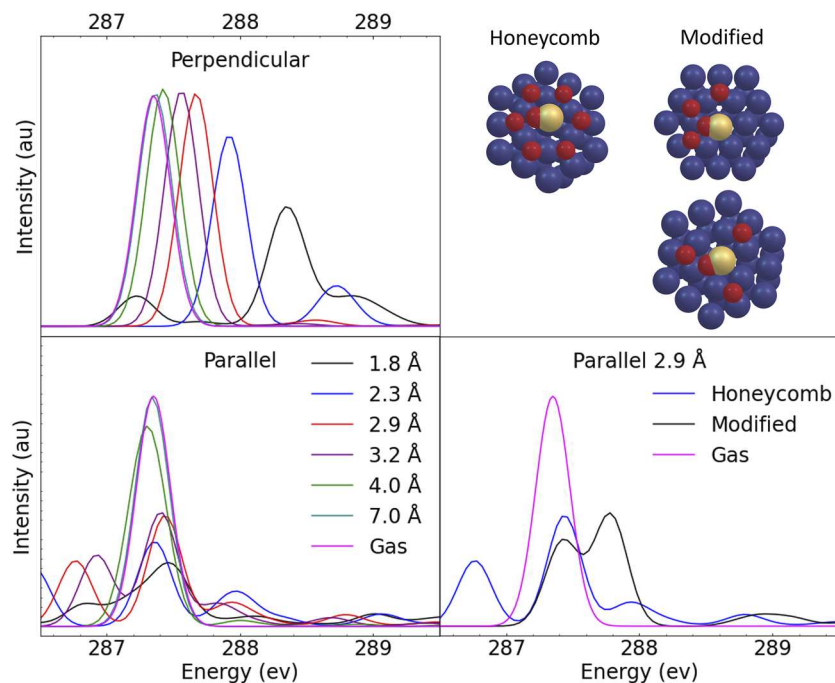


FIG. 6. Calculated XAS spectra at the C K-edge. A range of CO-surface distances for (top left) perpendicular CO and (bottom left) parallel CO on O/Ru(0001) in the honeycomb structure. Top right: The honeycomb structure of O/Ru(0001), and two modified structures with half the O coverage of the honeycomb CO coverage and by another 0.1 eV from the intermediate to high CO coverage. This decrease arises from the CO-CO dipole interaction that competes against CO binding to the surface. With the high CO exposure, surface CO would more quickly block O adsorption sites, increasing the concentration of CO on the surface and pushing the system toward the high CO coverage behavior predicted by Tetenoire *et al.*

287 eV for CO_(B), while the main peak intensity is at 287.7 eV. There is a much smaller chemical shift from the gas phase to the interacting state for parallel CO compared to perpendicular CO. As the surface-CO distance increases, there is a significant lowering of the main peak intensity for parallel CO compared to perpendicular CO, where we almost have a gas phase CO $2\pi^*$ character at 2.3 Å. For parallel CO, the bonding interaction is almost absent by 4.0 Å although still weakly observed. At 7.0 Å, as expected, the surface interactions disappear for both orientations, and the CO is in the gas phase.

We have previously reported TR-XAS CO oxidation at the O K-edge under similar conditions where the pressure of CO was three times lower than reported here (2×10^{-8} Torr) while maintaining the same O₂ pressure.^{1,29,44} It is important to note that these experiments were not polarization sensitive. We refer to these prior studies as the “low CO exposure” data and the current study as the “high CO exposure” data.

For the previously reported low CO exposure, virtually no gas-like CO was detected¹ although some gas-like CO may have been present as a small shoulder of the main CO peak between 534 and 536 eV. If present, this would indicate a low concentration of gas-like CO. The $2\pi^*$ region was dominated by states along the CO oxidation pathway. In stark contrast, the results presented here show almost exclusively CO desorption dynamics in the $2\pi^*$ region, with little evidence of CO oxidation. It appears that the high CO exposure strongly favors CO desorption over oxidation, in contrast with low CO exposure.

In a recent paper by Tetenoire *et al.*,⁵⁰ the energy barriers associated with CO oxidation and desorption on the O/Ru(0001) surface were calculated as a function of CO coverage. The authors studied CO coverages of 0.25 ML (low), 0.375 ML (intermediate), and

0.50 ML (high) on the $p(2 \times 1)$ O structure (0.5 ML O) and the honeycomb structure, which has a CO coverage of 0.25 ML. They found that the desorption barrier drops significantly with the CO coverage by 1.0 eV from the low and honeycomb CO coverages to the intermediate CO coverage and by another 0.1 eV from the intermediate to high CO coverage. This decrease arises from the CO-CO dipole interaction that competes against CO binding to the surface. With the high CO exposure, surface CO would more quickly block O adsorption sites, increasing the concentration of CO on the surface and pushing the system toward the high CO coverage behavior predicted by Tetenoire *et al.*

Tetenoire *et al.* also predicted the existence of a physisorption well for CO desorption at intermediate and high coverages. The minimum of the CO-surface physisorption potential well varies with the CO adsorption site and surface coverage but is generally 1–5 Å above the equilibrium CO-surface bond distance. One of the most favorable physisorption wells arises from the intermediate coverage with CO desorbing from a location between a top site and a fcc site, with a tilt toward the fcc site. At these CO-surface distances, our calculated XAS spectra show that the $2\pi^*$ peak for the perpendicular CO has gas-like behavior.

Between 2.8 and 3.3 Å, the calculated XAS spectra for parallel CO with O in the honeycomb structure show that the higher energy $2\pi^*$ antibonding state remains constant at an energy higher than the gas phase CO peak. For the structures with half the O coverage, the calculated shift is even higher in energy. The experimental shift is between the two, indicating that we likely have an O coverage between 0.25 ML and 0.5 ML. The lower energy $2\pi^*$ bonding peak has a strong dependence on the CO-surface distance between 2.3 and 3.3 Å. A collection of molecules in this range would give rise to XAS spectra that feature a narrow higher-energy antibonding peak

and a broader, lower-intensity, lower-energy bonding peak, corresponding to our observations. This suggests that the more parallel $\text{CO}_{(\text{A})}$ is trapped within these CO-surface bond distances.

Under low CO exposure, little gas-like CO was observed. On the other hand, experiments probing gas-like products have shown that the primary species leaving the surface in laser-induced chemistry on CO/O/Ru(0001) is CO, not CO_2 .² The origin of the lack of signatures of gas-like CO in the low CO exposure TR-XAS data remains unclear. It may be that the existence of a physisorbed (precursor) state, where CO concentration can build up, is a requirement for strong detection of gas-like CO in TR-XAS, similar to that found in CO desorption on Ru(0001).¹¹ The likely different surface coverages of CO and O also play a key role in the balance between CO desorption and CO oxidation.

Tetenoire *et al.* showed that the CO oxidation transition-state barrier initially decreases from the low CO coverage to intermediate CO coverage by 0.4 eV but then sharply increases by 1.2 eV at high CO coverage. The CO oxidation transition state barrier for both the low and intermediate CO coverages is lower than for the honeycomb structure, which is still 0.34 eV lower than the high coverage limit. In the low CO exposure experiments, O was readsorbing on the surface just above 100 K,¹ well below the honeycomb transition temperature of around 214 K.²² The low CO exposure experiments may be closer to the intermediate CO coverage with an O structure of $p(2 \times 1)$ than to the honeycomb structure. At higher x-ray energies, between 293 and 294 eV, we directly observe the adsorbed bent CO_2 state. The intensity of this feature steadily increases over 10 ps. It is likely that the CO oxidation signature is present in the $2\pi^*$ region but is simply drowned out by large CO gas-like features. As CO desorbs from the surface immediately after laser excitation, the system would transition from the high coverage limit to intermediate or low coverages, bringing down the activation barrier for CO oxidation. In other words, some CO may need to desorb prior to the CO oxidation channel becoming favorable.

CONCLUSION

We recorded TR-XAS spectra showing the time evolution of CO desorption and CO oxidation on O/Ru(0001). The $1s-2\pi^*$ resonance of adsorbed CO rapidly undergoes a redshift and decrease in intensity after laser excitation, potentially from the excitation of the frustrated rotation, internal stretch, and/or moving to more highly coordinated sites. At longer timescales, some CO molecules detach from the surface with a reduced π^* interaction with the surface. Two states are observed having differing orientations. These results are in stark contrast with similar experiments performed previously under lower CO exposure conditions, where no physisorbed or gas-like CO was observed. We expect the higher CO exposure of this study to lead to a higher CO coverage and lower O coverage, decreasing the barriers for CO desorption and potentially increasing the barriers for CO oxidation. While the dominant pathway is CO desorption, we do still observe a relatively weak feature at high x-ray energies associated with bent CO_2 .

SUPPLEMENTARY MATERIAL

See the [supplementary material](#) for mass spectrometer data, calculation of CO tilt angles, and details of XAS spectra calculations.

ACKNOWLEDGMENTS

Research by the SLAC participants was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, Chemical Sciences, Geosciences, and Biosciences Division, Catalysis Science Program to the Ultrafast Catalysis FWP (100435) at SLAC National Accelerator Laboratory under Contract No. DE-AC02-76SF00515. Research based in Sweden was supported by the Knut and Alice Wallenberg Foundation under Grant No. 2016.0042 and the Swedish Research Council under Grant No. 2013-8823. The research used resources of the National Energy Research Scientific Computing Center, a DOE Office of Science User Facility supported by the Office of Science of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231. The authors acknowledge the continuous support of the FERMI team during the setting up and operation of the XFEL source for the experiment. M.B. and P.S.M. acknowledge funding from the Helmholtz association (Grant No. VH-NG-1005). M.D.A. and R.C. acknowledge support from the SIR grant SUNDYN (Grant Nos. Nr RBSI14G7TL and CUP B82I15000910001) of the Italian MIUR. Part of the calculations was performed using resources provided by the Swedish National Infrastructure for Computing (SNIC) at the HPC2N and NSC centers.

AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

Author Contributions

Jerry LaRue: Conceptualization (equal); Formal analysis (equal); Investigation (equal); Methodology (equal); Writing – original draft (equal). **Boyang Liu:** Formal analysis (equal); Investigation (equal); Writing – original draft (equal). **Gabriel L. S. Rodrigues:** Formal analysis (equal). **Chang Liu:** Formal analysis (equal). **Jose Antonio Garrido Torres:** Formal analysis (equal). **Simon Schreck:** Conceptualization (equal); Investigation (equal). **Elias Diesen:** Formal analysis (equal). **Matthew Weston:** Investigation (equal). **Hirohito Ogasawara:** Conceptualization (equal); Formal analysis (equal); Investigation (equal); Methodology (equal). **Fivos Perakis:** Investigation (equal). **Martina Dell'Angela:** Investigation (equal). **Flavio Capotondi:** Investigation (equal). **Devon Ball:** Formal analysis (equal). **Conner Carnahan:** Formal analysis (equal). **Gary Zeri:** Formal analysis (equal). **Luca Giannessi:** Methodology (equal). **Emanuele Pedersoli:** Methodology (equal). **Denys Naumenko:** Methodology (equal). **Peter Amann:** Investigation (equal). **Ivaylo Nikolov:** Methodology (equal). **Lorenzo Raimondi:** Methodology (equal). **Carlo Spezzani:** Methodology (equal). **Martin Beye:** Investigation (equal). **Johannes Voss:** Supervision (equal). **Hsin-Yi Wang:** Formal analysis (equal). **Filippo Cavalca:** Investigation (equal). **Jörgen Gladh:** Investigation (equal). **Sergey Koroidov:** Investigation (equal). **Frank Abild-Pedersen:** Supervision (equal). **Manuel Kolb:** Investigation (equal). **Piter S. Miedema:** Methodology (equal). **Roberto Costantini:** Methodology (equal). **Tony F. Heinz:** Funding acquisition (equal). **Alan C. Luntz:** Supervision (equal). **Lars G. M. Pettersson:** Formal analysis (equal); Supervision (equal). **Anders Nilsson:** Conceptualization (equal); Funding acquisition (equal).

DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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