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| Journal: | *Physical Chemistry Chemical Physics* |
| Manuscript ID | CP-ART-06-2019-003677.R2 |
| Article Type: | Paper |
| Date Submitted by the Author: | 05-Sep-2019 |
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# *Time-Resolved Observation of Transient Precursor State of CO on Ru(0001) using Carbon K-edge spectroscopy*

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## Abstract

The transient dynamics of carbon monoxide (CO) molecules on a Ru(0001) surface following femtosecond optical laser pump excitation has been studied by monitoring changes in the unoccupied electronic structure using an ultrafast x-ray free-electron laser (FEL) probe. The particular symmetry of perpendicularly chemisorbed CO on the surface is exploited to investigate how the molecular orientation changes with time by varying the polarization of the

FEL pulses. The time evolution of spectral features corresponding to the desorption precursor state was well distinguished due to the narrow line-width of the C K-edge in the x-ray absorption (XA) spectrum, illustrating that CO molecules in the precursor state rotated freely and resided on the surface for several picoseconds. Most of the CO molecules trapped in the precursor state ultimately cooled back down to the chemisorbed state, while we estimate that ~14.5 ± 4.9% of the molecules in the precursor state desorbed into the gas phase. It was also observed that chemisorbed CO molecules diffused over the metal surface from on-top sites toward highly coordinated sites. In addition, a new "vibrationally hot precursor" state was identified in the polarization-dependent XA spectra.

## Introduction

The interaction between small gas molecules and metal surfaces is of great interest for understanding relevant heterogeneous catalytic reactions.[1] Among various elementary surface reaction steps, the desorption of gas molecules and/or their dissociated fragments from the surface into the gas phase by means of a chemical bond-breaking event is regarded as one of the most fundamental processes.[2] Probing the dynamics during desorption of chemisorbed molecules by time-resolved spectroscopic techniques is a powerful means to achieve deeper insight.[3, 4] Notably, the interaction of CO with a transition metal surface has often been selected as the model in theoretical and experimental studies since this surface reaction is essential for two readily commercialized catalytic reactions: the oxidation of CO for car exhaust catalytic converters and the Fischer-Tropsch reaction for hydrocarbon and methanol synthesis.[5] Previous studies using pump-probe sum-frequency generation (SFG) spectroscopy have observed the frustrated rotational motion of CO molecules through a large redshift of the C-O vibrational frequency during thermal excitation on a Ru single-crystal surface, leading to desorption of the surface-adsorbed CO.[6, 7]

The existence of a short-lived and weakly bonded CO precursor state that could reside on the surface prior to desorption has been intensively discussed for a long time.[8-11] This transient state is generally interpreted as an intermediate state that assists the adsorbed molecule in regaining rotational and translational energy before completely breaking the adsorption bond to the surface and entering the gas phase. Recently, this transient surface species has been directly identified in soft x-ray free-electron laser (FEL) experiments using an ultrafast optical laser pump followed by an FEL probe.[12] Upon excitation of the Ru(0001) substrate by the femtosecond optical laser pulses, the changes in electronic structure of the CO molecules were monitored by x-ray spectroscopic techniques at the O K-edge. Most of the observed features are in line with the characteristics of a weakening interaction between the CO molecules and the substrate without a notable complete desorption of CO, thus experimentally confirming the existence of the precursor species for the first time. The identification of the precursor state consolidates the foundation that rationalizes the kinetics for various interactions of gas and metal surfaces. The translational motion of the CO molecule parallel to the surface was observed to be induced on short time scales prior to entering the precursor state.[13] Furthermore, an entropy barrier between the chemisorption state and the precursor state was proposed based on free-energy density functional theory (DFT) calculations.[12] Although the aforementioned results have demonstrated time-resolved FEL experiments as a powerful tool to reveal short-lived surface species, the broad O K-edge resonance peak in the x-ray absorption spectrum (XAS), due to many excited vibrational states being populated after the creation of the O1s core-hole,[14] could unfortunately hinder the investigation of several underlying spectroscopic details of the precursor state as it evolves with time. Additionally, the existence of the precursor state has recently been questioned in molecular dynamics (MD) simulations of a molecular beam (MB) experiment, where the complete sticking of CO to ruthenium (Ru) at low incidence energy is observed with a feature of a deep chemisorption well, yet lacking early reaction barriers.[15]

In the present work, we re-inspect the transient precursor state in the system of CO binding to Ru(0001) using an ultrafast pump-probe fluorescence x-ray absorption spectroscopic (XAS) technique at the C K edge with a focus on the C 1s → π* resonance.[16] Exploiting the fact that the CO molecule is perpendicularly chemisorbed to the metal surface with the C atom facing down, we use x-ray laser pulses with the E-vector oriented either horizontal or vertical with respect to the surface to investigate how the molecular orientation changes with time upon the optical laser pumping. As previously suggested,[9, 11, 12] the precursor state is expected to be in a fully rotationally isotropic state and therefore no polarization-dependent spectral feature should thus be observed. The C K-edge XAS measurements offer an advantage in comparison to the previous O K-edge XAS study conducted at LCLS[12, 13, 17] as the C K-edge is known to generate sharper features than the O K-edge due to less vibrational broadening after the creation of the core-hole at carbon.[14, 18] This results in enhanced spectral contrast. The narrow spectral features together with the polarization dependence give the possibility that more detailed spectroscopic information on how the precursor state develops with time could be obtained from the C K-edge XA spectra.

In a typical pump–probe measurement, the optical laser pump pulse heats up both electrons and phonons of the substrate, leading to vibrational excitation of the adsorbate driven by the hot electrons within the first picosecond, followed by the weakly adsorbed molecules populating the precursor state on the surface prior to desorption.[13] The dynamic features of the excited CO molecules diffusing over the metal surface are observed in our time-resolved x-ray spectra as previously seen in scanning tunneling microscopy (STM)[19], where the frustrated rotation excited by the hot electrons couples to frustrated translational motion. Furthermore, a new resonance feature ascribed to a “hot precursor” state, where the ground state is thermally excited due to the heated surface, can also be identified in the x-ray polarization-dependent XA spectra.

## Experimental method

The time-resolved optical pump – x-ray probe experiment was conducted using an endstation denoted as TIme resolved x-ray sTudies of reActioNs (TITAN) at the DIPROI beamline of the Free Electron laser Radiation for Multidisciplinary Investigations (FERMI) facility in Elettra, Italy.[20] The FEL is seeded by a tunable solid state laser system and the photon energy is multiplied through a two-stage high-gain harmonic generation (HGHG) process,[21] extending the operation capability into the soft x-ray regime whilst allowing for a high level of synchronization between the optical pump and soft x-ray probe. We used variably polarized soft x-ray pulses of around 287 eV energy (4.32 nm, which is close to the Carbon K-edge of chemisorbed CO) with less than 50 fs duration and delivered at a repetition rate of 10 Hz as the "probe". Two polarizations of the E-vector of the x-ray pulses with respect to the surface were used: in plane and out of plane. A portion of the seed laser is separately transported into the experimental station acting as the "pump" with the same repetition rate and 100 fs duration. It is noteworthy that the time jitter between the laser and the FEL is less than 6 fs.[22] The XA spectra were recorded by stepwise varying the incident energy and detecting fluorescence using a large area detector based on a previously reported configuration[23] with a perylene filter to remove the background UV light.

Prior to all the pump–probe measurements, the Ru single-crystal sample was cleaned using a procedure established from previous experiments.[12, 13] The base pressure inside the ultra-high vacuum (UHV) chamber was always kept below $3\times10^{-10}$ torr. A commercial Ru(0001) single-crystal disk with 10 mm diameter (SPL, Netherlands) was repeatedly cleaned by multiple cycles of $Ne^+$ sputtering (30 min), oxygen annealing at 600 K (10 min), and flashing up to 1030 K in UHV. The contamination level of the sample was determined by employing the XAS technique, which has high sensitivity to atomic oxygen / carbon. A saturated CO adlayer (~0.66 ML) was prepared on the clean Ru(0001) surface by pressurizing the UHV chamber with $1.0\times10^{-8}$ torr of CO while cooling the crystal down to ~100 K.[24] The crystal was frequently cleaned between different measurements to avoid any buildup of contaminations from potential CO dissociation. During the pump-probe measurement, we continuously flowed in liquid $N_2$ to maintain the sample temperature always below 150 K.

To magnify the probing area on the Ru(0001) crystal and enhance the sensitivity toward the surface reaction between CO and Ru, the small x-ray beam spot size of 30 μm (horizontal) ×30 μm (vertical) was irradiated on the sample at a grazing incidence angle of around $2^{o}$, resulting in a projected elliptical footprint of around 30 μm ×770 μm on the surface. The x-ray pulses were delivered to the surface with a delay time ranging from -2 picoseconds (ps) to +150 ps relative to the optical laser pump pulses of 400 nm central wavelength and pulse energy of 150 μJ (estimated at the sample position). The laser fluence was set close to the damage threshold of the Ru crystal (which was estimated to be 91 $J/m^2$) and the polarization of the laser is always vertical (out of plane) to the surface in order to maximize the probability of initiating the surface reaction. To ensure that a fresh surface spot is utilized for every pump-probe event, the crystal sample was continuously scanned at a speed of 1.5 mm/s, with a constant CO background pressure of $1.0\times10^{-8}$ torr during the entire experiment to re-dose CO onto the surface. To acquire an XA spectrum, the desired excitation energy of the probe x-ray pulses was selected by changing the UV seeding wavelength and the resonance conditions of the undulators accordingly, whilst different pump–probe delays were produced by adjusting the pump laser delay stage. The XA spectrum was thus obtained by plotting out the total number of emitted photons recorded as a function of the excitation energy for every desired pump–probe delay. Each data point in the collected XA spectra was subsequently normalized to its corresponding number of incident x-ray pulses.

Carbon 1*s* XA spectra of CO were computed for the chemisorbed state and a sampling of structures in the precursor region from ref.[12] using the transition potential approach of Triguero *et al.*[25] as implemented in the GPAW code.[26, 27] The calculations were performed using a grid spacing of 0.2 Å, and the exchange–correlation functional RPBE. An extended 2 × 2 Ru(0001) surface four-layer model with CO adsorbed on-top of a ruthenium was used for structure optimization, while for the XAS calculations the model was repeated in the *a*- and *b*-directions of the super cell twice (and hence became 4×4). For the case when CO is perpendicular to the surface, the sampling started with the chemisorbed state where C is 1.96 Å above the surface, but for the parallel case, the sampling started with the geometry where CO is 4.21 Å above the surface. The *k*-point sampling scheme was Monkhorst-Pack, the k-point sizes for the 2×2 and 4×4 models were 4×4×1 and 2×2×1, respectively and both are $\Gamma$ -centered. The absolute energy position of the spectra was determined with ΔKohn-Sham calculations. The onset of the computed spectra depends on the exchange–correlation functional while relative peak-positions have been shown to be independent of the selected functional.[28]

## Results and Discussion

The most stable state for CO molecule adsorbing on Ru(0001) is a standing up geometry at an on-top site where the C atom coordinates toward the Ru atom.[29] The unoccupied hybridized 2p orbitals with π symmetry, which are perpendicular to the CO center axis and thus parallel to the surface, are only dipole active to in-plane XAS. We evaluated the transient linear dichroism by employing in-plane (lin horizontal, lin H) and out-of-place (lin vertical, lin V) XAS to investigate how the molecular orientation changes upon excitation with an optical laser pulse.

Fig. 1 shows in-plane and out-of-plane XA spectra evolving with pump-probe delay time, where spectra in a range of selected time delays were combined and averaged together for better statistics to allow for comparison. First, let us focus on the spectral observations during the first picosecond time delay. As shown in the top panel of Fig. 1a with lin H spectra, before the arrival of the pump laser pulse, the unpumped delay spectrum depicts a strong C 1s → $\pi^*$ resonance peak centered at around 288 eV due to the fact that most of the chemisorbed CO molecules are in the standing up geometry. After the surface is optically pumped, a sudden decrease of intensity in the C 1s → $\pi^*$ resonance is observed in the 0-1 ps probe delay spectrum. This change is associated with the tilt of CO stimulated by hot electrons generated by the optical laser that excite frustrated rotational motion of the chemisorbed molecules[6, 19] leading to the molecules becoming rotationally excited and thereby in less up-right instantaneous orientations. We also observe a redshift of the peak position (from 288 eV to 287.92 eV) illustrating that the CO molecules are getting translationally excited and move from the on-top site towards higher-coordinated positions, e.g., bridge or hollow sites, due to differences in the potential energy surface between differently coordinated sites.[30, 31] Such phenomena have been experimentally observed in the adsorption-site-dependent XA spectra of C K-edge,[31] and this redshift was also observed in the previous O K-edge study and related to a core level shift due to bonding of CO in higher coordination to metal atoms.[13] Meanwhile, a lower resonance intensity also indicates a more populated $\pi^*$ orbital induced by the interaction with the highly coordinated sites.[32] The lin V XA spectra shown in Fig. 1b provide additional information, allowing us to complete the picture of the early evolution of the dynamics. Before the arrival of the pump laser pulses, the lin V spectrum is in principle expected to have low intensity due to the perpendicular geometry of CO. However, a weak C 1s → $\pi^*$ resonance intensity can still be found due to the fact that the high coverage, corresponding to a packed CO layer, leads to some weak tilting of the molecules,[33] resulting in some projection of the atomic $2p_{x,y}$ orbitals also along the normal direction with the surface. After the surface was optically pumped we observe a monotonic increase of the C 1s → $\pi^*$ resonance intensity in the lin V spectra together with a redshift (from 288 eV to 287.92 eV). This confirms that adsorbed CO molecules are shaken and move towards the high coordination sites, and therefore more resonance intensity projected on the vertical direction can be seen. This reflects the highly excited rotational and translational motion, and what was lost in the lin H spectrum is now regained in the lin V spectrum. In particular, we note that the lin V spectrum shows a more obvious intensity increase on the low energy side as compared to the lin H spectrum after optical pumping during the first ps, reflecting that we are probing the rotationally hot molecules that have gained excitation energy and become translationally hot.

Next we turn our focus to longer time delays in the range of a few picoseconds where O K-edge spectra have previously been described as showing the appearance of the precursor state.[13] In the lin V spectra shown in Fig. 1b, a new resonance peak centered at 287.42 eV and growing with time is clearly observed. On the other hand, the lin H spectra show that the $\pi^*$ resonance intensity of the chemisorbed CO gradually recovers after the first ps with an additional resonance feature emerging at the lower energy side, indicating that the intramolecular bond of chemisorbed CO is reinforced by decreasing the interaction with the substrate together with the appearance of a new species populating the surface. We first conclude that the energy position of this new surface species should be centered at 287.42 eV based on the lin V spectra even though it is not easily defined in the lin H spectra. The influence from the adsorbate C 1s $\rightarrow\pi^*$ resonance background centered at 287.92 eV is greatly mitigated in the lin V spectra due to the symmetry selection rule for the perpendicularly chemisorbed CO, and therefore, the detailed features of the new species on the lower energy side can be more easily resolved. The energy position of 287.42 eV is in fact corresponding to CO in gas phase.[14] However, the resonance intensity of this new state gradually decreases on a time-scale up to 150 ps in both the lin H and lin V spectra (shown in the bottom panel of Fig. 1a and 1b) and the peak center of the chemisorbed state shifts back to the original position with a similar intensity as that in the unpumped spectrum, illustrating that the excited surface species cooled down and most of the new species re-adsorbed to the surface. Such spectral observations unequivocally confirm that this new species should be CO in a precursor state rather than in gas phase, since most of the CO precursors just resided on the surface and re-adsorbed without immediately escaping away into the gas phase.[12] Otherwise this resonance intensity corresponding to gas phase should remain at the maximum.

In Fig. 2 we show the results of the spectrum calculations where the chemisorbed CO is found to have the C 1s → π* excitation ca. 2.0 eV higher than in the gas phase which is consistent with experiment qualitatively. The fact that the π* excitation for C 1*s* in chemisorbed CO is higher than for CO in gas phase, while for O 1*s* it is lower, may be rationalized by the antibonding character of the π* with the surface[34], which dominates for C 1*s* excitation whilst the metallic screening dominates for O 1*s*. As the CO distance to the surface is increased from the chemisorbed state in Fig. 2, the π* excitation moves down in energy and as the molecule enters the precursor state the energy coincides with that of the gas phase. For the precursor states where CO is physisorbed, whether CO is perpendicular or parallel to the surface does not produce any significant differences. In summary, the calculated spectra support the interpretation that in the precursor state of CO desorbing from Ru(0001) the π* peak moves down to coincide with the gas phase position.

To refine the understanding of this spectral observation, the spectra are decomposed into several symmetric Gaussian peaks as shown in the middle panel of Fig. 1, where the components of the fit for the 8-10 ps delay spectrum are shown. The π* resonance of the CO precursor can be probed by both lin H and lin V FEL pulses, indicating that CO molecules in the precursor state are nearly free to rotate in all directions on the surface. The red peak, centered at 287.42 eV, is thus ascribed to the precursor state based on the aforementioned conclusion, where the excitation is from the ground state to the lowest vibrational state (denoted as $v_0$ - $v_0$') with a side peak (green color) centered at 287.67 eV corresponding to an excitation from the $v_0$ - $v_1$'.

Since the electronic behavior of the weakly adsorbed CO in the precursor state is believed to be quite similar to free CO gas molecules due to the similar energy position and dynamic behavior, the C K-edge XA spectrum of CO gas phase[14] is employed here as the reference for the fitting process, in which the peak area ratio between the first resonance ($v_0$ - $v_0$') to the second resonance ($v_0$ - $v_1$') is fixed to 5.8. Moreover, since CO molecule in precursor state is believed to freely rotate in an isotropic fashion, all corresponding spectral features of precursor state must be equally seen in lin V and lin H spectra. The line-width of all precursor-related peaks can only be limited to 0.3 eV owing to the resolution of the FEL pulses (averaged FWHM = 0.3 eV) even though the practical linewidth for the C K-edge of CO gas is usually smaller than 0.18 eV in the XA spectrum.[14]

After the spectra were analyzed with these restrictions, the lin V spectra show a resonance peak centered at 287.16 eV (pink color) which can be further decomposed on the lower energy side next to the main precursor peak (middle panel, Fig. 1b). We associate this resonance with a so-called "hot precursor" state where the excitation is from the thermally excited ground state ($v_1$) to the lowest vibrational state in the excited state ($v_0$'). Interestingly, this hot precursor state is hard to define in the lin H spectra (middle panel, Fig. 1a). Such a discrepancy can be ascribed to the huge background from the strong C 1s → π* resonance in the lin H spectra, which unfortunately limits the spectral contrast. We will discuss this hot state more in detail in a subsequent publication (ref.[35]).

Most interestingly, the fitting process, as demonstrated in the Supplementary Information Fig. S1, reveals that in both in-plane and out-of-plane spectra, there must be an additional state (orange color) between the chemisorbed and precursor state, which acts to fill up the overall spectrum profile after the peak decomposition. This new finding based on the result of the curve fitting leads us to a deeper discussion regarding the formation of the precursor state. We emphasize that the peaks used in the fit are only those that can be seen in the raw data.

To discover the underlying reason for the additional resonance intensity existing between the chemisorption peak and the precursor peak, the lin H and lin V XA spectra at 8-10 ps delay, where the resonance intensity of the precursor state reached its maximum, are plotted on top of each other with appropriate scaling for comparison. As shown in Fig. 3, the highest intensity in the lin H XA spectrum is not on top of the precursor peak, but on the higher energy side next to the precursor state, indicating that this additional resonance intensity, denoted as new adsorbed state (NAS), should be more visible by lin H FEL probing. Thus, species in the NAS are expected to mostly keep a perpendicular orientation as the normal chemisorbed CO, which can also be seen in the result of the fit. As revealed in Fig.1 a and b (middle panel), the ratio between the NAS resonance peak (orange color) and main precursor peak ($v_0$-$v_0'$, red color) is bigger in the lin H spectra compared to that in the lin V spectra. It has been proposed that the two minima in the potential of mean force, i.e. the chemisorbed state and precursor state, are separated by an entropy barrier,[12] where it is reasonable to expect that some excited CO molecules are trapped before crossing the barrier. Meanwhile, it is also noted that after the laser pumping, the peak shape of the resonance intensity of the chemisorbed state becomes asymmetric with a shoulder emerging at lower energies due to a considerable portion of CO molecules becoming rotationally and translationally hot and moving to high coordination sites. The hot CO molecules hop over the adsorption sites to bridge/hollow sites and could stay there with a certain life time.[30] More detailed information can be extracted from the spectra at longer time delay, up to 150 ps. As shown in the Supplementary Information Fig. S2, the fitting result reveals that some NAS intensity is still visible in the lin H spectra, while in the lin V spectra NAS is absent due to the upright orientation of the CO molecules as the surface temperature rapidly becomes lower and they readsorb. Since the potential energy surface is very flat with small difference in effective binding energy between on-top and bridge/hollow sites at high CO coverage surface owing to the repulsive CO-CO interactions,[36] the temperature of around several hundred K should allow to populate also the higher-coordination sites. In this sense, together with the spectral observation, this new adsorbed state can thus be realized, which is characterized by a π* excitation energy lower than the chemisorbed state but higher than the precursor state, and the C atom is still facing down and sitting at the high coordination site.

Fig. 4 further shows a quantitative time-evolution analysis of the ultrafast transient response of chemisorbed CO on Ru(0001) to the laser pump irradiation. It has been well established that photo-induced surface reactions are typically mediated by the metal substrate, since a single adsorbate layer is not capable of efficiently absorbing the light energy whilst the metal substrate can do so. The substrate electrons are excited by the pump laser pulses and thermalize at the metal surface within ~ 100 fs, initiating a surface reaction leading to the diffusion of rotationally and translationally excited CO from on-top sites toward more highly-coordinated bridge or hollow sites on a picosecond time scale. Following that, the phonon system within the metal crystal is more slowly heated up by the hot electrons, triggering the dynamics in terms of stimulating the chemisorbed CO molecules into the precursor state which will remain interacting with the surface for several picoseconds.[13] The top panel of Fig. 4 shows that the integrated peak area of the chemisorbed state analyzed from lin H XA spectra rapidly decreased within the first picosecond and slowly recovered with time. This correlates with the transient response of the hot electrons coupling to the frustrated rotational molecular motion leading to surface diffusion, which is then followed by a relatively slower phonon-system-mediated surface reaction.[13] The lin V XA spectra show a monotonic increase of the C1s → π* resonance intensity within the first 10 picoseconds simply owing to the disturbance of the chemisorbed CO orientation after the laser pumping, and therefore more and more π* orbital can be detected by the lin V FEL pulses. Beyond 10 ps, both lin H and lin V XA spectra show a decreasing intensity in the precursor state as the system recovers back to the original chemisorbed state on a time scale of 150 ps.

The amount of CO molecules in the precursor state estimated from the evolution with time of the lin H and lin V XA spectra is also compared and plotted in the bottom panel of Fig. 4. The similarity between the two curves evidences that CO molecules in the precursor state are nearly free to rotate in an isotropic fashion and therefore the C 1s → $\pi^*$ transition in $\pi$ symmetry perpendicular to the molecular axis can be equally probed by both lin H and lin V FEL pulses. The population of molecules in the precursor state saturated between 6 to 10 ps and slowly decayed, which, together with the nearly fully recovered intensity in the chemisorbed state, indicates that most molecules in the precursor state cool down and re-adsorb back to the surface; the remaining intensity at 150 ps is reasonable to be considered as due to the free CO gas phase. After a detailed analysis of the time-resolved pump–probe FEL spectra, the transient dynamics of laser excitation on chemisorbed CO molecules over a Ru(0001) surface can thus be deduced and illustrated in Fig. 5. Upon arrival of the pump laser pulses, the chemisorbed CO molecules sitting at on-top sites are suddenly excited and become rotationally and translationally hot, diffusing toward highly coordinated sites with a wobbling molecular motion during the first picosecond. After a portion of excited adsorbates successfully crosses the entropy barrier, which separates the chemisorbed and precursor state, the isotropically rotating CO molecules in the precursor state then repopulate the surface with time. Around 14.5 ± 4.9%, which is calculated based on the ratio of precursor (($v_0$ - $v_0$’) peak intensity between 8-10 ps and 150 ps including the corresponding error, of the CO molecules in precursor state could finally break away from the surface into gas phase. This is estimated based lin V XA spectra due to the fact that they are selectively sensitive to the precursor state since the C 1s → $\pi^*$ transition in $\pi$ symmetry of the chemisorbed CO in the standing up geometry is dipole forbidden.

## Conclusion

In summary, the transient dynamics of chemisorbed CO on Ru(0001) as initiated via 400 nm optical laser pumping has been studied by monitoring the changes in the unoccupied electronic structure in C K-edge XA spectra at different pump–probe delays. The rotationally and translationally excited CO molecules diffuse from the on-top site toward the highly coordinated sites in the first picosecond, followed by a phonon-mediated surface reaction stimulating a fraction of chemisorbed CO into the precursor state. It is revealed by polarization-dependent XA spectra that CO molecules in the precursor state are free to isotropically rotate and interact with the surface for several picoseconds prior to desorption or readsorption. Owing to the sharp resonance peak feature of the C K-edge, the hot precursor state where the ground state was already thermally and vibrationally excited, and a new adsorbed state (NAS) existing between the chemisorbed and precursor states can be well resolved.

## Conflicts of interest

There are no conflicts of interest to declare.

## Acknowledgements

This work was supported by the Knut and Alice Wallenberg Foundation, the Swedish Research Council, and the U.S. Department of Energy, Office of Science, Office of Basic Energy Science, under Contract No. DE-AC02-76SF00515. The authors acknowledge the continuous support of FERMI team during the setting and the operation of the FEL source for the experiment. M.B and P.S.M acknowledge funding from the Helmholtz association (VH-NG-1005). M.D.A and R.C. acknowledge support from the SIR grant SUNDYN [Nr RBSI14G7TL, CUP B82I15000910001] of the Italian MIUR. S.K. would like to thank The Knut and Alice Wallenberg Foundation (KAW 2014.0370) for financial support.

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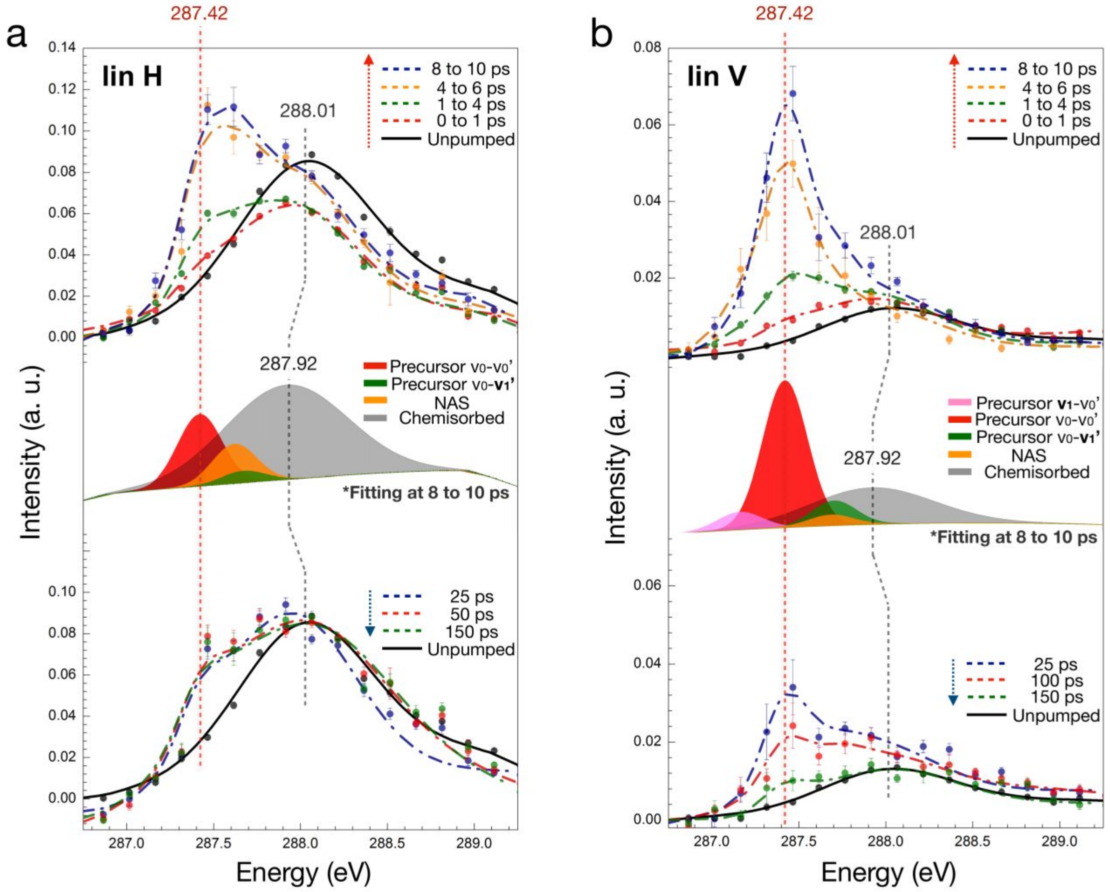

**FIG. 1.** Time-resolved XA spectra of chemisorbed CO on Ru (0001) following excitation by optical laser irradiation probed by (a) lin H FEL pulses and (b) lin V FEL pulses. The top panel shows the pump–probe spectra evolving from negative delay (unpumped) to +10 ps delay where the spectra are averaged over a desired range of delays as indicated in the figure. The middle panel shows the decomposed spectral distribution of characteristic states and only the fitting result for the spectrum at 8-10 ps delay is specifically plotted. Most of the spectral features slowly recovered back to their original state in the longer delay, as shown in the bottom panel where the spectrum at negative delay (unpumped) is also plotted for comparison. The vertical line at 287.42 eV indicates the position of the gas phase π* resonance.

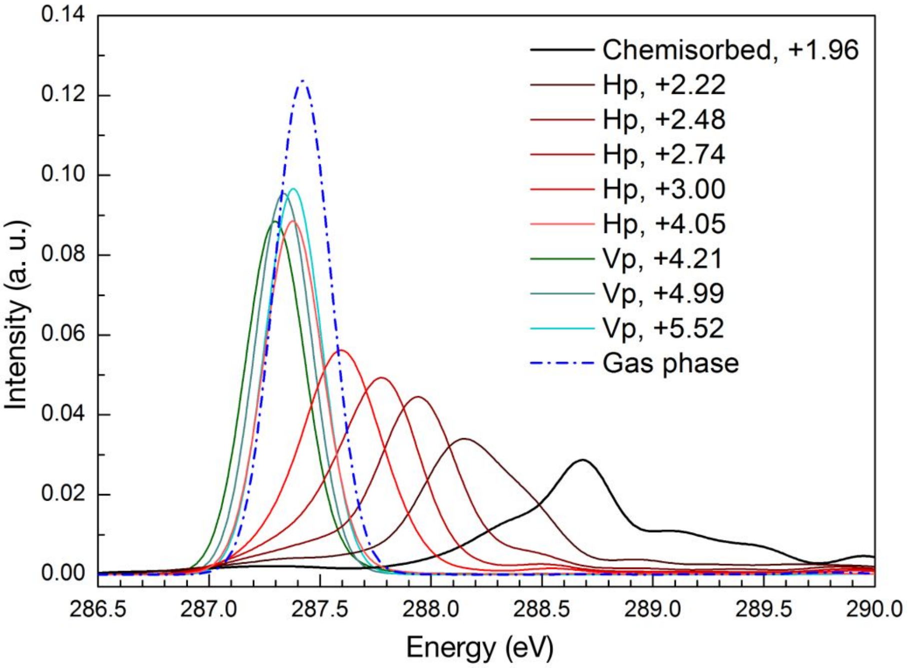

**FIG. 2.** Computed C 1*s* XA spectra showing the development of the π* resonance going from chemisorbed (black) towards the precursor region, i.e. a vertical displacement from the on-top site by amounts as given (Ångström, center of carbon), for the cases when CO is perpendicular (Hp) and parallel (Vp) to the metal surface, respectively. Please be noted that here, Hp denotes horizontal polarization - chemisorbed region, and Vp denotes vertical polarization - precursor region. The computed gas phase spectrum is shown as reference.

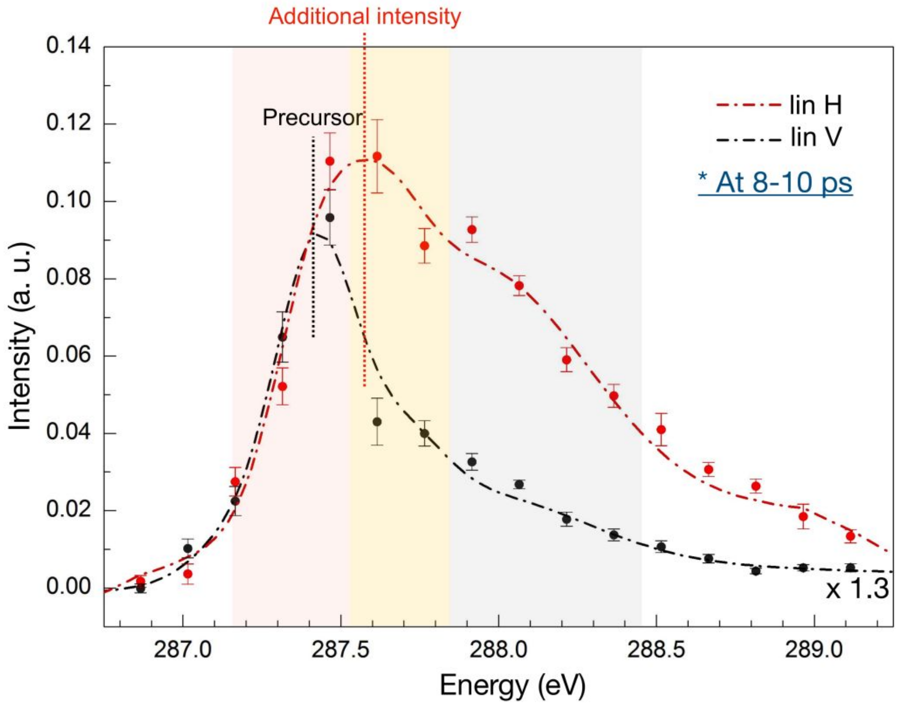

**FIG. 3.** Comparison between the lin H XA spectrum and lin V XA spectrum at 8-10 ps delay. The gray region is mainly contributed by the chemisorbed state, and the pink region is dominated by the precursor state. It can be seen that there must be an additional state existing between the chemisorbed and precursor states as clearly indicated in the lin H XA spectrum. The intensity of the lin V XA spectrum is scaled up by 1.3 for better comparison.

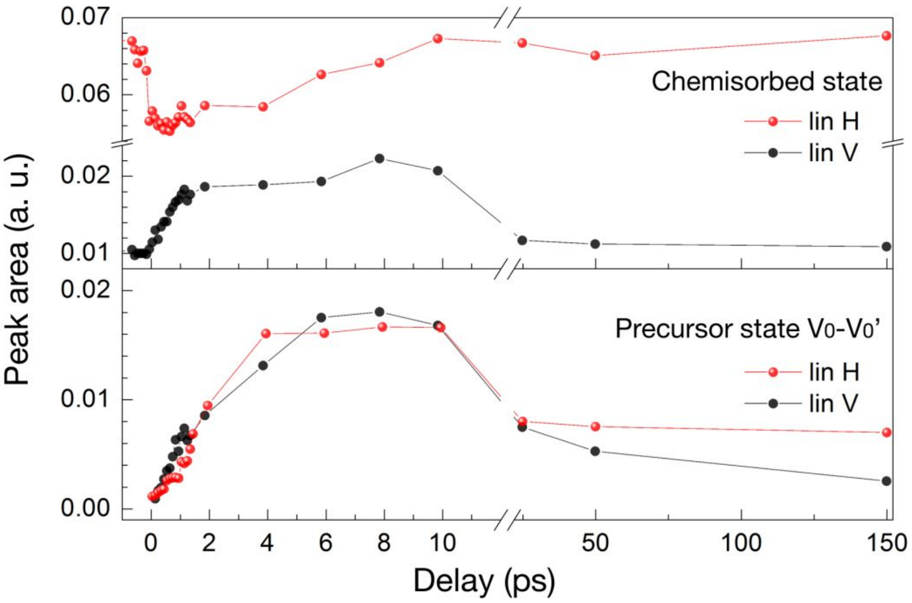

**FIG. 4.** Evolution of the integrated intensity of the characteristic states estimated from lin H and lin V XA spectra as a function of pump–probe delay. The top panel shows that in the first picosecond the trend of the chemisorbed state is different when probed by lin H FEL pulses as compared to when probed by lin V FEL pulses. The bottom panel shows that both lin H and lin V FEL pulses give a similar intensity of CO in the precursor state, indicating an isotropic rotation behavior. We refer to ref.[13] for calculated electron and phonon temperature as function of pump-probe time at absorbed laser fluence of 100 J/m$^2$ which is similar to the 91 J/m$^2$ used in the present work.

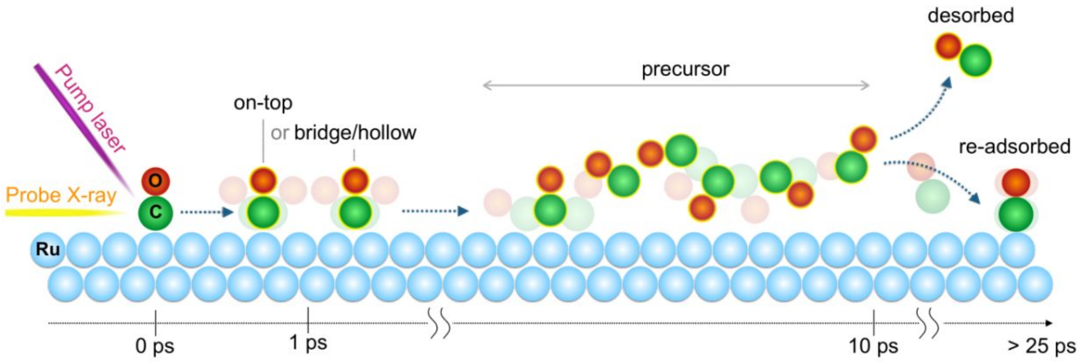

**FIG. 5.** Dynamic evolution as function of pump–probe delay for CO chemisorbed on Ru(0001) following optical laser excitation. After the laser irradiation on Ru(0001), CO molecules are shaken and diffuse from the on-top sites towards more highly coordinated sites, followed by isotropically rotating precursor state CO populating the surface. A fraction of CO in the precursor state proceeds to desorption while the majority re-adsorb back onto the surface.