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Optical laser-induced CO desorption from Ru(0001) monitored with a free-electron X-ray laser: DFT prediction and X-ray confirmation of a precursor state

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ABSTRACT

We present density functional theory modeling of time-resolved optical pump/X-ray spectroscopic probe data of CO desorption from Ru(0001). The BEEF van der Waals functional predicts a weakly bound state as a precursor to desorption. The optical pump leads to a near-instantaneous (<100 fs) increase of the electronic temperature to nearly 7000 K. The temperature evolution and energy transfer between electrons, substrate phonons and adsorbate is described by the two-temperature model and found to equilibrate on a timescale of a few picoseconds to an elevated local temperature of ~2000 K. Estimating the free energy based on the computed potential of mean force along the desorption path, we find an entropic barrier to desorption (and by time-reversal also to adsorption). This entropic barrier separates the chemisorbed and precursor states, and becomes significant at the elevated temperature of the experiment (~1.4 eV at 2000 K). Experimental pump-probe X-ray absorption/X-ray emission spectroscopy indicates population of a precursor state to desorption upon laser-excitation of the system (Dell'Angela et al., 2013). Computing spectra along the desorption path confirms the picture of a weakly bound transient state arising from ultrafast heating of the metal substrate.

1. Introduction

CO bonding to a metal surface is a prototypical process relevant to a large number of important chemical transformations, such as, *e.g.*, the water gas shift reaction converting CO and H_2O to CO_2 and H_2, the Fischer–Tropsch process to synthesize alkanes as synthetic fuels, as well as in conversion of CO to CO_2 in car emission control catalysts. The adsorption, bonding and desorption of CO at a metal catalyst surface thus become of fundamental importance to understand in detail.

The static CO bond to a metal surface has been studied by a large number of authors, both experimentally, *e.g.*, refs.[1–5], and theoretically, *e.g.*, refs.[6–16]. The bonding is popularly described in terms of σ-donation and π* back-donation in a frontier orbital scheme, but detailed experimental measurements using X-ray emission spectroscopy (XES) in combination with density functional theory (DFT) spectrum simulations have revealed a different picture. The bonding is found to occur in the π-system where the three interacting orbitals (1π, 2π* and metal $3d_\pi$) hybridize to form totally bonding $(1\tilde{\pi})$, non-bonding $\left(\tilde{d}_\pi\right)$ and totally antibonding $(2\tilde{\pi}^*)$ states in an allylic configuration [1,2,4–6,16,17]; the tilde (~) indicates that the orbital has been modified through the metal-adsorbate interaction. The closed-shell 5σ orbital, on the other hand, generates exchange repulsion against the *d*-states of the metal [1,2,4,10,17]. We note here that the π-bonding in terms of the allylic model was described already by Blyholder [6]

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using extended Hückel theory while the σ-repulsion became most evident from experimental XES studies of CO adsorption in different sites on Ni(100) [2].

Here we will expand on previous reports [18,19] on the time-resolved electronic structure changes in CO desorption from a transition-metal surface, Ru(0001), studied using the Linac Coherent Light Source (LCLS) free-electron X-ray laser. We will, in particular, focus on the interplay between theory and experiment in the analysis of time-resolved XES and X-ray absorption spectroscopy (XAS) data measured subsequent to heating the substrate with an optical pump laser. DFT calculations of the temperature-dependent free-energy potential energy surface were performed and XE and XA spectra calculated along the path to desorption. Through this interplay between experiment and theory we could unambiguously spectroscopically identify the proposed precursor state to desorption and adsorption [18,19].

2. Methods

2.1. Computational methods

The Ru(0001) surface was modeled as periodically repeated three-layer slabs of which the bottom two layers were kept fixed during structure relaxation (unit cell given in the Supplementary Material). Increasing the slab with one layer leads to no significant difference in the simulated spectra and the variations in CO adsorption energy were deemed negligible for the results in the present study. A 2×2 cell with periodic boundary conditions was used in which a CO molecule was adsorbed at the atop site, hence a coverage of 0.25 ML. From the top of the CO molecule to the bottom of the adjacent slab a separation of 10 Å of vacuum was employed in the surface normal direction. The DFT calculations of the potential energy surface of CO desorption were performed using the BEEF-vdW exchange-correlation (XC) functional [20] as implemented in the grid-based real-space projector-augmented wave GPAW code [21,22]. BEEF-vdW includes van der Waals (vdW) interactions through a functional describing non-local correlation; to establish the effects of including the vdW interaction, the generalized gradient approximation (GGA) XC functional RPBE [23] was also applied. A grid-spacing of 0.18 Å, and 0.12 eV Fermi smearing were used in the calculations. To converge the adsorption energy as well as the simulated spectra, a k-point mesh of $4 \times 4 \times 1$ was found to be sufficient. In determining the minimum energy path (MEP) 0.05 eV/Å was used as acceptance criterion on the maximum force on each relaxed atom; tightening the criterion to 0.02 eV/Å only changes the total energy of chemisorbed CO by 0.1 meV.

O K-edge XE spectra were calculated using GPAW [24] from the ground state orbitals [25] and summed over p_{xy} and p_z symmetries; the RPBE functional was used in this case. To compare with the experimental spectra a broadening with a Gaussian function of 1 eV full-width at half-maximum (FWHM) was employed. Geometries of the chemisorbed state and the precursor state were taken from the MEP of desorption and to obtain an absolute energy scale the computed spectra were shifted so that the energy position of the $1\tilde{\pi}$ state is aligned with that of the experiment; note that in the experimental spectrum the deconvolved $1\tilde{\pi}$ peak remains fixed in energy.

O K-edge XA spectra and core-excited state wave functions were obtained using the StoBe-deMon [26] DFT code using a three-layer cluster model containing 17 Ruthenium atoms to represent the Ru(0001) surface (coordinates given in the Supplementary Material). Triple-zeta basis sets were used in combination with a 14 electron relativistic effective core potential for Ruthenium, while carbon was described by an all-electron triple-zeta basis with one d-function added. Oxygen was described by the IGLO III basis of Kutzelnigg and coworkers [27] to allow for relaxation of the core after removal of one $1s$ electron. Spectra were computed within the transition potential approach of Triguero et al. [28,29]. A Gaussian broadening of 0.5 eV FWHM was applied up to 534 eV and then linearly increased to 3 eV until 539 eV and constant beyond that. The energy scale was adjusted by shifting the spectrum at the chemisorbed equilibrium geometry to have its $2\tilde{\pi}^*$ peak aligned with that of the unpumped experiment; the same shift was then applied to all other spectra. The XAS calculations used the exchange by Becke [30] and the correlation functional by Perdew [31]; it has been shown [32] that the spectral shape does not depend significantly on the choice of functional.

2.2. Experimental setup and method

The optical pump/X-ray probe experiment was conducted at the Surface Chemistry Endstation of the soft X-ray materials science instrument (SXR) [33–35] at the LCLS facility [36]. The preparation of the sample and the details about the experimental procedure can be found elsewhere [18,19].

3. Results

3.1. Minimum energy path

In Fig. 1 we present the computed minimum potential energy surface (corresponding to 0 K) along the desorption coordinate of CO along the surface normal from the atop site. Depending on the choice of XC functional, *i.e.* if non-local correlation is included to describe vdW interactions or not, the long-range behavior differs significantly. As seen in Fig. 1, RPBE actually produces a small barrier at a CO-Ru distance of ~3.1 Å after which the potential energy trails off to zero. The BEEF-vdW functional, on the other hand, yields an attractive plateau starting at a C-Ru distance around 3 Å which can be populated in the desorption process. This long-range attraction is absent when using standard GGA functionals such as RPBE. The equilibrium Ru-C distance for the favored atop adsorption was obtained as 1.94 Å.

As seen from the inset in Fig. 1, at distances beyond ~4 Å the CO molecule becomes free to rotate in the shallow vdW-generated shelf which gives a significant contribution to the entropy in the desorption process, a discussion we will return to below. At distances smaller than 2.5 Å in the figure, CO is found to move from atop to bridge and hollow sites.

To simulate the desorption process at conditions relevant to the experiment we need to account for the temperature of the system after

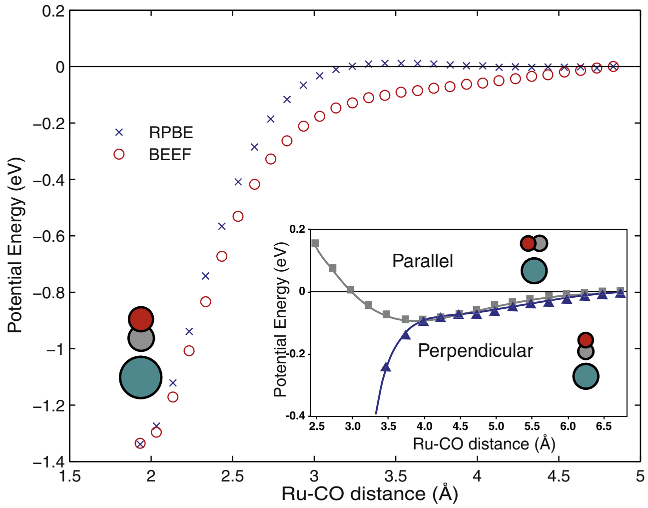

Fig. 1. Minimum energy path (MEP) of the CO desorption from the Ru(0001) surface using the RPBE (blue x-marks) and BEEF-vdW (red circles) exchange-correlation functionals. The potential energy is plotted as a function of the C-Ru distance. The inset shows a region of the desorption paths for CO perpendicular (blue triangles) and parallel (gray squares) to the surface calculated using the BEEF-vdW functional. At ~ 4Å (CO center of mass distance to the Ru surface), the attractive vdW plateau develops and the potential energy becomes independent of the CO orientation relative the surface. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.).

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