Supporting Information

The Influence of a Changing Local Environment during Photoinduced CO₂ Dissociation

Michael Vyshnepolsky, Zhao-Bin Ding, Prashant Srivastava, Patrik Tesarik, Hussain Mazhar, Matteo Maestri, and Karina Morgenstern*

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EXPERIMENTAL METHODS

The experiments were performed with a home-built low-temperature STM at 7K in UHV (base pressure $< 2 \times 10^{-10}$ mbar) [1]. Both surfaces are cleaned by standard sputtering and annealing cycles. 45 min sputtering is performed with Ne$^+$ ions at $3 \times 10^{-5}$ mbar and 1.0 keV, 3.0 µA for Ag(100) or 1.3 keV, 3.5 µA for Cu(111), followed by annealing at 630°C for 10 min. CO$_2$ is deposited on the sample inside the STM head, which is surrounded by LN2 and LHe shields. For deposition, a CO$_2$ pressure of $6 \times 10^{-5}$ mbar is established in a separately pumped chamber via a leak valve from a pressurized CO$_2$ gas bottle (manufacturer: Westfalen). The gate-through valve between this molecular deposition and the main chamber as well as the shutters of the shields around the STM head are opened for 50 s leading to a coverage of $(15 \pm 3)$% ML. The sample temperature rises from 7 to 21 K on opening the shields. All STM images were acquired using so-called modified tips that result from a transfer of a CO$_2$ molecule to the tip. Such a modified tip features an enhanced resolution as compared to a metallic tip, similar to tips modified by CO molecules [2]. Frequency-doubled light from a commercial laser (REGA 9050 from Coherent) provides 50 fs laser pulses at 400 nm with a repetition rate of 250 kHz at a power of up to 220 mW. A power between 0.07 mW and 0.4 mW is achieved via a combination of a polarizer and two beam splitters. The proportion of the p-polarized light in our setup amounts to 97% at the sample as determined in a parallel set-up. For laser illumination, the laser light is focused within the cold shields below the STM tip to an elliptical spot of $\approx 43\mu$m by $\approx 25\mu$m at its $1/e^2$ value and of $\approx 26\mu$m and $\approx 15\mu$m at half values. The maximum of the laser spot and the tip are aligned precisely with sub-micrometer precision with the aid of photo-electrons generated by the laser light from the sample and picked up by the tip, where the maximum of the photoelectron signal is at the maximum of the Gaussian-shaped laser spot. Note that for both surfaces the energy of a single photon is, at 3.1 eV, too low to overcome their respective work functions. Thus, the photoelectrons result from a two-photon process. This non-linearity increases the precision of laser alignment, a precision necessary to ensure that for a fluence-dependent quantification all images are recorded at the peak of the Gaussian-shaped laser spot.

To follow changes to individual molecules, the same spot of the surface is alternately imaged and illuminated for 4 s, corresponding to a train of $10^6$ laser pulses. For illumination, the tip is retracted from the scanned area and the incoming laser light as far as possible with-
out moving the scanner head. The described changes are not caused by the imaging process as concluded from images taken in the same procedure without intermediate illumination. At a similar incident power, the absorbed fluences for the two surfaces differ because the absorption of p-polarized light of 400 nm is, at an incident angle of 65° [1], 72% in copper, but only 5.6% in silver [3] due to the lower position of its d-band. We here state the peak fluences as we perform the experiment at the maximum of the Gaussian-shaped laser spot. For Ag(100), an absorbed peak fluence of between 8 and 12 µJ/cm² per pulse for the first illuminations is increased to around 20 µJ/cm² per pulse for the last two illuminations to account for the decreased efficiency of the reaction. For Cu(111), the absorbed fluence is increased from 90 µJ/cm² per pulse for the first illumination to 305 µJ/cm² per pulse for the last one. Because of these variances, we refer the yield to the peak fluence accumulated over all laser pulses up to the observation. This is a valid approach as the low absorbed photon density of the order between 0.2 to 7 photons per molecule, and a correspondingly smaller number of electrons, suggests single-electron processes over the whole investigated range. This non-linearity is confirmed by an experiment, where the pulse is lengthened to 705 fs by passing it through a piece of 50 mm glass (N-BK7, see below).

**COMPUTATIONAL METHODS**

All periodic DFT calculations in this work are performed with the Quantum ESPRESSO code [4] that is based on plane-wave basis sets and ultra-soft pseudo-potentials [5]. The exchange and correlation potential are approximated using the generalized-gradient approximation as formulated by the Perdew, Burke, and Ernzerhof (GGA-PBE) functional [6]. Bloch wave functions are expanded by plane waves with the cut-off of their kinetic energy to be 40 Ry (544 eV). The van der Waals (vdW) interactions that are not described with PBE are included using the Grimme-D2 approach [7]. The metal surface covered by 0.25 mono-layers (ML) of oxygen atoms is modelled with four-layer 2 x 2 slabs, and the surface covered by 0.33 ML of oxygen atoms is modelled with a four-layer 3 x 2 slab, where the bottom three layers are fixed at their atomic bulk positions. A 0.14 nm-thick vacuum layer is added between slabs in neighbouring supercells. The Brillouin zone of the supercell is sampled on a 6 x 6 X 1 and 4 X 6 X 1 Monkhorst-Pack grid [8] for the 0.25 and 0.33 ML model, respectively. The reaction energy is defined as the energy difference between the global minima
of the states that are on both sides of the transition state. Their structures are optimized until the force converges to 0.3 eV/nm. The transition states are then searched with the Climbing Image-Nudged Elastic Band (CI-NEB) algorithm [9]. The convergence threshold on the forces of each image is set to be 0.5 eV/nm. All the transition states are confirmed by ensuring that their vibrational spectra show only one imaginary mode. The vibrational frequencies are calculated by displacing the atoms on both, the adsorbate and the first layer of the metal surface using the Atomic Simulations Environment (ASE) [10]. The activation energy is then defined as the difference between the transition state energy and the initial state energy defined above.

APPARENT HEIGHT DISTRIBUTION OF CO$_2$ CLUSTERS

FIG. 1: Fluence dependent vertical changes to CO$_2$ clusters: Apparent height distribution as pixel histograms on (a) Ag(100) and (b) Cu(111) for increasing number of pulses $10^6$ in different colors as marked; average absorbed fluence on Ag(100) of 11.1 $\mu$J/cm$^2$ for the first five illuminations, 10.8 $\mu$J/cm$^2$ for the next three illuminations, and 19.6 $\mu$J/cm$^2$ for the last two illuminations; on Cu(111) of 130 $\mu$J/cm$^2$ for the first four and 260 $\mu$J/cm$^2$ for the last four illuminations. 0 pm corresponds to the surface level. $N_0$ is the total number of pixels in the image.

Vertical geometrical changes to the clusters are quantified in apparent height distributions
(Fig. 1b). On Ag(100) the apparent height distribution of the clusters exhibits a sharp maximum at around $(66 \pm 2)$ pm before illumination (magenta curve, Fig. 1a). The shoulder of the maximum at lower values represents the rim of the cluster and is thus an imaging artifact. The position of the maximum shifts to a slightly lower value of $(61 \pm 2)$ pm after the first illumination at a slightly reduced peak area (red curve). After the second illumination, the maximum, located at around $(63 \pm 4)$ pm, is broader than in the two previous distributions, and its area is decreased strongly to around one-third of its original value (orange curve). A broad symmetric distribution of around 90 pm in width is obtained after the fourth illumination (yellow curve). This distribution shifts, at the same width, monotonously to lower apparent height values within the next three illuminations to a mean of -7 pm, remaining around this value for the last two illuminations.

The increase of lower apparent height values is attributed to different effects. An overall increase of all values results from the cluster’s perimeter increase at decreasing compactness and the corresponding imaging artifact. Specific apparent height values in the range between 35 pm and 50 pm, showing up during the first illuminations, are attributed to a change in the adsorption sites of the CO$_2$ molecules, possibly due to reduced order. Such a relation between apparent height and adsorption site was observed for CO$_2$ on Ni(110) [11]. The lower values between 25 pm and 35 pm result from the apparent depressions (AD) in the clusters (c.f. Fig. 1c of the main manuscript), attributed either to missing CO$_2$ molecules or dissociation products. Negative values, indicative of products, exist starting from the third illumination at an accumulated fluence of around 30 $\mu$J/cm$^2$ (orange curve). They are visible in substantial amounts only after the next illumination (c.f. Fig. 2e of the main manuscript).

On Cu(111), the change in apparent height follows similar trends like the one on Ag(100) (Fig. 1b). A sharp maximum with a shoulder is present prior to laser illumination (magenta curve). The negative values result here from a dark rim around the cluster (c.f. Fig. 4 of the main manuscript) because of a differently modified tip. The maximum likewise broadens and shifts to lower values for the first two illuminations (red and orange curves), from $(109 \pm 2)$ pm to $(85 \pm 4)$ pm. Also here, these changes are attributed to a shift of the CO$_2$ to other adsorption sites, which is possible within the less ordered cluster. After the next illumination, the apparent height exhibits a broad distribution ranging from around -20 pm to 77 pm (yellow curve). A new broad maximum starts to grow out of this distribution at around -3 pm for the next illumination (light yellow curve). This maximum shifts to
around -13 pm in the following illuminations, pointing again to apparent depressions caused by products. The distributions of the last three illuminations remain almost constant, as on Ag(100), indicating that changes to the shape are finalized.

DISSOCIATION ON AG(100) AT LONGER PULSE LENGTH

FIG. 2: Dissociation of CO$_2$ on Ag(100) at a pulse length of 705 fs: (a,b) STM image before (a) and after (b) a laser illumination of $4 \cdot 10^6$ pulses at 11 $\mu$J/cm$^2$ per pulse, 100 mV, 7.4 pA (c,d) STM image before (a) and after (b) a laser illumination of $6 \cdot 10^6$ pulses at 14.7 $\mu$J/cm$^2$ per pulse, 100 mV, 6.9 pA; Markers: red circles: CO molecules; yellow dashed circles: oxygen atoms; cyan pentagons: agglomerations of CO$_2$ at CO; orange triangles: agglomerations of CO at O; one structure each is enlarged for better visibility by a factor of 3 and shown at enhanced contrast in the green squares, purple arrows point to an apparent depression within a CO$_2$ cluster.

For the illumination powers below 1 mW, as used in the main manuscript, the number of
photons absorbed by the metals is at the repetition rate of 250 kHz less than one per pulse. As only a fraction of the induced electrons are close enough to the surface to attach to an adsorbed molecule, the dissociation needs to be induced by a single-electron process. If it was a multi-electron process, it should degrade substantially when the pulses are stretched in time. Passing the laser through a 50 mm (N-BK7) stretches the pulse to 705 fs. Despite this lengthening, the same changes are observed as for the short laser pulses described in detail in the main manuscript (Fig. 2). These include a disordering of the clusters, additional species created on the terrace, and the appearance of oxygen (black regions) in the vicinity of the clusters. This confirms that the process is a one-electron process and not limited to ultra-short laser illumination.

* Electronic address: karina.morgenstern@rub.de, www.rub.de/pc1
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