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Real-Time Observation of Molecular Motion on a Surface

Ellen H. G. Backus,1 Andreas Eichler,2 Aart W. Kleyn,1,3 Mischa Bonn1,4

The laser-induced movement of CO molecules over a platinum surface was followed in real time by means of ultrafast vibrational spectroscopy. Because the CO molecules bound on different surface sites exhibit different C–O stretch vibrational frequencies, the site-to-site hopping, triggered by excitation with a laser pulse, can be determined from subpicosecond changes in the vibrational spectra. The unexpectedly fast motion—characterized by a 500-femtosecond time constant—reveals that a rotational motion of the CO molecules, rather than pure translation, is required for this diffusion process. This conclusion is corroborated by density functional theory calculations.

The motion of molecules from one adsorption site to another is the most elementary process of bond-breaking and-making on a surface and is a key step in processes such as catalysis and crystal growth. A fundamental understanding of surface molecular motion requires insights on both the molecular length and time scales, necessitating subnanometer spatial resolution and subpicosecond temporal resolution.

Real-space observations of site-to-site surface molecular motion are readily obtained by scanning tunneling microscopy (STM) (1). Recent STM experiments have even demonstrated control over molecular motion on a surface, induced by electrons from the STM tip (2–5) or by a femtosecond laser (6). These studies have provided detailed insights into the energetics, local directionality, and site dependence of molecular surface motion.

In contrast, the direct real-time observation of surface molecular motion has not been reported to date, although such data would provide important insights into the dynamics and molecular mechanism behind surface molecular motion. Indeed, a recent time-resolved study by Stépán et al. (7) and combined laser-STM experiments by Bartels et al. (6) have revealed detailed quantitative information on surface motion induced by an ultrashort laser pulse, as also shown previously for other surface reactions (8–12). However, in these studies the time coordinate was probed indirectly, by monitoring the equilibrated system after the induction of molecular motion with a laser pulse.

The direct time-resolved study of surface processes would allow the observation of energy flow between the substrate and the vibrational and rotational modes of the adsorbed molecule, and elucidate how these modes are coupled to the reaction coordinate (such as diffusion). Such information would unambiguously reveal the detailed molecular mechanism and intrinsic rates of surface reactions.

Here we report the direct real-time observation of surface molecular motion by means of time-resolved vibrational spectroscopy to provide real-time “snapshots” of the process. We observed subpicosecond hopping of CO molecules from step sites to terrace sites. Both the experiments and density functional theory (DFT) calculations reveal that, in contrast to the common belief that lateral motion is preceded by excitation of only the translational mode, excitation of the rotational mode of the molecules is a crucial step in the hopping process.

Our approach relies on CO molecules having a different internal C–O stretch vibrational frequency when adsorbed on the different sites of a stepped Pt(533) surface (Fig. 1A) (13), which provides indirect subnanometer spatial resolution along the coordinate perpendicular to the steps, as shown previously (14, 15). The Pt surface consisted of 7 Å-wide flat terraces separated by monatomic steps. The C–O stretch vibrations of CO on steps and terraces monitored with femtosecond sum-frequency generation (SFG) (16) differed by ~20 cm⁻¹ (Fig. 1B), so that CO molecules on the two sites were readily distinguished.

To obtain a surface with preferential occupation of the step sites, we made use of the stronger binding of CO molecules on steps (~2 eV) as compared to terrace sites (~1.5 eV) for isolated molecules (13, 17). Brief heating of a fully CO-saturated surface to 420 K preferentially removed CO molecules from the terrace sites; CO molecules at the steps desorbed at a higher temperature. The heating was terminated when the SFG spectrum (Fig. 1B, black line) revealed only CO on step sites at 2080 cm⁻¹ (13). The spectrum for a CO-saturated surface, where the majority of CO is adsorbed on terrace sites, shows a resonance at 2100 cm⁻¹ (13), which is the vibrational frequency of CO on terraces. The CO molecules bound to the step sites are invisible because of the effects of dipole-dipole coupling: The vibrational intensity from the oscillating CO dipoles on the step sites is transferred to the CO dipoles on the terrace sites.

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more quickly oscillating COs (at higher frequency) on the terrace sites (18).

In our experiment, we induced the energetically uphill motion of CO molecules from step to terrace sites by exciting the substrate with an ultrashort laser pulse (fluence, 60 J m\(^{-2}\)). To achieve maximum sensitivity for the CO hopping process, we started with occupancies of \(\sim 100\%\) of the steps and \(\sim 10\%\) of the terrace sites, the spectrum for which is shown as the dotted line in Fig. 1C. Estimates of the occupation of the step and terrace sites were obtained from an uptake curve and the dipole-dipole coupling model (18). Because desorption [binding energy \(E_{\text{bind}}\) = 1.5 to 2 eV] by laser-induced heating is readily achieved (19), and the activation energy for diffusion is typically a fraction of \(E_{\text{bind}}\), we expect diffusion to be triggered at lower fluences. Indeed, pump excitation of the Pt surface with CO preferentially at the step sites resulted in a steady-state situation, with CO more evenly distributed on step and terrace sites, as is apparent from comparing the gray curves (pump on/pump off) in Fig. 1C. After excitation, the terrace peak is even larger than the step peak, because the terrace CO (\(\sim 15\%\) occupation of the terrace sites) efficiently borrows vibrational intensity from the step CO (\(\sim 90\%\) occupation of the step sites) (18). Thus, the system is extremely sensitive to the motion of CO from steps to terraces.

The CO molecules can clearly undergo laser-induced movement from step to terrace sites. We also find that blocking the pump laser allows the molecules to diffuse back to the step sites in \(\sim 10\) s, in agreement with (20). If the motion is induced at an initial surface temperature of 400 K rather than 100 K, re-population of the step sites occurs on \(\sim 100\)-ps time scales because of thermal diffusion; that is, \(\sim 10^{11}\) times faster than at 100 K, which is consistent with the diffusion coefficients reported in (21).

The fraction of molecules that moves from step to terrace sites in a single laser shot can be determined by comparing pump-probe spectra directly before and after the excitation pulse. Figure 1C depicts spectra 10 ps before the pump pulse (negative delay, under steady-state conditions with \(\sim 90\%\) occupation of the step sites and \(\sim 15\%\) occupation of the terrace sites) and 170 ps after excitation. At 170 ps, the terrace peak has gained intensity and the step peak is reduced by a factor of 2. Taking into account that, at 170 ps, the system is still at slightly elevated temperature, we can reproduce the spectrum using the dipole-dipole coupling model (18), with \(10^{1\pm 10}\%\) of the CO molecules on the steps hopping to terrace sites. The calculated curve (18) is shown as the solid curve in Fig. 1D. Hopping of 10\% of the step CO molecules to the terrace sites results in a disproportionately large intensity decrease of 20\% of the step peak (compare dotted and solid lines in Fig. 1D) because of dipole-dipole coupling effects. The observed intensity change cannot be explained by desorption, because at the fluence used, less than 0.1\% of the molecules desorbs in a single shot. Also, the time scale of signal recovery is not consistent with readsoption of CO from the background or the relaxation of laser-induced changes in the orientation of molecules. Diffusion to or from bridge sites can be excluded as well, because no change is observed in the bridge peaks for step and terrace around 1900 cm\(^{-1}\) (13).

The dynamics of the motion of the CO molecules from step to terrace sites is obtained from pump-probe spectra near zero delay, shown in Fig. 1E for steady-state occupation of 75 and 20\% of the step and terrace sites, respectively. It is evident that the ratio of step and terrace peaks changes on ultrafast time scales: The step peak disappears almost completely within a picosecond, indicating that the motion from step to terrace sites occurs on this time scale. The observation that the effect of the pump pulse appears in the spectra already before the pump pulse (negative delay, under steady-state conditions) confirms that the motion of the CO molecules is still ongoing when the laser pulse is on (22). The time scale of signal recovery is not consistent with the diffusion coefficients reported in (21).

The details of the mechanism and rate of the laser-induced diffusion process can be derived from the SFG spectra of Fig. 1E, with inclusion of the hopping process. To reproduce the dynamic behavior of the terrace peak, the magnitude of its peak shift and line width change have to be divided by 2, presumably because of the appearance of additional terrace CO molecules during the hopping process. The time scale of the peak shift and line width is unchanged, however. In the
modeling, the time-dependent hopping probability from the step site to the terrace site is approximated by a function that is formed by a Gaussian rising edge, followed by an exponential decay (26). The integral of this function gives the time-dependent step site occupation.

The calculations confirm quantitatively that, in order to reproduce the data at short delays (Fig. 1E), a subpicosecond change of the site occupation is required, as is already evident from the raw data. The resulting step site occupation is plotted in Fig. 3A. The shape of the curve of Fig. 3A is very sensitive to the spectra at small positive delay. The time-dependent calculated SFG spectra are plotted in Fig. 1E and are in good agreement with the experimental data. As is the case in Fig. 2A, the calculated intensity is slightly too low at small negative delays. The exponential time obtained from the calculation is 500 ± 150 fs.

It has been generally assumed that molecular diffusion of diatomic adsorbates is controlled by excitation of the frustrated translation (inset in Fig. 3) (4, 5, 7). Although this model is intuitively appealing, the actual reaction coordinate may involve a more complex combination of modes. We calculated the time-dependent hopping probability expected for motion controlled by the frustrated translational mode. Using the τ = 4 ps coupling time derived from Fig. 2 for CO on steps, we can directly calculate the time-dependent temperature associated with the frustrated translational mode (Ttran) (Fig. 3B) and calculate the hopping probability according to an Arrhenius-type expression

\[
P_{\text{hop}}(t) = \theta(t)k_b\exp[-E_a/(k_bT_{\text{tran}}(t))],
\]

where \(E_a\) is the activation energy (0.4 eV (21)) and the prefactor (\(k_b\)) of 1002 s⁻¹ (20).

Remarkably, the agreement between the calculated result and the experimentally observed hopping probability (Fig. 3C, obtained by differentiating the hop fraction of Fig. 3A) is very poor, despite the independent calibration of the temperature of the frustrated translational mode with SFG (Fig. 2). However, quantitative agreement between model and data is obtained for a hopping process controlled by excitation of the frustrated rotational mode [mode (ii), τ = 411 cm⁻¹ (24), inset in Fig. 3]. This mode (see Fig. 3B for its time-dependent temperature) is coupled to the hot electrons in the Pt, with τ = 0.1 ps as established in (19) and also in agreement with the coupling time previously reported for this mode on Pt(111) (23). Because of this very efficient coupling, hopping can occur on the observed fast time scale. Not only was the temporal evolution reproduced, but also the calculated total hop fraction of ~10% is in good agreement with our experimentally observed 10 ± 10%. No additional coupling to the frustrated translation is required to account for our experimental data (27). Thus, a rotational motion rather than a translational motion is essential for the hopping process of CO molecules from step to terrace sites.

These experimental observations are corroborated by DFT calculations (17), which reveal that the barrier for motion onto the terrace next to the step (< 0.4 eV) is substantially lower than that for motion onto the terrace down the step (< 0.6 eV); the majority of the hopping CO molecules will migrate onto the upper terrace. The calculated value of the diffusion barrier is in good agreement with the 0.4 eV observed experimentally for CO on a stepped Pt surface (27). The reaction pathway for the motion of CO onto the upper terrace is depicted in Fig. 4. From the initial (is) and intermediate (im) states, one can see that the CO molecules moving onto the upper terrace first perform a frustrated translational motion: The C and O atoms move in the same direction. This is a joint motion around the center of the underlying Pt atom (28), not parallel to the surface. At the first transition state (ts1), however, a rotational motion of the molecule, with the C and O atoms moving in opposite directions, compensates for this tilting, so that the reaction intermediate (ri), with CO bound in a bridge configuration, can be reached. To reach the final state (fs), a similar motion has to be performed. The entire process thus requires excitation of both the frustrated translation and frustrated rotation, but the former (frequency, 35 cm⁻¹) is thermally excited at 100 K, effectively resulting in a precursor state.

Hence, excitation of the frustrated rotation is pivotal for CO hopping, in agreement with our experimental observations. For diffusion on a flat surface as well, most likely the frustrated rotation is crucial. Because of the atomic corrugation of the surface, the frustrated translational mode always involves rotation of the molecular axis with respect to the surface normal. This rotation has to be compensated for in order for the molecule to settle on the neighboring site, which can only be achieved by excitation of the frustrated rotational mode. Our findings illustrate the intricacies of mode coupling at surfaces: Contrary to common belief, the frustrated rotational motion is strongly coupled to the
coordinate for diffusion, and, in the case of our experiment, dominates the diffusion away from the initial position.

References and Notes


16. The experiments were performed in an ultrahigh vacuum chamber with a base pressure of $2 \times 10^{-11}$ mbar, in combination with a Tsipple magnetic field scanning technique (Quantumix, Titan). For the femtosecond pump-probe SFG experiments, three laser pulses were used to induce the motion of CO molecules: the SFG probe pair (a combination of a weak infrared (IR) and weak visible beam) and an intense visible pump beam (130 fs). Both the IR pulses [800 nm, full width at half maximum (FWHM) = 200 cm$^{-1}$, 6.5 mJ], generated by a traveling-wave optical parametric amplifier, and the visible upconversion pulses (1250 cm$^{-1}$, 6.5 mJ) were p-polarized and focused onto the surface by the same parabolic mirror (f = 100 mm). 1.3 m of the 800-nm laser output was used as a pump pulse (p-polarized). The beam diameter of the pump beam was 1 mm, which is approximately four times larger than the diameter of the probe beams. The time resolution was better than 200 fs. The SFG signal was detected with a spectrometer and a charge-coupled device camera. To minimize steady-state heating effects of the substrate, the laser frequency was reduced to 83 Hz by a chopper. Unless otherwise noted, the experiments were performed at a surface temperature of 100 K. For the highest-excitation fluences, very small amounts (<1 pm per shot) of CO, dosed via background dosing at 100 K, were desorbing. Therefore, we assume that the CO background pressure of $10^{-5}$ mbar to keep a constant surface coverage.

17. Structures and binding energies were calculated with the Vienna Ab-initio Simulation Package (VASP) (see http://cms.mpipi-ueetr.at/vasp/). VASP is a plane wave–based density functional code employing the projector augmented wave method (20). The surface was modeled by a 19-layer slab in a 4 x 4 cell containing four atoms per layer, sampled by a grid of $(3 \times 2 \times 1)$ k points. A cutoff energy for the expansion of the plane waves of 400 eV was found to be sufficient for an accurate description. For exchange and correlation contributions, generalized gradient approximations according to Perdew et al. (31) were applied. Pathways and activation energies for diffusion of CO were determined with the nudged elastic band method (32).


26. The width of the Gaussian determines the rise time of the signal and corresponds to the rate of adsorbate heating; the exponential decay is caused by adsorbate cooling. Both are determined by the coupling time. Because cooling is the slowest process, the exponential time scale is the largest of the two, and therefore provides an upper limit for the time scale on which adsorbate motion occurs.

27. Coupling to the frustrated rotation is not observed in the SFG spectra of Fig. 1, because the anharmonic coupling between the frustrated rotation and the internal C-O stretch vibration is apparently too small. The data at low fluence [11 J m$^{-2}$] can be described with only anharmonic coupling to the frustrated translation without invoking any effect of the frustrated rotation. This allows us to determine an upper limit for the anharmonic coupling between the frustrated rotation and the internal C-O stretch vibration. Based on the known values for the frequencies of the different modes and the anharmonic coupling for the frustrated translation (24), the absolute value for the coupling of the frustrated rotation is less than 1 cm$^{-1}$. This will result in an additional shift to the spectra in Fig. 1E of at most 2.5 cm$^{-1}$.


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Multistep Synthesis of a Radiolabeled Imaging Probe Using Integrated Microfluidics

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Microreactor technology has shown potential for optimizing synthetic efficiency, particularly in preparing sensitive compounds. We achieved the synthesis of an [$^{18}$F]fluoride-radiolabeled molecular imaging probe, 2-deoxy-2-[$^{18}$F]fluoro-D-glucose ([$^{18}$F]FDG), in an integrated microfluidic device. Five sequential processes—[$^{18}$F]fluoride concentration, water evaporation, radiofluorination, solvent exchange, and hydrolytic protection—proceeded with high radiochemical yield and purity and with shorter synthesis time relative to conventional automated synthesis. Multiple doses of [$^{18}$F]FDG for positron emission tomography imaging studies in mice were prepared. These results, which constitute a proof of principle for automated multistep syntheses at the nanomolar to microgram scale, could be generalized to a range of radiolabeled substrates.

Continuous-flow microreactors (1–3) have recently been used to manipulate individual chemical processes on nanoliter to microliter scales. The advantages of such chemical reaction circuits include enhanced heat transfer performance, faster diffusion times and reaction kinetics, and improved reaction product selectivity (4–6). For example, in microfluidic environments, triphasic hydrogenation (7) can be achieved with higher reaction efficiency, the inorganic synthesis of high-quality CdSe nanocrystals has been demonstrated (8), and chemical processes involving highly reactive intermediates can be executed with superior reaction selectivity (9). However, challenges remain in applying the technology to sequential syntheses of fine chemicals and pharmaceuticals.

In multistep procedures, flow-through systems are plagued by cross-contamination of reagents from different steps; side reactions and poor overall yield result from the inability