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Time-Resolved Measurement of Surface Diffusion Induced by Femtosecond Laser Pulses

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Diffusion of atomic oxygen on a vicinal Pt(111) surface induced by femtosecond laser pulses has been studied using optical second-harmonic generation as a sensitive *in situ* probe of the step coverage. Time-resolved studies of the hopping rate for step-terrace diffusion with a two-pulse correlation scheme reveal a time constant of 1.5 ps for the energy transfer from the electronic excitation of the substrate to the frustrated translations of the adsorbate.

It has been demonstrated that a new regime of chemical reactions at metal surfaces can be accessed with intense femtosecond laser pulses [1–10]. For a time scale below that of electron-phonon coupling (≈ 1 ps) it is possible to maintain a high density of electronic excitations in a metal without substantial heating of the crystal lattice. The high density of electron hole pairs created in the metal causes multiple electronic transitions between the ground and excited states of the adsorbate-metal system on the time scale of nuclear motion. This leads to reaction yields that are typically orders of magnitude higher than in conventional photochemical reactions at metal surfaces. For experimental reasons this regime of femtochemistry at surfaces has so far been investigated mainly for desorption since desorbing atoms or molecules can be detected easily and efficiently in the gas phase with quadrupole mass spectrometry (QMS).

For many catalytic reactions, however, diffusion of adsorbates is an equally important elementary step. Moreover, the ability to induce surface diffusion electronically at low temperature could allow the growth of novel materials. Recently, several groups have studied electronically induced migration processes of molecular adsorbates with scanning tunneling microscopy (STM) [11–13]. In the case of CO/Pd(110) and NH_3/Cu(100) it has been shown that inelastic tunneling processes, which excite internal molecular vibrations, lead to diffusion by anharmonic coupling to frustrated translations [11,12]. In the case of CO/Cu(110), electronic excitations of the substrate induced by short laser pulses were shown to give rise to lateral motion parallel and even perpendicular to the close-packed rows of the surface [13].

In this Letter we report the first investigation of an electronically induced diffusion process in the time domain. We generate a nonequilibrium initial distribution of adsorbate atoms by dissociative adsorption of O_2 at the step edges of a vicinal Pt(111) surface (Fig. 1). While the substrate is excited by femtosecond laser pulses, step depletion caused by diffusion of oxygen atoms is monitored by optical second-harmonic generation (SHG), a technique that is very sensitive to the presence of regular steps and

their electronic structure [14,15]. Systematic studies of the hopping rate for step-terrace diffusion as a function of fluence and delay time of two pump laser pulses provide information about the coupling strength and the time scale of energy transfer from the electronic excitation to the lateral motion of the adsorbate. It will be shown that description of the coupling within the framework of an electronic friction model requires the use of a friction coefficient that depends on the excitation density. This, and the observation of a correlation time of 1.5 ps, suggests that the frustrated O-Pt translational modes are not directly excited by hot substrate electrons but are populated by coupling to an intermediate heat bath, most likely the O-Pt stretch vibrations.

The experiments were conducted under ultrahigh vacuum conditions with a Pt crystal miscut by 4° from the (111) plane in the $[1\bar{1}0]$ direction. The resulting (10,12,11) surface consisted of 12 unit-cell-wide terraces and step edges along the $[11\bar{2}]$ direction. Diffusion was induced by 50 fs pulses from a kHz Ti:sapphire amplifier system operating at 800 nm. The output was split into two orthogonally polarized beams, combined collinearly with variable time delay, incident on the sample at 40° from the surface normal and slightly focused to a spot of 1 mm in diameter. Femtosecond laser pulses at 800 nm were also
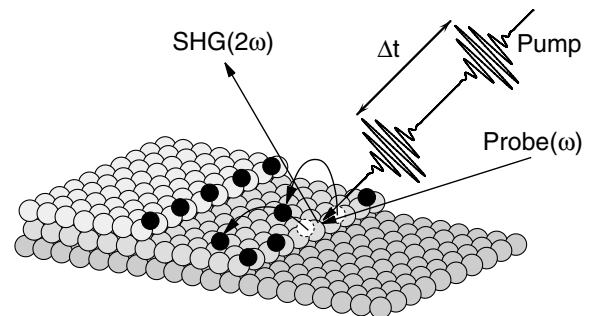

FIG. 1. Scheme of the experiment. Step sites are decorated selectively by dissociative adsorption. Intensive ultrashort laser pulses induce diffusion onto the terraces, which is monitored by second-harmonic generation of a probe beam.

used as the fundamental radiation for SHG. The SHG probe beam was p polarized and incident at 45° in a plane parallel to the step edges. The spot size was 10 times smaller than that of the pump beam and the absorbed fluence of the probe pulses was kept below 0.5 mJ/cm^2 in order to exclude any influence on the diffusion process. Detection of the p-polarized component of the second-harmonic radiation results in a SHG signal that originates predominantly from the steps [16].

Figure 2 displays several sets of raw SHG data as a function of time, showing first the decoration of the steps with atomic oxygen, and subsequently their depletion after switching on pump radiation of various absorbed fluences. For these measurements the sample was kept at 160 K and exposed to constant flux of molecular oxygen through a microcapillary array. At 160 K, chemisorbed O$_2$ is not stable on the terraces. It desorbs or it diffuses to the step edges where it preferentially dissociates and forms strongly bound atomic oxygen on top of the step edges [18]. Chemisorption of atomic oxygen at the steps leads to a strong reduction of the SHG signal until the steps are saturated ("dosing" regime in Fig. 2).

The selective decoration of the steps by atomic oxygen results in a nonequilibrium situation. The equilibrium distribution of oxygen on the vicinal surface depends on the binding energy differences and the relative abundance of adsorption sites on steps and terraces. Experimentally, we observe partial depletion of the steps by thermal diffusion when we heat the sample to 260 K and higher temperatures. For the study of laser-induced diffusion we cool the sample down to 80 K, where oxygen is immobile even on the terraces, and irradiate the sample with femtosecond laser pulses. We observe a continuous recovery of the SHG signal for pulses that exceed an absorbed fluence of 3.5 mJ/cm^2 (Fig. 2). The recovery of the SHG signal is due to the depletion of the step sites by oxygen diffusion onto the terraces and not due to desorption. When we scan the spot of the pump beam with a fluence of 6 mJ/cm^2 slowly over the whole sample surface, subsequently recorded temperature-programmed-desorption (TPD) spectra show no indication of a laser-induced decrease of the total oxygen coverage [19]. Since thermal desorption of atomic oxygen takes place recombinatively around 800 K, i.e., at a much higher temperature than diffusion, we expect that laser pulses exceeding the damage threshold of the sample would be required to induce desorption with our experimental setup. The fact that we observe almost complete step depletion at higher laser fluences indicates that the laser-induced diffusion process is not defect mediated, but affects all steps sites.

Although the recorded SHG signal averages over large surface distances, the use of a stepped surface allows us to deduce diffusion rates on the atomic scale. The quantity discussed in the following is the hopping probability p_{dif} per laser shot for migration from the step sites onto the terraces. In principle, this quantity can be determined directly from the initial slope $d\theta_s/dt$ of the SHG data
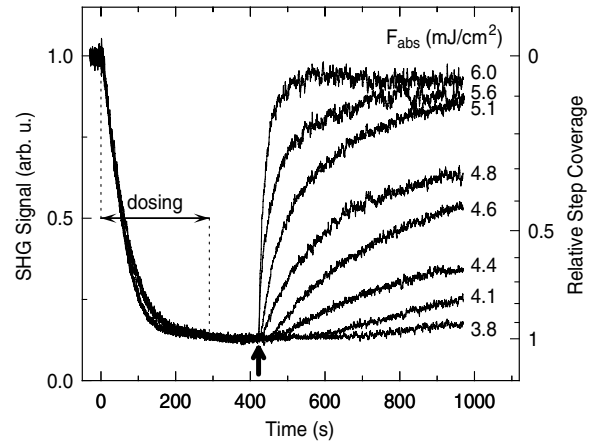

FIG. 2. Second-harmonic response of the Pt sample during dissociative adsorption of O$_2$ at the steps (dosing) and diffusion of atomic oxygen induced by femtosecond laser pulses of various absorbed fluences F_{abs}. The pump pulses had a repetition rate of 1 kHz and were switched on at the time marked by the vertical arrow. The right y scale gives the conversion of the SHG signal into the relative step coverage [17].

recorded after switching on the pump pulses. For an absorbed fluence of 4.4 mJ/cm^2 the data shown in Fig. 2 have a slope $d\theta_s/dt \approx 0.002$ s^{-1} which results in $p_{dif} \approx 2 \times 10^{-6}$. In order to exploit the excellent statistics of the whole data sets we have determined p_{dif} by describing the diffusion kinetics using a simple one-dimensional rate equation model [17]. We note that with our method of continuously monitoring the step coverage with SHG we achieve an accuracy for the determination of laser-induced diffusion rates that is comparable or even higher than the best measurements of desorption rates using QMS detection [6–8].

The measured hopping probability p_{dif} depends in a strongly nonlinear way on the pump fluence F_{abs} [Fig. 2, cf. Fig. 4(a)]. It increases by more than 2 orders of magnitude in the fluence range 3.8 mJ/cm^2 to 6.0 mJ/cm^2 and can be described by a power law of the form $p_{dif} \propto F_{abs}^{15}$. This is an extremely strong nonlinearity compared to previous laser-induced desorption experiments where typical exponents were within the range of 3–8 [1–9].

The nonlinear dependence of p_{dif} on laser fluence enables the application of a two-pulse correlation scheme [2]. For these experiments the pump pulse is split and the step depletion rate is determined as a function of the time delay between the two pulses (Fig. 3). The width of such a two-pulse correlation provides information about the energy transfer time from the initial excitation of the electrons to the adsorbate motion. Only for delays in which the system retains memory of the first excitation, the second pulse generates an enhanced yield compared to independent excitations.

The two-pulse correlation displayed in Fig. 3 has a high contrast between p_{dif} at zero and large delays, which is related to the high nonlinearity of the fluence dependence.

The width of 1.45 ps (FWHM) is much larger than the cross correlation of the two laser pulses and has the value of a typical electron-phonon coupling time. This unambiguously shows that diffusion is driven by the laser-excited electrons of the metallic substrate. An energy transfer which is mediated by substrate phonons would typically be slower by 1 order of magnitude [8].

Like for most of the laser-induced desorption experiments we analyze the energy transfer mechanism in two steps. First, the dynamics of the laser-excited electrons and the energy flow between the electronic and phononic system of the substrate is described by applying the widely used two-temperature model [2–5,7–10,20]. This allows the assignment of time-dependent electronic and ionic temperatures $T_e(t)$ and $T_i(t)$ assuming instantaneous equilibration in each subsystem. Then the (vibrational) excitation of the adsorbate is described within the modified electronic friction model [21], where the population of the adsorbate modes is characterized by a temperature T_a, which is coupled to the electron temperature T_e by an electronic friction coefficient η_e

$$\frac{\partial}{\partial t} T_a(t) = \eta_e [T_e(t) - T_a(t)]. \tag{1}$$

In principle, η_e is time dependent and has to be calculated using microscopic models. However, most of the laser-induced desorption experiments can be well described using a constant empirical friction coefficient [5,7,8,10]. Solving Eq. (1) gives a time-dependent adsorbate temperature which is then used to calculate the rate $R(t)$ of an activated process [21],
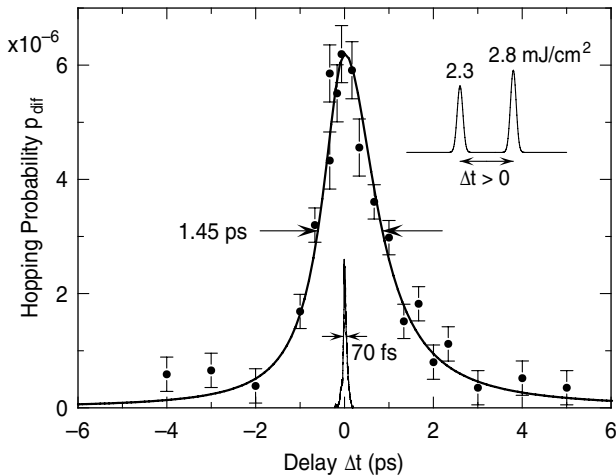
$$R(t) = \eta_e \frac{E}{kT_a(t)} e^{-E/kT_a(t)}. \tag{2}$$

In our case, E is the diffusion barrier and the measured hopping probability is the time integral $p_{dif} = \int R(t)dt$.

We have performed model calculations using material parameters for platinum reported in Ref. [20]. From our thermal diffusion experiments we estimate the diffusion barrier from step to terrace sites as $E \approx 0.8$ eV which is ≈ 0.3 eV larger than the barrier for hopping between terrace sites [22]. Results for different η_e's are plotted in Fig. 4. As shown by the thin dashed and dotted lines, the fluence dependence and the two-pulse correlation cannot be described simultaneously with a constant η_e. A narrow two-pulse correlation can only be modeled with strong friction. However, this results in a hopping probability which is too large by several orders of magnitude, and in a poor contrast between zero and large delays. A strong fluence dependence and a high contrast of the two-pulse correlation can only be obtained with a small η_e. This, however, results in a two-pulse correlation that is much broader than measured.

Reasonable agreement with the experimental data can be achieved if we assume an empirical dependence of η_e on electron temperature, $\eta_e(T_e) = \eta_e^0 T_e^2$ with $\eta_e^0 = 1.8 \times 10^5$ K^{-2} ps^{-1}. In particular, the high nonlinearity of the fluence dependence can be well reproduced with this assumption [Fig. 4(a)]. We note that the best parametrization of $\eta_e(T_e)$ depends on the diffusion barrier E. With a higher value than 0.8 eV, the required exponent of T_e drops below 2 but does not vanish. For all reasonable parametrizations of $\eta_e(T_e)$ the width of the two-pulse correlation remains somewhat smaller than the experimental one [Fig. 4(b)].
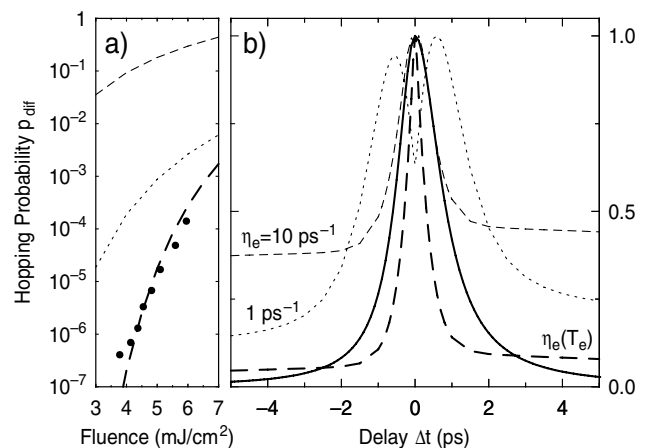

FIG. 3. Hopping probability p_{dif} per laser shot as a function of delay between the p- and s-polarized pump beams with absorbed fluences of 2.3 and 2.8 mJ/cm^2, respectively, (symbols). At positive delays, the weaker excitation precedes the stronger one (inset). The thick solid line is a guide to the eye. The thin line shows the SHG cross correlation of the two pump pulses generated at the sample surface.

FIG. 4. Calculated hopping probability p_{dif} (a) as a function of absorbed fluence and (b) as a function of time delay between two pump pulses for two constant friction coefficients (thin dotted and dashed lines) and an electron temperature dependent η_e (thick dashed line). Experimental values are indicated by symbols (a) and the solid line (b).

Because of the lack of a microscopic description of the electronic friction for O on Pt(111) we can only speculate about the reasons for the temperature dependence of η_e in the present stage. One possibility is inherent in the modified electronic friction model: As pointed out by Brandbyge *et al.* [21], a dependence of η_e on T_e can be expected when the relevant adsorbate level lies significantly far above the Fermi level such that its excitation probability increases strongly with T_e. However, the unoccupied resonance of atomic oxygen on Pt(111) is broad and lies very close to E_F [23]. In fact, all systems like $O_2/Pd(111)$, $CO/Cu(100)$, and $O + CO/Ru(0001)$, where desorption has been successfully modeled by a constant η_e, have higher lying resonances than O/Pt [5,7,8].

Another mechanism leading to a strong temperature dependence of η_e would be an indirect excitation of the frustrated translations via anharmonic coupling to primary excited O-Pt stretch vibrations. Since the anharmonicity of vibrations generally increases with amplitude, the coupling will become more efficient with increasing excitation density. In such a scenario the overall coupling will depend effectively on electron temperature, while the primary electronic excitation of the O-Pt stretch vibrations could still be mediated by a constant η_e. This mechanism is plausible for several reasons. First of all, the STM experiments mentioned above have shown that direct electronic excitation of diffusive motion is inefficient [11–13]. Second, in the case of CO/Cu(100) also, calculations show that the direct coupling of electronic friction to frustrated translations is weak [24]. Third, there is evidence for the presence of strong anharmonic coupling in the system O/Pt(111) because the vibrational linewidth of the perpendicular O-Pt stretch was found to increase substantially with temperature [25].

An important difference between the molecular adsorbates investigated by STM and the O/Pt system studied here, concerns the vibrational energy. Whereas one quantum of internal vibrational energy exceeds the diffusion barrier for these systems, the O-Pt stretch frequency (60 meV) is only slightly higher than the frequency of frustrated O-Pt translations (50 meV) [25]. For this reason, many quanta of vibrational energy need to be excited before they can couple efficiently to lateral motion and before the diffusion barrier of ~0.8 eV can be overcome. Therefore, the model not only explains the strong nonlinearity of the fluence dependence of the diffusion rate, but also the rather broad two-pulse correlation that we observe.

In conclusion, we have shown that diffusion of strongly chemisorbed atomic oxygen from step to terrace sites of a vicinal Pt(111) crystal can induced electronically with femtosecond laser pulses. By applying a time-resolved two-pulse correlation scheme in combination with optical second-harmonic generation, an effective coupling time of 1.5 ps between the electronic excitation of the substrate and the diffusive motion of the adsorbate has been determined. The necessity to introduce a temperature dependent electronic friction coefficient for the consistent modeling

of the results is interpreted in terms of an indirect excitation mechanism. We propose that the substrate electrons primarily excite O-Pt vibrations which then couple anharmonically to the frustrated translations required to overcome the barrier for lateral motion.

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