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Time-domain investigation of laser-induced diffusion of CO on a vicinal Pt(111) surface

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We report on a time-domain study of diffusion of CO on a vicinal Pt(111) surface at low substrate temperature induced electronically via substrate electrons, which have been optically excited by femtosecond-laser pulses. Hopping rates from step sites to terrace sites have been determined using optical second-harmonic generation as a sensitive probe of the step coverage. The dynamics of the electronic energy transfer between the excited substrate electrons and the adsorbate degrees of freedom have been investigated by the application of a two-pulse correlation scheme. We observe a nonlinear dependence of the hopping rate on the laser fluence ($\propto F^6$) in a fluence range of $F=1.9-4.3$ mJ/cm^2 and a narrow two-pulse correlation with a width of below 0.5 ps that increases with increasing laser fluence. It will be shown that the broadening of the two-pulse correlation with laser fluence is a general phenomenon for substrate mediated laser-induced surface reactions.

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I. INTRODUCTION

Hopping of atoms or molecules between different adsorption sites on a surface is one of the most elementary steps in surface reactions such as catalysis and crystal growth. Usually, adsorbate motion is induced by the coupling of the vibrational modes of the adsorbate to lattice vibrations of the substrate. Electronic excitations, however, can play an even more important role, particularly at metal surfaces. This has been studied in detail for the process of desorption induced by electronic transitions (DIET) where the reaction is initiated by single electronic transitions.[1,2] Optical excitation with femtosecond-laser pulses can create a high density of electronic excitations, which causes repetitive electronic transitions between the ground and excited states of the adsorbate-metal system on the time scale of nuclear motion. This regime of desorption induced by multiple electronic transitions (DIMET) (Ref. 3) is characterized by reaction yields, which are many orders of magnitude higher than in conventional photochemical reactions at metal surfaces[4–6] and has founded a new field of femtochemistry at metal surfaces.[7] One of the most interesting aspects of femtosecond-laser excitation is the possibility of performing time-resolved experiments that often take advantage of the nonlinear fluence dependence of the reaction rate for the application of a two-pulse correlation (2PC) scheme.[8] Such experiments gain information about the energy-transfer time from the electronic excitation to the adsorbate degree of freedoms and are often interpreted within models that describe the nonadiabatic coupling between the electronic system of the metal substrate and the adsorbate degrees of freedom by electronic friction.[9–15]

The first observation of femtosecond-laser-induced diffusion used the scanning tunneling microscopy (STM) to detect adsorbate motion. Bartels *et al.*[16] were able to show for the system CO/Cu(110) that electronic excitation of the substrate induced by absorption of short laser pulses gives rise to diffusion of CO parallel and perpendicular to the close-packed rows, while thermal excitation leads to diffusion only along the rows.[16] The STM, however, cannot readily be used to monitor laser-induced diffusion during irradiation, which makes the application of a 2PC scheme very time consuming. By using optical second-harmonic generation (SHG) as a sensitive probe for the step coverage, we could recently show for the system of atomic oxygen on a vicinal Pt(111) surface that femtosecond-laser-induced diffusion of adsorbates from step to terrace sites can also be monitored during laser irradiation with a high dynamic range.[17] The *in situ* optical probe made it possible to use a 2PC scheme for a time-resolved investigation of the energy transfer between laser-excited electrons and the diffusive motion.[18] Although optical techniques cannot observe the motion of individual atoms, they can nevertheless provide averaged information about diffusion on a nanometer scale if the optical signal can discriminate between different adsorption sites. Second-harmonic generation does not only show a high surface sensitivity that is to a large extent caused by the break of the crystal symmetry at the surface. Regular steps on a vicinal surface additionally break the symmetry parallel to the surface that makes them to very efficient sources for SHG.[19,20] This makes it possible to use SHG as a sensitive monitor of the occupation of step sites with adsorbates, where the simultaneous and continuous observation of a large number of sites allows the determination of even very small hopping rates.[21]

Our experiment on O/Pt(111) revealed an extremely strong nonlinear dependence of the hopping rate on laser fluence (F^{15}) and a narrow 2PC with a width of 1.5 ps, which has shown that the diffusive motion is driven by the laser-excited hot electrons of the substrate. In contrast to typical laser-induced desorption experiments, the 2PC and the fluence dependence of the hopping rate could only be reproduced within the electronic friction model by introducing a temperature dependence of the friction coefficient. It has been suggested that this temperature dependence is only an effective one and appears due to the neglect of the coupling between different vibrational modes.[22] An indirect excitation mechanism has been proposed that is based on a primary excitation of the O-Pt vibration by the hot electrons, which then couples anharmonically to the frustrated translation (FT) mode required to initiate lateral motion. Such indirect excitation due to vibrational mode coupling has been found in inelastic scanning tunneling experiments where hopping of small molecules on metal surfaces has been induced by excitation of their internal stretch vibrations.[23,24] The proposed mechanism introduces a coupling that depends on excitation density and would therefore explain the observed effective dependence of the electronic friction on electron temperature. Such temperature-dependent friction has also been shown to give a superior description of the 2PC and the fluence dependence observed for femtosecond-laser-induced desorption of molecular oxygen from a Pd(111) surface.[25]

Relevance for the contribution of different vibrational modes to femtosecond-laser-induced diffusion has been also found by Backus *et al.*[26] for hopping of CO from step to terrace sites on a highly stepped Pt surface. For this system, Jänsch *et al.*[27] performed the first systematic study of electronic induced surface diffusion in which they have observed migration of CO from terrace to step sites induced by irradiation with an electron gun. Backus *et al.*[26] used sum-frequency generation as a time-resolved optical monitor for the occupation of step and terrace sites by CO and found a fast transfer time of about 500 fs from the optical excitation of the substrate electrons to the diffusive motion of the CO molecules. This was unexpected since the direct coupling between the hot electrons and the FT mode is too weak to initiate hopping on a subpicosecond time scale. Based on calculations using the electronic friction model, it has been concluded that the frustrated rotation (FR) mode, which is strongly coupled to the electronic excitation, plays an important role for the fast energy transfer. However, it has been shown that the initiation of lateral motion requires the combined excitation of the FR as well as the FT mode.[28] The latter was already thermally excited in this experiment, effectively resulting in a precursor state.

The experimental results of both femtosecond-laser-induced diffusion experiments have been recently reanalyzed by Ueba *et al.*[29,30] under consideration of vibrational mode coupling. It has been shown that the introduction of a coupling between two vibrational modes can lead to a substantial heating of both modes even if only one of the modes is coupled to the hot electrons. For CO on Pt(111) such coupling can explain a heating of the FT mode through electronic excitation of the FR mode. According to that, only electronic excitation of the FR mode is essential for the initiation of lateral motion on a subpicosecond time scale.

In this contribution we report on femtosecond-laser-induced diffusion of CO from step to terrace site on a Pt(111) surface with low step density at a substrate temperature of 60 K. Hopping from step to terrace sites is observed using sensitive SHG detection, which makes it possible to study diffusion at low pump-laser fluence where desorption can be neglected. The hopping rate is measured as a function of laser fluence and as a function of time delay between two pump pulses in a 2PC scheme. The high dynamic range of the SHG-detection scheme allowed for the recording of 2PCs at two different laser fluences. We find a strong dependence of the hopping rate on laser fluence F, which can be described by a power law $\propto F^6$. The 2PCs have a narrow width of below 0.5 ps, which confirms the fast energy transfer from the hot electrons to the lateral motion observed by Backus *et al.*[26] It will be shown that the width of the 2PC depends on the fluence of the pump laser, which demonstrates that the strength of the electronic friction has to be extracted from such experiments with care. We will discuss the experimental results within the electronic friction model and show that the small width and high contrast of the 2PC can only be described by assuming a friction coefficient that depends on electron temperature. Similar to the case of O on Pt(111), we interpret this temperature dependence as an empirical description of the indirect heating of the FT mode by anharmonic coupling through the FR mode.

II. EXPERIMENT

The experiments were performed in an ultrahigh vacuum chamber at a base pressure below 1×10^{-10} mbar using a Pt(11,12,10) crystal with a terrace width of 11 unit cells and step edges parallel to the $[11\bar{2}]$ direction. The sample was cleaned by standard sputter-anneal cycles and oxygen treatment[17] and could be cooled down to 60 K. Surface cleanness and order have been verified by Auger spectroscopy, low-energy electron diffraction (LEED), and temperature-programmed desorption (TPD) of atomic oxygen. The latter is particularly sensitive to carbon contaminations that strongly suppress dissociative adsorption of oxygen. A gas-dosing system has been used to expose the surface with a controlled and uniform flux of CO through a microcapillary array. The amount of adsorbed CO was determined by TPD.

The optical setup is similar as used in Ref. 17. It is based on an amplified Ti:sapphire laser system that generates laser pulses with a duration of 60 fs and a central wavelength of 800 nm. Two optical paths were set up for pump and probe-laser pulses, respectively. The strong pump beam was split into two orthogonally polarized beams, which were combined collinearly with introduction of a variable time delay. The slightly focused pump beams were incident on the sample at 42.5° from the surface normal and formed a spot of 1.16 mm diameter [full width at half maximum (FWHM)]. The spot diameters have been determined by the knife-edge method. The total absorbed pump fluence could be varied between $0.5-5\ \mathrm{mJ/cm^2}$ by a combination of a half-wave plate and a thin-film polarizer. Absorbed fluences have been calculated from the measured average powers with the help of the optical constants of Pt (Ref. 31) and by assuming a perfect Gaussian beam profile. The weak p-polarized probe pulses were incident at 45° from the surface normal and were focused into a spot of 90 μm in diameter. The absorbed fluence was kept below $0.4\ \mathrm{mJ/cm^2}$ to prevent laser-induced diffusion due to the probe pulses. The p-polarized component of the specular reflected SH that was generated by the probe pulses on the sample surface was separated from the fundamental and detected with a photomultiplier tube using boxcar technique.

A well-defined initial distribution of CO molecules on the Pt surface has been generated by taking advantage of the higher binding energy of CO at step sites compared to terrace sites. The large difference of 0.5 eV (Refs. 27, 32, and 33) makes it relatively easy to prepare a selective occupation of step sites by dosing CO at elevated temperatures. Figure 1 shows a series of TPD spectra for different uptakes of CO dosed at substrate temperatures of 80 and 430 K, respec-

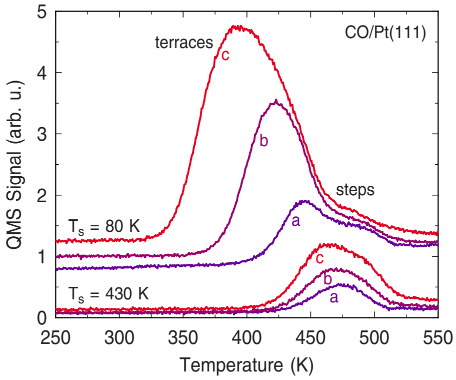

FIG. 1. (Color online) (a)–(c) Thermal programmed desorption spectra for increasing amount of CO dosed on vicinal Pt(111) at a substrate temperature of T_s=430 K (three lower curves) and T_s=80 K (three upper curves), respectively. The latter data have been vertically shifted for clarity. (c) Dosage corresponds to the saturation coverage at T_s=80 K, whereas (b) and (a) are smaller by a factor of 5/3 and 5, respectively.

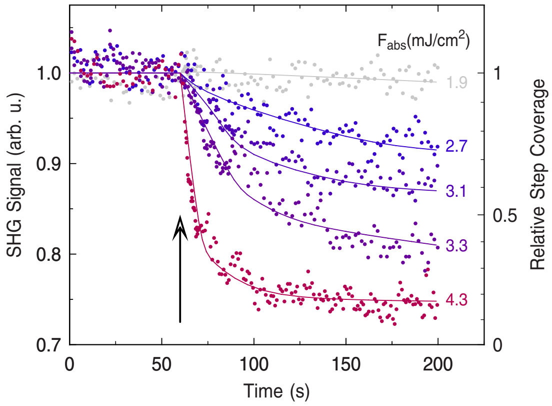

FIG. 2. (Color online) SH signal as a function of time for various absorbed fluences of the pump-laser pulses applied on a Pt surface with CO-covered step edges. The pump-laser pulses were applied at t=60 s, which leads to a reduction in the SH signal due to the depletion of the step sites. All measurements were done at a substrate temperature of 60 K.

tively. The 80 K data consist of a main peak that shifts to lower temperatures with increasing coverage and a shoulder at a temperature of about 480 K. The first can be assigned to CO desorbed from terrace sites, whereas the latter can be attributed to desorption of CO from step sites.[34] The small fraction of CO desorbed from step sites reflects the rather low step density of our sample. Fully occupied step edges have been prepared by dosing CO at a substrate temperature of 430 K where CO molecules attaining the surface perform fast terrace diffusion due to the low diffusion barrier[33] until they are trapped at step sites or desorb from the terraces. The corresponding TPD spectra show almost only desorption from step sites. This high adsorption temperature has been chosen in order to exclude delayed adsorption of CO onto terrace sites due to the elevated background pressure of CO right after the dosing. For the laser-induced diffusion experiments, the sample has been cooled down to 60 K in order to exclude thermally induced diffusion. This temperature is well below the threshold for significant migration onto the terraces.[27,33] In this way the distribution of CO molecules on the surface is frozen in between the laser shots and can be continuously monitored by SHG.

III. RESULTS

Figure 2 shows the SH signal during induced diffusion as a function of time for different pump fluences at a substrate temperature of 60 K. Initially, the step edges were covered with CO as described above. For each measurement, the pump beam path was unblocked at t=60 s. Only one of the pump beams has been used for these measurements. The repetitive excitation of the surface at a rate of 1 kHz led to a continuous reduction in the SH signal due to the depletion of the step sites that became faster with increasing laser fluence. The depletion could be clearly related to diffusion from steps onto the terraces since this process could be reversed by subsequent annealing of the sample to temperatures well above 80 K where CO becomes mobile on the terraces of Pt(111).[27] For adsorbed fluences below 5 mJ/cm^2 such cycles of laser-induced diffusion onto the terraces and thermally induced diffusion back to the steps result in a reproducible SH signal. Therefore, desorption can be neglected in the investigated fluence regime. At an absorbed fluence of 6 mJ/cm^2, Backus *et al.*[26] estimated that about 0.1% of the molecules desorb in a single laser shot. The comparison of the SH signal levels for the clean surface and for the surface with fully occupied step edges has been used to relate the SH signal to the step occupation as indicated by the right scale in Fig. 2. For this purpose we have assumed a linear relation between the nonlinear susceptibility and the step coverage that leads to a quadratic dependence of the SH intensity on step coverage as in the case of O/Pt(111).[17] In the case of oxygen adsorption, however, the SH signal was increasing with step depletion for the same polarization combination of a p-polarized fundamental beam and a p-polarized SH beam.[17,18] This difference is related to the opposite change in the work function on adsorption, which is, for metal surfaces, often directly related to the change in the SH signal.[35] Whereas the adsorption of O increases the work function of Pt, the adsorption of CO leads at first to a decrease in the work function.[36]

Hopping probabilities per laser shot from the fully occupied steps onto the terraces have been determined for each data set from the initial temporal change in the relative step coverage $d\theta/dt$ by $P=-(d\theta/dt)T$ where T=1 ms is the time between two sequent laser shots. Figure 3 shows the dependence of P on the absorbed laser fluence F in the investigated range of F=1.9–4.3 mJ/cm^2. In this range the fluence dependence can be described by a simple power law $\propto F^6$ as illustrated by the solid line. This is a much weaker dependence on laser fluence compared to laser-induced diffusion of O on Pt(111) (Ref. 17) where an extraordinarily strong nonlinear dependence $\propto F^{15}$ has been observed. Typical laser-induced desorption experiments, on the other hand, could be described by power laws with exponents in the range of 3–8.[37–40] Such a simple power law, however, is applicable only in a limited fluence range. The electronic friction model

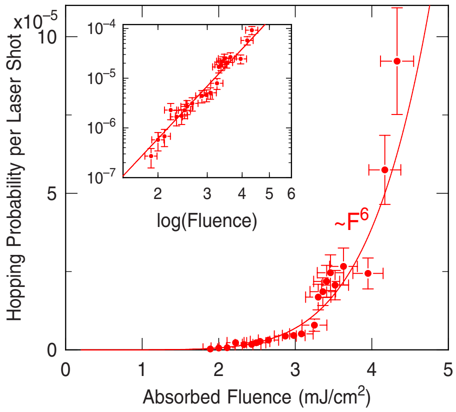

FIG. 3. (Color online) Fluence dependence of the extracted probabilities per laser shot for hopping of CO from the fully occupied steps onto the initially empty terraces of the vicinal Pt(111) surface induced by the fs-laser pulses. The solid line depicts a power law $\propto F^6$ where F is the absorbed laser fluence. The inset shows the same data in a double-logarithmic scale.

predicts in general an attenuating nonlinearity with increasing fluence.[22]

For a comparison with the experiment of Backus *et al.*[26] on Pt(533), we have to extrapolate our data to a fluence of 6 mJ/cm^2 where Backus *et al.*[26] reported a hopping probability of 10% per laser shot. At this fluence the desorption probability has been estimated to 0.1%, which made it necessary to use a CO background pressure for repetitive measurements. From our data at lower fluences we extrapolate a hopping probability, which is smaller by a factor of more than 2 orders of magnitude. This seems to be a very large difference. Due to the strong fluence dependence of F^6, however, even a change in the fluence scale by a factor of 2.15 changes the hopping probability by 2 orders of magnitude. In our experiment, we carefully determined the absorbed fluence by measuring the pulse energy using a power meter (uncertainty ≈5%), the beam profile using the knife-edge method (uncertainty ≈20%), and the optical absorption using the optical constants of platinum[31] under the assumption of an intensity-independent absorption, which has been verified by Her *et al.*[41] for absorbed fluences up to several mJ/cm^2. Yield averaging of the laser fluence[40] was not necessary in our experiment since we probed only the central part (≈1%) of the pumped area. We estimate that the absolute values of our fluence data are accurate within 30%, while relative changes could be determined better than 2%. Therefore the uncertainty of our fluence data cannot explain the difference between the two experiments. Another difference between the two experiments is the step density of the Pt surface, which is a factor of 3 lower in our case. This might result in slightly different diffusion barriers at the step edges, which could significantly change the hopping probability due its exponential dependence on the diffusion barrier.

The nonlinear dependence of the hopping probability on laser fluence is the prerequisite for the application of a two-pulse correlation scheme,[8] which makes it possible to analyze the dynamics of the energy transfer between the initially excited electrons and the adsorbates. For this purpose, diffusion has been induced for different time delays between both pump beams. In laser-induced desorption experiments two-pulse correlations were typically recorded only at one particular fluence due to the limited dynamic range of the particle detection scheme that does not allow much averaging. In contrast to that, the large dynamic range of the SHG-detection scheme of diffusion used here made it possible to record two-pulse correlations for different laser fluences as shown in Fig. 4 for two total absorbed fluences of 2.9 and 3.9 mJ/cm^2, respectively. Both data sets show a high contrast between zero and large delays and a narrow peak with a width below 0.5 ps (FWHM). This is about a factor of 3 narrower than observed for O/Pt(111) (Ref. 18) and also narrower than observed in laser-induced desorption experiments.[8,40,42–45] As indicated by the solid lines in Fig. 4, the width of the 2PCs is larger for the higher laser fluence.

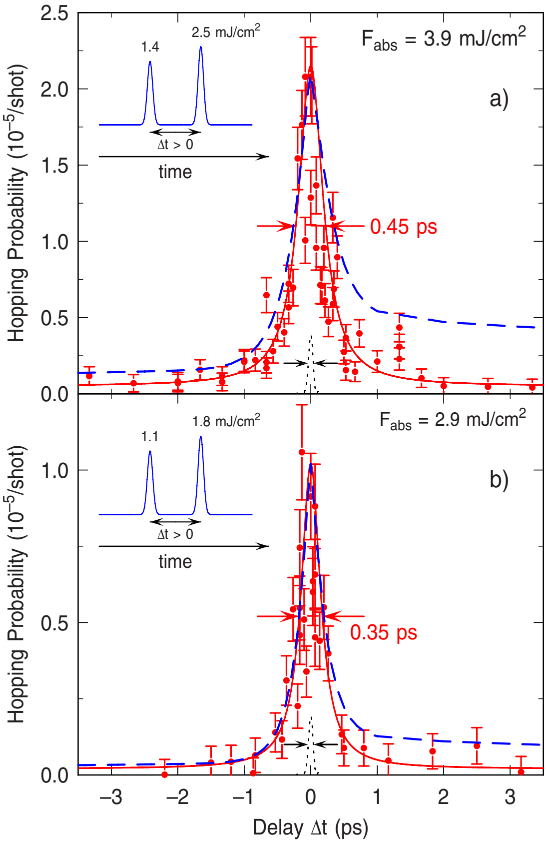

FIG. 4. (Color online) Two-pulse correlation traces (data points) for a total absorbed fluence of (a) 3.9 and 2.9 mJ/cm^2 (b). Solid red Lorentzian lines are to guide the eyes. The time resolution is illustrated by the cross-correlation trace of the pump pulses in both panels (black dotted lines). The insets show the partitioning of the absorbed fluence between the two pump pulses. Model calculations are depicted by blue dashed lines, respectively (see text).

IV. DISCUSSION

The width of a 2PC is often used as an estimation of the time scale on which sufficient energy flows from the laser-excited metal substrate to the adsorbate and makes it possible to distinguish between an electron- and a phonon-mediated excitation process.[7] A width below a few picoseconds is a clear indication that the coupling between the substrate and the motion of the CO molecules is electron mediated since the electron temperature cools down after laser excitation on a time scale of typically 1 ps due to electron-phonon coupling and diffusive motion into the substrate. The phonon system, on the other hand, can store the energy for much longer times, which results in a width of the 2PC of several picoseconds for phonon-mediated coupling.[44] The small width of below 0.5 ps observed in the present experiment qualitatively confirms a fast electronic energy transfer from the optically excited substrate electrons to the lateral motion as reported by Backus *et al.*[26] As will be shown below, it is, however, not possible to identify the energy-transfer time directly with the width of the 2PC. This is demonstrated by the fact that the width of the 2PC depends on laser fluence. For weaker excitation, the 2PC becomes narrower.

The narrowing of the 2PC with decreasing laser fluence can be well reproduced by model calculations within the generalized friction model of Brandbyge *et al.*,[13] which follows the same line as described in Ref. 22. The results are shown as dashed lines in Fig. 4. Similar to the case of O/Pt(111) the narrow width and the high contrast of the 2PC observed in the present experiment can be only reproduced by introduction of an electronic friction coefficient η_e that depends on excitation density. Interestingly, we find good agreement between data and model if we use the same empirical dependence of η_e on electron temperature T_e of the form $\eta_e = \eta_0 T_e^2(t)$ as has been used to successfully describe the data for hopping of O on Pt(111).[18,22] The curves shown in Fig. 4 have been calculated using $\eta_0 = 10^5\ \mathrm{K}^{-2}\ \mathrm{s}^{-1}$ and a diffusion barrier of $E_{\mathrm{diff}} = 0.5$ eV as has been reported by Ma *et al.*[46,47] using linear optical diffraction from adsorbate gratings of CO on stepped Pt(111). The model calculations show a clear narrowing as well as an increased contrast of the 2PC for the lower fluence. Only the asymmetry between positive and negative delays due to the different absorbed fluences of the two pump pulses is slightly overestimated by the model. The asymmetry, however, is less pronounced for the low-fluence data.

As discussed for the modeling of diffusion of O/Pt(111) (Refs. 18 and 22) the introduced dependence of η_e on electron temperature might be hypothetical and give only an effective description of an anharmonic coupling between different vibrational modes. Ueba *et al.*[49] showed that the consideration of a general anharmonic potential for the adsorbate motion results in a heat transfer coefficient that depends on the adsorbate temperature T_a and not on the electron temperature T_e.[48,49] Additionally they showed that a coupling between different vibrational modes results in an effective electronic friction that depends on the temperature of the coupling partner mode.[30] Since the optical excitation results at first in a heating of the substrate electrons, an explicit dependence of the friction on adsorbate temperature can be, however, also viewed as an implicit dependence on electron temperature.

The narrowing of the 2PC with decreasing fluence is a general phenomenon of electronically induced surface reactions and does not only appear within the electronic friction model for a temperature-dependent friction. In order to illustrate this effect Fig. 5 shows results of a model calculation using a constant electronic friction, which corresponds to the empirical friction model.[10,11] The curves in Fig. 5 show the reaction rate R, electron temperature T_e, and ion temperature T_i as a function of time for two different absorbed laser fluences. The time dependence of T_e and T_i has been calculated with the two-temperature model[50] using material parameters for Pt reported in Ref. 51 (electron-phonon coupling parameter $g = 6.76 \times 10^{17}\ \mathrm{W\ K^{-1}\ m^{-3}}$, electronic specific heat $\gamma = 748\ \mathrm{J\ K^{-2}\ m^{-3}}$, thermal conductivity at 77 K $\kappa_0 = 71.6\ \mathrm{W\ K^{-1}\ m^{-1}}$, and Debye temperature $T_D = 240$ K). In the empirical friction model the reaction rate is given by an Arrhenius-type expression of the form $R(t) = k_0 \exp[-E_{\mathrm{diff}}/k_B T_a(t)]$ where k_0 is a constant prefactor, T_a is the adsorbate temperature, and the time integral $p = \int R(t)dt$ corresponds to the hopping probability per laser shot. The adsorbate temperature was coupled to the electron temperature for this calculation using a constant electronic friction of $\eta_e = 10\ \mathrm{ps}^{-1}$. The time dependence of T_e and T_i reflects the different magnitude and temperature dependence of electron and ion specific heat. For an absorbed fluence of $4\ \mathrm{mJ/cm^2}$ the electron temperature rises above 2000 K while the ion temperature remains below 500 K. Due to the linear dependence of the electronic specific heat on temperature, the maximum of T_e is increased only by a factor of about $\sqrt{2}$ when the laser fluence is doubled, whereas the maximum of T_i increases nearly linear with laser fluence. Clearly, the increase in the laser fluence considerably changes the dynamics of the reaction rate. The rise as well as the fall of $R(t)$ are slowed down for the higher fluence. This slowdown is mainly caused by the exponential dependence of the R on the inverse adsorbate temperature and would also occur if the adsorbate temperature is governed by the ion temperature. The reduced increase in T_e with laser fluence, however, further enhances this effect. Even if the peak magnitude of the reaction rate as well as its time integral increase nonlinear with laser fluence,

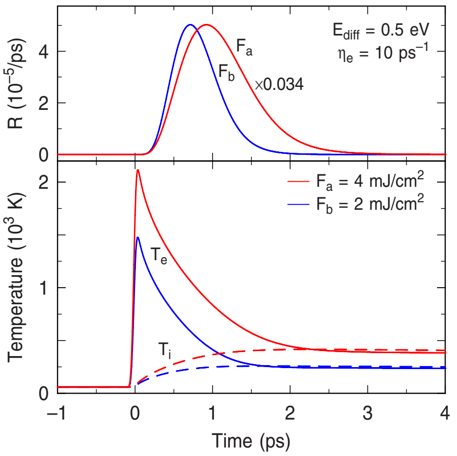

FIG. 5. (Color online) Time dependence of electron temperature T_e, ion temperature T_i, and reaction rate R for two different absorbed fluences of 2 (blue curves) and $4\ \mathrm{mJ/cm^2}$ (red curves), respectively. R has been calculated for a barrier height of $E_{\mathrm{diff}} = 0.5$ eV, a constant electronic friction of $\eta_e = 10\ \mathrm{ps}^{-1}$, and a prefactor of $k_0 = 1\ \mathrm{ps}^{-1}$. The rate for $F_a = 4\ \mathrm{mJ/cm^2}$ has been scaled for better comparison.

its delayed response for increasing fluence results in a broadening of the two-pulse correlation. This broadening should occur in all kinds of laser-induced surface reactions at metal surfaces, which are driven by either the hot electrons or ions of the substrate. It shows that the extraction of a friction coefficient from two-pulse correlations requires not only an appropriate modeling of the energy-transfer dynamics but also careful determination of the absorbed laser fluence.

V. SUMMARY

In summary, we have studied femtosecond-laser-induced diffusion of CO from steps onto terraces of a Pt(111) crystal with low step density in a low-fluence regime of $F = 1.9-4.3\ \mathrm{mJ/cm^2}$. In this fluence range the hopping probability shows a nonlinear dependence on laser fluence of the form F^6. The recording of two-pulse correlations for two different laser fluences revealed a dependence of their width on laser fluence. This dependence is a general phenomenon in laser-induced substrate mediated surface reactions and can be qualitatively described even within the empirical friction model with constant electronic friction. A reasonable description of the narrow width and high contrast of the two-pulse correlation, however, requires the introduction of a friction coefficient that depends on excitation density. Similar to the case of O/Pt(111) we interpret this dependence as an effective description of the coupling between different vibrational modes that might additionally show anharmonicity.

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