

Lateral hopping of CO molecules on Pt(111) surface by femtosecond laser pulsesM. Hayashi,¹ Y. Ootsuka,¹ M. Paulsson,^{1,2} B. N. J. Persson,³ and H. Ueba^{1,*}¹*Division of Nanotechnology and New Functional Material Science, Graduate School of Science and Engineering, University of Toyama, Toyama 930-8555, Japan*²*Division of Physics, School of Pure and Applied Natural Science, University of Kalmar, 391 82 Kalmar, Sweden*³*IFF, FZ-Jülich, 52425 Jülich, Germany*

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Theory of heat transfer between adsorbate vibrational degrees of freedom and ultrafast laser heated hot electrons including vibrational intermode coupling is applied to calculate two-pulse correlation, laser fluence dependence and time dependence of lateral hopping of CO molecules from a step to terrace site on a stepped Pt (111) surface. The intermode coupling is a key ingredient to describe vibrational heating of the frustrated translation mode responsible for the CO hopping. The calculated results are in good agreement with the experimental results, especially if we scale down the experimentally determined absorbed fluence. It is found that CO hopping is induced by indirect heating of the FT mode by the FR mode with a strong frictional coupling to hot electrons.

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I. INTRODUCTION

Real space and/or real time monitoring of adsorbate motions and chemical reactions on a metal surface are the ultimate techniques to study adsorbate reaction dynamics.¹ The first real-space observation of molecular motion induced by femtosecond laser pulses has been made with a scanning tunneling microscope (STM) by Bartels *et al.*² for the system CO/Cu(110). They demonstrated a possibility of combining direct imaging of a single CO molecule on a Cu (110) by STM with access to its lateral hopping induced by femtosecond laser excitation, and found that electronic excitation of the substrate induced by absorption of short laser pulses gives rise to hopping of CO parallel and perpendicular to the close-packed rows, in addition to desorption with weaker probability compared to lateral hopping. An STM, which permits a direct imaging of a single molecule before and after laser irradiation, cannot be used to monitor laser induced adsorbate motions in ultrafast time scale, while nonlinear time-resolved optical spectroscopy with unique high-surface sensitivity enables adsorbate motions to be monitored in a time scale of adsorbate dynamics (see recent reviews on ultrafast surface spectroscopies [two-photon photoemission,³ sum-frequency generation (SFG),^{4,5} and second-harmonic generation (SHG)⁶] of surfaces and adsorbates). The combination of these techniques holds great promise to gain deeper insights into adsorbate dynamical processes at surfaces.

The interesting area of this so-called surface femtochemistry includes processes such as diffusion and desorption of adsorbed atoms/molecules and association between coadsorbed reactants, respectively. The central questions of such studies are how and on what time scale is the initial energy of the exciting laser pulse transferred to the actual reaction coordinate. The vibrational properties of chemisorbed CO molecules on metal surfaces have received a great deal of interests over decades.^{4,7} In particular, the low-frequency modes such as the frustrated translational (FT) and frustrated rotational (FR) mode to which the C-O stretch mode anhar-

monically couples are known to be responsible for the temperature dependence of the frequency shift and the width in the infrared absorption spectra of C-O stretch mode. As will we demonstrate here, both modes now play a key role in CO hopping on surfaces.

Recently two different groups have carried out time-resolved measurement on lateral motion of CO molecules on an ultrafast laser heated Pt surface.^{8,9} Employing pump-probe SFG spectroscopy Backus *et al.* observed hopping of CO molecules from step to terrace site on a Pt (533) surface.⁸ A femtosecond pump pulse induces the motion of CO molecules on the surface, and the motion is followed in real time with variably delayed probe pulses. Their awkward construction of a stepped Pt surface, and the fact that the internal C-O stretch frequency depends on the precise location of the CO molecule on this type of surface, have enabled a real-time monitoring of CO hopping at simultaneous high temporal and spatial resolution. The adsorbate motion is brought about by the heating of Pt electrons with ultrafast laser pulses. Because the heat capacity of the electrons is very low, they reach high enough temperatures faster than 1 ps. These hot electrons transfer energy to the adsorbates low frequency FT and FR mode involved in hopping motion, and these modes are characterized by their time dependent temperatures. They found that the excitation of the FR mode is essential in the CO hopping process.⁸ Direct excitation of the FT mode is significantly too slow to cause the hopping motion of the CO within the subpicosecond time scale observed in the experiment. Because of the atomic corrugation of the surface, the FT mode always involves rotation of the molecular axis with respect to the surface normal. This rotation has to be compensated in order for the molecule to settle on the neighboring site, which can only be achieved by excitation of the FR mode.

The hopping motion is like a dance, in which the CO molecules execute concerted rocking and translational steps.¹⁰ It should be mentioned here that long before this experiment Dobbs and Doren¹¹ have demonstrated using classical molecular dynamics that the bending and the lateral translational motions are strongly coupled near the transition

state for diffusion in a model system of CO/Ni(111). This mechanism permits excitation of the FT mode by the FR mode. The subtleties of the coupling of low frequency modes to reaction coordinate in surface-adsorbate systems may be generally more complex than we imagine. The idea behind such anharmonic coupling between different modes whereby only one of them needs to be initially excited has been originally used to rationalize hopping experiments of CO molecules on a Cu(111) surface by electron attachment during vertical manipulation with a STM.¹² This picture is quite general and has been applied to various other systems as we describe hereafter.

A theory of energy (heat) transfer between the laser heated hot electrons in metals and the vibrational modes of adsorbates in the presence of the vibrational mode coupling has been successfully applied to calculate the transient behavior of the CO hopping probability.¹³ It was shown that, although energy exchange solely via excitation of the FT mode is significantly too slow to cause the hopping motion of the CO molecule, the strong coupling to the FR mode heats up the FT mode enough to induce hopping. It is important to note that high excitation of the FR mode by hot electrons is absolutely required for the FT mode to be heated high enough for the hopping motion within a subpicosecond time scale. It should also be mentioned that in the harmonic approximation the FT and FR modes of a CO molecule on metal surfaces are orthogonal modes in a sense that energy cannot flow from one mode to another. When we include the coupling to the substrate electronic degrees of freedom, it becomes possible that energy can flow from one mode to another via substrate electronic excitations, i.e., electron-hole pair excitations in metal substrates.

A technique of the time resolved SHG has been employed to study lateral hopping of atomic oxygen on a vicinal Pt(111) surface induced by femtosecond laser pulses.¹⁴ The experimental results of the two-pulse correlation (2PC) and the fluence dependence of the hopping probability were compared to that calculated using an empirical temperature dependent electronic friction coefficient $\eta_e[T_e(t)]$ in the conventional heat transfer equation. The necessity to introduce $\eta_e[T_e(t)]$ for the consistent modeling of the results was interpreted in terms of an indirect excitation mechanism. They proposed that the substrate electrons primarily excite O-Pt vibrations which then couple anharmonically to the FT mode required to overcome the barrier for lateral motion. This scenario of the elementary processes of indirect activation of the FT mode via the mode coupling to the O-Pt mode having a efficient heat transfer from the hot electrons is supported by a successful reproduction of the experimental results using a theory of heat transfer via vibrational mode coupling.¹⁵

Recently Lawrenz *et al.*⁹ revisited a time resolved study of CO hopping on a Pt(111) surface. Using the advantage of high sensitivity of SHG, they observed a nonlinear dependence of the hopping rate on the laser fluence F (i.e., $\propto F^6$) and a narrow 2PC width of below 500 fs. The result is compared well to the unexpectedly fast motion with a time constant 500 ± 150 fs estimated from the time-dependent step site occupation determined by the time-resolved SFG spectra by Backus *et al.*⁸ Similar to the case of O/Pt(111) the narrow width of the 2PC has been reproduced by introduction of an

electronic friction coefficient $\eta_e(t) = \eta_0 T_e^2(t)$ that depends on excitation density. For CO molecules on the stepped Pt surfaces the most representative nonlinear time-resolved spectroscopies (SFG and SHG) have been employed to observe time-dependent hopping rate, 2PC and fluence dependence and these experimental results deserves to be analyzed in terms of an appropriate modeling of energy (heat) transfer dynamics, i.e., as described above excitation of the FR mode plays a key role in lateral motion of CO molecules.

In this work, we revisit lateral hopping of CO molecules from a step edge to terrace site on a stepped Pt (111) surface. The heat transfer equations for coupled harmonic oscillators are used to calculate the 2PC and the fluence dependence of the as well as the time-dependent hopping rate in order to establish comprehensive analysis of this system. It is found that all the calculated results nicely reproduce the experimental results using the same set of the parameters (for the 2PC and fluence dependence if the systematic scaling down of the absorbed fluences is permitted) including the barrier height, the frictional coupling of the FT and FR mode to hot electrons and the coupling constant between these modes.

II. THEORY AND RESULTS

According to our general formula¹⁶ of the energy transfer between modes **a** (with the energy of $\hbar\omega_a$) and **b** ($\hbar\omega_b$) excited by the frictional coupling $\eta_{a(b)}$ to the hot electrons, the transient temperature $T_a(t)$ and $T_b(t)$ of each mode is calculated by the following coupled equations,

$$\frac{dT_a(t)}{dt} = \left[\eta_a + \eta_{ab} \frac{k_B T_b}{\hbar\omega_b} \right] (T_e - T_a), \quad (1)$$

$$\frac{dT_b(t)}{dt} = \left[\eta_b + \eta_{ba} \frac{k_B T_a}{\hbar\omega_a} \right] (T_e - T_b), \quad (2)$$

where the indirect frictional couplings between two different modes have a relation $\eta_{ab}/\eta_{ba} = \omega_a/\omega_b$. The mode coupling plays a dominating role in the heating of mode **a**, responsible for a motion even when its direct heating via η_a is small, as is often the case for parallel adsorbate vibrations. It is also important to remark here that, in the harmonic approximation, the FT and FR modes of CO on metal surfaces are orthogonal modes in a sense that energy cannot flow from one mode to another. However, when we include the coupling to electron-hole pair excitations in substrates, it becomes possible that energy can flow from one mode to another via substrate electronic excitations. It is also noted that after a long enough time the adsorbate-metal system reaches thermal equilibrium $T_e = T_a = T_b$, as expected because of the coupling to the substrate electrons. Equations (1) and (2) are combined with the so-called two-temperature model (2TM)¹⁷ to calculate the laser heated hot-electron temperature $T_e(t)$.

We first calculate $T_e(t)$ for a Pt surface using the material parameters (electron-phonon coupling, electronic and ion heat capacities, electronic thermal conductivity, and Debye temperature) reported in Ref. 18 at the initial substrate temperature of 60 K for a Gaussian shaped laser pulse (the wavelength of 800 nm and the pulse width of 50 fs) at the

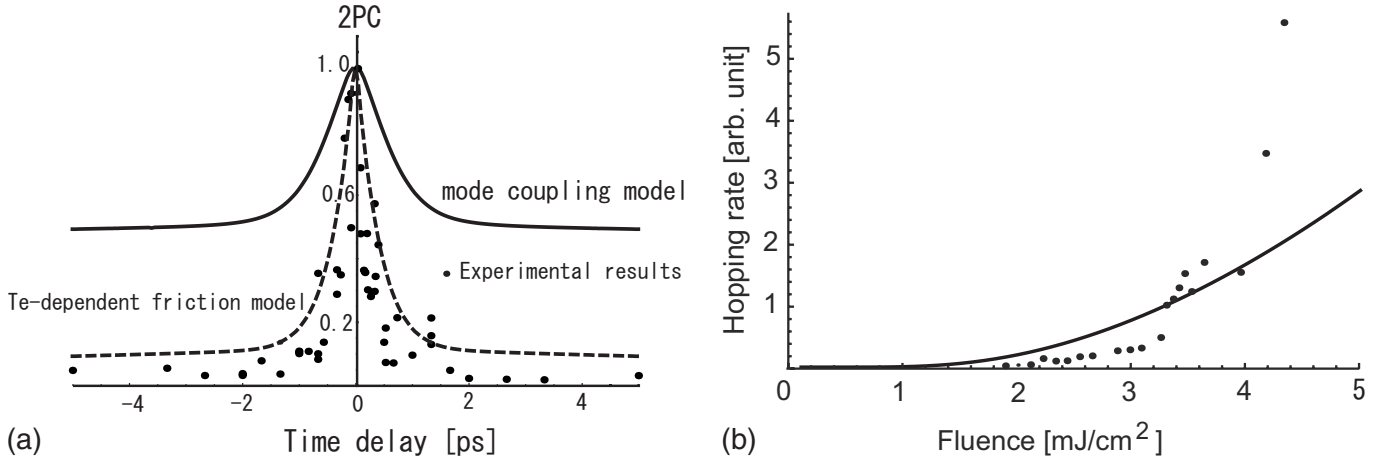


FIG. 1. (a) Calculated 2PC of CO hopping using mode coupling model (solid curve) and T_e -dependent friction model (dashed curve) compared to the experimental results (black dots) from Ref. 9. (b) Calculated fluence dependence of the hopping rate (solid curve) using mode coupling model compared to the experimental results (black dots) from Ref. 9. See the text for the parameters used herein.

fluence $F=2 \text{ mJ}/\text{cm}^2$. The $T_e(t)$ thus calculated enters into Eqs. (1) and (2) to obtain $T_a(t)$ for the FT mode ($\hbar\omega_a=4.4 \text{ meV}$) and $T_b(t)$ for the FR mode ($\hbar\omega_b=51 \text{ meV}$) for the CO molecule on the Pt(111) surface.⁸ Among three friction constants $\eta_a=0.25/\text{ps}$ and $\eta_b=5/\text{ps}$ are fixed for the FT and FR mode at the step site,^{8,19,20} respectively, and we take η_{ab} as a free parameter. It is remarked here that such a strong coupling time ($\tau_b=1/\eta_b=0.2 \text{ ps}$) of the FR mode to the hot electrons was reported on Pt (111) in the pump-probe SFG spectra of the C-O stretch mode during photodesorption.²⁰ For CO molecules on metal surfaces it has been widely accepted that the C-O stretch and FR modes relax rapidly due to electron-pair excitations in substrates, while FT modes have considerably longer lifetimes.²¹ For example on Cu(100) the lifetimes are about 1ps and 40 ps for the FR and FT modes, respectively.²²⁻²⁴

We calculate the 2PC and the fluence dependence of the hopping rate using a simple Arrhenius type formula $R(t)=R_0 \exp[-U_0/k_B T_a(t, t_d)]$, here $T_a(t, t_d)$ shown in Fig. 2 is calculated using a set of friction constants $\eta_a=0.25/\text{ps}$, $\eta_{ab}=4/\text{ps}$ and $\eta_b=5/\text{ps}$. In Ref. 13 we used a barrier height $U_0=0.4 \text{ eV}$ for hopping from a step site to a terrace site at the CO coverage $\theta=0.3 \text{ ML}$.²⁵ In the present calculation we take $U_0=0.5 \text{ eV}$,^{26,27} which was used in the analysis by Lawrenz *et al.*⁹ Figure 1(a) compares the calculated 2PC(t_d) at the fluence $F_1=F_2=2 \text{ mJ}/\text{cm}^2$ using the mode-coupling model (solid curve) with the experimental results⁹(black dots), here both are normalized at $t_d=0$. In spite of using a similar set of parameters (η_a , η_{ab} , η_b , and U_0), which could reproduce the transient behavior of CO hopping rate on a Pt (533),^{8,13} the 2PC calculated using the mode-coupling model exhibits too broad width at $t_d=0$ and too large wings at long delay times compared to the experimental results. The width of a 2PC provides us with a time scale of heat transfer from hot electrons and/or from phonons in the substrate to the adsorbate vibrational degree of freedoms, and its dependence on the laser fluence and on the barrier height is of general importance irrespective to any kind of modeling of adsorbate dynamics induced by ultrafast laser heating. Here, one should bear in mind that this is not a time constant of adsor-

bate reaction, which is estimated from the time-dependent reaction rate as shown below in Fig. 5. The fluence dependence of the hopping rate shown in Fig. 1(b) (solid curve) also exhibits a large deviation from the experimental results (black dots) at the higher fluences. Here, a prefactor k_0 is chosen to fit the numerical result to the experimental data at $F=3.5 \text{ mJ}/\text{cm}^2$.

Also shown (dashed curve) in Fig. 1(a) is the 2PC calculated using a modified heat transfer equation

$$\frac{dT_a(t)}{dt} = \eta_e[T_e(t)](T_e - T_a), \quad (3)$$

with $\eta_e[T_e(t)]=\eta_0 T_e^2(t)$, $\eta_0=10^5 \text{ K}^{-2} \text{ s}^{-1}$ with $U_0=0.5 \text{ eV}$ (Ref. 9) for the same fluences. This empirical modeling quite nicely reproduces their experimental result as shown in Fig.

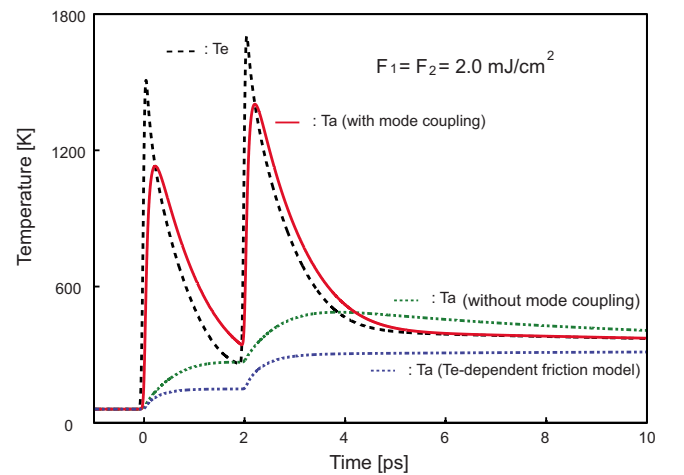


FIG. 2. (Color online) Transient profile of the hot-electron temperature $T_e(t)$ (black dashed curve) and $T_a(t)$ calculated with (red solid curve) and without (green dotted curve) mode coupling, and with the modified friction model with $\eta_e[T_e(t)]$ (blue dotted curve) using the same set of parameters as in Fig. 1. The $T_b(t)$ mode temperature $T_b(t)$ for the FR mode (not shown here) immediately follows $T_e(t)$ due to a strong frictional coupling.

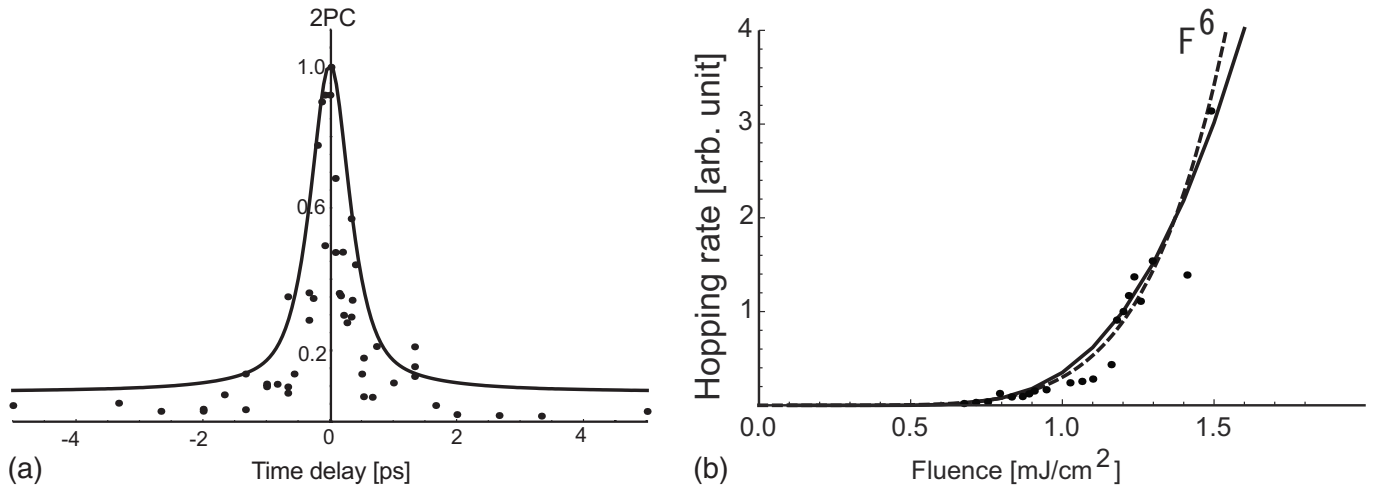


FIG. 3. (a) Comparison of the calculated 2PC (solid curve) with the experimental result (black dots). (b) Comparison of the calculated fluence dependence of the hopping rate (solid curve) with the experimental result (dashed dots). The black dotted curve is a power law of F^6 .

1(a). The FT-mode temperature $T_a(t)$ (the blue dotted curve in Fig. 2) calculated by Eq. (3), however, shows a slow and gradual heating and cooling so that the FT mode temperature cannot be heated high enough to induce hopping within subpicosecond time scale. Figure 2 also shows $T_e(t)$ (black dashed curve), $T_a(t)$ with (red solid curve) and without (green dotted curve) mode-coupling using the same set of parameters in Fig. 1. Here, $T_b(t)$ (not shown) follows almost the same transient profile as $T_e(t)$. It is clear that $T_a(t)$ of the FT mode is heated up high enough via the mode coupling with the FR mode having a strong frictional coupling to hot electrons. Backus *et al.*⁸ found that the transient shape and intensity of the experimental hopping probability as a function time obtained from the time-resolved SFG are in excellent agreement with the time dependent temperature of the FR mode whose time dependent temperature was calculated using a conventional heat transfer equation. This finding led to a conclusion that a rotational motion of the CO molecule, rather than translation, is pivotal for this hopping process. Before this work, no one has ever been able to make such a direct comparison between a transient behavior of an ultrafast surface reaction and that of a temperature of the vibrational degrees of freedom. On the other hand, $T_a(t)$ calculated using $\eta_e[T_e(t)]$ exhibits slow heating and cooling compared to that calculated by the mode coupling model. This was also for the O/Pt system (see Fig. 2 in Ref. 15). This seems to indicate that CO hopping does not occur within the subpicosecond time scale. Based on these reasoning's we cannot identify the low adsorbate temperature obtained by the modified friction model with a real FT mode excitation.

The narrowing of the 2PC with decreasing (increasing) fluence (barrier height) is known to be a general phenomenon of electronically induced surface reactions.^{9,24} Among many parameters in our modeling we are not permitted to increase U_0 over 0.6 eV according to the available experimental data^{25,28} and the references therein. We also confirmed that an increase η_{ab} (a free parameter in our modeling) does not cause an appreciable narrowing as far as we

assume a strong η_b . An important experimental issue concerns the difficult to determinate absorbed laser fluence, which has been shown to be a critical experimental parameter.² There is a general agreement that a systematic uncertainty in the experimentally determined fluence may exist. Moreover, it has also been shown that the actual temperatures at the surface may vary from those calculated using the 2TM.²⁹ This deviation from the 2TM is expected only for small fluences, but the overestimation of a temperature does not occur at higher fluences.³⁰

In order to achieve a better agreement with both the 2PC and the fluence dependence with the same set of parameters, we attempt to recalculate them by scaling down the experimentally determined fluence, while keeping the rest of the parameters same as before, i.e., $U_0=0.5$ eV, $\eta_a=0.25$ /ps, $\eta_{ab}=4$ /ps, and $\eta_b=5$ /ps. The scaling is motivated by the preceding discussion and the difficulty of accurately determining the absorbed fluence.⁹ The calculated 2PC(t_d) and the fluence dependence $R(F)$ of the hopping rate using $F_1=F_2=0.7$ mJ/cm² (scaling down by a factor of 2.7–2.8 from Ref. 9) are shown in Fig. 3(a). The calculated 2PC (solid curve) is little bit broader than the experimental results (black points) by a factor of 1.7. The further narrowing can be obtained either by lowering U_0 or the laser fluence. One more remark here is that usually 2PC experiment is performed with different pulse intensities F_1 and F_2 . The positive consequence is that the 2PC trace becomes asymmetric at the wings as seen in the $T_e(t)$ -model calculation (see Fig. 4 in Ref. 9). The calculated 2PC(t_d) using the same fluence $F_1=F_2$ and the experimental data exhibit almost no asymmetry.

The solid curve in Fig. 3(b) shows the calculated fluence dependence $R(F)$ in nice agreement with the experimental results (black points) which follow the power-law of $R(F) \propto F^6$ (dashed curve). It is also found that $R(F) \propto F^6$ reproduces the result by Backus *et al.*⁸ at their fluence $F=6$ mJ/cm². The fluence dependences of the hopping probability observed by two different groups consistently follows $R(F) \propto F^6$ when the scaling down of the fluence in Ref. 9 is permitted. Without scaling down of the fluence Lawrenz *et*

*al.*⁹ extrapolated their data to a fluence of 6 mJ/cm²,⁸ and found a hopping probability, which is smaller by a factor more than two orders magnitude. They also noted that a change of the fluence scale by a factor of 2.15 changes the hopping probability by two orders of magnitude. With the best estimated absolute values of their fluence data are accurate within a factor of 0.3 so that the uncertainty of their fluence data cannot explain the difference between the two experiments. As possible origins of this difference they suggested a difference of the step density of the Pt surface and diffusion barrier at the step edges between the two experiments, which may change the hopping probability due its exponential dependence on the diffusion barrier. As noted earlier there is a certain uncertainty in determining the absolute fluence so that to compare the absolute fluence between two different measurements is prone to certain variability.

This strong nonlinearity of the yield with increasing laser fluence is a characteristic of femtosecond laser initiated surface process. It is noted, however, that a power n of the nonlinear fluence dependence of the reaction yield ($R \approx F^n$) does not allow one to draw conclusions regarding the excitation mechanism.¹ Using this scaling down of the fluence, we obtain the 2PC width of ≈ 750 fs (an increase in η_{ab} gives more narrow width), which is wider than the experimental result of about 500 fs.⁹ Such ultrashort time scale is a clear evidence of the heat transfer from the electronic excitation of the substrate to the FT mode via the coupling to the FR mode.

Now, one may ask if the excitation of the FT mode by hot electrons is required no matter how weak it is. Because of the quite low energy ($\hbar\omega_a = 4.4$ meV) the FT mode is thermally excited at low temperatures in the experiments, and can be a precursor state for hopping.^{8,10} In order to examine this idea we have made the whole calculations with $\eta_a = 0$ (no direct heat transfer from hot electrons). It is found that the results shown above remain unchanged. The energy needed to activate the FT mode above the barrier is supplied from the partner FR mode excited by hot electrons. This reminds us of a single electron process of CO hopping on Pd(110)³¹ and NH₃ hopping on Pd(110) on Cu(100)³² using a STM, where excitation of the C-O (N-H) stretch mode (these vibrational energies are larger than the barrier for hopping) by a single tunneling electron activates the FT mode above the barrier via the anharmonic mode coupling. Observation of the FT and FR modes of CO on Cu(100) by scanning tunneling microscope-inelastic electron tunneling spectroscopy (STM-IETS)³³ is clear evidence of that a direct excitation of these modes by tunneling electrons does not lead to any motion of a CO molecule. Because of quite low energies of these frustrated modes compared to the hopping barrier and the rapid vibrational damping rate compared to tunneling current rates, it is mostly unlikely for the FT mode to climb up many vibrational ladders by multielectron process. It is also mentioned that, because of the population (energy) relaxation time $T_1 (=1/\eta_a, \text{ due to electron-hole pair excitation, } \approx 2.2 \text{ ps})$ for the C-O stretch mode of CO in the on-top position on a flat Pt(111) surface,³⁴ it is unlikely that the temperature of the C-O stretch mode is heated high enough to activate the FT mode above the barrier within subpicosecond time scale. The vibrational line shapes of the C-O stretch

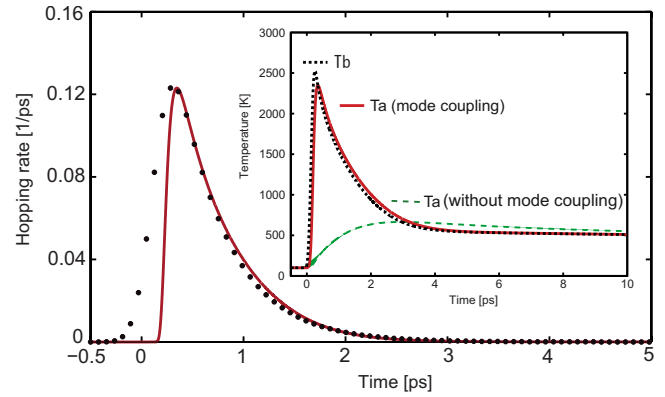


FIG. 4. (Color online) The calculated time dependence of the hopping rate $R(t)$ (solid curve) compared to the experimental result (black points).⁸ Here the time for $R(t)$ is manually shifted to give the peak at the same point of the experimental result. The inset shows the transient profiles of $T_b(t)$ (black dotted curve) and $T_a(t)$ with (red solid curve) and without (green dashed curve) mode coupling. See the text for the parameters used herein.

mode exhibit an increase in the width of infrared absorption peak with increasing temperature, thereby suggesting vibrational dephasing via anharmonic coupling to the low-frequency FT or FR modes. Schweizer *et al.*³⁵ reported detailed measurements of the lineshapes and the intensities of the C-O stretch mode in the CO/Pt(111) system using infrared absorption spectroscopy. The change of the line-width and frequency as a function of temperature has been explained in terms of vibrational dephasing model. They found that the anharmonic coupling to the FT mode is very small (only 2 cm⁻¹ corresponding to $\eta = 0.36/\text{ps}$ for the on-top CO molecules).³⁵ The evidence of a coupling to the FR mode was not observed. This makes an efficient heat transfer unlikely from the C-O stretch mode to the low-frequency frustrated modes involved in laser-induced hopping of CO on Pt(111) surface. However, this was not the case for CO on a Ru(001). A transient redshift, a broadening and a decrease in intensity of the C-O stretch mode observed by time-resolved SFG during femtosecond near-IR laser excitation leading to desorption have been explained in terms of the weak (strong) anharmonic mode coupling to the FT (FR).³⁶

Figure 4 shows the calculated time dependence of the hopping rate (solid curve), $R(t) = k_0 \exp[-U_0/k_B T_a(t)]$, calculated using a prefactor $k_0 = 1.46 \times 10^{12}/\text{s}$ and $U_0 = 0.5$ eV. Here we calculate $T_a(t)$ for the FT mode using the same set of the frictional couplings for the initial substrate temperature at $T_0 = 100$ K and the laser pulse width = 130 fs and $F = 6$ mJ/cm². $T_a(t)$ (red solid curve shown in the insert) thus calculated reaches the maximum of 2350 K at $t = 350$ fs, while $T_b(t)$ (dashed curve) for the FR mode immediately follows $T_e(t)$ (black dotted curve) because of the strong coupling $\eta_b = 5.0/\text{ps}$. The insert also plots $T_a(t)$ (green dashed curve) without mode coupling. The excellent agreement with the experimental result (black points)⁸ permits us to estimate the time constant of the CO hopping. The decay slope $\tau = 480$ fs assuming $R(t) \propto e^{-t/\tau}$ agrees well with the time constant 500 ± 150 fs of CO hopping estimated from a measurement of the time-dependent step site occupation of CO mol-

ecules on the Pt surface.⁸ This demonstrates that, although energy exchange *solely* via excitation of the FT mode is significantly too slow to cause CO hopping, the strong coupling to the FR mode heats up the FT mode high enough to induce hopping within a subpicosecond time scale.

Figure 5 shows $R(t)$ (solid curve) and $T_a(t)$ (dashed curve), respectively, calculated using $T_e(t)$ -dependent friction model at $F=6$ mJ/cm² and $T_0=100$ K. Because of its weak coupling it is found that $R(t)$ is three orders magnitude smaller than the experimental results,⁸ and exhibits a quite slow decrease with increasing time due to extremely slow cooling rate of $T_a(t)$. These transient behaviors are not compatible with the experimental result shown in Fig. 4. This indicates that a nice reproduction of the 2PC [shown in Fig. 1(a)] using $T_a(t)$ calculated with $T_e(t)$ -dependent friction model is not consistent with the experimental results of the time dependence of CO hopping rate.

III. CONCLUDING REMARKS

Recent femtochemistry and STM experiments^{31,32} and theory^{37,38} demonstrate the role of anharmonic coupling between different vibrational modes as a key mechanism for energy transfer from one preferentially excited coordinate to the reaction coordinate. Depending on the anharmonicity and time scales of energy exchange between different adsorbate degrees of freedom, the reaction dynamics may be dominated by excitation of a particular mode (energy accepting mode) followed by anharmonic coupling to the reaction coordinate mode.

For a lateral hopping of CO molecules on a stepped Pt(111) surface, the present analysis combined with the previous ones^{13,16} demonstrates that the FT mode (the reaction coordinate mode) is highly excited via the mode coupling to the FR mode. This mode coupling provides a predominant source of heating leading to the hopping motion. The time constant of about 480 fs obtained from the time-dependent hopping rate is clear evidence that the FT mode are not directly excited by hot substrate electrons, but are populated by coupling to the FR mode of the CO molecule.

In the present model, the hopping rate is only governed by $T_a(t)$ as expected for Arrhenius type reaction rate. This is more similar to an experiment near thermal equilibrium and corresponds more to the intuition that a high excitation of the relevant mode leads to an enhanced reaction. The modified friction model using an empirical $T_e(t)$ dependent friction is unable to identify the low-adsorbate temperature with a real mode excitation. Lawrenz⁹ argues that since the optical excitation results at first heating of the substrate electrons, an explicit dependence of the friction on adsorbate temperature can be viewed as an implicit dependence on electron temperature. As we have found here that the $T_e(t)$ -dependent friction is not able to give a high adsorbate temperature within a time scale of hopping as shown in Figs. 2 and 5. The fast dynamics comes in due to the dependence of the hopping rate on the temperature-dependent friction coefficient, not due to fast dynamics of the adsorbate temperature. In this model the adsorbate temperature cannot describe the vibrational excitation of the adsorbate as one observes with time-

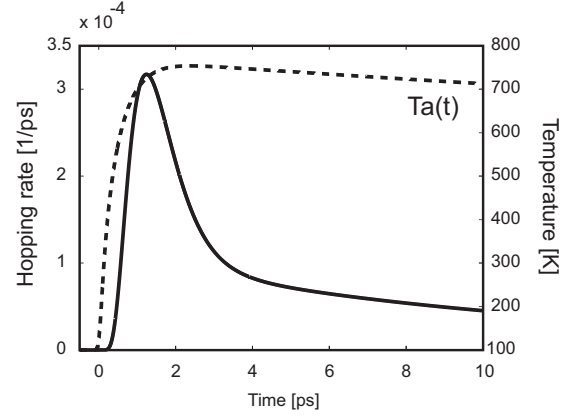


FIG. 5. The time-dependence of the hopping rate $R(t)$ (solid curve) and $T_a(t)$ (dashed curve) calculated using the T_e -dependent friction model. See the text for the parameters used herein.

resolved vibrational spectroscopy. These drawbacks in $T_e(t)$ -dependent friction model are all overcome in the mode-coupling model presented here. Nevertheless, we may be able to relate $T_e(t)$ -friction model to the present model. As shown in Eq. (1) the effective friction coupling $\eta_a^{\text{eff}}(t)$ to the \mathbf{a} -mode can be expressed as $\eta_a^{\text{eff}} = \eta_a + \eta_{ab}(k_B T_b(t)/\hbar\omega_b)$. When one assumes a strong coupling η_b for the accepting mode, $T_b(t)$ immediately follows $T_e(t)$, and gives a time-delayed rapid increase in $T_a(t)$ of the accepting mode responsible for motion. For a large friction coefficient η_0 in Eq. (3), we can expect $\eta_e[T_e(t)] \rightarrow T_b(t)$ in our heat transfer equations with mode-coupling. This suggests a heat transfer via mode coupling as an elementary process behind the empirical $T_e(t)$ -friction model.¹⁴

Lastly, it is still an open question how the width of a 2PC can be related to the reaction rate in order to understand the elementary processes of adsorbate dynamical motions driven by ultrafast laser excitation. The width of a 2PC is used as an estimation of the time scale, on which energy flows from the laser-excited metal substrate to the adsorbate. A width below a few picoseconds is a clear indication that the CO motion is electronically mediated through coupling between the substrate and hot electrons. However, it is still neither possible to identify the energy transfer time directly with the width of the 2PC, nor to relate it to the time constant of the motions. Lawrenz *et al.*⁹ observed that the width of the 2PC depends on laser fluence. This is confirmed in comparison of the calculated 2PC shown in Figs. 1 and 3 for different fluences. The 2PC and the fluence-dependent yield data are simultaneously fitted by adjusting the coupling strength/frictional coefficient, the activation energy and the fluence. These parameters have a different influence on the full width at half maximum (FWHM) and the wings of the 2PC. The FWHM gives us something like the energy storage time in heat bath (electronic vs phononic), and is not the reaction time. Recently, Wagner *et al.*³⁹ quantitatively compared associative desorption $\text{C} + \text{O} \rightarrow \text{CO}$ from Ru(001) induced by femtosecond laser pulses rates with the conclusion that both electronic and phononic contributions have to be taken into account in order to reproduce experimental data. For desorption it is impossible to perform a real-time measurement which enable

the hopping rate to be directly determined.⁸ Recently, with additional information from molecular trajectory calculations Luntz found that the FWHM of the 2PC gives the reaction time for a particular case of H+H associative desorption from Ru(001).⁴⁰ In hot electron-mediated surface reactions, $T_a(t)$ peaks after $T_e(t)$ has already reached its maximum. This is also true for slower phonon-mediated processes characterized by prolonged cooling leading to a large wing in 2PC at longer time delay. What Luntz *et al.* found with a three-dimensional model based on molecular dynamics is that this time separation between the T_e maximum and the T_a maximum [then, $R(t)$] is essentially the time the nascent H_2 molecule needs to climb out of the adsorption well. In terms of the heat path picture, this delayed rise and peaking of the adsorbate temperature with respect to T_e basically reflects the time which is needed to heat up the energy reservoir of the relevant adsorbate motion leading to reaction. In the present analysis the decay slope of $R(t)$ depends on the decline of the $T_a(t)$ and U_0 , while the 2PC width depends on the laser fluence and can be related to the energy storage and dissipation time. The extraction of a coupling time and a reaction rate from a 2PC requires more appropriate modeling of the ultrafast heat transfer and adsorbate dynamics. In our model, it is difficult to do so because of an indirect and predominant heat flow via a mode coupling accompanied with a nonadiabatic excitation of electron-hole pairs in a substrate.

Nevertheless, our theoretical work establishes a mode coupling scheme between an easily excited (energy accepting) mode (here, the frustrated rotational mode) and a subsequently excited second mode via anharmonic coupling. This latter mode (the frustrated translational mode) is of course necessary for the overall diffusion process to occur. However, only this coupling between both mode enables the hopping of the CO molecules to take place on a subpicosecond time scale.

The present work have consistently reproduced CO hopping on stepped Pt surfaces observed by two different

groups.^{8,9} Moreover, the comparison of the theoretical findings with the experiment shows how critical it is to reliably obtain the absorbed laser fluence. The present theoretical model partially contradicts the previous modeling,⁹ but it also resolves some of the existing inconsistencies. It is noted, however, that if scaling down of the fluence is not permitted,⁴¹ at the present stage we are not able to reproduce both experiments^{8,9} with the same set of parameters. There are several ways to improve the present analysis assuming a harmonic potential for the FT and FR mode. The mode coupling will become stronger for the higher vibrational levels,⁴² in particular, in the anharmonic potentials.¹³ It is clear that the excitation of the FR mode plays indispensable role so that the actual reaction coordinate cannot be described with a simple one-dimensional coordinate anymore.

The generalization of the mode-coupling model is capable to consider the anharmonicity of the potential for the adsorbate motion,¹³ which is an important issue for the comprehensive description of an activated process such as lateral hopping, since the adsorbate particularly probes the anharmonic part of the potential when it goes over the barrier. Combined observation of a time-resolved reaction rate, 2PC and their laser fluence dependence and more systematic theoretical work will provide deeper insights into the temporal evolution of ultrafast adsorbate dynamical processes by electronic excitation at surfaces.

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