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Lateral hopping and desorption of a single CO molecule on a Cu(110) surface induced by femtosecond laser pulses

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Lateral hopping and desorption of a single CO molecule on a Cu(110) surface [Bartels *et al.*, Science **305**, 648 (2004)] induced by femtosecond laser pulses are studied using an indirect heat-transfer model. In addition to a direct heating of the reaction coordinate (RC) mode [frustrated translation (FT) mode for hopping and center-of-mass (CM) mode for desorption] by laser-generated hot electrons in the substrate, we consider an indirect heating of the RC mode through intermode coupling between the frustrated rotation (FR) mode and the RC mode. We calculate the transient behavior of the effective temperature of the FT and the CM modes, and of the normalized reaction yield. The experimental result of a ratio of the hopping yield along and across a row on a Cu(110) surface is nicely calculated. Although no information is available for the attempt frequency in a form of the Arrhenius equation for thermally activated reactions, it is predicted under which condition the desorption rate becomes in the same order of magnitude as the hopping rate, although the barrier height for desorption is much higher than for hopping. The present analysis highlights the role of excitation of the FR mode in reactions of a CO molecule as has been confirmed in the real-time observation [Backus *et al.*, Science **310**, 1790 (2005)].

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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. The first real-space observation of a single molecular motion induced by femtosecond laser pulses has been made in combination with a scanning tunneling microscope (STM) by Bartels *et al.* for a system CO/Cu(110).[1] They demonstrated a possibility of combining direct imaging of a single CO molecule 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 on the surface, in addition to desorption with weaker probability compared to lateral hopping. It seems rather surprising that the desorption yield is found to be the same order of magnitude in spite of the fact that the barrier height for desorption is much higher than for diffusion. It should be mentioned here that a single CO molecule on a Cu(110) surface does not move by a tunneling electron from a STM tip which excites the C-O stretch mode because of the negligible small anharmonic coupling of the frustrated translation (FT) mode to the C-O stretch mode.[2] A STM, which permits a direct imaging of a single molecule before and after laser irradiation, can not 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. A clever choice of CO on a stepped Pt surface and the fact that the internal CO stretch frequency depends on the precise location of the CO molecule on the surface enables Bonn *et al.*[3] to monitor CO hopping in simultaneous high temporal and spatial resolution. A femtosecond pump pulse induces the motion of CO over the surface, and the motion is followed in real time with variably delayed probe pulses. The probe consists of nonlinear surface vibrational sum-frequency generation (SFG) spectroscopy to look inside the CO molecules at the C-O stretch vibration, as these are excited and displaced as a result of femtosecond laser excitation. Their most striking finding is an indispensable role of excitation of the FR mode in contrast to intuitive expectation that only excitation of the FT mode is responsible for hopping on a surface. They found that the energy- (heat-) transfer rate occurs much more slowly than the time scale on which actual hopping occurs. Hence, the experimental results are incompatible with the FT mode being the relevant mode responsible for hopping motion. The results are, however, perfectly compatible with the rate at which energy is transferred from the electrons to the FR. It should be noted here that the experiments have been done at the substrate temperature of 100 K so that the FT mode is thermally excited.

Mehlhorn *et al.* also investigated a femtosecond laser-induced hopping of a single CO molecule on a Cu(111) surface using a scanning tunneling microscope.[4] They observed that as a function of the absorbed fluence F, the hopping yield per pulses $Y(F)$ exhibits a strongly nonlinear increase at high $F = 4$–$5.2\ \mathrm{J/m^2}$. The increase was analyzed using a hot electron temperature $T_e(t)$-dependent friction model. Such empirical friction model has also been used to explain the two-pulse correlation and the fluence dependence of atomic oxygen and CO hopping on a stepped Pt(111) surface[5,6] and desorption of oxygen molecules from a Pd(111) surface.[7] In spite of these quantitative reproductions of their experimental results, the level of understanding of the process behind $T_e(t)$-dependent friction model remains at the phenomenological level. Güdde and Höfer suggested in their study of atomic oxygen hopping on a step Pt surface that a possible elementary process is an indirect excitation by anharmonic coupling between the O-Pt stretch and the O-Pt translation mode.[8]

In a series of recent works on the adsorbate motions induced by femtosecond laser excitation, we proposed a theory including an indirect heating of the reaction coordinate mode (RC) mode via the intermode coupling in addition to a direct heating of the RC mode by laser excitation.[9–13] Indirect heating of the FT mode (which is assumed to be the reaction coordinate for surface hopping) by the frustrated rotation (FR) mode has nicely reproduced the experimental results of the real-time monitoring[3,10] and two-pulse correlation[6,11] for a CO hopping on a stepped Pt(111) surface. We also found that neither the electronic heating via friction coupling nor the phonon coupling alone can explain the experimental result. Both heatings are cooperatively responsible for CO hopping on Cu(111). The electronic heat transfer dominates over the phononic one at high F, where the effective electronic friction coupling becomes larger than the phononic coupling so that there is a crossover from phonon-mediated to hot-electron-mediated heat transfer for a single CO hopping on Cu(111).[13] One possible reason of the stronger friction coupling (shorter lifetime) of the FR mode than that of the FT mode is that the FR mode has higher frequency so there is a larger phase space for exciting electron-hole pairs. It should be mentioned here that long before these experiments, Dobbs and Doren[14] 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). In the abstract, they described the following: "The adsorbate bending (frustrated rotation: FR) mode is strongly coupled to lateral translational motion. This molecular mode provides an important source of energy for reaching the transition state to diffusion." In this model, the molecular bending mode is a more important source of lateral translational energy than the surface at short times. This result is interpreted as a consequence of directional bonding to surface, and it should be generally important in surface diffusion of chemisorbed molecules. They concluded that this mechanism permits excitation of translational motion via the FR mode. The FR mode thus mediates energy transfer between the surface and the reaction coordinate. 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.[15] This picture is quite general and has been applied to various other systems as we have done before and in this work.

II. THEORY AND RESULTS

We study hopping and desorption of a single CO molecule on a Cu (110) surface induced by femtosecond laser pulses. Bartels *et al.*[1] observed a lateral hopping of a single CO molecule along and across the row on Cu(110) surface at $F = 30 \pm 3$ J/m^2 using 405-nm excitation (200-fs pulse duration) at the substrate temperature 22 K.[1] CO hopping perpendicular to the atomic rows has not been observed under conventional thermal conditions.[16] This indicates that thermal diffusion in the perpendicular direction does not occur due to a larger energy barrier associated with the increased hopping distance to the next site. The observed ratio of the hopping yield $Y = Y_{\mathrm{ac}}/Y_{\mathrm{al}}$ (across the rows to along the rows) was estimated to be 0.34, and the desorption yield Y_{des} compared to Y_{al} was found to be about 0.5.

We assume the transient reaction profile is defined as

$$R_i(t) = A_i \int \exp\left[-E_{\mathrm{B}}^i / k_{\mathrm{B}} T_i(t)\right], \quad (1)$$

where A_i is an attempt frequency, E_{B}^i is a barrier, and $T_i(t)$ is a time-dependent temperature of a reaction coordinate mode after pulse laser excitation at $t = 0$ (here, i = al, ac, and des stand for hopping along and across a row, and desorption, respectively). The reaction yield par pulse is then given by

$$Y_i = \int R_i(t) dt, \quad (2)$$

where time integral is made over the time interval until the initial temperature is recovered. This formula enabled Bartels *et al.*[1] to estimate the barrier height $E_{\mathrm{B}}^{\mathrm{al(ac)}} = 97$ (128) meV along (across) the row [here, $E_{\mathrm{B}}^{\mathrm{al}} = 97$ meV along the row is almost the same as determined from the slope of an Arrhenius plot for hopping rate of a single CO molecule on Cu(110) observed at the substrate temperature range between 42 and 53 K].[16]

A heat transfer from hot electrons and substrate phonon to the adsorbate vibrational degrees of freedom (FT mode for lateral hopping and CM mode for desorption) is widely studied using a constant electronic and phononic friction (η_{el}, η_{ph}) model[17]

$$\frac{dU_{\mathrm{FT(CM)}}(t)}{dt} = \eta_{\mathrm{el}}(U_{\mathrm{el}} - U_{\mathrm{FT(CM)}}) + \eta_{\mathrm{ph}}(U_{\mathrm{ph}} - U_{\mathrm{FT(CM)}}), \quad (3)$$

where

$$U_x = \hbar\Omega/[\exp(\hbar\Omega/k_{\mathrm{B}}T_x) - 1] \quad (4)$$

denotes the energy of a harmonic oscillator corresponding to the FT mode and the CM mode at the temperature T_x (here, x = FT, CM, el, and ph). Bartels *et al.* calculated $T_{\mathrm{el}}(t)$ and $T_{\mathrm{ph}}(t)$ for Cu using the two-temperature model,[18] and $T_{\mathrm{FT}}(t)$ using $\hbar\Omega_{\mathrm{FT}} = 4$ meV, $\eta_{\mathrm{el}} = 1/(5.1\ \mathrm{ps})$, and $\eta_{\mathrm{ph}} = 1/(4.2\ \mathrm{ps})$ at $F = 30$ J/m^2 and at the substrate temperature of 22 K. These coupling times to the electronic and phononic heat baths were deduced from the infrared response of the C-O stretch mode on Cu(100) to heating of the substrate.[19]

In what follows, we present the full formula we use here in order to reproduce $T_{\mathrm{el}}(t)$ and $T_{\mathrm{ph}}(t)$ calculated by Bartels *et al.*[1] The simulation done by Bartels *et al.* is necessarily repeated in detail to share the same $T_{\mathrm{el}}(t)$, $T_{\mathrm{ph}}(t)$, and $R_{\mathrm{al,ac}}(t)$ with them and to demonstrate an indispensable role of an excitation of the FR mode in CO hopping on Cu(110) surface as confirmed in real-time observation on a stepped Pt surface.[3]

The well-established two-temperature model reads as

$$C_{\mathrm{el}}(T_{\mathrm{el}})\frac{\partial}{\partial t}T_{\mathrm{el}} = \frac{\partial}{\partial z}\left(\kappa\frac{\partial}{\partial z}T_{\mathrm{el}}\right) - H(T_{\mathrm{el}},T_{\mathrm{ph}}) + S(z,t), \quad (5)$$

$$C_{\mathrm{ph}}(T_{\mathrm{ph}})\frac{\partial}{\partial t}T_{\mathrm{ph}} = \frac{\partial}{\partial z}\left(\kappa\frac{\partial}{\partial z}T_{\mathrm{ph}}\right) + H(T_{\mathrm{el}},T_{\mathrm{ph}}) + S(z,t), \quad (6)$$

where the heat capacity of the electron is $C_{\mathrm{el}} = \gamma T_{\mathrm{el}}$ ($\gamma = 98$ Jm^{-3} K^{-2} for Cu) and that of the phonons C_{ph} (T_{ph}) is calculated with a Debye formula using $\theta_D = 343$ K for Cu, and z is the distance below the substrate surface. For a temperature dependence of the thermal conductivity κ, we use an empirical formula by Mehlhorn.[20] The temperature

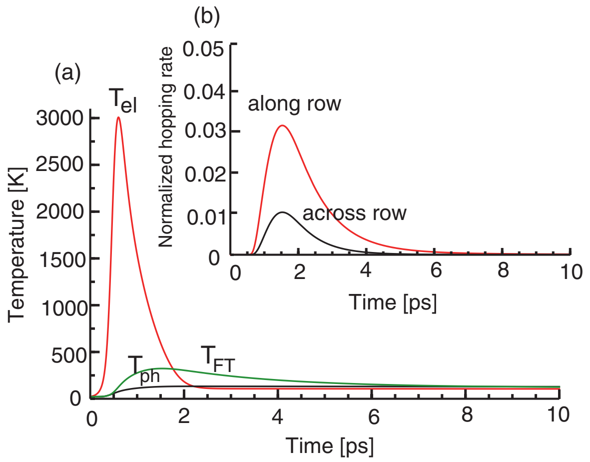

FIG. 1. (Color online) (a) Transient temperature of $T_{\rm el}$ (red curve), $T_{\rm ph}$ (black curve), and $T_{\rm FT}$ (green curve) calculated using direct heating transfer equation (1) with $F = 30$ J/m^2 and initial temperature at 22 K. See the text for the rest of the parameters used herein. (b) Normalized hopping rate along (red curve) and across (black curve) the row on Cu(110), respectively. See the text for the rest of the parameters used herein.

dependence of the electron-phonon coupling is calculated using a formula

$$H(T_{\rm el},T_{\rm ph}) = f(T_{\rm el}) - f(T_{\rm ph}), \tag{7}$$

$$f(T) = 4g_\infty\theta_D\left(\frac{T}{\theta_D}\right)^5\int_0^{\theta/T}\frac{x}{e^x-1}dx, \tag{8}$$

where $g_\infty = 1\times10^{17}$ W/m^3 K.[19,21] At high-temperature limit $H(T_{\rm el},T_{\rm ph}) = g_\infty(T_{\rm el}-T_{\rm ph})$. The laser source term is given by

$$S(z,t) = \frac{F}{2\Delta t\lambda}e^{-z/\lambda}\mathrm{sech}^2\left(\frac{t-t_0}{\Delta t}\right), \tag{9}$$

where F is the absorbed fluence, the skin depth $\lambda = 15$ nm, and the pulse temporal full width at half maximum $\Delta t = 113$ fs for the pulse duration of 200 fs in Ref. 1. We use a set of parameters for a Cu (Debye temperature $\theta_D = 343$ K), electronic specific heat $\gamma = 98$ Jm^{-3} K^{-2}, phonon specific heat calculated using the Debye model, skin depth $= \lambda = 15$ nm for a wavelength of 400 nm of laser pulse. Thus, calculated $T_{\rm el}(t)$ (red curve) and $T_{\rm ph}(t)$ (black) and $T_{\rm FT}(t)$ (blue curve) using the same $\eta_{\rm el} = 1/(5.1$ ps) and $\eta_{\rm ph} = 1/(4.2$ ps) as in Ref. 1 shown in Fig. 1 are almost the same as Fig. 4(A) in Ref. 1. A peak electronic temperature $T_{\rm el} = 3000$ K is reached, in contrast to a peak phonon temperature $T_{\rm ph} = 140$ K. Figure 1(b) shows the normalized hopping probability using $T_{\rm FT}(t)$, $E_{\rm B}^{\rm al} = 97$ meV, and $E_{\rm B}^{\rm ac} = 128$ meV used in Ref. 1. With these parameters, an electronically driven process yields a branching ratio for diffusion across the rows of 0.25, which is comparable to experimental finding of 0.34.[1] Unlike a CO hopping on Pt(111) (Ref. 3) where indirect heating of the FT mode by the FR mode with a strong frictional coupling to hot electrons plays an indispensable role,[10] direct heating of the FT mode seems to give the acceptable hopping ratio along and across the row as far as we use $\eta_{\rm el} = 1/(5.1$ ps) for the FT mode. However, this electronic friction is too large in view of the dissipation rate of the FT mode of a CO molecule on a Cu surface. From the synchrotron infrared studies of the CO/Cu(100), one can determine the electronic friction $\eta_{\rm FT} = 1/(60$ ps).[22] By considering the friction interaction of substrate electrons with low-frequency vibrations, Persson[23] has used CO-induced changes in thin Cu film resistivity and Cu(100) infrared reflectivity[22] to derive an expression relating the change in resistivity of thin metal film. He estimated the friction coupling time between the FT mode and the substrate electrons to be in the range of 36–56 ps. On Cu(111), Mehlhorn *et al.* used 40 ps for the FT mode.[4]

The importance of an electronic coupling in the vibrational damping is well established.[24] Another exciting application of electronic friction involves excitation by tunneling electron from a STM. This process has successfully permitted single-atom or molecule manipulation, including a triggering of single-molecule reactions at surface with a STM.[25] The friction is produced by rapid fluctuations of the adsorbate motion between two potential energy curves differing as an electron or hole moves into and out of the adsorbate resonance level.[24] The energy is ultimately dissipated through the available continuum of electron-hole pairs in the metal. It has been well established that a hopping of a single CO molecule on Pd(110) is induced by initial excitation of the C-O stretch mode by tunneling electron, which is followed by the anharmonic coupling to the FT mode in competing vibrational energy dissipation into excitation of electron-hole pairs.[2] Lorente[26] used density functional theory (DFT) to calculate the lifetimes of CO vibrations due to electron-hole damping:

$$\frac{1}{\tau_\lambda} = \frac{2\pi}{\hbar}\Sigma_{m,n.k}f_n(1-f_m)\left|\langle m,k|\frac{\partial H}{\partial Q_\lambda}\partial Q_\lambda|n.k\rangle\right|^2 \times\delta(\varepsilon_{m.k}-\varepsilon_{n,k}-\hbar\omega_\lambda), \tag{10}$$

where ∂Q_λ is the eigenvector of the dynamical matrix for the mode λ, normalized to the root-mean-squared displacement of the mode, and H is the full adiabatic Hamiltonian. The electron-vibration coupling is then given by $\frac{\partial H}{\partial Q_\lambda}\partial Q_\lambda$. The electronic states of different band index $n \rightarrow m$ are accompanied with exchanging one quantum of vibration $\hbar\omega_\lambda$. The Fermi factors f_m and f_n take care of the occupied states n and the unoccupied states m, i.e., electron-hole pair excitation. The lifetimes thus calculated are $\tau = 2.2$ ps, 2.37 ps, and 77 ps for the ST (C-O stretch), FR, and FT modes, respectively. The vibrational lifetime basically follows the mode's frequency. One factor for why the lifetime is shorter for the FR mode than the FT is that it is at higher frequency so there is a larger phase space for exciting electron-hole pairs. The lifetime of the FR mode is, however, almost as short as the C-O stretch mode. This is due to the large electron-vibration coupling of the FR mode, as has been observed in STM-IETS (inelastic tunneling electron spectroscopy) for a single CO on Cu(100) (Ref. 27) and Cu(110) (Ref. 28). It has been noted that the electron-vibration damping does not seem to be much affected by the actual surface orientation, but rather by local bonding geometry to the surface. The damping rates of the FR mode are extremely rapid compared to the FT mode for all the Cu surfaces of the Cu(100),[29] Cu(110),[26] and Cu(111).[30] This is also true for CO on Pt(111) so that indirect heating of the FT mode via the mode coupling to the FR mode has been shown to reproduce the experimental result of a time-resolved observation of CO hopping on Pt(111).[3,6,10,12] In our following analysis, we assume that frictional coupling originates from vibrational energy dissipation due to electron-hole pair excitation,[31,32] i.e., $\eta_{\lambda(\mathrm{ST,FR,FT})} = 1/\tau_\lambda$ as electronic friction coupling rate to hot electron of each mode.

The intermode coupling rate of the ST mode to the low-lying modes (FR and FT) of CO on Cu(110) was also calculated by

$$\frac{1}{\tau_{\mathrm{ST},i}} = \frac{2\pi}{\hbar}\Sigma_{m,n.k} f_n(1-f_m) \times \left|\langle 1,0,m|\delta Q_{\mathrm{ST}}\frac{\partial^2 H}{\partial Q_{\mathrm{ST}}\partial Q_i}\delta Q_i|0,1,n\rangle\right|^2 \times \delta(\varepsilon_m-\varepsilon_n+\hbar\omega_{\mathrm{ST}}-\hbar\omega_i). \tag{11}$$

Here, i stands for the FR or FT mode, and the electron-vibration coupling that depends on the two normal-mode sets of coordinates Q_{ST} and Q_i. The energy conservation is satisfied in terms of excitation of the continuum of electron-hole pair excitation. The combined electronic and nuclear states are initially the ST mode one time excited and the electron in the occupied state n, as given in the $|0,1,n\rangle$, and the final state is the i mode once excited and the electron in the unoccupied state m, as given in the bra $\langle 1,0,m|$. The calculated intermode coupling rate of the ST mode via electron-hole excitation is 1.1×10^{10}/s and 0.15×10^{10}/s for the FR and FT modes, respectively. It was found that the FR mode has a larger coupling by the very large electron-vibration coupling when the FR mode is involved in an electronic transition. This strength of the FR-mode coupling suggests that the FR mode may have a leading role in the dynamics of CO motion on metallic surfaces.

We employ the same model of heat transfer in the presence of the coupling between A and B modes as used before:[10–13]

$$\frac{dU_{\mathrm{A}}(t)}{dt} = \eta_{\mathrm{A}}^{\mathrm{eff}}(t)[U_{\mathrm{el}}(t) - U_{\mathrm{A}}(t)], \tag{12}$$

$$\frac{dU_{\mathrm{B}}(t)}{dt} = \eta_{\mathrm{B}}^{\mathrm{eff}}(t)[U_{\mathrm{el}}(t) - U_{\mathrm{B}}(t)], \tag{13}$$

where $\eta_{\mathrm{A}}^{\mathrm{eff}}(t) = \eta_{\mathrm{A}} + \eta_{\mathrm{AB}}/\hbar\Omega_{\mathrm{B}}U_{\mathrm{B}}(t)$ and $\eta_{\mathrm{B}}^{\mathrm{eff}}(t) = \eta_{\mathrm{B}} + \eta_{BA}/\hbar\Omega_{\mathrm{A}}U_{\mathrm{A}}(t)$ is an *effective* friction coupling of the A and B mode to hot electrons, respectively, and $\eta_{\mathrm{AB}}/\eta_{\mathrm{BA}} = \Omega_{\mathrm{A}}/\Omega_{\mathrm{B}}$. In the high-temperature limit, this reduces to[10]

$$\frac{dT_{\mathrm{A}}(t)}{dt} = \left[\eta_{\mathrm{A}} + \eta_{\mathrm{AB}}\frac{k_{\mathrm{B}}T_{\mathrm{B}}}{\hbar\Omega_{\mathrm{B}}}\right][T\mathrm{el}(t) - T_{\mathrm{A}}(t)], \tag{14}$$

$$\frac{dT_{\mathrm{B}}(t)}{dt} = \left[\eta_{\mathrm{B}} + \eta_{\mathrm{BA}}\frac{k_{\mathrm{B}}T_{\mathrm{A}}}{\hbar\Omega_{\mathrm{A}}}\right][T\mathrm{el}(t) - T_{\mathrm{B}}(t)]. \tag{15}$$

We first examine indirect heating of T_{FT} by the ST-FT mode coupling. Because of very strong (efficient) electron-ST mode coupling, T_{ST} immediately follows T_{el} and T_{FT} is found to be heated up to about 1900 K at around 1 ps after laser excitation as shown in Fig. 2(a), and the normalized hopping probability along (blue curve) and across (red curve) are shown in Fig. 2(b). The calculated ratio of the hopping yield 0.78 is too large compared to the experimental result.

Using $\eta_{\mathrm{FT}} = 1/(77\ \mathrm{ps})$, $\eta_{\mathrm{FR}} = 1/(2.7\ \mathrm{ps})$, and $\eta_{\mathrm{FT,FR}} = 1/(7.8\ \mathrm{ps})$, Fig. 3(a) shows $T_{\mathrm{FT}}(t)$ and $T_{\mathrm{FR}}(t)$ and the transient effective frictions $\eta_{\mathrm{FT}}^{\mathrm{eff}}(t)$ (green curve) and $\eta_{\mathrm{FR}}^{\mathrm{eff}}(t)$ (blue curve) are shown in Fig. 3(b). Because of a strong coupling to the FR mode, $T_{\mathrm{FR}}(t)$ is heated up above 1400 K at 1 ps. This results in indirect heating of the FT mode by $\eta_{\mathrm{FT,FR}}$. [Note that without coupling to the FR mode, $T_{\mathrm{FT}}(t)$ is only heated up to around 80 K.] This manifests itself in a peak profile of $\eta_{\mathrm{FT}}^{\mathrm{eff}}(t)$. Because of the weak heating rate of the FT mode, it takes a quite longer

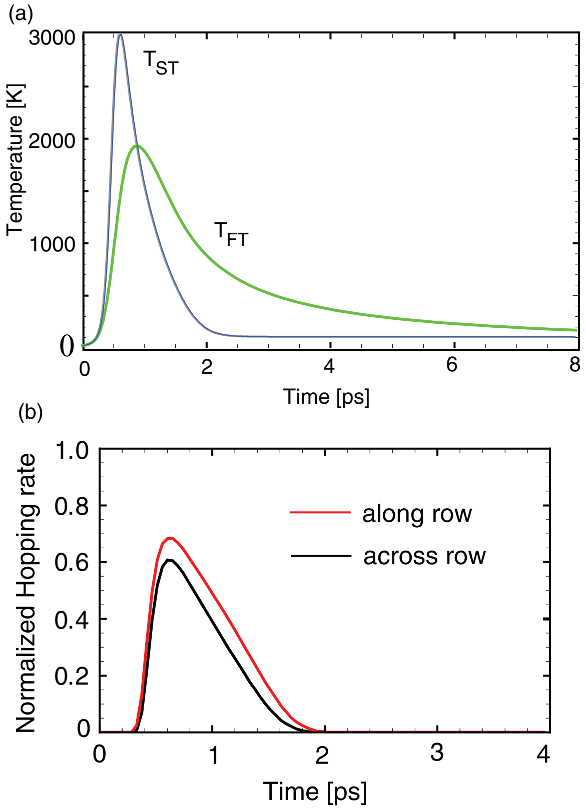

FIG. 2. (Color online) (a) Transient temperature of T_{ST} (blue curve), T_{FT} (green curve) calculated using $F = 30\ \mathrm{J/m^2}$ and initial temperature at 22 K. See the text for the rest of the parameters used herein. (b) Normalized hopping rate along (red curve) and across the row on Cu(110).

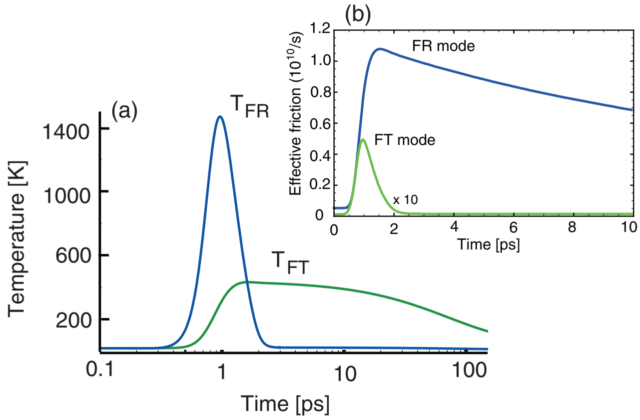

FIG. 3. (Color online) (a) Transient temperature of T_{FR} (blue curve) and T_{FT} (green curve) calculated using $\eta_{\mathrm{FT}} = 1/(77\ \mathrm{ps})$, $\eta_{\mathrm{FR}} = 1/(2.7\ \mathrm{ps})$, and $\eta_{\mathrm{FT,FR}} = 1/(7\ \mathrm{ps})$. (b) Time-dependent effective friction $\eta_{\mathrm{FT}}^{\mathrm{eff}}(t)$ (green curve) and $\eta_{\mathrm{FR}}^{\mathrm{eff}}(t)$ (blue curve). See the text for the rest of parameters used herein.

time until the initial temperature is recovered. The normalized transient behaviors of the hopping rate along and across the raw calculated using $T_{\rm FT}(t)$ are shown in Fig. 4. Here, we assume $A_{\rm ac} = A_{\rm al}$ as in Ref. 1. Strictly speaking, a prefactor (attempt frequency) $A_{\rm ac,al}$ is different along the rows and perpendicular to the rows because of the difference of the FT mode energy along and across the row,[26] respectively. Thus, calculated $T_{\rm FT}(t)$ gives a hopping ratio 0.339 in excellent agreement with the experimental finding of 0.34.[1] The small difference, however, does not affect the calculatation of the ratio given above. Although both (constant friction and effective friction) modelings are able to reproduce comparable hopping ratio, the transient profiles $T_{\rm FT}(t)$ and $R(T)$ exhibit quite different behaviors. Such difference, however, is washed away after the time integral of Eq. (2).

A more interesting report in Ref. 1 is that the desorption yield is in the same order of magnitude as the hopping rate although the barrier height for desorption is much higher than for hopping. This surprising observation has not been discussed before, but reminds us that Stipe *et al.*[33] observed that a single oxygen molecule on the Pt(111) surface dissociates at the same bias voltage that induces rotation. This suggests that excitation of the FR mode forms a precursor state for dissociation of an oxygen molecule if there is a strong coupling between the FR mode and O-O stretch mode. A similar scenario can be applied to desorption of CO from the Cu(110) surface. The DFT calculation gives the energy of 47 meV and the friction coupling $\eta_{\rm CM} = 1/(10.75 \times 10^3$ ps) for the CM mode: CO-Cu.[26] Figure 5(a) shows the transient behavior of the effective temperature $T_{\rm eff\,des}(t)$ of CM mode with several intermode couplings $\eta_{\rm FR\text{-}CM}$ and without it. As expected, $T_{\rm eff\,des}(t)$ increases with $\eta_{\rm FR\text{-}CM}$ and exhibits the rapid heating at about 1 ps after laser excitation. After reaching the maximum temperature, $T_{\rm eff\,des}(t)$ exhibits rapid cooling with an increase of $\eta_{\rm FR\text{-}CM}$. We need to know a prefactor $A_{\rm des}$ and a desorption barrier $E_{\rm B}^{\rm des}$ to calculate the transient behavior of the desorption rate $R_{\rm des}(t) = A_{\rm des}\exp[-E_{\rm B}^{\rm des}/(k_{\rm B}T_{\rm eff\,des})]$ and the yield $Y_{\rm des} = \int R_{\rm des}(t)dt$. A previous second-harmonic generation experimental results as a time-resolved probe of the laser-induced desorption of CO molecules from a Cu(111) (Ref. 34) and two-pulse correlation (2PC) experiments for desorption of CO molecules from a Cu(100) (Ref. 35) have been analyzed using $E_{\rm B}^{\rm des} = 0.4$ and 0.57 eV, respectively. On a Cu(110) surface, an optical differential reflectance method has been employed to study CO desorption kinetics as a function of submonolayer coverage and obtained $E_{\rm B}^{\rm des} = 0.72$ eV at low coverage.[36] Thermal desorption spectroscopy for CO adsorbed on different site on Cu(110) determined 0.56 eV from the atomic row.[37] Thus, $E_{\rm B}^{\rm des}$ is very sensitive on the coverage and adsorption cite.

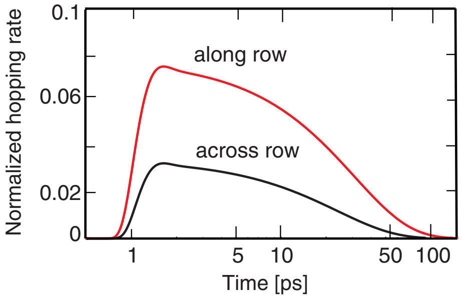

FIG. 4. (Color online) Hopping probability along (red curve) and across (black curve) the row calculated using FR-FT mode coupling. See the text for the parameters used herein.

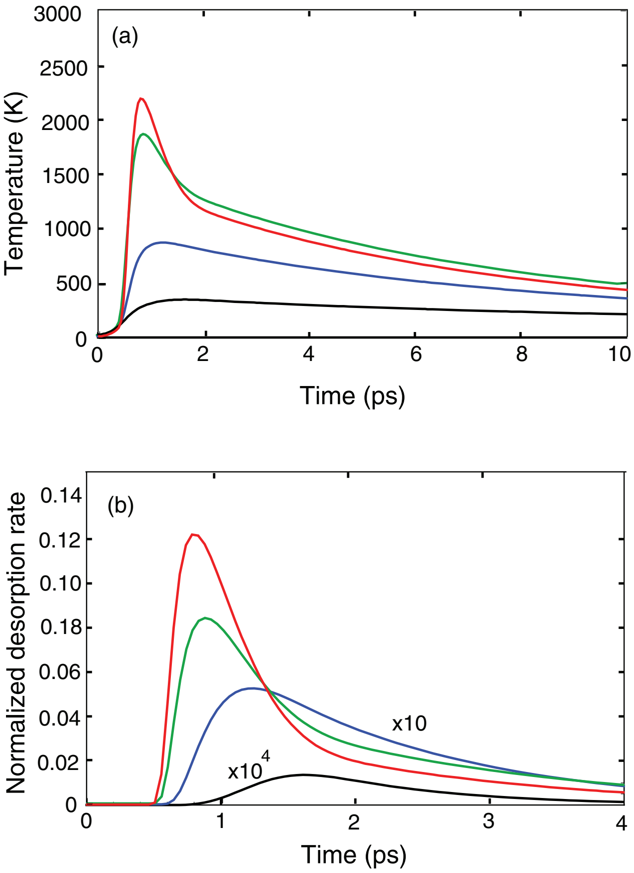

FIG. 5. (Color online) (a) Effective temperature of the CM mode for $\eta_{\rm FR\text{-}CM} = 0$ (black curve), $1/(10^4$ ps) (blue curve), $5/(10^4$ ps) (green curve), and $8/(10^4$ ps) (red curve). (b) Transient profile of the normalized desorption rate corresponding to the effective temperatures shown above. See the text for the parameters used herein.

In this work, we are concerned with the relative reaction probability between hopping along the row and desorption so that we take $E_{\rm B}^{\rm des} = 0.56$ eV. Figure 5(b) shows $\tilde{R}_{\rm des}(t) = R_{\rm des}(t)/A_{\rm des}$ for different $\eta_{\rm FR\text{-}CM}$ corresponding to $T_{\rm eff\,des}(t)$ in Fig. 5(a). The peak of $\tilde{R}_{\rm des}(t)$ shifts from $t \simeq 1.5$ ps for $\eta_{\rm FR\text{-}CM} = 0$ to below $t = 1$ ps, and orders of magnitude increase of $\tilde{R}_{\rm des}(t)$ with an increase of $\eta_{\rm FR\text{-}CM}$. Time integral of $R_{\rm des}(t)$ up to $t = 150$ ps where all temperatures reach at thermal equilibrium gives the normalized desorption yield $\tilde{Y}_{\rm des} = 2.2 \times 10^{-3}$ (for $\eta_{\rm FR\text{-}CM} = 0$), 10.1 $[1/(10^4$ ps)], 117 $[5/(10^4$ ps)], and 119 $[8/(10^4$ ps)]. These values are compared to a time integral of the normalized hopping yield $\tilde{Y}_{\rm al} = \int R_{\rm al}(t)/A_{\rm al}dt$ from $R_{\rm al}(t)$ shown in Fig. 4. This gives $\tilde{Y}_{\rm al} = 491$. The experimental result in Ref. 1 reported $Y_{\rm des} \simeq 0.5Y_{\rm al}$, a very large desorption yield in spite of the fact that the barrier height for desorption is much higher than for hopping. For CO hopping from terrace to step sites on Pt(111) surface, $A_{\rm hop} = 10^{12}$/s was determined.[38] For a single CO hopping on Cu(111), $A_{\rm hop} = 10^{12.6}$/s was used to reproduce the fluence dependence.[4] It is also noted that $A_{\rm des}$ generally corresponds to the period of vibration of the bond between the adsorbed molecule and substrate and is frequently taken to be about 10^{13}/s. The following arguments should be considered as tentative. If one assumes that desorption occurs via direct heating of the CM mode ($\eta_{\text{FR-CM}} = 0$), the above analysis requires $A_{\rm des} \simeq 10^5 A_{\rm al}$. This is quite unlikely and a very broad and low-temperature profile of the FT mode. On the other hand, if we are allowed to assume $\eta_{\text{FR-CM}} = 1/(10^4\ \text{ps})$, a relation $A_{\rm des}/A_{\rm al} \simeq 24$ is able to explain the experimental result, and is consistent to the order of magnitude intuitively expected for the attempt frequency for hopping and desorption of CO molecules on metal surfaces (it is not a present aim to choose the proper value of $\eta_{\text{FR-CM}}$ to obtain the experimental value of $Y_{\rm des} \simeq 0.5 Y_{\rm al}$).

III. CONCLUDING REMARKS

For lateral hopping on a surface, we expect that the adsorbate needs sufficient excitation in a direction parallel to the surface for hopping, and intuitively we might expect that only the translational mode is responsible. There is no doubt that the reaction pathway involves translational motion, which is populated thermally even at low temperatures and/or even at weak friction coupling to hot electrons. This forms a precursor state coupled to the rotational motion excited by strong coupling to hot electrons and induces hopping. The rate limiting process of ultrafast laser-induced CO hopping on metal surfaces is an excitation of the FR mode. The lateral motion is like a dance in which the CO molecules execute concerted rocking and translational steps.[39] Now, a question arises as to whether excitation of the FR mode only induces lateral hopping. In the real-time monitoring of CO hopping on a Pt(111) surface,[3] the initial substrate was 100 K, where thermal excitation of the FT mode is sufficient to reveal the role of the rotational mode, which would otherwise remain obscured by the slower coupling to the FT mode.

It is generally observed that for CO adsorbed on metals, the electronic friction of the FT mode is much smaller than for the FR mode and the other adsorbate vibrational modes. The potential energy surface for CO adsorption on metals is usually very flat. This may indicate that a jellium type of picture may be valid as a first approximation. Within the jellium model, where the ions of the substrate are smeared out into a semi-infinite continuum, the energy of the adsorption bond does not change during CO parallel translation, and the magnitude of the orbital matrix elements, which couple the CO to the substrate, are constant. However, the phase of the matrix element changes and in the jellium picture this is the origin of the nonadiabatic coupling which results in the damping of the FT mode. For the FR mode (and the other CO vibrational modes), the situation is very different since for these modes the magnitude of the CO-metal coupling matrix elements changes with the vibrational normal mode coordinate. We believe that the origin for why $\eta_{\rm FR} \gg \eta_{\rm FT}$ is related to this qualitative difference is in the nature of the mode coupling to the substrate electrons. The electronic friction is particularly strong when an adsorbate-induced resonance state appears close to the Fermi energy, and if the position (and width) of the adsorbate state is strongly modulated by the variations in the normal mode vibrational coordinate.

The mode coupling parameter $\eta_{\rm FT,FR}$ we used in order to fit the experimental data is larger than what one would expect from the simple qualitative arguments presented in Ref. 10. We believe that this may be due to strong coupling between the CO translational and rotational degree of freedom in the vicinity of the transition state, i.e., close to the top of the barrier along the reaction coordinate. Electronic-structure calculations have shown that as the center of mass of the CO molecule is displaced from one symmetry cite to another along the path in configuration space which minimizes the total energy, the C-O bond tilts away from the surface normal, initially slowly, but close to the transition state very fast, as a function of the lateral CO position.[40] This may enhance the mode-coupling parameter $\eta_{\rm FT,FR}$ close to the transition state. In addition, the study by Dobbs and Doren[14] indicates that kinetic effects may be important close to the transition state. That is, because of the moment of inertia of the CO molecule, close to the transition state the CO molecular axis may be oriented differently than expected from the ground-state potential surface, which could also enhance the energy transfer between the translational reaction coordinate and the CO frustrated rotation.

We have studied a hopping and desorption of a single CO molecule on Cu surfaces induced by ultrafast laser pulse excitation of hot electrons. In the heat-transfer equation with friction coupling (a basic assumption in models based on electronic friction is that a thermalized hot-electron gas interacting with molecules), one should use a temperature-independent electronic friction. If the friction model can not describe the experimental data with a temperature-independent electronic friction, the surface reaction involves more complex processes, e.g., involving two anharmonically coupled adsorbate modes as assumed before and in this work. Because of a weak friction coupling to the FT mode or the CM mode of CO molecule on Cu surfaces, the indirect heating via the coupling to the FR mode is required to induce CO hopping and desorption. The same processes have been successfully applied for CO hopping on Pt surfaces.[10,12] Since the details of the transient behavior of the adsorbate temperature are washed away after integration of $R(t)$ over the time, it is needless to note that experiments using nonlinear time-resolved pump-probe spectroscopy are mostly desired in order to gain insights into elementary processes of heat transfer. Unfortunately, it is impossible to combine it with a static STM observation of single-molecule reactions.

We conclude that neither excitation of only the FT mode or the CM mode is not able to explain the experimental results. We believe that our model with intermode coupling between the FT and FR modes for hopping and between the CM and the FR modes for desorption capture the essential elementary process behind CO hopping and desorption. This is based on the fact that the FR mode has the largest coupling to the laser-generated hot electrons; we propose that excitation of the FR mode forms a precursor state for desorption of a single CO molecule from Cu(110). In order to reinforce our modeling, detailed electronic-structure calculations and electron-vibration interactions are required for CO on Cu surfaces to estimate the FT-FR mode and CM-FR mode coupling accompanied with electron-hole pair excitations in the substrate. As seen above, the present analysis needs many parameters. This is not, however, a case of a famous saying.[41] The FR-FT and FR-CM mode couplings are the only free parameters to calculate the hopping and desorption yield, and the rest of the parameters are taken from relevant experimental and theoretical results for CO on Cu(110). As for surprising observation of desorption with the similar magnitude of yield compared to hopping, a lack of the relevant attempt frequency leaves room for more elaborated theoretical work.

A final remark is addressed for adsorbate motions induced by vibrational excitation.[9] A CO hopping induced by inelastic tunneling electrons from a tip of a STM and by ultrafast pulse laser excitation. In the former, we have proposed a model where the FT mode is excited above a barrier via an anharmonic mode coupling to the C-O stretch mode excited by tunneling electrons,[2,42] while in the latter case indispensable role of excitation of the FR mode has been established in both experiments and their theoretical analysis. The bias voltage of about 240 mV to excite the C-O stretch (ST) mode is large enough to excite the FR mode to high enough (in a coherent way) to activate the FT mode over the barrier. It is also noted that an extensive density functional theory calculation for the electronic and vibrational properties of a CO molecule on a Cu(110) surface obtained the anharmonic coupling between ST and FR modes (1.1×10^{10}/s) is an order of magnitude larger than that between ST and FT mode (0.15×10^{10}/s).[26] Although no clear experimental evidence suggesting a role of excitation of the FR mode and its coupling to the FT or CM mode is available, there is no reason to exclude a reaction pathway of CO hopping through vibrational energy transfer: ST mode → FR mode (in higher level than the hopping barrier) → FT mode. The detailed microscopic mechanism, i.e., how the relevant vibrational modes are responsible for a simple motion of lateral movement of a CO molecule on metal surfaces remains to be clarified. We should note, however, that a clear distinction between the direct and indirect heating (via mode coupling) model of the reaction coordinate mode is only possible by an experiment that probes the dynamics of the different modes in real time rather than the static outcome achieved by combination of ultrafast pulse laser excitation and STM. Nevertheless, the present analysis highlights the role of excitation of the FR mode in reactions of CO molecule as has been confirmed in the real-time observation by Backus *et al.*[3] We will be able to expect more insights into the elementary processes of a single-molecule reaction induced by ultrafast laser excitation and monitored with the use of a static STM by observing its laser fluence dependence.[4,13]

Note added in proof. Recently real time observation (with free-electron x-ray laser) of a surface bond breaking of CO molecules on a Ru(0001) surface[43] has confirmed a transient precursor state where the CO molecule is nearly free to rotate and to move parallel to the surface prior to desorption.

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