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Heat transfer between adsorbate and laser-heated hot electrons

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Abstract

Strong short laser pulses can give rise to a strong increase in the electronic temperature at metal surfaces. Energy transfer from the hot electrons to adsorbed molecules may result in adsorbate reactions, e.g. desorption or diffusion. We point out the limitations of an often used equation to describe the heat transfer process in terms of a friction coupling. We propose a simple theory for the energy transfer between the adsorbate and hot electrons using a newly introduced heat transfer coefficient, which depends on the adsorbate temperature. We calculate the transient adsorbate temperature and the reaction yield for a Morse potential as a function of the laser fluency. The results are compared to those obtained using a conventional heat transfer equation with temperature-independent friction. It is found that our equation of energy (heat) transfer gives a significantly lower adsorbate peak temperature, which results in a large modification of the reaction yield. We also consider the heat transfer between different vibrational modes excited by hot electrons. This mode coupling provides indirect heating of the vibrational temperature in addition to the direct heating by hot electrons. The formula of heat transfer through linear mode–mode coupling of two harmonic oscillators is applied to the recent time-resolved study of carbon monoxide and atomic oxygen hopping on an ultrafast laser-heated Pt(111) surface. It is found that the maximum temperature of the frustrated translation mode can reach high temperatures for hopping, even when direct friction coupling to the hot electrons is not strong enough.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

The heat transfer between a liquid and a solid, or between thin adsorbed layers and the solid substrate, is a topic of great practical importance. For example, if two solids are squeezed together in a liquid, the solids in the contact regions will in general be separated by a few layers of adsorbed molecules. During sliding, a very large amount of energy can be dissipated in the confined molecular layer, resulting in a strong increase in the effective temperature of the adsorbed layer. The (heat) energy transfer between the adsorbed layer and the solid body is determined by the heat transfer coefficient α . In general, the energy transfer between adsorbed molecules and the substrate is given by

$$\frac{dQ}{dt} = J_{s \rightarrow a} - J_{a \rightarrow s}. \quad (1)$$

Here $Q(t)$ is the heat in the adsorbate, and $J_{s \rightarrow a}$ and $J_{a \rightarrow s}$ are the heat flows from the substrate to the adsorbate and from the adsorbate to the substrate, respectively. If we consider high temperatures, and if the temperature difference between the substrate and the adsorbate is small, then

$$J_{s \rightarrow a} - J_{a \rightarrow s} = \alpha(T_s - T_a), \quad (2)$$

where we have assumed local thermal equilibrium so that we can speak about an adsorbate temperature T_a and a substrate surface temperature T_s . The heat transfer coefficient α can be related to the adsorbate vibrational energy relaxation times (which determines the average time for an adsorbate vibrational mode to decay by transferring the energy to the substrate). For adsorbates on metals the continuum of low-energy electronic excitations may result in very fast energy transfer from the adsorbate to the substrate (energy relaxation

via excitation of electron–hole pairs). It is clear that for small adsorbed molecules, the different vibrational modes of an adsorbed molecule will, in general, exhibit different temperatures, so that each molecular vibrational mode ν may be characterized by a different temperature T_ν . In this case the energy Q_ν in a mode ν satisfies

$$\frac{dQ_\nu}{dt} = \alpha_\nu(T_s - T_\nu). \quad (3)$$

At very high temperatures, the adsorbate modes may be highly excited, and in this case strong intra-molecular anharmonic coupling may lead to a transfer of energy between different adsorbate modes, in general (in order to conserve the energy) involving some energy exchange with the substrate. For example, if a coupling occurs between modes ν and ν' , then

$$\frac{dQ_\nu}{dt} = \alpha_\nu(T_s - T_\nu) + f(T_s, T_\nu, T_{\nu'}), \quad (4)$$

$$\frac{dQ_{\nu'}}{dt} = \alpha_{\nu'}(T_s - T_{\nu'}) + g(T_s, T_\nu, T_{\nu'}), \quad (5)$$

where the functions f and g result from the anharmonic coupling between modes ν and ν' . These functions will in general depend on the substrate temperature, because the transfer of energy between modes ν and ν' must involve absorbing or emitting some energy (elementary excitations) to the substrate.

In this paper we first present a general theory for the heat transfer coefficient α_ν , assuming that the coupling between the adsorbate vibrations and the substrate is via the electronic excitations. This seems to be the case in many femtosecond laser pulse experiments. Experiment and model calculations have shown that laser pulses in the femtosecond range can generate very high effective surface temperatures at metal surfaces [1, 2]. The laser photons are mostly absorbed in the substrate within a skin depth (~ 100 Å) and may lead to an effective electronic temperature of the order of several thousand kelvin. Because of heat transfer to the ions (i.e. to phonons) and heat diffusion into the bulk, the high electronic temperature only exists for ~ 1 ps. Because of the small heat capacity of a degenerate electron system, the increase in the phonon temperature is quite small. For this reason it is believed that laser-induced adsorbate reactions are caused by the interaction between the adsorbates and the hot electron system, rather than interaction with phonons.

Experimental data of the type discussed above are usually analyzed by assuming instantaneous equilibrium in each subsystem so that the surface region of the solid exhibits time-dependent electronic and ionic temperatures $T_e(t)$ and $T_i(t)$. The population of vibrational levels in the adsorbate system is also assumed to be in (local) equilibrium so that one can speak about an adsorbate temperature $T_a(t)$ which, however, may differ for different adsorbate vibrational modes. We note that this is likely to be a good approximation with respect to the type of application that interests us here. We are interested in reactions (e.g. desorption or diffusion) involving going over a reaction energy barrier. However, before going over the barrier an adsorbate will in general perform many jumps between its

vibrational levels. Thus, the ensemble of adsorbates will be (nearly) thermalized (except for the levels close to the barrier top, where the population is non-equilibrium because of the transfer over the barrier), and we can speak about the (time-dependent) adsorbate temperature $T_a(t)$. When $k_B T_a \gg \hbar\omega_0$ and $k_B T_e \gg \hbar\omega_0$ (where $\hbar\omega_0$ is the vibrational quantum; the numerical data presented below indicate that these inequalities are satisfied for the low-frequency modes involved in the adsorbate motions), the adsorbate temperature $T_a(t)$ is usually calculated using the *heat transfer equation* [1] with a friction coupling η_e between hot electrons and the adsorbate vibrational degree of freedom, i.e.

$$\frac{dT_a}{dt} = \eta_e [T_e(t) - T_a]. \quad (6)$$

Gordon and Tully [3] found, using molecular dynamics with electronic frictions, an agreement between the frictions and the lifetime of excited adsorbate vibrations at metal surfaces. Most experiments described above have been analyzed using $T_a(t)$ calculated from equation (6), where the electronic temperature $T_e(t)$ is calculated using the well-known two-temperature model [4]. From $T_a(t)$ the reaction rate $R(t)$ can be calculated using the standard theory of activated processes; $R(t) \propto \exp[-U_0/k_B T_a(t)]$. We will show later that for a harmonic oscillator at high temperature (classical limit) the energy $Q = k_B T_a$, so that (3) reduces to (6) if $\alpha = k_B \eta_e$.

Femtochemistry at surfaces, i.e. adsorbate reactions induced by hot electrons generated by femtosecond laser heating, has so far been used mainly to investigate desorption processes, since desorbing atoms or molecules can be detected easily in the gas phase using mass spectrometry. Recently, time-resolved nonlinear spectroscopy has been employed for real-time monitoring of adsorbate hopping at surfaces. Backus *et al* [5] employed sum-frequency generation (SFG) to follow the hot-electron-induced hopping of CO molecules on a stepped Pt surfaces. The observed hopping probability (or transition rate) was reproduced using $T_a(t)$ calculated for the the CO frustrated rotation (FR) mode from equation (6). Direct energy transfer between the hot electrons and the frustrated translation (FT) mode was found to be too slow to cause the hopping motion of the CO within the subpicosecond timescale. Thus, contrary to the usual expectations, the excitation of the FR mode, rather than the parallel translation, was proposed to be essential in the CO hopping process.

The work by Stépán *et al* [6] on the femtosecond-laser-induced hopping of atomic oxygen on a stepped Pt(111) surface also serves as an instructive example where equation (6) seems to fail. In addition to a high nonlinearity of the fluency dependence of the hopping probability, they reported that the two-pulse correlation of the hopping probability cannot be described by a constant frictional coefficient, η_e . However, if an empirical electronic temperature dependence of $\eta_e(T_e)$ is assumed, both the fluency dependence and the two-pulse correlation could be much better reproduced. As pointed out by Brandbyge *et al* [7], a dependence of η_e on T_e can be expected when the relevant adsorbate level lies far above the Fermi level. However, the unoccupied resonance of atomic oxygen on Pt(111) is broad and lies very close to

ϵ_F [8]. Culver *et al* [9] suggested that the vibrational damping due to coupling to electron–hole pair excitations becomes temperature dependent when the vibrational frequency ω_0 of the adsorbate mode satisfies $\hbar\omega_0 < k_B T_e$. Persson and Gadzuk [10] examined this issue critically. They showed that this result is overstated, and that the vibrational lifetime is strictly temperature independent, at least as long as the vibrational mode is treated as a harmonic oscillator and $k_B T_e \ll \epsilon_F$.

One possible explanation for the apparent T_e -dependent friction was given in [6]: an indirect excitation of the FT mode via anharmonic coupling to primary excited O–Pt stretch vibrations, which is excited via the friction coupling to the hot electrons. Such anharmonic coupling has been demonstrated to play a key role in several earlier processes, such as the hopping of CO on Pd(110) [11] and NH₃ on Cu(100) [12], where energy transfer from the C–O (N–H) stretch vibration (excited by a tunneling electron using a scanning tunneling microscope) to the FT mode induces hopping. However, another possibility is that the assumptions behind the derivation of equation (6) may not be valid.

Here we present a simple theory for the time-dependent evolution of the vibrational energy of an adsorbate due to the friction coupling to hot electrons in a metal. We present a formula for the energy transfer from femtosecond-laser-heated hot electrons to the adsorbate in terms of a newly introduced heat transfer coefficient, α . It is proved explicitly that our formula reduces to equation (6) if we assume a harmonic potential and a linear electron–vibration coupling. Both α and $T_a(t)$ are calculated numerically for a Morse potential. We compare the calculated laser fluency dependence of the reaction yield obtained using our new formula with the result obtained using the conventional heat transfer equation (6).

Our theory is also extended to a case where there is heat transfer between different vibrational modes excited by hot electrons. This mode coupling provides indirect heating of the vibrational temperature in addition to direct heating due to hot electrons. This permits us to explore the relative contribution to the vibrational heating depending on the friction coupling and the mode coupling. An approximated formula of such indirect heating derived for the linear coupled harmonic oscillators is applied to the recent real-time observations of carbon monoxide molecule and atomic oxygen hopping on an ultrafast laser-heated stepped Pt(111) surface [5, 6]. It is found that the transient temperature of the reaction coordinate mode can be high enough on the timescale of the adsorbate motion, even for the weak friction coupling to the hot electrons.

2. Heat transfer at surfaces

2.1. General formula

Let P_n be the probability that an adsorbate is in the vibrational excited state $|n\rangle$. The function $P_n(t)$ satisfies the rate equation

$$\frac{dP_n}{dt} = \sum_m P_m w_{m \rightarrow n} - \sum_m P_n w_{n \rightarrow m}, \quad (7)$$

where $w_{m \rightarrow n}$ is the transition rate from the vibrational state $|m\rangle$ to the state $|n\rangle$, caused by the interaction with hot electrons

in the metal. We assume local thermal equilibrium on the adsorbate so that

$$P_n = Z_a^{-1} e^{-\beta_a E_n}, \quad (8)$$

where $\beta_a = 1/k_B T_a$ and E_n ($n = 0, 1, \dots$) are the vibrational energy levels (for a harmonic oscillator $E_n = n\hbar\omega$). Substituting equation (8) in equation (7) and multiplying with E_n and summing over n gives an evolution of the vibrational energy $Q_a = \sum_n E_n P_n$:

$$\frac{dQ_a}{dt} = \sum_{nm} [e^{-\beta_a(E_m - E_n)} w_{m \rightarrow n} - w_{n \rightarrow m}] E_n P_n. \quad (9)$$

We assume that the coupling between the adsorbate vibrational normal mode coordinate u and the electronic excitations (electron–hole pair excitations, treated as bosons) in the substrate is of the form,

$$V(u) = \sum_q \lambda_q (b_q^\dagger + b_q) f(u), \quad (10)$$

where λ_q is the coupling constant and b_q^\dagger (b_q) is a creation (annihilation) operator of the substrate electronic excitations with the energy ω_q .

Using the Golden Rule formula, we obtain the rate for the vibrational transition $n \rightarrow m$ while emitting or absorbing ω_q ,

$$w_{n \rightarrow m} = \frac{2\pi}{\hbar} \sum_q |\lambda_q|^2 [(\langle n_q \rangle + 1) \delta(E_m - E_n + \omega_q) + \langle n_q \rangle \delta(E_m - E_n - \omega_q)] |\langle m | f(u) | n \rangle|^2, \quad (11)$$

where $\langle n_q \rangle = n(\omega_q) = 1/(e^{\beta_e \omega_q} - 1)$ ($\beta_e = 1/k_B T_e$) is the Bose–Einstein distribution function characterized by the electronic temperature T_e . Let us define the (weighted) density of states of the substrate electronic excitations

$$\rho_\lambda(\omega) = \sum_q |\lambda_q|^2 \delta(\omega - \omega_q), \quad (12)$$

so that equation (11) is rewritten as

$$w_{n \rightarrow m} = \frac{2\pi}{\hbar} \int d\omega [(n(\omega) + 1) \rho_\lambda(\omega) + n(-\omega) \rho_\lambda(-\omega)] \times \delta(E_m - E_n + \omega) |\langle m | f(u) | n \rangle|^2. \quad (13)$$

In a similar way we obtain

$$w_{m \rightarrow n} = \frac{2\pi}{\hbar} \int d\omega [(n(-\omega) + 1) \rho_\lambda(-\omega) + n(\omega) \rho_\lambda(\omega)] \times \delta(E_m - E_n + \omega) |\langle m | f(u) | n \rangle|^2. \quad (14)$$

Using that $n(\omega) + 1 = -n(-\omega)$, we can also write (13) and (14) as

$$w_{n \rightarrow m} = -\frac{2\pi}{\hbar} \int d\omega n(-\omega) [\rho_\lambda(\omega) - \rho_\lambda(-\omega)] \times \delta(E_m - E_n + \omega) |\langle m | f(u) | n \rangle|^2, \quad (15)$$

$$w_{m \rightarrow n} = \frac{2\pi}{\hbar} \int d\omega n(\omega) [\rho_\lambda(\omega) - \rho_\lambda(-\omega)] \times \delta(E_m - E_n + \omega) |\langle m | f(u) | n \rangle|^2. \quad (16)$$

Substituting equations (15) and (16) into equation (9) gives

$$\begin{aligned} \frac{dQ_a}{dt} &= \frac{2\pi}{\hbar} \sum_{nm} |\langle m|f(u)|n\rangle|^2 \\ &\times \int d\omega \delta(E_m - E_n + \omega) [\rho_\lambda(\omega) - \rho_\lambda(-\omega)] \\ &\times \left[e^{-\beta_a(E_m - E_n)} + \frac{n(-\omega)}{n(\omega)} \right] n(\omega) E_n P_n. \end{aligned} \quad (17)$$

For high temperatures we can expand

$$\begin{aligned} e^{-\beta_a(E_m - E_n)} &\simeq 1 - \beta_a(E_m - E_n), \\ \frac{n(-\omega)}{n(\omega)} &= -e^{\beta_c \omega} \simeq -(1 + \beta_c \omega), \end{aligned} \quad (18)$$

$$n(\omega) \approx 1/\beta_c \omega$$

so that, after ω -integration of equation (17), we obtain

$$\begin{aligned} \frac{dQ_a}{dt} &= \frac{2\pi}{\hbar} \sum_{nm} |\langle m|f(u)|n\rangle|^2 E_{nm} [\rho_\lambda(E_{nm}) \\ &- \rho_\lambda(-E_{nm})] \frac{\beta_c - \beta_a}{\beta_c E_{nm}} E_n P_n, \end{aligned} \quad (19)$$

where $E_{nm} = E_n - E_m$. We assume electron-hole pair excitations as a substrate heat bath and take $\rho_\lambda(\omega) = \bar{\lambda}^2 \rho^2(\epsilon_F) \omega$, where $\rho(\epsilon_F)$ is the substrate density of states at the Fermi level and $\bar{\lambda}$ is some average coupling parameter. Using this, equation (19) takes the form

$$\frac{dQ_a}{dt} = \alpha(T_a)(T_e - T_a), \quad (20)$$

where the *heat transfer coefficient*

$$\alpha(T_a) = \frac{2\pi}{\hbar} 2k_B [\bar{\lambda} \rho(\epsilon_F)]^2 \sum_{nm} |\langle m|f(u)|n\rangle|^2 (-E_{nm}) \beta_a E_n P_n, \quad (21)$$

depends on T_a but *not* on T_e . If we introduce the electronic friction $\eta_e = (8\pi \omega_a) [u_0 \bar{\lambda} \rho(\epsilon_F)]^2$ (where $u_0 = (\hbar/2m_a^* \omega_a)^{1/2}$ is the amplitude of the zero-point adsorbate vibration), we get from equation (21)

$$\alpha(T_a) = k_B \eta_e \frac{\beta_a}{\hbar \omega_a} \sum_{nm} |\langle m|\bar{f}(u)|n\rangle|^2 (-E_{nm}) E_n P_n, \quad (22)$$

where $\bar{f} = f/u_0$. Note that we can write

$$\begin{aligned} &\sum_{nm} |\langle m|\bar{f}(u)|n\rangle|^2 (-E_{nm}) E_n P_n \\ &= \frac{1}{2} \sum_{nm} |\langle m|\bar{f}(u)|n\rangle|^2 (-E_{nm}) (E_n P_n - E_m P_m) \\ &= \frac{1}{2} \sum_{nm} |\langle m|\bar{f}(u)|n\rangle|^2 (-E_{nm}) (E_n - E_m e^{-\beta_a(E_m - E_n)}) P_n \\ &\approx \frac{1}{2} \sum_{nm} |\langle m|\bar{f}(u)|n\rangle|^2 E_{nm}^2 P_n. \end{aligned} \quad (23)$$

Substituting this in equation (22) gives

$$\alpha(T_a) = k_B \eta_e \beta_a \sum_n M_n E_n P_n, \quad (24)$$

where

$$M_n = \sum_m |\langle m|\bar{f}(u)|n\rangle|^2 \frac{E_{nm}^2}{2E_n \hbar \omega_a}. \quad (25)$$

The factor M_n takes into account that when the adsorbate temperature increases, the adsorbate will probe regions in u far away from the equilibrium position $u = 0$, and this will result in a modified coupling (overlap) between the adsorbate orbitals and the metal electrons. This picture is particularly clear when u corresponds to the vertical displacement of the adsorbate. In this case, as $u \rightarrow \infty$, the overlap between the adsorbate and the substrate will vanish, i.e. $f(u) = 0$, and in this limit $M_n = 0$. In earlier studies based on the electronic friction concept (equation (6)), this effect was usually taken into account by assuming that the electronic friction, $\eta_e(z)$, depends on the separation z between the adsorbate and the substrate, with $\eta_e(z) \rightarrow 0$ as $z \rightarrow \infty$.

If we assume that the adsorbate mode can be treated as a harmonic oscillator and if we assume a linear coupling $f(u) = u = u_0(b + b^\dagger)$, then we get from equation (25) that $M_n = 1$. Using this and that at high temperatures $\sum_n E_n P_n = 1/\beta_a$ for a harmonic oscillator, equation (24) reduces to $\alpha(T_a) = k_B \eta_e$. Since for a harmonic oscillator at high temperatures $Q_a = k_B T_a$, we obtain from (20) and (24)

$$\frac{dT_a}{dt} = \eta_e (T_e - T_a), \quad (26)$$

which agrees with equation (6). The present simple theory demonstrates that the equation (6) is only valid for a harmonic oscillator with linear electron-vibration coupling. We note that earlier experiments [1, 2] and recent ones (e.g. CO hopping and desorption on Cu(100) [13], CO hopping on a stepped Pt surface [5]) have been successfully analyzed using equation (6) with a time-independent (or temperature-independent) friction η_e . However, this assumption is not valid even when the adsorbate mode is treated as a harmonic oscillator. In addition, if the temperature T_a becomes so high that the levels in the anharmonic part of the potential well are strongly populated, then one may expect a strong temperature dependence of α . This is likely to be the case (for a very short time) in many high-fluency ultrafast laser spectroscopy experiments.

In a general case, the sum over n in equation (24) must be performed numerically. However, the m -sum in equation (25) can be performed analytically. Using that

$$\sum_m E_{nm}^2 |\langle m|f(u)|n\rangle|^2 = \langle n|[f(u), H][H, f(u)]|n\rangle,$$

and

$$[H, f(u)]\Psi_n = -\frac{\hbar^2}{2m_a^*} [f''(u)\Psi_n(u) + 2f'(u)\Psi_n'(u)],$$

we get

$$M_n = \frac{\hbar \omega_a}{2E_n} \int du \Phi_n^2(u), \quad (27)$$

where

$$\Phi_n = u_0 [f''(u)\Psi_n(u) + 2f'(u)\Psi_n'(u)]. \quad (28)$$

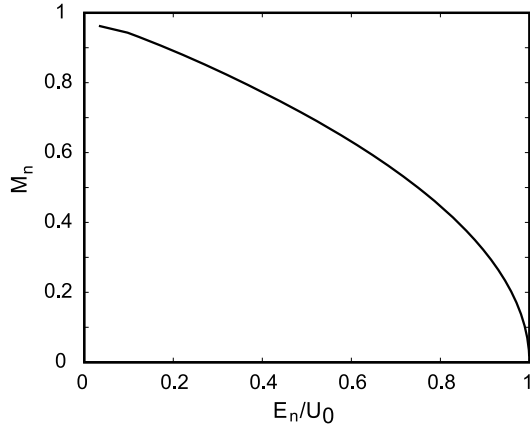


Figure 1. The factor M_n as a function of E_n/U_0 calculated using the normalized vibrational wavefunctions for a Morse potential with $U_0/\hbar\omega_0 = 15$.

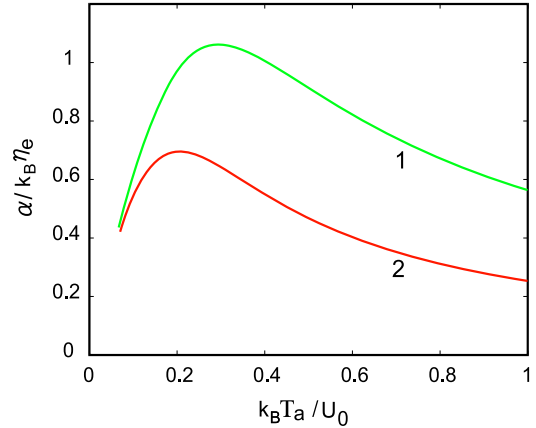


Figure 2. The heat transfer coefficient α (in units of $k_B\eta_e$) as a function of $k_B T_a/\hbar\omega_0$. Curves **1** and **2** are calculated from equation (21) with $M_n = 1$ and M_n given by equation (25) for a Morse potential equation (29), respectively, for $U_0/\hbar\omega_0 = 15$.

2.2. Model calculation for Morse potential

Let us consider the desorption of an adatom (mass m) from a metallic substrate and assume that the substrate can be considered as being rigid. Assume that the interaction potential is well approximated by a Morse potential

$$U(u) = U_0 (1 - e^{-u/u_0})^2, \quad (29)$$

with the vibrational energies

$$E_n = (n + 1/2)\hbar\omega_0 - (n + 1/2)^2(\hbar\omega_0)^2/4U_0, \quad (30)$$

where U_0 is the depth of the potential well and u is the displacement of the atom normal to the substrate surface, and $\omega_0 = (2U_0/m^*)^{1/2}/u_0$ is the frequency of small-amplitude vibrations in the bottom of the well. The Schrödinger equation for $H = p^2/2m^* + U(u)$ is solved numerically to obtain the normalized vibrational wavefunction $\Psi_n(u)$. In a first approximation, the interaction energy $U(u) \sim |f(u)|^2$, so we take $f(u) = u_0(1 - e^{-u/u_0})$.

We first show in figure 1 the result of the calculation of $M_n(E_n)$ as a function of U_0/E for a Morse potential. In the calculation we have used $U_0/\hbar\omega_0 = 15$, which gives 30 vibrational levels in the potential well. Note that M_n decreases with increasing vibrational energy E_n . This simply reflect that the (average) position of the atom moves further away from the surface as the vibrational excitation energy increases, which reduces the atom–surface interaction.

The heat transfer coefficient α of equation (21) is calculated for a linear electron–phonon coupling $f(u) = u$ (this gives $M_n = 1$) and for $f(u) = u_0(1 - e^{-u/u_0})$. Figure 2 shows α (in unit of $k_B\eta_e$) as a function of $k_B T_a/\hbar\omega_0$ calculated from equation (21) with $M_n = 1$ and M_n given by equation (25), respectively. It is noted that for a classical harmonic oscillator $\alpha/k_B\eta_e = 1$, but in the present case α gets modified as a result of anharmonicity (as manifested in curve **1**) and by the fact that $M_n < 1$ (curve **2**).

We first calculate $T_a(t)$ using our newly proposed energy (heat) transfer equation (20). The hot electron temperature

$T_e(t)$ (the red curve in figure 3) is calculated using the well-known two-temperature mode [4] with a laser pulse width (full width half maximum, FWHM) of 0.13 ps and wavelength of of 800 nm, and an absorbed laser fluency of 70 J m^{-2} irradiated on a Pt metal at the initial temperature $T_{el} = 100 \text{ K}$. The blue and black curves are the adsorbate temperature $T_a(t)$ calculated using the conventional (black curve) and the newly proposed heat transfer equation (blue curve) for a constant friction $1/\eta_e = 0.2$ and 1.0 ps . The typical timescale of energy transfer from the hot electrons in the substrate to the different adsorbate vibrational modes is characterized by friction parameters, η_e , which differ for each mode. The efficient coupling time of $1/\eta_e = 0.2 \text{ ps}$ gives rise to a higher and quicker increase in $T_a(T)$ than that at $1/\eta_e = 1.0 \text{ ps}$.

We have found in figure 3 that, although the qualitative transient profiles of $T_a(t)$ are similar, our model gives substantially lower adsorbate peak temperature than that calculated using equation (6) for a harmonic potential. The reason why our theory gives a smaller maximal adsorbate temperature than the previous model due to the smaller heat transfer coefficient predicted by our model. This results from the fact that when the adsorbate temperature increases, the adsorbate will, on average, move away from the substrate, leading to a weaker adsorbate–substrate coupling. The same effect is the reason why, for long times, the adsorbate temperature in our model is higher than in the model that assumes a temperature-independent heat transfer coefficient. That is, α determines not only the heat transfer from the substrate to the adsorbate (when the substrate is hotter than the adsorbate), but also the energy transfer from the adsorbate to the substrate when the adsorbate is hotter than the substrate. So the reduced magnitude of α in our model implies that the transfer of the adsorbate heat to the substrate occurs more slowly than in the previous model, so the adsorbate temperature will be higher than in the previous model for large times.

Since the reaction (e.g. desorption) rate depends exponentially on the adsorbate temperature, the difference in $T_a(t)$ will result in a large modification of the reaction yield. Figure 4 shows the desorption yield $Y(F)$ for $1/\eta_e = 0.2$

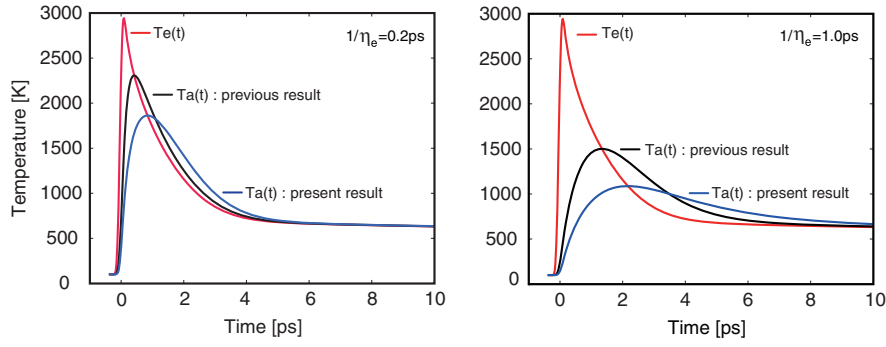


Figure 3. Time dependence of electron temperature T_e (red curve) and adsorbate temperature T_a calculated using a conventional (black curve), and newly proposed heat transfer equation (blue curve) for friction coupling $1/\eta_e = 0.2$ and 1 ps.

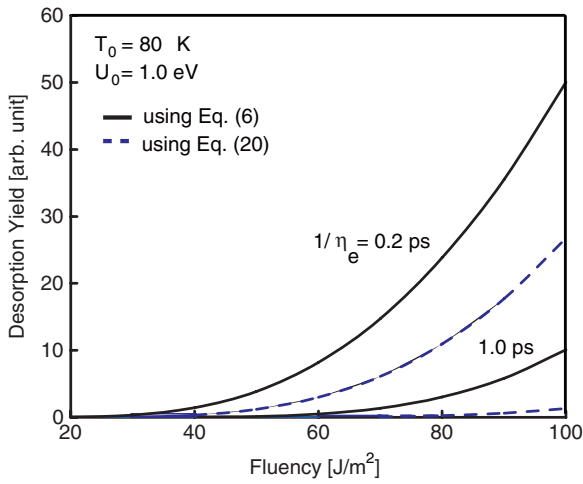


Figure 4. Desorption yield $Y(F) = \exp[-U_0/k_B T_a(t)]$ for $1/\eta_e = 0.2$ and 1.0 ps as a function of laser fluency at the initial substrate temperature 80 K and the barrier height $U_0 = 1.0$ eV. The black and blue dotted curves are calculated from $T_a(t)$ obtained from equations (6) and (20), respectively.

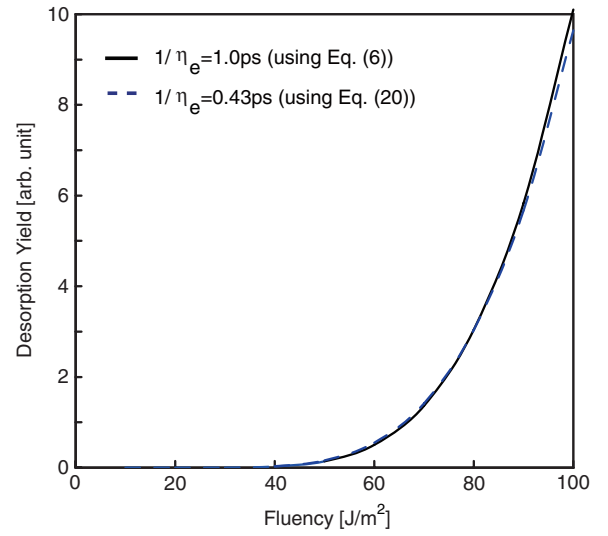


Figure 5. Desorption yield as a function of fluency. The black and blue dotted curves are calculated using $T_a(t)$ obtained from equation (6) with $1/\eta_e = 1$ ps and from equation (20) with $1/\eta_e = 0.43$ ps, respectively.

and 1 ps as a function of the laser fluency F at the substrate temperature $T_0 = 80$ K:

$$Y(F) = \int R(t, F) dt, \quad (31)$$

where we assume a simple Arrhenius expression, $R(t) = \exp[-U_0/k_B T_a(t)]$, with $U_0 = 1.0$ eV. Here we neglect the prefactor, since the absolute yield is not a very important parameter for these types of simple one-dimensional models. As a result of the lower $T_a(t)$ for the Morse potential (blue dotted curves) than for a harmonic potential (black solid curves), the desorption yield exhibits a smaller nonlinear increase with fluency. However, it seems like the shape of the fluency dependence is very similar for the two cases, and almost the same results are obtained using $1/\eta_e = 0.43$ ps in equation (20) for a Morse potential and $1/\eta_e = 1$ ps in equation (6) (blue dotted and black solid curve, respectively, in figure 5).

The transient behavior of $T_a(t)$ calculated using the newly proposed heat transfer equation may not directly manifest

itself in the analysis of experiments like desorption where the reaction yield is obtained by the time integration of the time-dependent reaction rate $R(t)$ as a function of the laser fluency. An appropriate choice of η_e (and also U_0) may reproduce the experimental results using a simple heat transfer equation (6). The present theory will be appreciated in the time-resolved observation that is directly related the transient profile of $T_a(t)$.

2.3. Energy transfer via mode–mode coupling

Backus *et al* [5] showed, with the help of calculations of the hopping probability derived from transient temperatures for the FT and FR modes of CO, that excitation of the FR mode is essential in the CO hopping process. Excitation of the FT mode is significantly too slow to cause the hopping motion of the CO within the subpicosecond timescale observed in the experiment. The primary step therefore involves hot electrons exciting the FR mode, followed by energy transfer to the FT mode. The reason why this indirect reaction path dominates is the much stronger electronic friction coupling to the FR mode.

The reaction pathway may nevertheless involve mode–mode coupling between the frustrated translation (thermally excited in their experiment performed at 100 K) and the frustrated rotation.

Stépan *et al* [6] reported that the two-pulse correlation of the hopping probability of O atoms on a stepped Pt surface could not be described in terms of the transient temperatures of the frustrated mode calculated using equation (6) with a single constant friction coefficient η_e . However, if an appropriate hot electron temperature dependence of $\eta_e(T_e)$ was assumed, the experimental data was much better reproduced. They proposed as a possible explanation for the apparent temperature-dependent friction that the O–Pt stretch mode is first excited by the hot electrons, followed by excitation of the translation mode of the O atom via anharmonic coupling to the O–Pt stretch mode.

These two experimental studies, and the elementary processes suggested therein, motivates us to explore the energy transfer in the presence of the coupling between two different vibrational modes excited by hot electrons [14].

Consider an adsorbate with two different vibrational modes ω_a and ω_b , excited by hot electrons via the friction couplings η_e^a and η_e^b , respectively. We assume anharmonic coupling between the modes so that energy can be transferred directly between the two modes. In order to conserve the total energy, the vibrational transitions are accompanied by the emission or absorption of elementary substrate excitations. The processes that we will consider here are illustrated schematically in figure 6. We assume the Hamiltonian to be of the form $H = H_a + H_b + V$, where H_a is related to the vibrational mode **a** (normal mode coordinate u_a) and similarly for H_b . We will assume that H_a commutes with H_b . The anharmonic coupling V between modes **a** and **b** is assumed to be of the form

$$V(u) = \sum_q \tilde{\lambda}_q (b_q^\dagger + b_q) f(u_a, u_b), \quad (32)$$

where the coupling constant $\tilde{\lambda}_q$ is temperature independent. The nucleus–electron interaction is, in general, of the form $\sum_{\alpha,\beta} V_{\alpha,\beta}(u_1, u_2 \dots) c_\alpha^\dagger c_\beta$ (where u_1 and u_2 , are, for example, normal mode or reaction coordinates of the nucleus and $c_\alpha^\dagger c_\beta$ represents the electronic excitation from level ϵ_β to level ϵ_α in the substrate) and, since here we treat the electronic excitations as bosons (b_q^\dagger, b_q), we get terms of the form $\sum_q V_q(u_1, u_2 \dots) (b_q^\dagger + b_q)$. The lifetimes of the low-frequency adsorbate modes are determined by the same coupling [10], but with $V_{\alpha,\beta}(u_1, u_2, \dots)$ expanded to linear order in u_1, u_2, \dots (this has been studied in great detail in many earlier papers [15, 16]). The linear order terms, however, cannot give rise to the process of energy transfer between different adsorbate vibrational modes. We therefore consider the leading nonlinear term in the expansion of $V(u)$ which can give rise to mode–mode coupling and energy transfer from one mode to another. The new term that we study only becomes important when the substrate electron system is very hot.

Let us now calculate the probability rate $w_{n_a \rightarrow m_a}$ that a vibrational quantum is transferred between mode **a** and **b**, while mode **a** makes a transition from state n_a to m_a accompanied by

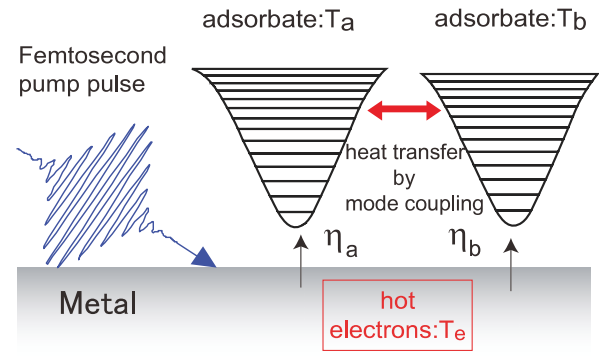


Figure 6. Heat transfer in the presence of mode coupling between different vibrational mode **a** and **b** excited by hot electrons via friction coupling η_a and η_b , respectively.

emission or absorption of a bulk elementary excitation ω_q . We get

$$w_{n_a \rightarrow m_a} = - \int d\omega [\rho_\lambda(\omega) - \rho_\lambda(-\omega)] n(-\omega) W_{n_a m_a}(\omega), \quad (33)$$

where

$$\rho_\lambda(\omega) = \sum_q |\tilde{\lambda}_q|^2 \delta(\omega_q - \omega),$$

and

$$\begin{aligned} W_{n_a m_a}(\omega) &= \frac{2\pi}{\hbar} \sum_{n_b, m_b} |\langle m_a, m_b | f(u_a, u_b) | n_a, n_b \rangle|^2 \\ &\times \delta(E_{m_a} + E_{m_b} + \omega - E_{n_a} - E_{n_b}) P(n_b) \\ &= \sum_{n_b, m_b} F_{n_a m_a}(n_b, m_b, \omega) P(n_b), \end{aligned} \quad (34)$$

and

$$w_{m_a \rightarrow n_a} = \int d\omega [\rho_\lambda(\omega) - \rho_\lambda(-\omega)] n(\omega) W_{m_a n_a}(-\omega), \quad (35)$$

where

$$\begin{aligned} W_{m_a n_a}(-\omega) &= \frac{2\pi}{\hbar} \sum_{n_b, m_b} |\langle m_a, m_b | f | n_a, n_b \rangle|^2 \\ &\times \delta(E_{n_a} + E_{n_b} - \omega - E_{m_a} - E_{m_b}) P(m_b) \\ &= \sum_{n_b, m_b} F_{n_a m_a}(n_b, m_b, \omega) P(n_b) e^{-\beta_b(E_{m_b} - E_{n_b})}. \end{aligned} \quad (36)$$

Substituting equations (35) and (33) into equation (9) gives a heat transfer equation for the **a**-mode:

$$\begin{aligned} \frac{dQ_a}{dt} &= \sum_{n_a m_a} \sum_{n_b m_b} \int d\omega [\rho_\lambda(\omega) - \rho_\lambda(-\omega)] F_{n_a m_a}(n_b, m_b, \omega) \\ &\times \left[e^{-\beta_a(E_{m_a} - E_{n_a})} e^{-\beta_b(E_{m_b} - E_{n_b})} + \frac{n(-\omega)}{n(\omega)} \right] \\ &\times n(\omega) E_{n_a} P(n_a) P(n_b). \end{aligned} \quad (37)$$

Since at high temperatures $n(\omega) \approx 1/\beta_e \omega$ so that $[\rho_\lambda(\omega) - \rho_\lambda(-\omega)] n(\omega) \approx 2\tilde{\lambda}^2 \rho^2(\epsilon_F)/\beta_e$, we obtain

$$\begin{aligned} \frac{dQ_a}{dt} &= 2\tilde{\lambda}^2 \rho^2(\epsilon_F) \frac{1}{\beta_e} \sum_{n_a m_a} \sum_{n_b m_b} n_b m_b \\ &\times \int d\omega F_{n_a m_a}(n_b, m_b, \omega) [-\beta_a(E_{m_a} - E_{n_a}) \\ &- \beta_b(E_{m_b} - E_{n_b}) - \beta_e \omega] E_{n_a} P(n_a) P(n_b). \end{aligned} \quad (38)$$

Performing the ω -integral gives

$$\begin{aligned} \frac{dQ_a(t)}{dt} &= \frac{S}{2} \sum_{n_a m_a} \sum_{n_b m_b} |\langle m_a, m_b | \bar{f} | n_a, n_b \rangle|^2 \\ &\times \left[\left(\frac{\beta_a}{\beta_e} - 1 \right) (-E_{m_a n_a}) + \left(\frac{\beta_b}{\beta_e} - 1 \right) (-E_{m_b n_b}) \right] \\ &\times E_{n_a} P_{n_a} P_{n_b}, \end{aligned} \quad (39)$$

where $S = 8\pi [u_{a0} u_{b0} \bar{\lambda} \rho(\epsilon_F)]^2$ (where u_{a0} and u_{b0} are the zero-point vibration amplitudes of mode **a** and **b**, respectively), $\bar{f} = f/(u_{a0} u_{b0})$, $E_{m_a n_a} = E_{m_a} - E_{n_a}$, $E_{m_b n_b} = E_{m_b} - E_{n_b}$. Using the analog of equation (23) we get

$$\begin{aligned} M_{aa} &= \frac{1}{2} \sum_{n_a m_a} \sum_{n_b m_b} |\langle m_a, m_b | \bar{f} | n_a, n_b \rangle|^2 (-E_{m_a n_a}) E_{n_a} P(n_a) P(n_b) \\ &\approx \frac{1}{4} \sum_{n_a m_a} \sum_{n_b m_b} |\langle m_a, m_b | \bar{f} | n_a, n_b \rangle|^2 E_{m_a n_a}^2 P(n_a) P(n_b), \end{aligned} \quad (40)$$

and

$$\begin{aligned} M_{ab} &= \frac{1}{2} \sum_{n_a m_a} \sum_{n_b m_b} |\langle m_a, m_b | \bar{f} | n_a, n_b \rangle|^2 (-E_{m_b n_b}) E_{n_a} P(n_a) P(n_b) \\ &\approx \frac{1}{4} \sum_{n_a m_a} \sum_{n_b m_b} |\langle m_a, m_b | \bar{f} | n_a, n_b \rangle|^2 E_{m_b n_b} E_{m_a n_a} P(n_a) P(n_b). \end{aligned} \quad (41)$$

Substituting this into equation (37) gives

$$\begin{aligned} \frac{dQ_a(t)}{dt} &= \alpha_a (T_e - T_a) + k_B S [(T_e - T_a) M_{aa} \beta_a \\ &+ (T_e - T_b) M_{ab} \beta_b], \end{aligned} \quad (42)$$

where we have added the contribution $\alpha_a (T_e - T_a)$ due to the direct coupling between mode **a** and the substrate excitations (see section 2.1). In a similar way, we obtain

$$\begin{aligned} \frac{dQ_b(t)}{dt} &= \alpha_b (T_e - T_b) + k_B S [(T_e - T_b) M_{bb} \beta_b \\ &+ (T_e - T_a) M_{ba} \beta_a], \end{aligned} \quad (43)$$

where $M_{ba} = M_{ab}$ and

$$M_{bb} = \frac{1}{4} \sum_{n_a m_a} \sum_{n_b m_b} |\langle m_a, m_b | \bar{f} | n_a, n_b \rangle|^2 E_{m_b n_b}^2 P(n_a) P(n_b). \quad (44)$$

Note that M_{aa} , M_{ab} and M_{bb} depend on T_a and T_b but not on the substrate temperature T_e . It is also remarked that if $T_e \neq T_a$ (or $T_e \neq T_b$), then the second terms of equations (42) and (43) do not vanish even for two identical modes ($\omega_a = \omega_b$) with the same temperatures $T_a = T_b$. This can be understood as follows. Assume first that there are no direct frictional coupling between modes **a** and **b** and the substrate, i.e. $\eta_a = \eta_b = 0$ (so that $\alpha_a = \alpha_b = 0$ in equations (42) and (43)). However, we will assume that higher-order terms in the expansion of $f(u_a, u_b)$, which couple mode **a** to mode **b**, are nonvanishing. Assume now that $T_a = T_b \neq T_e$. In that case, if the new terms that we derived (the second terms in equations (42) and (43)) vanish when $T_a = T_b$, then $dQ_a/dt = 0$ and we would *never* reach thermal equilibrium, in spite of the fact that there is a coupling between the adsorbed molecule and the electronic excitations of the substrate. However, the terms that we calculated do not vanish unless $T_e = T_a = T_b$, so

we will, after a long enough time, reach thermal equilibrium as expected because of the coupling to the substrate electrons.

As a simple illustration, assume that both modes can be treated as harmonic oscillators and assume the lowest-order coupling $f(u_a, u_b) = u_a u_b$. Substituting this into equations (40), (41) and (44) gives:

$$\begin{aligned} M_{aa} &= \frac{\omega_a}{\omega_b} (\beta_a \beta_b)^{-1}, & M_{bb} &= \frac{\omega_b}{\omega_a} (\beta_a \beta_b)^{-1}, \\ M_{ab} &= \omega_a \omega_b, \end{aligned}$$

so that

$$\frac{dT_a(t)}{dt} = \eta_a (T_e - T_a) + S \omega_a \left[\frac{(T_e - T_a)}{\omega_b \beta_b} + (T_e - T_b) \omega_b \beta_b \right], \quad (45)$$

$$\frac{dT_b(t)}{dt} = \eta_b (T_e - T_b) + S \omega_b \left[\frac{(T_e - T_b)}{\omega_a \beta_a} + (T_e - T_a) \omega_a \beta_a \right]. \quad (46)$$

We define indirect friction parameters $\eta'_a = S \omega_a$ and $\eta'_b = S \omega_b$ so that $\eta'_a / \eta'_b = \omega_a / \omega_b$. Notice that the second terms in the [...] brackets in equations (45) and (46) are, in general, negligible compared to the first terms. Thus we can write

$$\frac{dT_a(t)}{dt} \approx \left[\eta_a + \eta'_a \frac{k_B T_b}{\hbar \omega_b} \right] (T_e - T_a), \quad (47)$$

$$\frac{dT_b(t)}{dt} \approx \left[\eta_b + \eta'_b \frac{k_B T_a}{\hbar \omega_a} \right] (T_e - T_b). \quad (48)$$

Note that the *effective friction*, $\eta_a^{\text{eff}} = \eta_a + \eta'_a (k_B T_b / \hbar \omega_b)$, depends on the temperature of the coupling partner mode. In general, one expects $S \sim (\eta_a \eta_b / \omega_a \omega_b)^{1/2} (u_{a0} u_{b0} / a^2)$ so that $\eta'_a \sim (\eta_a \eta_b)^{1/2} (\omega_a / \omega_b)^{1/2} (u_{a0} u_{b0} / a^2)$, where a is some atomic distance. Since for low-frequency vibrations $u_{a0} \sim 0.1 \text{ \AA}$, we typically get $\eta'_a / \eta_a \sim 0.01 (\eta_b / \eta_a)^{1/2}$. However, this estimate is very rough and much larger values for η'_a may be expected under some circumstances.

Figure 7 shows the time dependence of T_a and T_b calculated using equations (47) and (48) in the presence of the mode coupling term between the adsorbate modes and the substrate. We show results for several strengths of the coupling parameter, $\eta'_a = 0.1, 0.2, 0.5$ and 1.0 ps^{-1} . We have assumed that there is no direct coupling between the mode **a** and the hot electrons, i.e. $\eta_a = 0$. Note that, as expected, with increasing η'_a the temperature of mode **a** increases more quickly with time and reaches higher maximal values. It is clear that the mode coupling $V = u_a u_b \sum_q \lambda_q (b_q + b_q^+)$ can, for physically reasonable values of the coupling parameters, give a strong temperature increase and may give the dominant contribution to the heating of mode **a** when the direct coupling η_a between mode **a** and the hot electrons is small, as is often the case, for example, for parallel adsorbate vibrations.

As mentioned before, Backus *et al* [5] reported an indispensable role of the excitation of the FR mode with an efficient friction coupling rather than the FT mode in laser-activated hopping of CO molecules on a stepped Pt surface. This conclusion was supported by the transient temperature profile of each mode. As depicted in figure 8, the observed

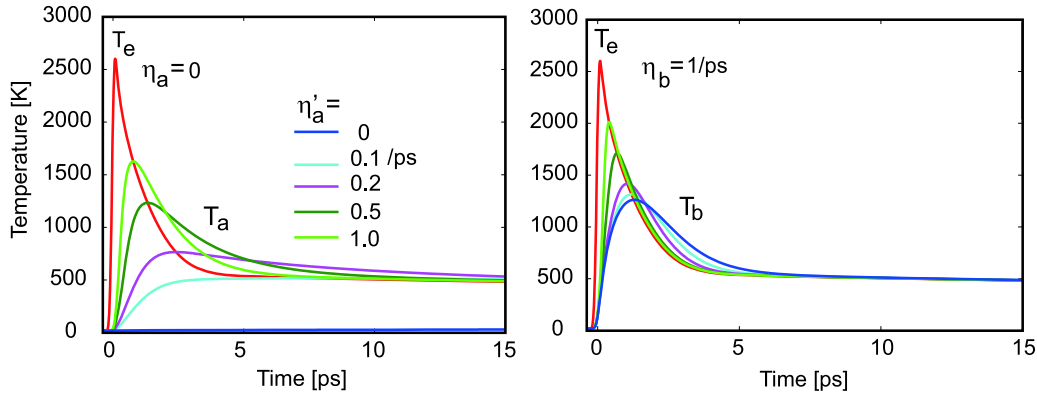


Figure 7. Time dependence of T_a and T_b in the presence of the energy transfer between modes and the substrate calculated using equations (47) and (48). The initial substrate temperature $T_0 = 20$ K, the laser fluency is 70 J m^{-2} , $\omega_a = 20 \text{ meV}$, $\omega_b = 50 \text{ meV}$, $\eta_a = 0 \text{ ps}^{-1}$ (i.e. no direct coupling between mode **a** and the hot electrons), $\eta_b = 1.0 \text{ ps}^{-1}$, $\eta'_a/\eta'_b = \omega_a/\omega_b$, and for several strength of the mode coupling $\eta'_a = 0.1, 0.2, 0.6$ and 1.0 ps^{-1} .

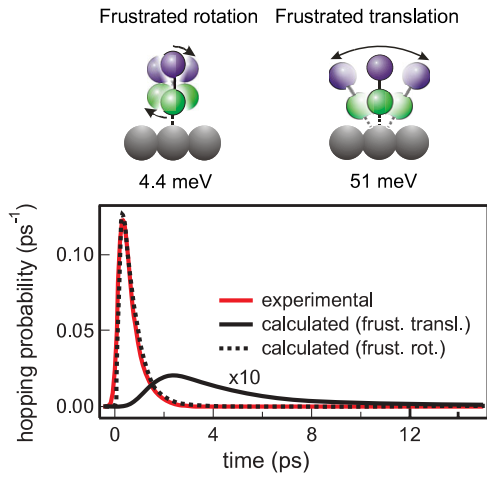


Figure 8. CO hopping probability as a function of time. The red curve is the experimental result [5] and the dashed curve is calculated using equation (6) with $1/\eta = 0.1 \text{ ps}$ for the FR mode, while the solid curve is for the FT mode with $1/\eta = 4 \text{ ps}$. Courtesy of M Bonn.

transient hopping probability was nicely reproduced using the FR mode temperature calculated using equation (6) with $1/\eta_c = 0.1 \text{ ps}$. It is noted here that the initial substrate temperature is 100 K, so the FT mode is thermally excited in their experiment. We apply equations (47) and (48) to this system. The hopping probability for CO on a Pt(111) surface at 100 K and a laser fluency 70 J m^{-2} is calculated using $U_0 = 0.4 \text{ eV}$, $\omega_a(\text{FT mode}) = 4.4 \text{ meV}$ and $1/\eta_a = 3.8 \text{ ps}$, $\omega_b(\text{FR mode}) = 51 \text{ meV}$ and $1/\eta_b = 0.1 \text{ ps}$ [5], and $1/\eta'_a = 0.8 \text{ ps}$. The result shown in figure 9 is found to be in good agreement with the experimental result. Although energy exchange *solely* via excitation of the FT mode is significantly too slow to cause the hopping motion of the CO within a subpicosecond timescale observed in the experiment (see figure 8), the strong coupling to the FR mode heats up the FT mode enough to induce hopping. It is also very important to emphasize that the excitation of the FR mode by hot electrons is absolutely required for the FT mode to become excited within a picosecond for hopping motion. The present

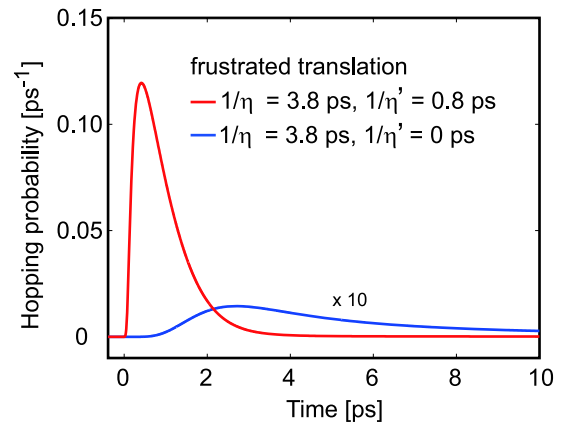


Figure 9. The calculated hopping probability calculated for the FT mode with mode coupling to the FR mode ($1/\eta' = 0.8 \text{ ps}$) using equations (47) and (48). The blue curve is calculated for the FT mode without mode coupling. See the text for the parameters used herein.

analysis suggests the possibility of substantial heating of the FT mode through mode coupling to the FR mode that has a strong coupling to hot electrons.

We also refer to the recent work by Stépán *et al* [6] on the femtosecond-laser-induced hopping of atomic oxygens on a stepped Pt(111) surface. In addition to a high nonlinearity of the fluency dependence of the hopping probability, they reported that the two-pulse correlation of this hopping probability could not be described by $T_a(t)$ calculated by equation (6) using a constant η_a . However, if an empirical electronic temperature dependence of $\eta_c(T_e)$ was assumed, the experimental data could be better reproduced. The temperature-dependent friction was postulated to be associated with anharmonic coupling between the primary excitation of the O–Pt stretch vibration by hot electrons and the frustrated translation (reaction coordinate) of the O atoms. Our theory predicts the adsorbate temperature dependence of a heat transfer coefficient. Even for coupled harmonic oscillators with linear coupling to the heat bath (substrate), the effective friction coupling of one mode (the prefactors in equations (47)

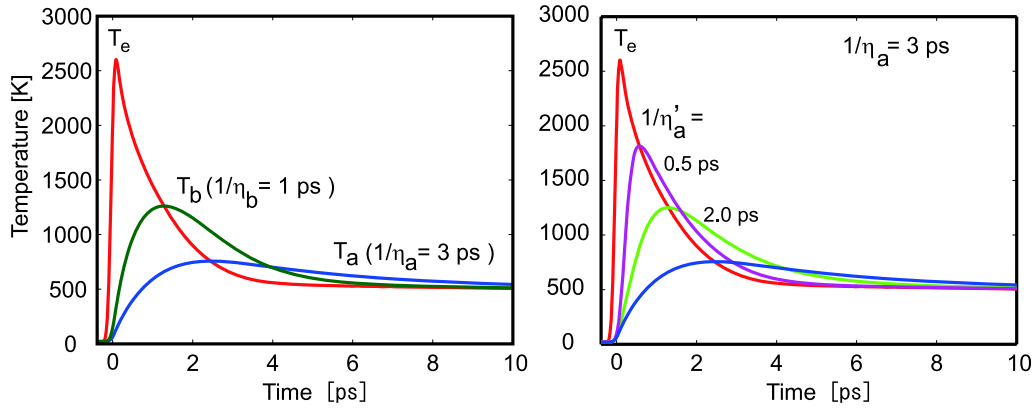


Figure 10. Left: the adsorbate temperature $T_a(t)$ ($1/\eta_a = 3$ ps) and $T_b(t)$ ($1/\eta_b = 1$ ps) without mode coupling ($1/\eta'_a = 0$), where $\omega_a = 50$ meV and $\omega_b = 60$ meV. The rest of the parameters are the same as before. Right: the adsorbate temperature $T_a(t)$ ($1/\eta_a = 3$ ps) for $1/\eta'_a = 0.5$ and 2.0 ps.

and (48)) depends on the temperature of the other mode in the presence of the mode coupling.

Figure 10 shows an example where modes **a** and **b** have insufficient friction coupling to the substrate, so that T_a and T_b do not increase enough to induce a motion (left), while T_a gets heated up through mode coupling to the **b** mode (right). Here we use $\omega_a = 50$ meV and $\omega_b = 60$ meV, which correspond to the atomic oxygen FT mode and the O–Pt stretch mode on a Pt(111) surface [17]. There is experimental evidence for anharmonic mode coupling between these modes from the temperature dependence of the O–Pt stretch mode observed by infrared absorption spectroscopy [18]. We also take $1/\eta_b = 1$ ps from the low-temperature limit of the linewidth of the O–Pt stretch mode. It is interesting to find that T_a increase with η'_a , and will reach high enough for hopping.

3. Summary and perspective

We have proposed a theoretical model for the energy (heat) transfer between adsorbate molecules and a metallic substrate irradiated by femtosecond laser pulses based on a frictional coupling under the assumption of local thermal equilibrium (coupling of heat baths). This extends existing theories of heat transfer to the adsorbate from hot electrons via electronic friction coupling by considering a general anharmonic oscillator potential for the adsorbate motion and coupling between different vibrational modes of the adsorbate. The coupling to the substrate is expressed in terms of a heat transfer coefficient α , which considers that the wavefunctions and energy of the vibrational mode in the reaction potential well in terms of M_n depend on the adsorbate temperature T_a , not on the electron temperature T_e . The factor M_n takes into account that when the adsorbate temperature increases, the adsorbate will probe regions far away from the equilibrium position, and this will result in a modified coupling between the adsorbate orbitals and the metal electrons. For desorption processes we expect the coefficients M_n to decrease with increasing n due to the fact that the position of the atom moves further away from the surface as the vibrational excitation energy increases, which reduces the atom–surface interaction.

This is, however, not necessarily the case for other processes such as diffusion with a corrugated periodic potential well along the surface [19].

The theory can be used to analyze laser femtosecond pulse experiments, where adsorbate reactions are induced by energy transfer from a hot electron system created by a strong laser pulse. The theory is general and accurate, and can be applied for diffusion with a knowledge of the vibrational wavefunction of the corrugated adsorbate–substrate potential and the friction coupling to the electronic excitation in metals. It is shown that our model reduces to the conventional heat transfer equation with a temperature-independent heat transfer coefficient (friction coefficient) in the case of a harmonic oscillator potential and a linear electron–vibration coupling.

We have also proposed a general formula for heat transfer at a surface when there is a coupling between two vibrational modes with different friction couplings to hot electrons. Such a mode coupling provides indirect heating or cooling of the vibrational temperature in addition to the direct heating due to hot electrons. We examined the anharmonic coupling between two different modes (equation (32)) accompanied by energy transfer between the heat bath of the substrate. One may also consider different forms of the anharmonic mode coupling $V(u) = V_{a,b}f(u_a, u_b) = \sum_{m,n} V_{a,b}^{m,n} u_a^m u_b^n \rightarrow u_a^2 u_b^1 + u_a^1 u_b^2 + \dots$, and each mode is heated by direct friction coupling (equations (10) and (24)). In this case we need to calculate the heat transfer matrix element by the anharmonic mode coupling in the second-order processes in a similar way to what we did for a theory of single molecule hopping induced by the anharmonic coupling between the mode excited by tunneling electrons from STM and the low-frequency FT mode [14, 20].

The proposed formula and the numerical results for a harmonic oscillator and a linear coupling to the substrate heat bath of electron–hole pair excitations demonstrate strong heating of the mode even when its direct coupling to the hot electrons is small. The simplified coupled equations of heat transfer between two different modes have been applied for the description of recent experiments on femtosecond-laser-induced diffusion of CO and O on Pt surfaces. Here, the role of the coupling between different vibrational modes (the

frustrated rotation and translation for CO hopping, and the O–Pt stretch mode and the frustrated translation for atomic oxygen hopping) is emphasized. It is shown that, even if the direct electronic coupling to modes relevant for the considered reaction is small, the coupling to other vibrational modes can result in a significant indirect excitation. We have become aware of the importance of multidimensional dynamics, where the energy exchange between different vibrational degrees of freedom is involved in the reaction pathways [2]. Our theory of heat transfer between ultrafast-laser-heated hot electrons and adsorbates in the presence of vibrational mode coupling is a first step towards a better understanding of the multidimensional surface reactions of adsorbates on metal surfaces.

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