Comment on "Diffusion and Dimer Formation of CO Molecules Induced by Femtosecond Laser Pulses"

In a recent Letter [1], Mehlhorn *et al.* reported on femtosecond-laser induced diffusion yield $Y(F)$ of a single CO molecule on Cu(111) using a scanning tunneling microscope. As a function of the absorbed fluence F, they observed that $Y(F)$ exhibits a linear increase at low F followed by a strongly nonlinear increase at high F. They proposed that the linear increase is induced by single electronic transitions, while the strong increase can be described using a friction model where hot electrons transfer energy to the frustrated translation (FT) mode. They assumed the electronic friction η_e to depend on the electron temperature $T_e(t)$, in accordance with earlier suggestions [2]. However, it was proved that frictional coupling is temperature independent if it originates from electron-hole pair excitation [3]. The electronic friction is defined as $\eta_{el} = w_{1 \to 0} - w_{0 \to 1}$, where the decay rate $w_{1 \to 0}$ and the thermal excitation rate $w_{0 \to 1}$ between the vibrational excited state and the ground state are given by $\eta_e(n_B + 1)$ and $\eta_e n_B$, respectively, and where $n_B = [\exp(\hbar\omega/k_B T) - 1]^{-1}$ is the Bose-Einstein distribution function. It is clear that η_e is temperature *independent*, even when $w_{1 \to 0}$ and $w_{0 \to 1}$ depend on the temperature.

Here we show how one can understand the experimental results of Ref. [1] without using a temperature-dependent friction. We propose an indirect heating of the FT mode via the mode coupling to the frustrated rotation (FR) mode in addition to a direct heating of the FT mode by laser excitation [4]. We note that for CO diffusion on a Pt(111) indirect heating of the FT mode by the FR mode reproduced the experimental results of the real-time monitoring [4,5] and two-pulse correlation [6,7].

In the mode-coupling model we have two coupled equations: $dU_{FT}/dt = [\eta_{FT} + (\eta_{FT,FR}/\hbar\omega_{FR})U_{FR}](U_{el} - U_{FT})$ and $dU_{FR}/dt = [\eta_{FR} + (\eta_{FR,FT}/\hbar\omega_{FT})U_{FT}](U_{el} - U_{FR})$, where $U_x = \hbar\omega/[\exp(\hbar\omega/k_B T_x) - 1]$ denotes the energy of a harmonic oscillator corresponding to the FT and FR modes at the temperature T_x (where $x =$ FT, FR, and el). Without intermode coupling (i.e., $\eta_{FT,FR} = 0$), neither heating of the FT or FR mode can explain the experimental data of Ref. [1]. However, using the measured η_{FT} and η_{FR} [8] and a suitably chosen $\eta_{FT,FR}$ the calculated $Y(F)$ agrees very well with the experimental result (see Fig. 1). In this calculation we have used the diffusion barrier height $E_b = 87$ meV, which is close to the value $(97 \pm 4$ meV) deduced from diffusion data for CO on Cu(110) [9]. Also, the prefactor we use $(R_0 = 3 \times 10^{13}$ s$^{-1})$ is close to what one expects from Kramers theory of activated processes, which in the present case gives $R_0 \approx \omega_{FT}/2\pi \approx 10^{13}$ s^{-1}.

To summarize, in the friction model for heat transfer one should use a temperature-independent electronic friction. If the friction model cannot describe the experimental data
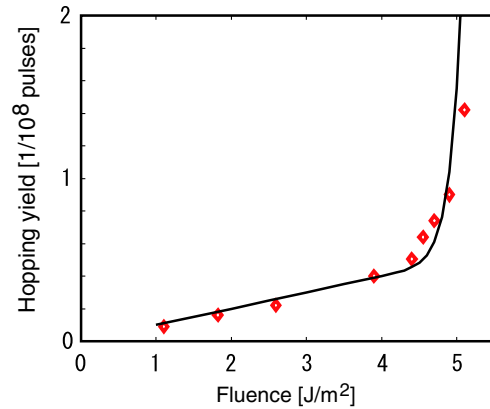

FIG. 1 (color online). Hopping yield per pulse as a function of fluence: experimental results (red diamond), calculated (black) by $Y(F) = \alpha F + \int R(t, F)dt$, where $R(t, F) = R_0 \exp[-E_b/k_B T_{FT}(t, F)]$ (black curve). The parameters are $\alpha = 1.0 \times 10^{-9}$ per pulse and per J/m^2 and $R_0 = 3 \times 10^{13}$ s^{-1} and $E_b = 87$ meV, $\eta_{FT} = 2.5 \times 10^{10}$ s^{-1},   and $\eta_{FR} = \eta_{FT,FR} = 1 \times 10^{12}$ s^{-1}.

with a temperature-independent electronic friction, the surface reaction involves more complex processes, e.g., involving two anharmonically coupled adsorbate modes as assumed above. We believe that our model with intermode coupling between the FT and FR modes captures the essential elementary process behind CO diffusion [10].

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