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Electron-hole pair contributions to scattering, sticking, and surface diffusion: CO on Cu(100)

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To assess the importance of coupling to electron-hole pair (ehp) excitations for molecular sticking, scattering, and diffusion dynamics at metal surfaces, simulations of the CO/Cu(100) system were performed using the ''molecular dynamics with electronic frictions'' method. Over a range of incident translational energies, energy losses to ehp excitations produce a moderate increase in sticking probability and account for 5%–10% of initial translational energy in scattered molecules, significantly less than phonon losses. Vibrational excitation and deexcitation of scattered molecules, while remaining a minor pathway for energy flow, is strongly affected by the inclusion of ehp excitations. Finally, although equilibrium diffusion constants are unaffected by the inclusion of coupling to ehp, it causes a significant quenching of transient mobility following adsorption of translationally hot molecules. © *1998 American Institute of Physics.* [S0021-9606(98)70533-1]

INTRODUCTION

The contribution of electronic excitations to energy transfer upon collision of an atom or molecule with a metal surface has been the subject of many studies.[1–10] A procedure to incorporate the effects of electron-hole pair (ehp) excitations in otherwise classical, full-dimensional molecular dynamics simulations has recently been developed. The method, called ''molecular dynamics with electronic frictions'' (MDEF)[11] relies on *ab initio* calculations of the nonadiabatic couplings between electronic and adsorbate nuclear degrees of freedom. These interactions have been calculated and parameterized for the CO on Cu(100) system, for which MDEF has been used to simulate adsorbate vibrational relaxation[12] and ultrafast laser-induced desorption.[13] In both cases, the model yielded results in reasonable agreement with experiment, adding further confirmation that these are processes for which coupling to ehp transitions cannot be ignored. In this study, we use the same interaction parameters to examine the influence of ehp transitions on other aspects of surface dynamics: sticking, scattering, surface diffusion, and transient mobility of CO on Cu(100). Nonelectronic (i.e., phonon) processes are expected to play a major role in energy transfer in all these cases, but the extent to which ehp transitions are also important is not known. It is the purpose of this study to evaluate the magnitude and nature of the influence of ehp transitions, as approximated by the MDEF scheme, on these dynamical processes.

The MDEF method approximates the flow of energy between nuclear motion and the electron bath with frictions and temperature-dependent fluctuating forces. Several assumptions are implicit in the treatment of the coupling of nuclear and electronic dynamics as a friction, notably that the coupling is weak and that the shapes of the nuclear potential energy surfaces (and hence, the forces experienced by the nuclei) are the same at all electronic energy levels that differ only in the extent of ehp excitation. The latter approximation is justifiable by the delocalized nature of ehp excitations, which diminishes their influence on the localized surface–adsorbate interaction.

DETAILS OF SIMULATIONS

Classical molecular dynamics trajectories, with or without electronic friction, were performed on the Cu(100) system with 108 surface atoms, with periodic boundary conditions parallel to the surface and stochastic boundary conditions representing interactions with the bulk. The same potential and friction parameters were used as in Ref. 12. Interactions among the copper atoms were modeled as pairwise harmonic potentials between nearest and next-nearest neighbors, with force constants (1.58×10^4 and 0.22×10^4 g s^{-2}, respectively) chosen to replicate the experimental bulk phonon spectrum. The empirical gas–surface interaction potential used is additive over all copper atoms, consisting of an exponential repulsion term for the Cu–O interaction and a modified Morse potential, which depends both on the Cu–C separation and the angle η between O–C and C–Cu bonds,

$$
\begin{aligned}
V_i(\mathbf{r}_C, \mathbf{r}_O, \mathbf{r}_i) = {} & A \, \exp(-\alpha |\mathbf{r}_i - \mathbf{r}_O|) \\
& + B\{\exp[-2\beta(|\mathbf{r}_i - \mathbf{r}_C| - r_e)] \\
& - 2\cos^2 \eta_i \exp[-\beta(|\mathbf{r}_i p - \mathbf{r}_C| - r_e)]\}.
\end{aligned}
$$

$$\tag{1}$$

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TABLE I. Values for parameters used in CO intramolecular and CO–surface potential energy function, referring to Eqs. (1) and (2).

Parameter	Value
A	$84\,300.0$ kJ mol^{-1}
α	3.36 Å
B	55.86 kJ mol^{-1}
β	3.0 Å^{-1}
r_e	1.9 Å
F	1070.0 kJ mol^{-1}
γ	2.3 Å^{-1}
r_{CO}	1.125 Å

TABLE II. Values used for parameters used in generating matrix elements of $\mathbf{K}(z_{COM},\theta)$, the electronic friction coupling matrix. Parameters correspond to those in Eqs. (3) and (4).

Parameter	$m=1$	$m=2$	$m=3$
c_{1m}	0.834	0.834	0.770
c_{2m}	0.096	0.096	0.120
c_{3m}	0.048	−0.174	0.200
e_{1m} (amu fs^{-1})	0.480	0.480	1.080
e_{2m} (amu fs^{-1})	0.300	0.300	0.610
e_{3m} (amu fs^{-1})	−0.280	−0.280	−0.750
e_{4m} (Å^{-1})	1.560	1.560	2.180

Here, $\mathbf{r}_C$, $\mathbf{r}_O$, and $\mathbf{r}_i$ refer to position vectors of the carbon atom, the oxygen atom, and the ith copper atom, respectively. The effect of the orientation factor $\cos^2 \eta_i$ in the attractive part of the C–Cu potential is that the full attraction is achieved only when the CO molecular axis points directly at the Cu atom, causing the minimum energy configuration to be CO bound perpendicular to the surface via the carbon end at an ''on-top'' site, in accordance with experiment.[14] The intermolecular C–O interaction was represented by the unmodified gas-phase Morse potential,

$$V_{CO}(|\mathbf{r}_C-\mathbf{r}_O|)=F\{\exp[-2\gamma(|\mathbf{r}_C-\mathbf{r}_O|-r_{CO})]$$
$$-2\exp[-\gamma(|\mathbf{r}_C-\mathbf{r}_O|-r_{CO})]\}. \quad (2)$$

Values used for the parameters in Eqs. (1) and (2) are listed in Table I. The potential reproduces the experimental binding energy at the potential minimum (0.59 eV).[15] Frequencies for the adsorbate vibrational modes[16] calculated using these parameters are likewise in reasonable agreement with experiment.

Electronic frictional forces were implemented using the parameterization described in Ref. 12, based on *ab initio* electronic structure calculations as described in Ref. 11. The friction tensor $\mathbf{K}$ is a 6×6 matrix, although in this parameterization it is approximated in terms of only three nonzero eigenvalues and their eigenvectors, which depend on the center-of-mass displacement of the molecule from the surface (z_{com}) and the angle of the molecule with respect to the surface normal (θ). The eigenvectors in the parameterization are separable in Cartesian coordinates in the molecular frame, in which z lies normal to the surface and x lies in the plane formed between the molecule and the surface. If the six degrees of freedom—one for carbon and one for oxygen for each molecular-frame Cartesian coordinate—are represented in the order x_C, x_O, y_C, y_O, z_C, z_O, the matrix takes on block-diagonal form with three 2×2 blocks. Each block is the product of an eigenvalue, e_m, with a matrix of the form

$$\begin{pmatrix} c_m^2 & -c_m\sqrt{1-c_m^2} \\ -c_m\sqrt{1-c_m^2} & 1-c_m^2 \end{pmatrix},$$

with $m=1,2,3$ representing the molecular-frame Cartesian coordinates described above. The eigenvectors depend (through c_m) on the tilt angle θ as

$$c_m(\theta)=c_{1m}+c_{2m}\cos\theta+c_{3m}\sin^2\theta, \quad (3)$$

while the eigenvalues depend on θ and on z_{com}, as

$$e_m(\theta)=(e_{1m}+e_{2m}\cos\theta+e_{3m}\sin^2\theta)\exp(-e_{4m}z_{com}). \quad (4)$$

The parameters associated with these equations are collected in Table II. A rotation of the matrix about the z axis of magnitude ϕ is then required to transform it from molecular- to lab-frame Cartesian coordinates.

The analytical expressions and parameters employed here are identical to those used in the studies reported in Refs. 12 and 13. We note that with this parameterization, the friction tensor is generally somewhat larger, on average, than the *ab initio* points to which it was fitted. The discrepancy is as large as a factor of two in some geometries. The *ab initio* (Hartree–Fock) coupling terms are not expected to be more accurate than a factor of two, however. In order to be consistent with previous work, we chose not to revise the parameterization for the present work. Therefore, the effects of ehp transitions in the results reported here are slightly larger than would be predicted using ''unsmoothed'' *ab initio* couplings.

A sense of the physical effects of the friction tensor can be obtained from the magnitude of its coupling to the degrees of freedom of the CO molecule (internal vibration, two rotations, three translations) as a function of its orientation and position. We emphasize that because the friction matrix $\mathbf{K}$ is not diagonal in these modes, its operation would not preserve their purity, and the lifetime of the modes cannot be directly obtained from the matrix elements of $\mathbf{K}$. We can estimate the strength with which a mode is coupled to the electron bath, however, by calculating the instantaneous rate at which a mode will be quenched,

$$k_i(z_{com},\theta)=\mathbf{u}_i^\dagger\mathbf{K}(z_{com},\theta)\mathbf{u}_i, \quad (5)$$

where $\mathbf{u}_i$ is a mass-weighted unit vector corresponding to an arbitrary mode i, and k_i has units of inverse time. Figure 1 shows $k(z_{com},\theta)$ for the internal vibration, ''cartwheel'' rotation (with the angular momentum vector parallel to the surface), center-of-mass displacement perpendicular to the surface, and center-of-mass displacement parallel to the surface. Note that the binding configuration of adsorbed CO is $\theta=0$ and $z_{com}=2.53$ Å. For this geometry, the z_{com} translation mode corresponds to the molecule–surface stretch, and the cartwheel rotation corresponds to the frustrated rotation mode.

Three important points are illustrated in Fig. 1. The effects of electronic friction are significant on the scattering times scale ($\sim$1 ps) only within chemical bonding range of the surface. They are strongest when CO is in its preferred
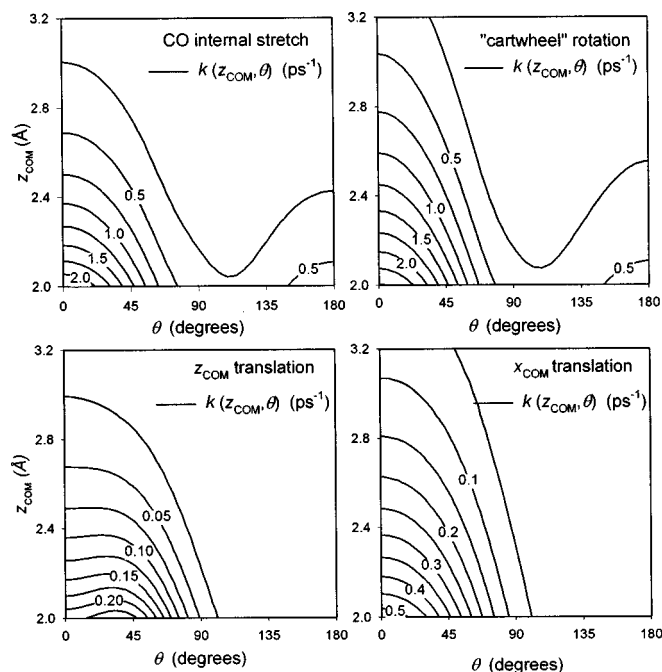
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FIG. 1. Contour plots of coupling of electronic friction to important adsorbate modes, calculated as in Eq. (5), as a function of z_{COM} and θ with respect to Cu(100) surface. Note that not all plots are on the same scale.

chemisorption orientation, for in that configuration the electronic structure of surface and adsorbate are strongly coupled; the importance of this orientation dependence can only be increased by the closer approach allowed molecules in the proper orientation by the form of the potential. Thus, the chemical interaction dominates the electrostatic dipole-induced dipole coupling to electron-hole pairs, and we can predict that for a scattering molecule to lose a significant amount of energy to electronic friction it must pass through the bonding orientation during collision. Finally, rotational and intramolecular vibrational modes are coupled roughly ten times as strongly as the z_{com}-translation mode.

With the potential V and friction matrix $\mathbf{K}$ in hand, the equation of motion for the adsorbate degrees of freedom r becomes

$$M_r \ddot{r} = -\frac{\partial V}{\partial r} - \sum_s K_{rs} \dot{s} + R_r(t),\qquad(6)$$

with $R_r(t)$ representing a stochastic fluctuating force designed to maintain the bath temperature by satisfying the fluctuation–dissipation theorem,

$$\langle R_r(t) R_s(t') \rangle = kT K_{rs} \delta(t-t').\qquad(7)$$

In all simulations, the time step used was 0.4 fs. Most simulations were initiated with zero initial rotational motion and zero intramolecular vibrational energy (i.e., neglecting zero-point energy), although in some instances initial angular momenta were chosen to give a Boltzmann distribution of rotational energies corresponding to a temperature of 700 K, and for the investigation of vibrational deexcitation CO was initialized with 0.265 eV (one vibrational quantum) of intramolecular vibrational energy.

In sticking/scattering simulations, trajectories were initiated with the gas molecule in a random orientation and position 10.0 Å above the surface, with a specified linear momentum and rotational energy distribution. The surface atoms were initiated in their lattice positions and each given a random initial velocity, selected from a Gaussian distribution to give a mean initial kinetic energy of 3 kT per atom, in order to allow the surface to adopt a thermal distribution of positions and velocities during the time the CO molecule was approaching the surface. When the molecule passed the bound minimum center-of-mass displacement above the surface plane (2.5 Å), it was considered to be in contact with the surface, and its lateral position with respect to that point and its velocity were saved at regular intervals for analysis of transient mobility. Trajectories were continued until either the molecule center of mass reached 10.5 Å above the surface plane or until 6 ps after the molecule first came into contact with the surface. At such a time, incident molecules were considered trapped, as examination of trajectories showed equilibration with the surface to be essentially complete. Four thousand trajectories were performed to yield statistics for each set of initial translational energy, angle of incidence, initial rotational temperature, and surface temperature conditions.

For surface diffusion simulations, the adsorbate was placed in a random position and orientation 2.9 Å above the surface plane and both adsorbate and surface allowed to equilibrate for 36 ps at a given temperature. The lateral center-of-mass coordinates of the adsorbate were then recorded at eight regularly spaced intervals over 200 ps, and the mean square displacement at equally spaced time points was averaged over 64 trajectories for each of four surface temperatures, with or without electronic friction (128 trajectories at the lowest temperature simulated). Adsorbed molecules were prevented from desorbing by reversing their velocity normal to the surface should they reach a center-of-mass displacement 2.9 Å above the surface plane. This was done in order to prevent the selective removal of more energetic adsorbates, which might bias the observed diffusion rate.[17] Only at the highest temperature simulated, and then in very few instances, were adsorbates prevented from desorbing in this manner. The mean square displacement was linear in time at all temperatures.

RESULTS

Sticking probabilities

Figure 2 shows the effect of electronic frictions on the sticking probability as a function of initial translational kinetic energy for normal and oblique trajectories incident to a surface at 100 K. Here, "sticking" refers to nondissociative chemisorption and equilibration with the surface, also referred to as "trapping." As the binding energy (0.59 eV) is much greater than kT (<0.01 eV), the lifetime of the adsorbate on the surface is very long, leaving little ambiguity in the distinction between "sticking" and "scattering" trajectories. The inclusion of electronic friction causes a small increase in sticking probability at all incident energies under these conditions, but does not affect the qualitative results.
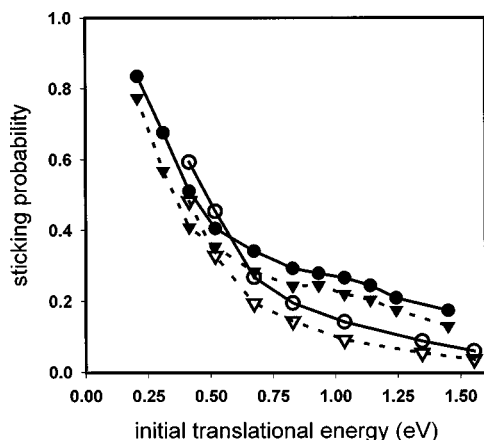
FIG. 2. Simulated trapping probability as a function of incident translational energy for CO on Cu(100) at a surface temperature of 100 K. Filled symbols: normal incidence; open symbols: 45 deg angle of incidence, [011] azimuthal direction. Solid lines/circles are for simulations incorporating electronic frictions, dashed lines/triangles are without electronic frictions.

The effect of electronic friction on sticking probabilities was similarly minor for simulations performed with higher surface temperature or nonzero initial rotational energy (data not shown).

We observed some unexpected results in the angular dependence of the sticking probability, unrelated to the effects of electronic friction. In particular, the sticking probability was greater at incident energies greater than 0.75 eV for trajectories with normal incidence ($\theta=0$) than for glancing trajectories ($\theta>0$). This contrasts sharply with the common expectation that the sticking probability will be a function of $E_T \cos^n \theta$, where $n=2$ for a flat surface ("normal energy scaling") and less than two (but greater than zero) in the presence of corrugation. While experimental data for CO on Cu(100) are not available, a decrease in sticking probability with increasing θ at fixed incident energy has been observed experimentally in similar molecular chemisorption systems, such as CO on Ni(100)[18] and NO on Pt(111),[19] as well as for Cl_2 trapping on Cl-saturated GaAs(110).[20] Other related systems, such as CO on Cu(110)[21] and CO on Pt(111),[22] exhibit little or no θ dependence of sticking probability, also indi-

cating a strong breakdown of the normal energy scaling. We believe this breakdown to be due to the strong orientational dependence of the binding potential.[23]

Inelastic scattering

The energy distribution after scattering for directly scattered trajectories, shown in Fig. 3, shows that electronic friction accounts for a relatively uniform proportional loss in incident energy, and does not affect trends in the distribution of energy to phonon or rotational channels. We anticipated a more significant effect on the level of rotational excitation of scattered trajectories, based on the previously calculated short lifetime (~ 1 ps) of the frustrated rotation mode of chemisorbed CO.[12] The absence of such an effect suggests that on average trajectories only spend a fraction of their collision time in the proper orientation for strong coupling. Indeed, it might be supposed that collisions in which the molecule maintains the energetically favorable, strongly coupled configuration are unlikely to generate the torque that will give rise to rotational excitation in the first place.

Energy transfer to the intramolecular stretching mode of CO is not shown in Fig. 3, because it is extremely small compared to other channels. In the absence of electronic frictions, intramolecular vibrational excitation of scattered molecules was below 1% of incident translational energy for incident translational energies of 4 eV and below. In the presence of electronic friction, intramolecular vibrational excitation showed a roughly linear dependence on surface temperature T_S at all incident energies (Fig. 4). At high incident energies (~ 6 eV and above), where vibrational excitation due to impact exceeds kT, the coupling to ehp actually decreased the intramolecular vibrational excitation. Qualitatively, the results reflect the fact that the coupling of the CO stretch to the surface electron bath can only bring the energy distribution of that mode toward the surface temperature. How close it comes to that equilibrium energy depends on the time the molecule spends at the surface, and more particularly on the time it spends near its bonding configuration, where the coupling is strongest. In the absence of electronic friction, there is no increase in vibrational excitation with T_S
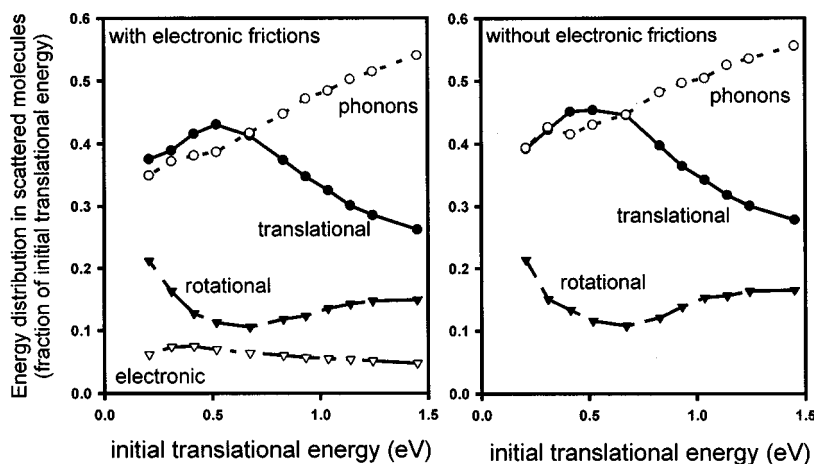

FIG. 3. Proportional distribution of initial translational energy into various channels following scattering of CO from Cu(100) at normal incidence at a surface temperature of 100 K, in the presence and absence of electronic frictions.

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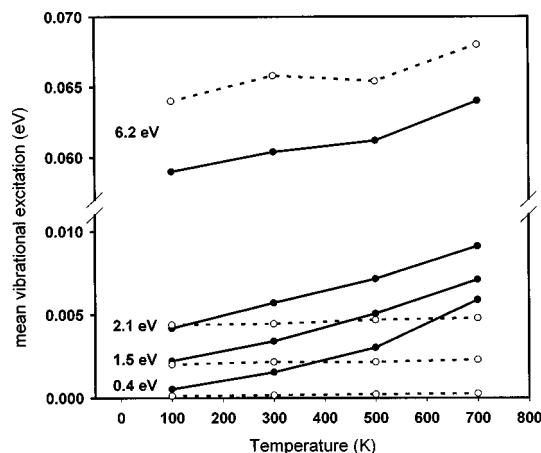
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FIG. 4. Mean intramolecular vibrational energy of CO scattered from Cu(100) at various incident translational energies and surface temperatures. Solid lines: electronic frictions included; dashed lines: no electronic friction. All points correspond to normal incidence, with zero initial intramolecular and rotational energy.
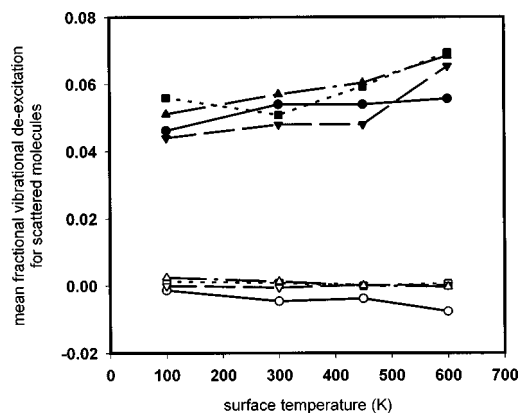

FIG. 5. Mean fractional decrease in intramolecular vibrational during normal incidence scattering of vibrationally excited (0.265 eV) CO on Cu(100), as a function of surface temperature, T_s. Filled markers: electronic frictions included; open markers; no electronic friction. Solid lines and circles: 2.1 eV incident translational energy; dotted/squares: 1.5 eV; dot-dash/triangles: 0.8 eV; dashed/inverted triangles: 0.4 eV.

for moderate incident translational energies, reflecting a very inefficient transfer of energy between the surface phonons and the CO stretch.

Although experimental data are not available for the CO/Cu(100) system, it is instructive to compare the present results with the experiments of Rettner *et al.* on the NO/Ag(111) system,[24] which similarly showed a pronounced increase in direct vibrational excitation with increasing T_S. The current study provides support to the interpretation given by Rettner *et al.*, that such a temperature dependence indicates the main source of vibrational excitation to be electronic in origin. The calculated probability of vibrational excitation is likewise of the same order of magnitude in simulation and experiment. At an incident energy of 1.5 eV, a surface temperature of 700 K, and in the presence of electronic friction, the mean calculated energy transfer (7 meV) to the CO stretching mode would represent a greater than 2% population of the $\nu=1$ state in the scattered CO; the maximum population of collisionally excited NO in the above experiments was 7%$\pm$5%. We note that the linear form of the temperature dependence in the simulation data reflects the use of a classical energy distribution for the electron bath; a quantized electron bath should give an exponential temperature dependence, as observed in the experiments. A framework that includes the temperature dependence of coupling to electron-hole pair excitations has been developed elsewhere.[25]

The formalism we employed neglects the local heating of the electron bath during collision, both by direct ehp excitation and by nonadiabatic transfer from the excited phonon bath (i.e., inelastic electron–phonon scattering, which would cause an additional damping in the phonon dynamics). This local heating might significantly increase the probability of vibrational excitation during the collision, but is unlikely to be important for degrees of freedom more strongly coupled to phonons.

Simulation of the scattering of vibrationally excited CO on Cu(100) was performed to assess the role of electronic

friction in vibrational deexcitation during surface scattering. Figure 5 shows the temperature dependence of vibrational deexcitation at several incident energies, in the presence and absence of electronic friction. In the absence of electronic friction, scattering has a negligible effect on the CO stretching energy; the exception is at very high incident energy, where a small fraction of the translational energy is transferred to the vibrational mode, giving a negative amount of deexcitation. Only when the effects of electron-hole pair excitations are included is there significant deexcitation of vibrationally hot scattered molecules. The degree of deexcitation is in qualitative agreement with experiments on NO/Ag(111), indicating a probability of 0.9 that molecules initially in the $\nu=1$ state would retain their single quantum of vibrational energy after surface scattering.[26] There are no obvious trends in the efficiency of vibrational deexcitation as a function of incident energy. There are several competing factors at play, including penetration deeper into the surface (where coupling to electronic frictions is stronger) for high incident energy collisions, longer duration of contact with the surface for low incident energy collisions, and the incident energy-dependent partition of trajectories into sticking or scattering outcomes. One discernible trend is that increasing T_s causes a moderate increase in deexcitation. This contradicts the expectation that energy will flow more rapidly to a colder bath. The explanation is to be found in the effect of a more energetic phonon bath on sticking and scattering dynamics: a collision that would result in a sticking event (with complete equilibration of the adsorbate to the surface temperature) at low T_s has a significant probability of being ejected from the surface before fully equilibrated by a hot surface atom when T_s is high. The result is that molecules scattered from hot surfaces are on average closer to equilibration than those scattered from cold surfaces. This is true in particular for low incident energies, consistent with Fig. 5, because the amount of surface phonon energy available is more significant in determining whether a molecule sticks or scatters.
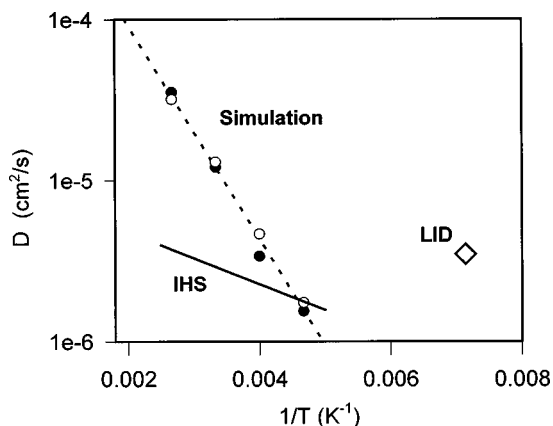
FIG. 6. Arrhenius plot for diffusion of CO on Cu(100) surface generated from molecular dynamics (MD) simulations. Filled circles: with electronic frictions; open circles: without electronic frictions. Also shown are a single point measurement by laser-induced desorption (Ref. 30) and a line corresponding to Arrhenius parameters determined by quasielastic helium scattering (Ref. 29; specific data points not reported).
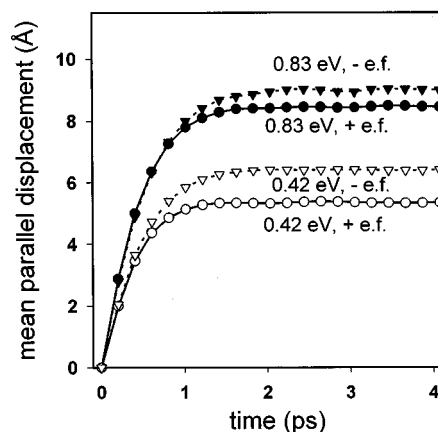

FIG. 7. Ballistic motion of nascent CO adsorbates, incident at 45 deg on Cu(100) along the [011] azimuth. The mean displacement along the surface projection of the incident velocity is plotted as a function of time following initial surface contact (as described in Details of Simulations). Surface temperature is 100 K.

Surface diffusion

The effect of electronic frictions on the dynamics of molecules bound to the surface was also investigated. Previous work[12] focused on the lifetimes of various normal modes for a molecule adsorbed on a particular surface site. Here we look at movement between sites: lateral mobility and surface diffusion. Molecules equilibrated at the surface show an Arrhenius dependence on temperature in their diffusion which, irrespective of the presence of electronic friction, yields an energy of activation of 0.132 ± 0.006 eV and a pre-exponential factor of $2.0\pm0.4\times10^{-3}$ cm^2/s; thus, the presence of energy transfer via ehp does not affect the diffusion rate.

The absence of an effect of electronic friction on diffusion rates does not indicate that diffusion does not couple to electronic friction, only that under this potential the phonon bath alone is sufficient to maintain energy equilibration between surface hops. In systems where multiple, correlated hops contribute significantly to the diffusion rate in the adiabatic approximation, electronic friction can influence the dynamics by providing an additional channel for thermal equilibration and decreasing the correlation between hops. This was found to be the case for hydrogen diffusion in bulk palladium by Li and Wahnström,[27] who were able to significantly improve their simulations' agreement with experiment by including an electronic friction term derived from calculations of hydrogen in the uniform electron gas.[28]

Widely divergent experimental values for diffusion have been reported for this system; as evident from Fig. 6, quasielastic helium scattering measurements[29] at low coverage (0.06 monolayer) have been interpreted as indicating a much lower energy of activation and preexponential factor (0.032 eV and 10^{-5} cm^2/s, respectively), while a single point laser-induced desorption measurement at 140 K and unspecified coverage[30] gives a much higher diffusion constant than predicted by extrapolation of either our Arrhenius plot or the helium scattering results. Therefore, we cannot say at present whether our results are in accord with experiment. The accu-

racy of our results depends almost entirely on the accuracy of our interaction potential, however, and not on ehp coupling strengths.

Transient mobility

The effect of electronic friction on mobility of molecules on the surface before they reach equilibrium is also of interest, with implications for thin film growth at surfaces and for reactions involving ''hot'' precursor or product species, as from a molecular beam or from other chemical or photochemical surface reactions. To study the transient mobility of nascent adsorbates, we monitored the movement of those molecules that were ultimately trapped to determine how far they travel after encountering the surface. An analysis of trajectories with an oblique angle of incidence is useful to separate the effects of ballistic transport (in which the adsorbate maintains its original momentum) and hot diffusion (in which the adsorbate has lost memory of its original momentum but transiently retains excess kinetic energy). Figure 7 shows the mean molecular displacement along the projection of the initial momentum on the surface plane, for molecules incident at 45 deg from the normal. Trapped molecules travel an average of roughly 1 Å (about one-third to one-half of a lattice spacing) farther along the direction of their initial parallel momentum in the absence of electronic friction than in its presence. In all cases, molecules lose memory of the direction of their initial momentum within 2 ps after impact. Hot diffusion, which continues to be important for several more picoseconds after this loss of memory in the absence of electronic friction, appears to be strongly damped in its presence. This is evident in Fig. 8, which shows that the root-mean-square (rms) spread of the lateral distribution of trapped molecules continues to increase noticeably beyond 2 ps in the absence of electronic friction, but remains essentially constant on this time scale in its presence. The extent of hot diffusion in these simulations is limited to several angstroms; this short transient mobility distance is in rough accord with conclusions of recent experiments on
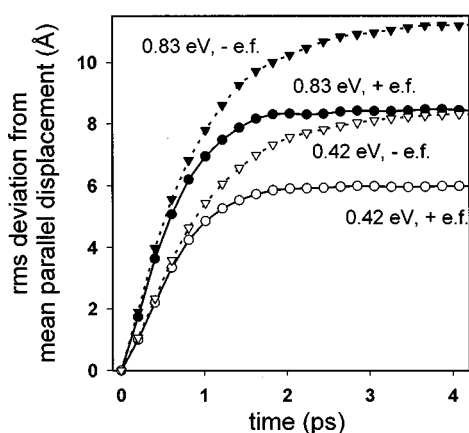
FIG. 8. Diffusive motion of nascent CO adsorbates, incident at 45 deg on Cu(100) along the [011] azimuth. The rms deviation from the mean of the displacement along the surface projection of the incident velocity, as a function of time following initial contact with surface. Surface temperature is 100 K.

CO/Pt(111).[31,32] The importance of electronic friction in the thermalization of trapped adsorbates, in contrast to its relatively minor effects on scattered molecules, comes from the adsorbate's adoption of the bonding orientation and position, in which it is highly coupled to the electron bath of the metal substrate.

The coupling of electronic friction to the so-called "frustrated translational" mode is weak,[12] and is therefore not responsible for these observed effects of electronic friction on lateral translation. We note that a detailed theoretical treatment of the coupling of this mode to surface phonons has confirmed that nonelectronic effects account well for its observed experimental relaxation time.[33] A much more likely candidate is the frustrated rotation, which is the adsorbate mode most strongly coupled to ehp formation. Correlations between this mode and translation across the surface, in fact, have been observed and discussed in regard to classical simulations of model CO/Ni(111).[34]

Previous simulations of transient surface mobility, of atomic oxygen on Al(111),[35] found similar distances for ballistic transport at roughly tenfold higher initial energies, in a system with correspondingly higher energy barriers to lateral motion. It was also concluded for that system that energy transfer to phonons dominated the damping of ballistic motion, with electronic frictional effects relatively unimportant. The relative importance of phonon and ehp contributions is expected to vary among systems depending on the strength (and mode specificity) of electronic coupling and on the adsorbate–substrate potential energy surface.

CONCLUSIONS

We have investigated the effects of nonadiabatic coupling to electron-hole pair excitations on the scattering, sticking, and surface mobility of CO on the Cu(100) surface using the molecular dynamics with electronic frictions formalism. Coupling to the electron bath accounts for significantly less energy transfer during molecule–surface collisions than does coupling to phonons, resulting in a correspondingly small increase in sticking probability at all incident energies over a range of surface temperatures. Similarly, the translational and rotational energy distributions of scattered molecules are only slightly affected by ehp coupling. Ehp's have a much larger influence, however, on vibrational energy transfer. At moderate incident energy ($\sim$1 eV) and high surface temperature, coupling to the surface electron bath was the major source of vibrational excitation of the CO stretch in scattered molecules, as well as the predominant pathway of vibrational deexcitation during scattering at all temperatures. Coupling to the electron bath does not influence equilibrium surface diffusion in the system, but did prove to have a significant effect on the transient mobility of molecules following adsorption, leading to a decrease in ballistic transport and hot diffusional motion during and after sticking.

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