

Role of Anisotropic Electronic Friction in Laser-Driven Hydrogen Recombination on Copper

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Ultrafast light-driven chemical dynamics at surfaces are governed by energy transfer from excited electrons to vibrational degrees of freedom. When this nonadiabatic energy transfer is anisotropic, it can lead to dynamical steering effects that affect reaction probabilities or nonthermal final energy distributions in molecules. Here, enabled by a machine-learning-based simulation framework, we compare isotropic and anisotropic models of electronic friction during laser-driven hydrogen evolution on the (111) facet of copper. While anisotropic electronic friction determines the rate of energy transfer into the adsorbate and the fluence dependence of desorption probabilities, final translational, vibrational, and rotational energy distributions are mainly governed by the potential energy landscape at the barrier and insensitive to nonadiabatic effects.

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Adsorption and desorption of molecular hydrogen from metal surfaces are important steps in heterogeneous catalysis and electrochemical processes [1]. Although these steps are thoroughly studied in thermally activated catalysis, many open questions remain for photocatalytic processes on metal interfaces [2]. Plasmonic metals such as copper, aluminium, or gold are often of particular interest due to their efficiency in converting incident light into electron-hole-pair excitations beyond thermal excitation thresholds [3,4]. These nonthermal excitations rapidly thermalize into a “hot” electron distribution through electron-electron scattering with an effective temperature above the surrounding lattice [5]. While hot electron thermalization typically occurs within several fs, electron-phonon scattering occurs over multiple ps [6]. Until the energy from electron-hole-pair (EHP) excitations is completely equilibrated with the surrounding lattice, energy can be transferred to adsorbates [5], driving chemical transformations [7].

In ultrafast pump-probe experiments, this nonthermal EHP-mediated energy transfer is signified by transient changes to adsorbate vibrational modes, e.g., the redshift of the CO stretch vibration frequency on a Cu(100)

substrate [8]. The anisotropy of coupling between hot electrons and adsorbate vibrations has been shown to affect dynamics in measured and calculated vibrational linewidths [9–11] of adsorbed hydrogen, atomic hydrogen scattering [12], and dissociative chemisorption of H₂ [13,14]. In laser-induced dynamics, isotope effects can be enhanced [15], trapping in precursor states can be promoted [16], or direction-specific diffusion can be induced [17]. In addition, laser-desorbed H₂ molecules generally have a nonthermal partitioning of energy across vibrational, rotational, and translational degrees of freedom [7]. However, it is still not clear if this nonequipartition of energy in the molecule results from nonadiabatic effects or from details of the barrier landscape during recombinative desorption.

Classical molecular dynamics simulations impose the Born-Oppenheimer approximation and are unsuitable to describe laser-driven dynamics, as they neglect nonadiabatic electron-nuclear coupling effects [18]. While a fully *ab initio* description of electron dynamics triggered by a laser pulse is possible [19], simulations of the ensuing coupled-electron nuclear dynamics of realistic interfaces are still computationally challenging [20]. A commonly employed mixed quantum-classical approach to study light-driven dynamics at surfaces is the molecular dynamics with electronic friction (MDEF) method [21–24]. In addition to the conservative dynamics governed by the potential energy surface (PES), V , the MDEF equation of motion includes nonadiabatic effects as a dissipative force mediated by an electronic friction tensor (EFT), $\Lambda(\mathbf{R})$, and a coupled random force term, $\dot{W}[T(t), t, \Lambda]$, as follows:

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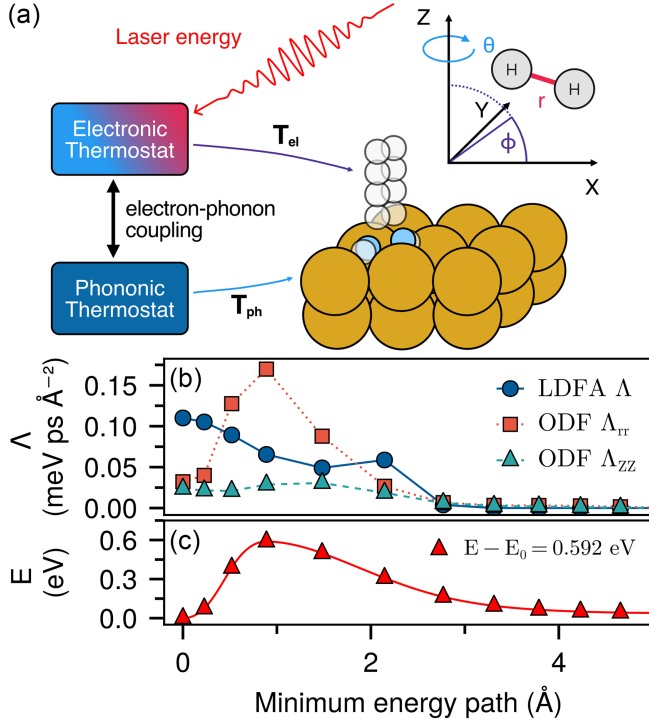


FIG. 1. (a) Geometries along the minimum energy path (MEP) for recombinative desorption of H₂ from a Cu(111) surface and a schematic of the electron and phonon bath in the two-temperature model. The transition state geometry is marked in blue. Only the first two of six total layers of the surface slab are shown. (b) Values of electronic friction tensor components along the MEP. (c) Potential energy along the MEP.

$$m\ddot{\mathbf{R}} = -\nabla V - \Lambda(\mathbf{R})\dot{\mathbf{R}} + \dot{W}[T(t), \Lambda]. \quad (1)$$

Light-driven surface dynamics can be simulated by coupling MDEF with the two-temperature model (TTM) [25], a parametrized set of coupled heat transfer equations for the electronic (T_{el}) and phononic (T_{ph}) subsystem temperatures [26,27] [see Fig. 1(a)].

Earlier dynamics studies were able to qualitatively match experimental desorption yields and nonthermal energy partitioning for H₂ evolution on Ru(0001) using low-dimensional PESs with static surfaces constructed from density functional theory (DFT) [22]. Recently, the emergence of high-dimensional machine learning (ML) potentials has enabled studies that include all degrees of freedom. Simulations of laser-activated CO diffusion on Cu(110) [17] and O diffusion on Pd(111) [28] have demonstrated how surface and adsorbate excitations cooperatively activate diffusion multiple ps after an incident laser pulse. In addition, a study by Lindner *et al.* on laser-driven H₂ evolution from Ru(0001) [15] recently showed how finite-size effects affect desorption yields, calling the accuracy of low-dimensional surrogate models into question. Virtually all TTM-MDEF simulations in the literature evaluate the

EFT with the isotropic local density friction approximation (LDFA), where friction coefficients are calculated from ion-scattering shifts in a homogeneous electron gas with the electron density of the substrate at the position of the adsorbate atom [29].

In this Letter, we perform full-dimensional TTM-MDEF simulations of laser-driven H₂ evolution from a Cu(111) surface at a coverage of 2/9 ML using a tensorial and anisotropic description of orbital-dependent friction (ODF) that is directly calculated from first-principles electron-phonon coupling [30–33]. ODF has been shown to accurately reproduce the mode dependence of vibrational lifetimes [12,32] and spatially anisotropic energy dissipation effects in reactive scattering of N₂ on Ru(0001) [34] and H₂ on Cu [35]. Previous LDFA-based simulations were able to predict the nonequipartition of energy for H₂ evolution from Ru(0001) surfaces [22]. However, LDFA is known to underestimate vibrational lifetimes of H atoms adsorbed on metals [9,12,32,35]. Here, we show that the nonequipartition of energy originates dominantly from the shape of the PES, while the rate of recombination and fluence dependence are determined by the employed electronic friction theory.

The TTM-MDEF simulations are enabled by previously reported machine learning models of the PES and the EFT [14,36,37] trained on accurate DFT data based on the SRP48 functional [38]. As a result, we are able to include all surface degrees of freedom and the effect of laser heating on the phonons. The models were originally developed to describe molecular scattering, but a detailed validation against DFT data for recombinative desorption showed that they are also transferable to laser-assisted desorption (see Supplemental Material [39]).

H₂ on Cu(111) exhibits a high desorption barrier [0.592 eV, see Fig. 1(c)] and strong anisotropy of friction across internal modes of molecular hydrogen during recombination [Fig. 1(b)]. Upon laser excitation [Fig. 2(a)], the electronic temperature T_{el} in the metal rapidly rises to over 5000 K within approximately 0.3 ps, while the phononic temperature T_{ph} rises more slowly. The rapid increase of T_{el} leads to activation of hydrogen atom diffusion already within the time span of the laser [15]. Adsorbed hydrogen atoms gain kinetic energy twice as quickly on average in LDFA simulations compared to ODF [Fig. 2(b)]. The rate of kinetic energy transfer is determined by the magnitude of the EFT, where, for the chemisorbed hydrogen atoms, the diagonal components of the ODF EFT are roughly half as large as the LDFA friction coefficient (see Figs. S11 and S12 in Supplemental Material [39]). The ODF is weaker perpendicular to the surface compared to components parallel to the surface (Fig. S13 in Supplemental Material [39]). The off-diagonal components of ODF are considerably lower during on-surface diffusion and only reach higher values around the transition to desorption. The magnitude of ODF only exceeds LDFA in the transition state region and

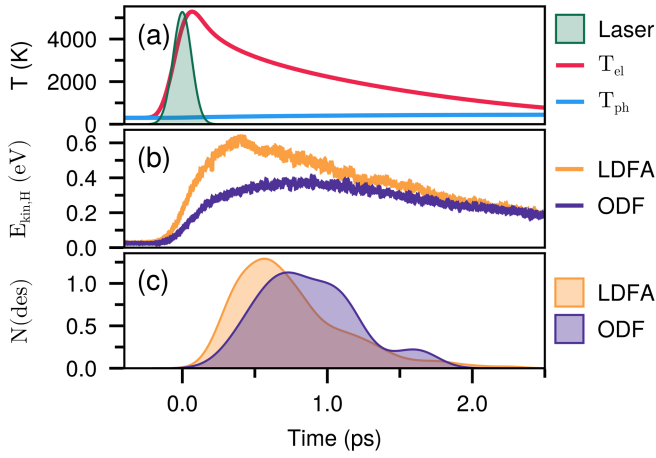


FIG. 2. (a) Temperature profiles for the phonon (T_{ph}) and electron (T_{el}) thermostats in the TTM for a starting temperature of 300 K and a laser fluence of 100 J m^{-2} . The laser intensity is indicated by the green shaded area and reaches the maximum at $t = 0$. (b) Average kinetic energies, $E_{\text{kin,H}}$, of adsorbed H atoms over time for both electronic friction approximations. (c) Normalized distribution of desorption events over time for both electronic friction approximations.

only along the recombination mode (intramolecular stretch), shown as Λ_{rr} in Fig. 1(b).

The increased kinetic energy of adsorbed hydrogen atoms can eventually lead to recombinative desorption if enough energy has been transferred to cross the recombination barrier. As a result, the rate of desorption [Fig. 2(c)] reaches a maximum shortly after the maximum kinetic energy transfer into the hydrogen atoms is reached (at 0.39 ps for LDFA, 0.89 ps for ODF). While the average kinetic energy of H atoms in ODF simulations relaxes more slowly after the laser pulse, we do not find strong evidence of delaying or dynamical trapping (Fig. S15 in Supplemental Material [39]).

The choice of electronic friction approximation also leads to almost an order of magnitude difference in desorption yields, with LDFA showing significantly higher reactivity across the range of fluences investigated. In desorptions induced by multiple electronic transitions [54], the desorption probability follows a power law relationship of the form $|A| \cdot F^n$ with the laser fluence. This relationship has not been measured experimentally for light-driven H_2 recombination from Cu(111). The TTM-MDEF simulations find values of $n = 3.051 \pm 0.201$ for LDFA and $n = 2.337 \pm 0.197$ for ODF simulations.

H_2 molecules formed through laser-driven desorption are known to desorb translationally hot, and with a preference for certain rotational and vibrational states; however, it is unclear whether the topology of the PES or the energy transfer due to electronic friction (or both) dominate this behavior [7,55]. Analysis of the translational, vibrational, and rotational energy of desorbing H_2 molecules in our simulations reveals only subtle

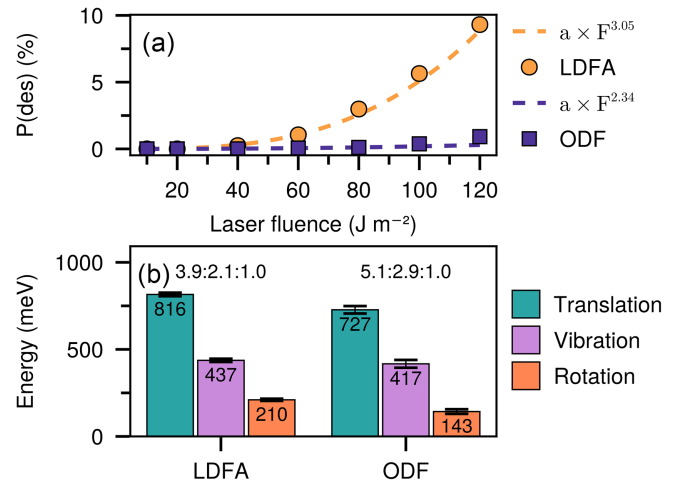


FIG. 3. (a) Single-shot desorption yields for hydrogen on a Cu(111) surface as a function of absorbed laser fluence for simulations with LDFA and ODF. Statistical uncertainties from bootstrapping analysis are indicated where they are larger than the markers used. (b) Mean internal energies of desorbing H_2 molecules determined from LDFA and ODF simulations for a Cu(111) surface with an initial temperature of 100 K and a laser fluence of 120 J m^{-2} .

differences in the energy partitioning between the two friction models [Fig. 3(b)]. In ODF simulations, H_2 molecules desorb with lower overall energy than in LDFA simulations. However, the absolute vibrational energy remains roughly equal for both methods. This may be a weak indication of the stronger nonadiabatic coupling along the bond axis for ODF [Fig. 1(b)] [14,56]. The total vibrational energy is likely somewhat overestimated in both sets of simulations due to the semiclassical Einstein-Brillouin-Keller [52] analysis rounding to integer quantum states [22]. Because of the high symmetry and lack of steps or edges on the Cu(111) surface, collision events between hydrogen atoms are most likely to occur when both atoms are at similar heights over the surface, and the MEP favors a concerted motion away from the surface. These two factors likely discourage cartwheel rotations on desorption from a terrace, leading to desorption with, on average, low rotation energy. This is slightly more pronounced for ODF, where the component of friction perpendicular to the surface is lower than for LDFA. Considering the significant difference in magnitude of friction between the two models, the resulting differences in the quantum-state-resolved energy distributions of desorbed molecules are surprisingly small.

As the choice of electronic friction approximation seems to strongly affect desorption probabilities, but only weakly affects the final state distributions of desorbed molecules, we return to the MDEF equation of motion to investigate the mechanism of desorption in more detail. The stochastic equation of motion contains ∇V , the potential gradient informing classical dynamics. The velocity-dependent

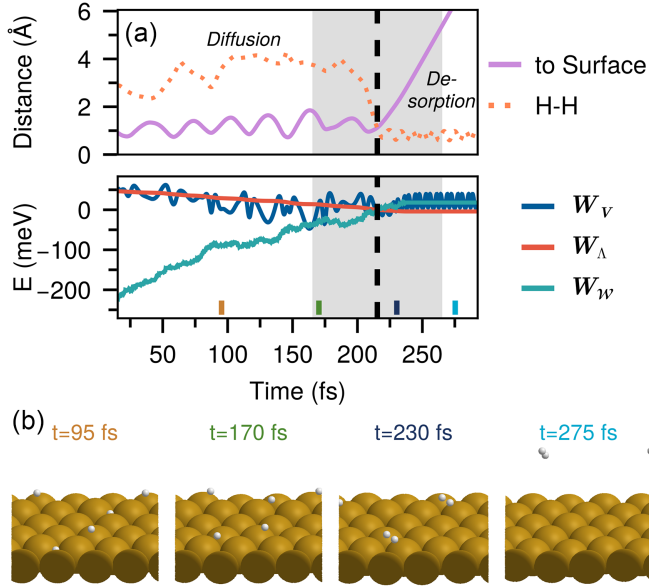


FIG. 4. (a) H-H distance and H_2 -surface distance as a function of time during a trajectory to indicate the two phases of desorption (diffusion and desorption, indicated with a gray box). Energy components due to the potential energy E_V , friction energy E_Λ , and thermal fluctuation energy E_W terms for two hydrogen atoms as a function of time during a recombinative desorption event. The EFT is represented with orbital-dependent friction. Equivalent figures for LDFA simulations are in Supplemental Material [39]. The energy contributions are shifted to zero at the transition state for clarity. The initial surface temperature was 100 K, and the laser fluence was 120 J m^{-2} . (b) Molecular dynamics snapshots throughout the trajectory.

friction term $\Lambda(\partial/\partial t)\mathbf{R}$ describes the frictional force caused by nonadiabatic effects, while $\mathcal{W}(\Lambda, T_{\text{el}}, \mathbf{R})$ describes stochastically distributed thermal random noise.

For a given simulation, we can determine the work of each of the three force terms described above as a function of time, which allows us to estimate the relevance of each contribution throughout the trajectory, as shown in Fig. 4. (Further details on work calculations are in Supplemental Material [39].) We can distinguish between two stages of a laser-driven desorption event: the “diffusion” region, where chemisorbed H atoms are mobilized by nonadiabatic energy transfer from EHPs, and the “desorption” region, where two H atoms enter the transition state region of the PES and recombine to H_2 . In the first region, the thermal fluctuation work W_W continuously transfers energy from hot electrons into the molecule and induces H atom diffusion. During this stage of the trajectory, W_Λ , the work from the velocity-dependent friction term, dissipates energy out of the system, but at a much lower rate. In the diffusion regime, where the distance between H atoms is large, off-diagonal elements of the ODF EFT are significantly lower than diagonal components, so differences between LDFA and ODF mostly depend on the magnitudes of diagonal EFT components. This in turn determines the

significant differences in the LDFA and ODF energy transfer rates.

During the desorption stage, i.e., the tens of femtoseconds before and after the onset of desorption [Fig. 4(b)], both contributions are eclipsed by the energy contribution from the PES (W_V), consistent with adiabatic, classical dynamics. Since the timescale between H-H collisions and recombinative desorption lies in the tens of femtoseconds, there is insufficient time for differences in the magnitude of the LDFA and ODF EFT models to significantly alter the energy distribution of the nascent molecule, in particular, as contributions are effectively zero once the recombination barrier is crossed and the molecule desorbs. Therefore, the actual process of desorption is insensitive to nonadiabatic effects. This is consistent with observations on the reverse process: the sticking probability of H_2 on copper is also insensitive to nonadiabatic effects [14,56].

In summary, we have compared machine-learning-accelerated TTM-MDEF simulations of H_2 recombination from Cu(111) surfaces using an isotropic and an anisotropic friction model. Both models yield differences in energy transfer, diffusion rates, and desorption probabilities, yet the desorption process itself is dominated by the barrier and the potential energy landscape. The choice of electronic friction approximation primarily determines how quickly the energy barrier to recombinative desorption will be reached, while the translational, vibrational, and rotational energy distribution of the desorbing H_2 molecules is mostly defined by the PES.

LDFA is known to underestimate vibrational lifetimes of adsorbed H atoms [12], and we expect that this also leads to an overestimated desorption yield in our simulations. However, our comparison only holds in the low coverage regime, where off-diagonal components in ODF are small. Vibrational lifetimes of adsorbates are sensitive to coverage [9], and further detailed studies at higher coverages as well as a comparison with experimental observables, e.g., as previously conducted on ruthenium surfaces [7], will be needed to show whether frictional steering and nonadiabatic energy transfer differ in high-coverage scenarios. As the rate of laser-assisted diffusion is a key indicator of the magnitude of friction, more experimental studies on diffusion rates, such as via Helium spin echo experiments [57,58], would be of great benefit in the future.

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Data availability—The software packages used in this work are described in the supporting material and are publicly available, with the exception of FHI-aims, which is subject to licensing conditions. Processed simulation data used to generate figures is available from Ref. [59].

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