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Energy loss in gas-surface dynamics: Electron–hole pair and phonon excitation upon adsorbate relaxation

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ABSTRACT

We study the effect of electron and phonon degrees of freedom on the relaxation dynamics of adsorption processes in gas-surface systems by using *ab initio* molecular dynamics that incorporates an electronic friction force (AIMDEF). As representative cases we have chosen three systems with different adsorption energies and adsorbate-to-surface atom mass ratios: H on Pd(100), N on Ag(111), and N_2 on Fe(110). We show, through inspection of the total energies and trajectories of the hot adsorbates on the surface, that electron–hole (e–h) pair excitations dominate relaxation of the light gas species, while the phonon channel is dominant for the heavy species. In the latter case e–h pairs become more important at the final thermalization stages.

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1. Introduction

During the adsorption of gas atoms or molecules on surfaces, the involved gas species have to dissipate their excess kinetic energy, which is sometimes increased by the surface attraction, into the two following energy loss channels: electron–hole (e–h) pair excitations and surface vibrations (phonons). During this relaxation process, the adsorbed *hot* species propagate on the surface, and their energy loss is dictated by the interplay between the e–h pair and phonon dissipation channels. Evidence of e–h pair excitations in the adsorption of thermal gas particles on metal surfaces is manifested experimentally in the so-called *chemicurrents*, which are electrical currents generated upon adsorption of atomic and molecular species on metal surfaces [1–3]. In other experiments the excited electrons are observed when the highly vibrational excited molecules collide with the metal surface [4,5]. The efficiency of the energy loss channels in dissipating the excess kinetic energy of the incoming particles will determine, for instance, whether the hot species can recombine with another adsorbate or whether thermalization occurs before recombination.

In a recent work, it was demonstrated to what extent e–h pairs and phonons dominate the relaxation process in gas-surface systems with a wide range of adsorption energies, E_{ads}, and adsorbate-to-surface atom mass ratios, $\gamma = m_A/m_S$ [6]. The chosen systems were hot H atoms on Pd(100) that originate from the dissociative adsorption of H_2 ($\gamma = 0.0094$ and $E_{ads} = 0.5$ eV), atomic N on Ag(111) ($\gamma = 0.13$ and $E_{ads} = 2.2$ eV), and N_2 molecules on Fe(110) ($\gamma = 0.5$ and $E_{ads} = 0.2 - 0.5$ eV). For H on Pd(100) it was shown that e–h pair excitations are the dominant energy loss channel [7] and that they dissipate energy at a five times faster rate than the phonons channel [8]. For heavier adsorbates, like N and N_2, it was shown that the phonon energy loss channel dominates, while the effect of the smaller but continuous dissipation into e–h pair excitations becomes apparent at long time scales.

In this paper, we revisit the above mentioned systems to analyse the problem from the point of view of the influence of e–h pairs and phonons on the adsorbates total energies and their trajectories. In particular, we are interested in learning on the mean traveled distance of the hot species on the surface. In principle, the in-plane distance between the initial and final positions of the adsorbate on the surface can be experimentally measured with scanning tunneling microscopy (STM) [9,10]. To obtain the above mentioned quantities we have employed the same *state of the art* methods used in Refs. [6,7] to perform the classical molecular dynamics (MD) at *ab initio* level.

This paper is organized as follows. In Section 2 we introduce the methodology and the results and discussions follow in Section 3. In Section 4 we give the conclusions.

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2. Methods

In *ab initio* molecular dynamics (AIMD) simulations, the adiabatic forces between the atoms in the system are calculated at each integration step of the classical dynamics equations using the Hellmann–Feynman theorem and density functional theory (DFT). This enables the description of the surface atom movements (phonons) in each of the simulation steps. Additionally, in the recently implemented AIMD with electronic friction (AIMDEF) [7], the non-adiabatic effects that come from the energy exchange between nuclear and electronic degrees of freedom are accounted through an electronic friction force included into the classical equations of motion [14]. To describe this electronic friction force at the position $\mathbf{r}_A$ of the projectile, $-\eta(\mathbf{r}_A)\dot{\mathbf{r}}_A$, we use the local density friction approximation (LDFA) [15]. In this approach, the friction coefficient $\eta(\mathbf{r}_A)$ at each time step of the simulation is uniquely a function of the bare surface electronic density at the position $\mathbf{r}_A$, $\rho_{\text{surf}}(\mathbf{r}_A)$. More precisely, $\eta(\mathbf{r}_A)$ is calculated for an atom traveling through a homogeneous free electron gas [16–19] with electronic density equal to $\rho_{\text{surf}}(\mathbf{r}_A)$. In case of a molecular projectile, the independent atom approximation is additionally performed, in which $\eta(\mathbf{r}_A)$ is calculated for each atom of the molecule independently. The LDFA is widely used to treat the effect of e–h pair excitations in many of the elementary processes that involve atoms and molecules at metal surfaces, e.g., adsorption and scattering events [6,7,15,20–26], recombination and desorption processes [27–29], as well as for quantifying the vibrational lifetime of adsorbates [30–32].

In simulations where the surface atoms are allowed to move, the surface electronic density will correspondingly vary with time. Thus, application of the LDFA requires in those cases the knowledge at any instant t of the bare surface electronic density, $\rho_{\text{surf}}(\mathbf{r}_A, t)$. The latter complicates the implementation of the LDFA in usual AIMDEF, because it is the electronic density of the whole system, i.e., gas species and surface atoms, and not the bare surface electronic density, what is self-consistently calculated at each integration step. This problem was tackled in Ref. [6], where the Hirshfeld partitioning scheme [33] was used to construct the bare surface electronic density *on the fly*. In this embedding scheme the contribution of the adsorbate to the electronic density is removed from the self-consistent (SCF) electron density of the whole system, $\rho^{\text{SCF}}(\mathbf{r}_A)$, at each time step of the simulation. The surface electron density then reads

$$\rho_{\text{surf}}(\mathbf{r}_A) = \rho^{\text{SCF}}(\mathbf{r}_A)\left[1 - \sum_n^{N_A} w_n(\mathbf{r}_A)\right],$$
$$w_n(\mathbf{r}_A) = \frac{\rho_n^{\text{atom}}(\mathbf{r}_A)}{\sum_m^N \rho_m^{\text{atom}}(\mathbf{r}_A)}, \tag{1}$$

where N and N_A are the total numbers of atoms in the system and in the adsorbate, respectively, and ρ_n^{atom} is the electron density of the isolated n-th atom. The weighting factor $w_n(\mathbf{r}_A)$ specifies the relative share at $\mathbf{r}_A$ of the n-th atom in the electron density of the whole system. Thus, the factor in square brackets of Eq. (1) defines the weight corresponding to the system without the contribution of the adsorbate. Recently, the Hirshfeld partitioning scheme was used to calculate the vibrational lifetimes of molecular adsorbates within the LDFA framework [32].

In the present work, all the simulations were performed using the DFT-based *Vienna Ab initio Simulation Package* VASP [34], which uses a plane wave basis set. The electron-core interaction was described by projector augmented wave potentials [35]. In each of the studied systems we use a different generalized gradient approximation (GGA) for the exchange and correlation functional, as detailed in Table 1. The functionals were chosen to facilitate

Table 1
DFT computational details for H/Pd(100), N/Ag(111) and N_2/Fe(110): functionals, energy cut-offs for the plane wave basis set ($E_{\text{cut-off}}$), cell sizes, numbers of surface layers, Monkhorst–Pack (MP) meshes for the Brillouin zone, and spin polarization.

	H/Pd(100)	N/Ag(111)	N_2/Fe(110)
Functional	PW91 [11]	PW91	RPBE [12]
$E_{\text{cut-off}}$	350 eV	400 eV	400 eV
Cell size	2×2	2×2	3×3
# layers	5	5	4
MP mesh [13]	$6 \times 6 \times 1$	$5 \times 5 \times 1$	$3 \times 3 \times 1$
Spin-polarized	No	Yes	Yes

the comparison of our AIMDEF calculations with previous works [7,36–38]. Further computational details can be found in Table 1. The classical equations of motion were integrated using the Beeman's predictor–corrector method for velocities [39]. The integration time steps are 0.1 fs for H/Pd(100), 0.5 fs for N/Ag(111), and 0.7 fs for N_2/Fe(110). These time steps were selected so that the drift in the total energy is negligible when compared to the corresponding energy loss due to e–h pair excitations.

In order to disentangle the relevance of each energy dissipation channel, we performed AIMDEF simulations in the frozen surface (FS + EF) and the non-frozen surface (NFS + EF) approaches. In the latter, the atoms in the two topmost layers were allowed to move during the simulation run. Non-frozen surface AIMD simulations without electronic friction (NFS) were carried out as well.

The simulations of hot H atom dynamics on the Pd(100) surface were performed with the initial coordinates and velocities corresponding to the already dissociated H_2 molecule on Pd(100), but keeping the H atoms independent from each other. These initial conditions were taken from adiabatic frozen surface MD simulations done on a six-dimensional potential energy surface (PES) (see Ref. [7,40]), where the H_2 molecule approaches the surface with $E_i(H_2) = 0.5$ eV at normal incidence. For each method, 50 trajectories were simulated. Non-spin-polarized calculations are justified here because, after dissociation, the H atoms propagate close to the surface and thus the spin is quenched.

The adsorption dynamics of N on Ag(111) was studied for normal incidence and initial kinetic energy $E_i = 0.1$ eV. These incidence conditions were shown to provide a high adsorption probability of around 0.9 [36]. A total of 20 trajectories, which start at a distance $z_i = 4$ Å above the surface, were simulated with randomly chosen initial lateral positions (x_i, y_i).

In the case of non-dissociative adsorption of a N_2 molecule on Fe(110), the sticking probability at normal incidence is maximised by an initial energy $E_i = 0.75$ eV [37,38]. A total of 80 trajectories starting from $z_i = 4$ Å above the surface were run with random initial (x_i, y_i) values and orientations.

3. Results and discussion

3.1. Total energy of the gas species

In Figs. 1(a), 2(a) and 3(a)–(c) we show the total energy of the adsorbates (A), $E_{\text{tot}}(A)$, as a function of integration time and averaged over the total number of trajectories. The total energy here is the sum of the kinetic and potential energies of the adsorbate, $E_{\text{tot}}(A) = E_{\text{kin}}(A) + E_{\text{pot}}(A)$. For all the cases the zero of potential energy is defined as the potential energy of the adsorbate when it is located in vacuum. For the H atom we also subtract one half of the H_2 binding energy in the gas phase to that reference potential, which is calculated considering the spin polarization of the H atom placed in the vacuum, in order to have the H atom in the H_2 molecule located far from Pd(100) as the potential energy reference.

The kinetic energy term $E_{\text{kin}}(A)$ is obtained *on the fly* during the simulation, but the potential energy term $E_{\text{pot}}(A)$ needs to be