Electronic Energy Dissipation During Scattering of Vibrationally Excited Molecules at Metal Surfaces: *Ab initio* Simulations for HCl/Al(111)

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In this Letter, *ab initio* molecular dynamics simulations based on time-dependent density functional theory for the electrons and Ehrenfest dynamics for the nuclei are reported that detail the interaction of a vibrating HCl molecule with an Al(111) substrate. The mechanism responsible for the strong electron-hole-pair (EHP)–vibrational coupling in case of highly vibrationally excited molecules is traced back to a large eigenenergy shift of the sp_z^*-like antibonding HCl lowest unoccupied molecular orbital with the bond length. As a consequence of this mechanism, the electronic excitation spectra turn out to be highly asymmetric. The simulations suggest an explanation of how to reconcile a strong EHP-vibrational coupling in case of highly vibrationally excited molecules with the small, but clearly evident, electronic contribution to the $v = 0 \rightarrow v = 1$ vibrational excitation observed experimentally during the scattering of HCl molecules at a hot Au surface by Ran *et al.* [Phys. Rev. Lett. **98**, 237601 (2007)].

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The mechanisms of electronic energy dissipation at metal surfaces are at the center of current experimental and theoretical research [1–5]. Sticking of atoms and molecules at metal surfaces is often described within the Born-Oppenheimer (BO) approximation. The effect of electronic energy dissipation channels on the scattering and sticking dynamics has been investigated and, in some cases, discussed controversially [6–11]. It has been pointed out that high-dimensional dynamics are essential [12,13]. In addition to indirect inferences, direct evidence of electronically nonadiabatic effects has emerged from various experiments. These comprise exoelectron emission [10,14] and chemicurrents induced by chemical reactions at metal surfaces [15,16]. When scattering vibrationally highly excited NO molecules at a cesiated Au surface, Wodtke *et al.* [10] have observed strong exoelectron emission for vibrational excitation energies of the NO molecules beyond the threshold for exoelectron emission. Shenvi *et al.* [17–19] have been able to describe the electron-hole-pair (EHP)–vibrational coupling within their independent electron surface hopping approach. In contrast to the open-shell NO molecule, for the closed-shell HCl molecule, the electronic coupling to the metal surface is expected to be different. For HCl molecules scattered at a Au surface, Ran *et al.* [20] have measured the surface-temperature dependence of the probability of $v = 0$ to $v = 1$ vibrational excitation. They found clear evidence for a contribution from EHP excitations of the hot metal substrate to the vibrational excitation at high surface temperature, which is, however, 2–3 orders of magnitude smaller that the effect estimated for NO/Au. In [21], vibrational relaxation of HCl from $v = 2 \rightarrow v = 1$ has been observed to have a probability probably larger than 0.1. It has been argued that HCl/Au may be intermediate between the region where electronic nonadiabaticity matters and where it is negligible [10]. The purpose of the simulations presented here is to identify the mechanism of EHP-vibrational coupling in the case of HCl/metal. From this, a clear explanation emerges, why the EHP-vibrational coupling is small for an HCl molecule in its vibrational ground state, while it increases steeply for high vibrational excitation.

Ab initio simulation of the coupled dynamics of electrons and ions is an intricate task due to the different time scales involved. In the case of small coupling, molecular dynamics with electronic friction [22] has often been applied in order to circumvent this problem. Monturet and Saalfrank [2] have successfully reproduced the final state distribution for vibrationally excited NO scattered at Au(111). In the case of vibrationally highly excited HCl molecules interacting with the EHP continuum of a metal substrate, however, the approximations required for electronic friction are not justified any more, as will become clear from the simulation results below. Mizielinski *et al.* [23], have pointed out that high orders of perturbation theory are required to obtain converged electronic excitation spectra in the case of a model Hamiltonian describing H atoms interacting with a metal surface. Consequently, we have chosen a nonperturbative approach, i.e., *ab initio* molecular dynamic simulations based on time-dependent density functional theory (TDDFT-MD) for the electrons, combined with Ehrenfest dynamics for the nuclei [24–26]. In view of its simple electronic structure, we have chosen the Al(111) surface as the metal substrate. Owing to the strong energy dissipation rate for highly vibrationally excited HCl molecules, we focus only on the incoming part of the trajectory and do not consider any dissociation dynamics of the molecule on the surface. The large computational expense of the simulations does not allow for statistical averaging over initial conditions of the molecule. Thus, we restrict ourselves to two orientations (but various initial vibrational excitations) of the molecule, which allow general conclusions about the energy transfer mechanism. The HCl bond is oriented perpendicularly to the surface, with the hydrogen atom pointing either towards (down configuration) or away from the surface (up configuration). The molecule impinges onto the surface at the fcc-hollow position of the unreconstructed Al(111). TDDFT-MD simulations have been performed with a version of the DFT total-energy code by Bockstedte *et al.* [27] generalized to time-dependent processes [24]. The surface is represented by a slab geometry. The periodically repeated supercell contains 14 layers of aluminum, and the size of the surface unit cell is $(2\sqrt{3} \times 2\sqrt{3})$. The supercell contains two HCl molecules, one impinging on either side of the slab. The Al and Cl atoms are represented by norm-conserving pseudopotentials [28]. For the H atom the $1/r$-Coulomb potential is used. The generalized gradient approximation by Perdew, Burke, and Ernzerhof [29] is applied to the time-independent exchange correlation (XC) functional. In the time-dependent Kohn-Sham equations, the adiabatic approximation is utilized for the XC functional. The convergence criteria have to be relaxed for the computationally expensive time-dependent calculations. Thus, we take a single special **k** point for the Brillouin-zone integration and limit the plane-wave expansion of the wave function to a kinetic energy cutoff of 10 Ry. The effect on the potential energy surface (PES) which, in general, is more sensitive than the Kohn-Sham eigenenergies, can be read from Fig. 1. Most importantly, the position of the physisorption minimum does not change significantly in the case of tighter convergence parameters.

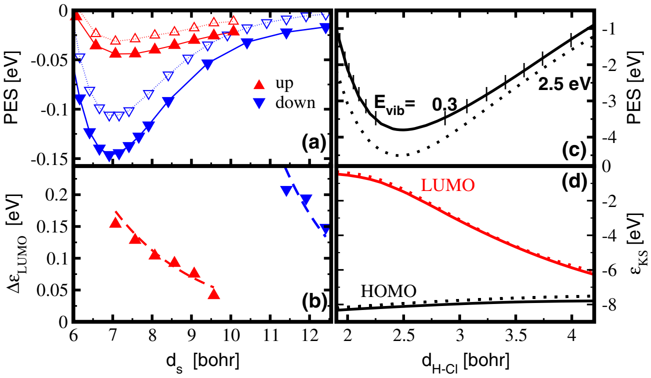

FIG. 1 (color online). (a) Potential energy of an HCl molecule (with $d_{\text{H-Cl}} = 2.48$ bohr) in the up or down configuration atop the fcc-hollow site of the Al(111) surface and (b) the width of its LUMO PDOS peak $\Delta\varepsilon_{\text{LUMO}}$ versus separation d_s between the surface and the center of mass of the molecule. (c) Potential energy of the HCl molecule and (d) Kohn-Sham eigenenergy of the HOMO and the LUMO as a function of the HCl bond length $d_{\text{H-Cl}}$. Full lines/Filled symbols: calculation with 10 Ry cutoff. Dotted Lines/Open Symbols: calculation with 30 Ry cutoff. A single special **k** point has been used.

Results for the free HCl molecule are summarized in Fig. 1. The variation of the eigenenergies is well described already at the relaxed convergence parameters. The important thing to note is the strong decrease of the energy position of the antibonding sp_z^*-like LUMO with increasing H-Cl bond length. For a vibration energy of about 2.5 eV, this shift covers a range of almost 6 eV. The Cl-$p_{x,y}$-like HOMO, on the other hand, depends only very little on the H-Cl bond length. This is consistent with its orbital character. These simple observations already offer the essential clue for the EHP excitation mechanism when the vibrating molecule interacts with a metal surface.

As remarked above, we study the energy transfer by means of *ab initio* TDDFT-MD. The complete scattering process of the HCl molecule at the Al surface has been estimated to last of the order of 400 fs. This is to be compared to the time step required for the integration of the Kohn-Sham equations of about 0.002 fs and the oscillation period of the HCl in the range of 13–19 fs. The finite size of the supercell and the resultant discreteness of the electronic eigenenergy spectrum can lead to artificial electronic coherence or a strong depopulation of a single specific electronic orbital, which is deteriorating the results for the dissipation for simulation times amounting to several vibrational periods. This will happen, in particular, in case of large dissipation. Thus, we limit our TDDFT-MD simulations to 1–2 vibrational periods. The simulations are started at discrete molecule-surface separations. In the case of the down configuration, initial separations range from $d_s = 9.41$ to 12.41 bohr [30]. For the up configuration, d_s is in the range from 7.57 to 9.57 bohr. Initially, the HCl molecule assumes its noninteracting equilibrium bond length of 2.48 bohr. The initial velocities are chosen such that the internal kinetic energy of the molecule vibration ranges from 0.3 to 2.5 eV. The kinetic energy corresponding to the center-of-mass motion of the HCl has always been set to 0.1 eV. As the simulation proceeds, energy is transferred from the motion of the nuclei to EHP excitations. The time-dependent nonadiabatic energy $E_{\text{nonad}}(t)$ is defined by the difference of the TDDFT total energy and the total energy after relaxation onto the Born-Oppenheimer surface at frozen-in nuclear coordinates $R_{\text{ion}}(t)$

$$E_{\text{nonad}}(t) = E_{\text{tot}}^{\text{TDDFT}}(t) - E_{\text{tot}}^{\text{BO}}(R_{\text{ion}}(t)). \qquad (1)$$

Results for the increase of the nonadiabatic energy within one vibration period of the HCl molecule have been collected in Fig. 2. The time interval for ΔE_{nonad} determination starts when the HCl bond length first passes its equilibrium value from below. Two important features of the TDDFT-MD results should be emphasized: (i) The energy dissipation into EHP rises steeply as a

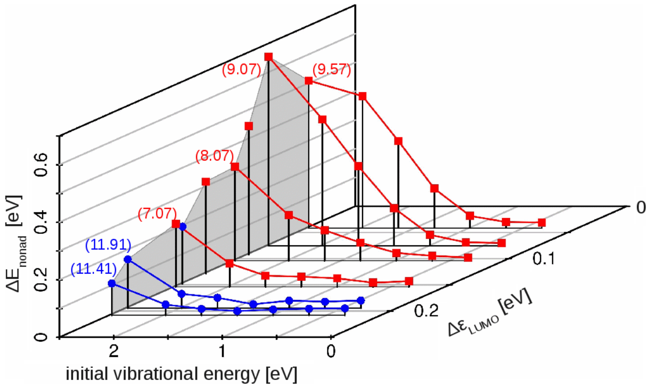

FIG. 2 (color online). Increase of nonadiabatic energy $\Delta E_{\mathrm{nonad}}$ during one period of the HCl vibration, plotted versus the initial vibrational energy of the molecule and the LUMO width $\Delta\varepsilon_{\mathrm{LUMO}}$. Molecule-surface separations ($d_s/[\mathrm{bohr}]$) are noted in parentheses. Squares denote results for HCl in the up configuration, circles results for the down configuration. Error due to the total energy drift and accuracy of BO relaxation is roughly estimated to be of the order of 20 meV.

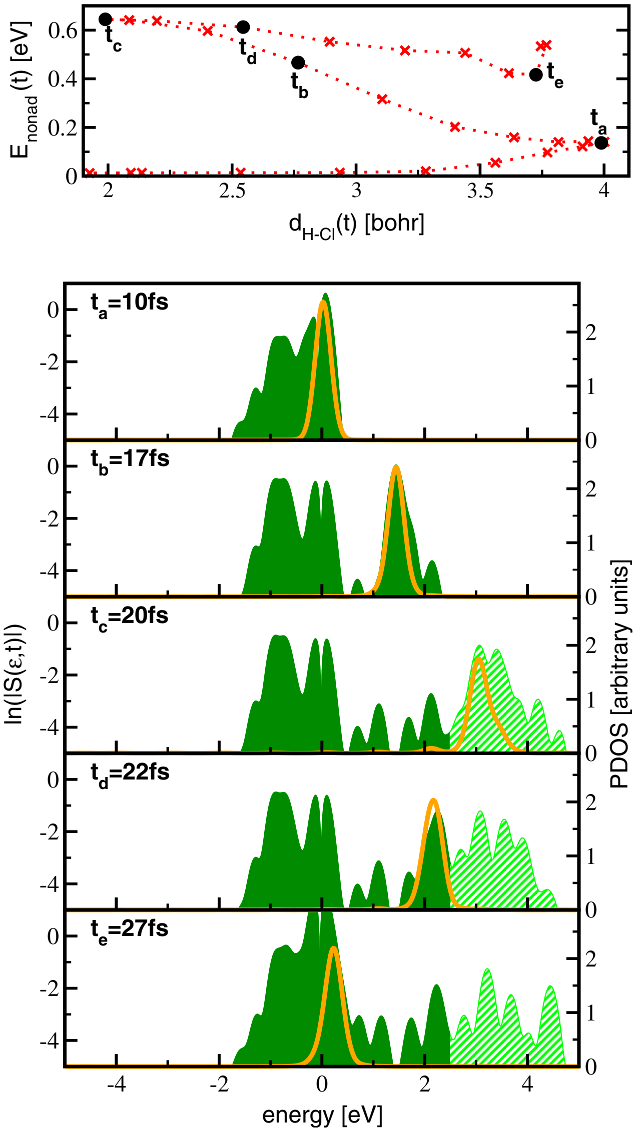

FIG. 3 (color online). Time evolution of EHP excitation. Upper panel: Nonadiabatic energy $E_{\mathrm{nonad}}(t)$ for an HCl molecule in up configuration versus its bond length $d_{\text{H-Cl}}(t)$. Initial molecule-surface separation 9.57 bohr, initial vibrational energy 2.5 eV. The dotted line is a guide to the eye. Lower panel: Snapshots of the electronic excitation spectra at times denoted by t_{a-e} in the upper panel. Parts of the spectra with energies beyond the initial vibrational excitation of the HCl molecule are denoted by hatched areas [33]. The PDOS for the HCl LUMO is denoted by the orange line.

function of HCl vibrational energy [31]. This reconciles the small nonadiabatic effect observed by Ran *et al.* [20] for $v = 0 \rightarrow v = 1$ excitations with the strong energy transfer into EHP calculated for highly vibrationally excited molecules. (ii) In the case of strongly vibrationally excited molecules, there occurs a maximum of the energy dissipation rate at a certain distance further away from the metal surface than the physisorption energy minimum. This nicely correlates to the experimental observation by Nahler *et al.* [32] of an 1/velocity-dependence of the exoelectron emission quantum yield during the scattering of $v = 18$ NO molecules at a Cs/Au surface. Slower molecules spend a longer time interval in the region of space where EHP-vibrational coupling is strong [1]. It should be noted, however, that Shenvi *et al.* [17] have suggested another explanation in the case of NO/Au(111). NO molecules with a small velocity are efficiently steered into orientations favorable for vibrational-EHP coupling very close to the substrate surface. This notably differs from the mechanism we observe for HCl/Al(111) where the maximum EHP-vibrational coupling occurs in a region of the PES where the molecule is much farther away from the surface.

In the case of the vibrating HCl molecule, the energy dissipation mechanism can be traced back to the periodic shift of the energy of the electronic resonance that arises due to the interaction of the HCl LUMO with the continuum of metal states. The shift is driven by the oscillation of the HCl bond length. The varying position of the projected density of states (PDOS) peak is visualized in the lower panel of Fig. 3. The excitation spectra have been calculated by subtracting the Born-Oppenheimer density of occupied states at frozen-in atomic positions $R(t)$ from

$$n(t,\varepsilon) = 2\sum_{i=1}^{n_{\mathrm{occ}}}\sum_{j}|\langle\psi_i(t)|\phi_j(R(t))\rangle|^2\delta(\varepsilon-\varepsilon_j(R(t))). \tag{2}$$

The factor of 2 accounts for spin degeneracy. The $\mathbf{k}$-point integration has been dropped as only a single special $\mathbf{k}$ point is used in the calculation. This circumvents the issue of configuration-dependent redistribution of electrons among different $\mathbf{k}$ vectors, a scattering process that would be symmetry forbidden in the case of TDDFT-MD and

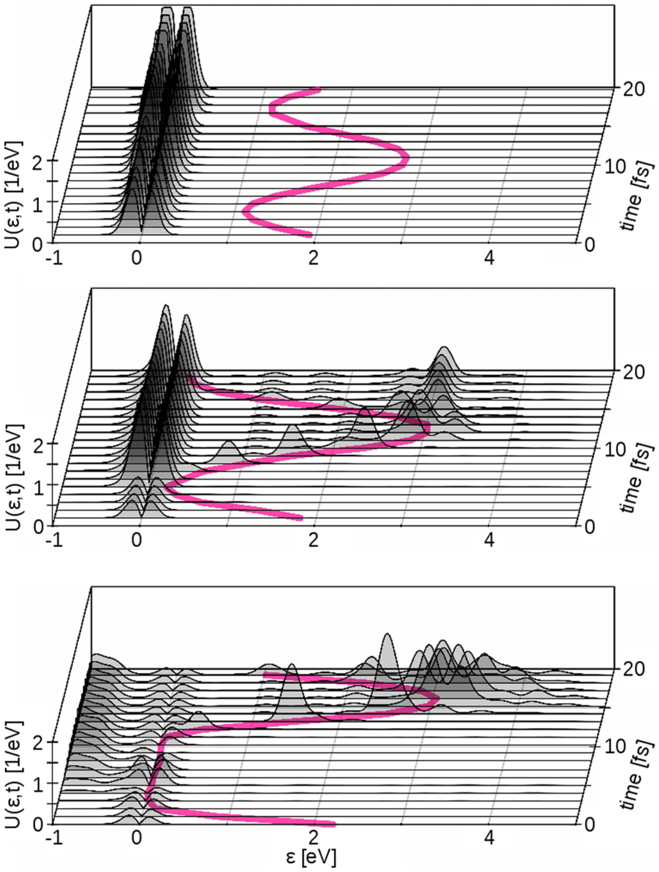

FIG. 4 (color online). Time evolution of EHP excitation spectra. Shown is $U(\varepsilon, t) := \varepsilon S(\varepsilon, t)/E_{\mathrm{nonad}}(20\ \mathrm{fs})$. It provides direct insight into the spectral distribution of the excitation energy. All three plots are for molecules in the up configuration starting at 9.57 bohr distance from the surface. Initial vibrational energies of the HCl molecule amount to, from top to bottom, 0.33 eV, 1 eV, and 2.5 eV.

spatially periodic perturbations (see also the definition of excitation spectra by Mizielinski and Bird in Ref. [23]). That two HCl molecules impinge onto the slab from either side has been accounted for by dividing the spectra by a factor of 2. For presentation, the discrete spectra have been convoluted with a Gaussian with a width of 100 meV. Results are denoted by $S(\varepsilon, t)$ and marked by the green shaded areas in Fig. 3, Eigenenergies refer to $\varepsilon_F = 0$. Evidently, in the case of a large initial vibrational excitation of the HCl molecule, the electron and hole part of the spectra evolve very differently. Hot electrons occur with a high probability. This is due to a mechanism, which resembles the vibrational electron autodetachment process suggested by Wodtke *et al.* [1,10,34] in the case of NO scattered at Cs/Au: The LUMO resonance becomes occupied with electrons when the HCl molecule is widely stretched such that the resonance is close to the Fermi level. When the bond length decreases, the LUMO resonance shifts away from the Fermi level to higher energy. Thereby, an electronically strongly nonadiabatic state is produced. Coupling to metal states results in energy dissipation. This dissipation mechanism is most effective at intermediate molecule-surface separations, when the hybridization of the HCl LUMO with the metal states is sufficiently large as to allow for a filling of the state, but at the same time the LUMO width is sufficiently small (i.e., the lifetime of the resonance sufficiently large) to allow for a shift of the electrons to high energies. This mechanism leads to an energy dissipation rate which is, at one and the same H-Cl separation $d_{\text{H-Cl}}$, much larger for $\dot{d}_{\text{H-Cl}} < 0$ than for $\dot{d}_{\text{H-Cl}} > 0$, as can be seen in the upper panel of Fig. 3 [35]. This is in strong contrast to the prediction of simple linear friction theory, where the energy dissipation rate is quadratic in the velocity and does not contain memory effects. The full nonadiabatic dynamics can even lead to an energy transfer from the electrons back to the vibrational energy of the molecule. This can occur when the still partially occupied LUMO resonance shifts from higher to lower energies (i.e., when $\dot{d}_{\text{H-Cl}} > 0$ between t_c and t_e). In Fig. 4, the time evolution of the EHP excitation is compared for three different initial vibrational excitation energies of the HCl molecule. In addition to the ubiquitous contribution from electronic friction, the energy dissipation mechanism explained above only becomes active for sufficiently large vibrational excitation energy. For small vibrational amplitudes, the HCl LUMO does not come close enough to the Fermi level to become occupied with electrons. Thus, in that case, the "pumping" mechanism cannot be active anymore. When the LUMO stays close to the Fermi level for some time, EHP excitation occurs due to the subsequent upward shift of the orbital. In Fig. 4, we observe that part of the excitation remains at high energies in this case.

To summarize, we have presented TDDFT-MD simulations of the nonadiabatic effects that occur during scattering of HCl molecules at a metal surface. A very efficient energy dissipation mechanism for vibrationally highly excited molecules has been identified. It is similar to the electron autodetachment mechanism proposed by Wodtke *et al.* [1,10,34]. For the closed-shell HCl molecule, we have found a characteristic strong increase of the coupling with the vibrational excitation energy. The results are qualitatively consistent with recent HCl/Au scattering experiments where the electronically nonadiabatic excitation [20] and deexcitation [21] has been measured. Quantitative comparison will require statistical averaging over all initial configurations.

Numerical simulations have been carried through at the Rechenzentrum der Christian Albrechts Universität.

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