

In the wake of collision

When atoms collide with metal surfaces, electron-hole pair excitations dissipate the adsorption energy

By Harald Brune

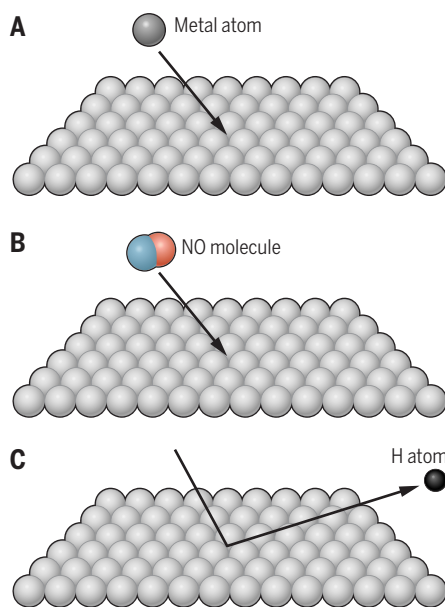
When a metal atom with thermal kinetic energy hits a metal surface, it adsorbs on it with a probability of one. Moreover, it sticks to its impact site and makes not even a single jump to neighboring lattice sites (1). The mechanism behind this observation is not fully understood. On page 1346 of this issue, Bünermann *et al.* study a simpler system that can help to elucidate the metal/metal case. In their study, energetic hydrogen atoms impact on a gold surface. Only a fraction of the H atoms adsorb on the surface (see the figure), but the reflected atoms still lose a substantial fraction of their incident kinetic energy. The authors unequivocally identify electron-hole pair excitation as the main dissipation mechanism in these collisions (2). Apart from its obvious model character, the H/metal system is important for fields as diverse as heterogeneous catalysis, interstellar H₂ production, and H storage.

For the metal/metal case, field ion microscopy studies have shown that the adsorption energy is dissipated instantaneously. Atoms deposited at low temperature (20 K) onto a close-packed single crystal surface populate two nonequivalent adsorption sites with equal probability, even when the two sites have slightly different binding energies (3). If the atoms were able to make only one lateral jump, the higher binding energy site would be occupied more often than the low-energy one. When the surface is heated to 45 K, thermal diffusion leads to the exclusive occupation of the energetically more favorable site. The complete absence of transient mobility at low temperature requires the entire adsorption energy—on the order of several electron volts (eV)—to be dissipated instantaneously. It is unlikely that collective lattice vibrations are fast enough to dissipate this energy. As in the H/metal system, electronically nonadiabatic effects, such as electron-hole pair excitations, are thus likely to play the dominant role.

In a binary collision of H and Au atoms, only 2% of the kinetic energy is transferred from H to Au. This is a result of the very dif-

ferent masses of both atoms. For the incident kinetic energy chosen in Bünermann *et al.*'s experiment, the expected energy loss from a binary ballistic collision on Au is 56 meV. However, the observed energy loss is almost 20 times higher, and the energy-loss distribution is much broader. It is centered at 910 meV and the maximum energy loss is larger than 2.0 eV, explaining why some atoms stick and therefore why this reaction takes place at all.

To illustrate the role of electron-hole pair excitation, the authors compare the reaction on a clean Au surface with one that has a thick layer of solid Xe adsorbed onto it. On Xe, the binary collision model gives an energy loss of 83 meV, and the observed loss is comparable (46 meV). Therefore, the H-Xe



Surface collisions. (A) When metal atoms collide with a metal surface with very small incident kinetic energy, every atom sticks. (B) For molecule-metal collisions, electron-hole pair excitations are the main mechanism through which adsorption energy is dissipated. (C) Hydrogen/metal collisions are similar to metal/metal ones; if the incident kinetic energy is small, every atom would probably stick. At the higher energies used by Bünermann *et al.*, only very few stick, making it possible to measure the energy of the backscattered atoms and to determine how much energy they have lost. The authors show that as for molecule/metal collisions, electron-hole pair excitation is the dominant mechanism for energy dissipation.

collision can be treated as a ballistic collision, but the H-Au collision clearly cannot.

Molecular dynamics calculations without electronic excitations essentially yield the ballistic loss spectrum that is in disagreement with the scattering data from Au(111). Once electron-hole pair creation is included, the calculations give excellent agreement with experiment. Similar to the experiment, these simulations are very demanding, because many trajectories have to be considered on a high-dimensional potential energy surface. The beauty of H as adsorbate is that it reduces the complexity because there is only translational kinetic energy; no rotations, vibrations, or steric effects such as orientations of the molecular axes need to be considered. The theory uses the ab initio potential energy surface in classical molecular dynamics simulations and applies the known scheme to introduce electronic friction (4). It thus has no adjustable parameters.

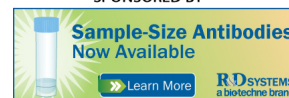
The interactions of molecules with metal surfaces are much more complicated because the molecules can dissociate, there might be activation barriers for this dissociation, and steric effects can play a role. However, energy dissipation in nondissociative molecular adsorption is in a way simpler than in atomic adsorption (5). The molecule gets distorted when binding to the surface starts to become significant. For example, near a surface, the bond in a simple diatomic molecule gets weakened and therefore stretched, thereby exciting the molecule's vibrational degrees of freedom. From this excited state, the energy can very efficiently be transferred to electronically nonadiabatic behavior, such as electron-hole pair excitation in the metal.

The central insight from the work of Bünermann *et al.* is that translational motion can be damped in the same way as intramolecular excitations (6). This is important in the energy dissipation of hot reaction products (7, 8). Electron-hole pair creation is also behind regular dry friction, and its effect can be suppressed by putting one of the sliding bodies into a superconducting state (9). Electron-hole pair excitations control the time and energy scale of surface chemical reactions, obviously also for the most elementary one of H on Au(111). ■

REFERENCES

- H. Brune, in *Physics of Covered Solid Surfaces*, H. P. Bonzel, Ed. (Springer, Berlin, 2001), vol. III/42 Subvolume A, Part 1 of Landolt Börnstein New Series, Group III: Condensed Matter, pp. 217–258.
- O. Bünermann *et al.*, *Science* **350**, 1346 (2015).
- A. Götzhäuser, G. Ehrlich, *Phys. Rev. Lett.* **77**, 1334 (1996).
- S. M. Janke *et al.*, *J. Chem. Phys.* **143**, 124708 (2015).
- K. Golibrzuch *et al.*, *Ann. Rev. Phys. Chem.* **66**, 399 (2015).
- S. P. Rittmeyer *et al.*, *Phys. Rev. Lett.* **115**, 046102 (2015).
- H. Brune *et al.*, *Phys. Rev. Lett.* **68**, 624 (1992).
- J. Wintterlin *et al.*, *Phys. Rev. Lett.* **77**, 123 (1996).
- M. Kiseil *et al.*, *Nat. Mater.* **10**, 119 (2011).

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