

Surface Science Perspectives

Bond breaking at surfaces: Electrons or phonons?

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The desorption of atoms and molecules is one of the most fundamental of all surface processes. A distinction is usually made between “thermal” desorption and desorption induced by energetic sources of excitation, such as incident photons or electrons, that induce electronic transitions. The paper by Trenhaile and co-workers in this issue shows the surprising result that the “thermal” desorption of Br from the Si(001) surface is in fact an electronic process in which the random statistical motion of phonons occasionally converges to excite an electron to an antibonding Si–Br σ^* state from which desorption of Br occurs [1]. Moreover, it is the entropy associated with the assembly of the phonons that is key to understanding how the desorption occurs. The results are important because they suggest that electronic transitions may have an important, but previously unrecognized, role in “thermal” desorption processes at surfaces.

Bond breaking at surfaces, like its gas-phase counterpart, has long been understood based on two distinct mechanisms. In the “electronic” mechanism, some source of energy induces a transition from a bound electronic state to an unbound state; one example would be a transition from the Si–Br σ state to a Si–Br σ^* antibonding state as illustrated in Fig. 1a. The second, “thermal” mechanism involves putting enough energy into a specific vibrational mode, such as an Si–Br stretching vibration, that a chemical bond literally breaks and desorption occurs; this process is illustrated in Fig. 1b. These mechanisms are usually distinct because the time scale for physical motion of an atom is quite long compared with the time needed for electrons to change their spatial distribution; this leads to the Franck–Condon approximation, which states that electronic transitions are usually not accompanied by a change in bond lengths and can usually be depicted as “vertical” transitions like that shown by the solid arrow in Fig. 1a.

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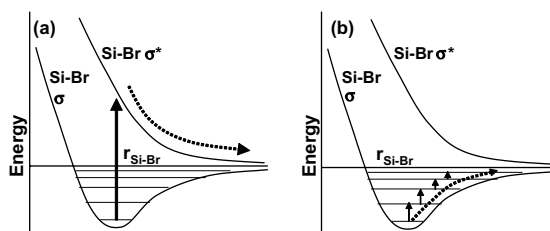


Fig. 1. Classical desorption processes. (a) Desorption induced by an electronic excitation, represented by the solid vertical arrow. (b) Desorption induced by thermal excitation of a vibrational mode.

In most systems, the bound and unbound electronic states are quite widely separated in energy. Consequently, processes involving excited electronic states usually are initiated by some form of direct energetic excitation such as electrons or photons that impinge on the surface and directly or indirectly (e.g., secondary electrons instead of the primary electrons) induce an excitation to a higher electronic state from which desorption occurs [2–4]. Because, thermal electrons usually have insufficient energy to promote a system to a new electronic state, the separability of thermal and electronic excitations is usually valid. However, Trenhaile et al. show that this separability is clearly violated for desorption of Br from the Si(001) surface, such that *neither* of the above mechanisms is correct; their results suggest that electrons may have a much more important role than had been previously recognized in desorption, adsorption and other surface chemical processes.

For semiconductors, the chemical potential of the electrons (Fermi level) is controlled by the doping. However, thermal desorption processes are typically not affected by the doping, because the pathway to desorption basically involves sitting in one electronic state and climbing a ladder in which vibrational energy is stochastically added and removed from the bond until some very small fraction of the time—the atoms are pulled far enough apart that the bond breaks. The atom displacements are all-important, and the electrons simply follow the lead.

The paper by Trenhaile and Weaver shows that the desorption of bromine from the (001) surface of silicon involves a thermally driven electronic excitation that is controlled by the *coupling* of phonons with the electrons—in short, it is the *breakdown* of the Franck–Condon principle that makes the reaction possible. They show that desorption occurs via a confluence of ~ 10 – 20 phonons, each of energy ~ 60 meV, that together are able to excite an electron to an antibonding Si–Br σ^* state from which desorption occurs. What is especially interesting is that the phonons do not directly induce desorption (as in a classical bond-breaking mechanism), but that the phonons excite an electron, which then does the work.

In order to prove this unusual mechanism, Trenhaile et al. performed a very interesting and novel analysis of how the rate of desorption changes with doping and with temperature. They show that desorption occurs more readily from n-type samples than from p-type samples at some temperatures but that there is a cross over in kinetics at ~ 700 K. The doping dependence and the agreement between the energy deduced from experiment and the separation between E_{σ^*} and E_F clinches that idea that electronic transition must be involved.

What is perhaps even more novel is how they establish the crucial role of *phonons* in controlling the desorption process. To do this, they note that the rate of desorption can be described in terms of a rate equation as $\text{rate} = A^* \exp(-\Delta G/kT)$, where ΔG , the activation barrier, represents the change in free energy in order to get to the transition state [5]. This activation barrier has a contribution from the enthalpy (the energy required to promote an electron from the Fermi energy to the Si–Br σ^* state) and from the change in entropy associated with the phonons. Since the number of ways that the phonons can be assembled is greater when the barrier is larger, the entropic and enthalpic contributions compensate one another; this

is a manifestation of the long-recognized Meyer–Neldel or compensation rule [6]. By separating the entropic and enthalpic contributions, Trenhaile and co-workers show that the crucial step in the desorption process is the rare event in which approximately 10–20 phonons simultaneously interact with one electron to promote it to the Si–Br σ^* level, which leads to Br desorption.

Similar multiphonon processes are quite common in many relaxation processes, such as the nonradiative relaxation of electrons from the conduction to valence band in bulk silicon, but their crucial role in controlling *chemistry* at surfaces has not been previously recognized.

The results of Trenhaile and co-workers have a number of important technological implications. Halogens can both etch and passivate surfaces of silicon and other semiconductors. If the doping has a big influence on the surface chemistry, it will strongly affect the conditions used for semiconductor processing, and may also enable the use of bromine and other species as a kind of dopant-selective mask. Perhaps more importantly, the work shows how one of the most common fundamental assumptions—the separability of electronic and vibrational degrees of freedom—is violated in an important chemical system. This result for desorption has implications about adsorption mechanisms as well, due to the principle of microscopic reversibility. The translational kinetic energy of a molecule or atom perpendicular to the surface must be lost in order for it to adsorb. This has generally been shown to occur via a mechanism whereby the gas phase momentum is lost by excitation of phonons in the solid. However, recent experimental [7–9] and theoretical [10] studies have also demonstrated the importance of electronic excitations created during chemisorption and physisorption of gases at surfaces [7–10], and by chemical reactions at surfaces [8,9]. Together, all these studies are pointing to the fact that making and breaking chemical bonds involves a complex interplay between lattice vibrations and electronic excitations, thereby breaking down the difference between “thermal” and “electronic” processes.

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References

- [1] B.R. Trenhaile, V.N. Antonov, G.J. Xu, K.S. Nakayana, J.H. Weaver, *Surf. Sci.* 583 (2005) L135.
- [2] Ph. Avouris, R. Walkup, *Ann. Rev. Phys. Chem.* 40 (1989) 173.
- [3] D. Menzel, R. Gomer, *J. Chem. Phys.* 41 (1964) 3311.
- [4] P.A. Redhead, *Can. J. Phys.* 42 (1964) 886.
- [5] S. Glasstone, K.J. Laidler, H. Eyring, *The Theory of Rate Processes*, McGraw-Hill, New York, 1941.
- [6] A. Yelon, B. Movaghar, H.M. Branz, *Phys. Rev. B* 46 (1992) 12244.
- [7] B. Gergen, H. Nienhaus, W.H. Weinberg, E.W. McFarland, *Science* 294 (2001) 2521.
- [8] H. Nienhaus, B. Gergen, W.H. Weinberg, E.W. McFarland, *Surf. Sci.* 514 (2002) 172.
- [9] B.R. Cuenya, H. Nienhaus, E.W. McFarland, *Phys. Rev. B* 70 (2004) 115322.
- [10] J.W. Gadzuk, *J. Phys. Chem. B* 106 (2002) 8265.