Chemically Induced Electronic Excitations at Metal Surfaces

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The energy released in low-energy chemisorption or physisorption of molecules on metal surfaces is usually expected to be dissipated by surface vibrations (phonons). Theoretical descriptions of competing electronic excitations are incomplete, and experimental observation of excited charge carriers has been difficult except at energies high enough to eject electrons from the surface. We observed reaction-induced electron excitations during gas interactions with polycrystalline silver for a variety of species with adsorption energies between 0.2 and 3.5 electron volts. The probability of exciting a detectable electron increases with increasing adsorption energy, and the measured time dependence of the electron current can be understood in terms of the strength and mechanism of adsorption.

Knowledge of the details of energy transfer and dissipation processes during reactions on metal surfaces is fundamental to a deep understanding of heterogeneous catalysis. Highly exothermic surface reactions in which energy transfer occurs by nonadiabatic processes giving rise to excited electronic states are well known (*1*); for example, gas reactions on alkali metals can give rise to exoelectrons and chemiluminescence. For low-energy processes (≤ 0.5 eV), however, electronic excitations are thought to play a minor role in energy dissipation, and at present there is no comprehensive theory to quantitatively predict the partitioning of the interaction energy of a reactant with a metal surface into the various dissipation modes. This problem has been addressed theoretically from several points of view, each with various ad hoc approximations, including a perturbation of an electron system by a time-varying electromagnetic potential from a gas phase species in transit (*2*), an electrodynamic effect of the polarization fields of a molecular charge outside a metal (*3*), and a secondary Auger electron process (*1*).

We have developed large-area, ultrathin-film, Schottky diode devices that have allowed us to show direct evidence of nonadiabatically generated charge carriers during chemisorption of both atomic [H, D, and O: adsorption energy (E_{ads}) ~ 2.5 to 3.5 eV] and, recently, molecular (O_2 and NO: E_{ads} ~ 0.5 to 1.0 eV) adsorbates on several metal surfaces on which E_{ads} is well below the metal work functions (*4, 5*). The device structure was designed so that electronic excitations generating electrons with sufficient energy to surmount the Schottky barrier could be measured as a chemically induced reverse diode current: a "chemicurrent" (Fig. 1A). In our ongoing work, we are investigating whether chemically induced charge carriers are a general feature of energy transfer during any chemical interaction (both bond-forming chemisorption and weaker physical adsorption) between an atom or molecule and a metal surface, even at low energies at which phonon production is of comparable energy. The presence of energetic electron-hole (e^-/h^+) pairs as a routine feature of gas-metal interactions suggests that local chemistry, mediated by hot electrons, is possible. We observed electronic excitations on Ag surfaces during reactions that represent a range of gas-metal interactions from chemisorption with E_{ads} of ~2 eV (for H, O, NO_2, and NO) to physical adsorption with E_{ads} of ~0.3 eV (for CO_2, C_2H_4, C_2H_6, C_3H_8, and Xe) that support our hypothesis that carrier generation is ubiquitous and is strongly correlated with E_{ads}.

We used phase-sensitive current detection to observe electrons excited from adsorption of mechanically chopped (91 Hz) reactant beams on polycrystalline Ag films. Typical beam fluxes were between 1×10^{13} and 5×10^{13} molecules cm^{-2} s^{-1}, depending on the molecule investigated. The Ag film was deposited in ultrahigh vacuum (~10^{-10} torr) on n-type (1 to 10 ohm-cm) Si(111) as a thin (6 to 8 nm) front contact in a Ag/Si Schottky diode configuration (*4, 5*). The active film area was 0.35 cm^2. We used a Si(111) surface modified by chemical oxidation with H_2O_2 (30%) to produce an approximately 1-nm-thick oxide that lowers the effective Schottky barrier (ϕ) to between ~0.2 and 0.3 eV (*6*). In our previous work, the Schottky diodes were formed on a hydrogen-terminated Si(111) surface with a typical barrier height of 0.5 to 0.6 eV, which was too high to allow us to observe the low-energy processes reported here. The chemical reaction–induced currents measured during the initial exposure of polycrystalline Ag to H_2O, NO_2, NO, and Xe at 125 ± 5 K are shown (Fig. 1). Upon exposure to H_2O, the initial peak intensity was followed by a decay in the current amplitude as the surface coverage of adsorbed water increased and the number of available vacant sites decreased. The adsorption of H_2O on Ag at temperatures below 150 K is molecular (*7*), and the E_{ads} for H_2O has been measured to be ~0.6 eV on Ag(110) (*8*).

The more complex adsorption of NO_2 on Ag is reflected in the transient features of the chemicurrent. NO_2 adsorbs dissociatively on Ag as NO and atomic O at temperatures above 25 K with an E_{ads} of ~2 eV (*9*). The initial adsorption transient behavior is similar to that of H_2O. As the fractional coverage increased, adjacent adsorbed NO reacted to form $(NO)_2$ dimers that rapidly produced a desorbing N_2O and a reactive atomic O (*10*). Atomic O chemisorption generates hot electrons (Fig. 2), and the observed second current maximum at 70 s is due to electrons from the fraction of oxygen chemisorption events that are temporally correlated to the chopped incident NO_2 beam. For the phase-sensitive detection system, a low-noise current-to-voltage preamplifier with band-pass filtering was used as an input to a lock-in amplifier. From the modulated beam, only electrons produced within approximately 0.1 s of the beam interaction could be detected. We observed a similar second signal maxima from the dimerization and subsequent O chemisorption for NO exposure on Ag (*5*), as observed for NO_2. However, the peak signal from NO was smaller and decayed more slowly than did the signal from NO_2, while sharing the presence of a delayed secondary peak from superimposed temporally correlated O chemisorption. This behavior is consistent with the lower E_{ads} and lower adsorption probability of NO on Ag (*5, 11*).

The signal from Xe exposure to Ag is relatively weak (Fig. 1). The E_{ads} of Xe on Ag(111) has been measured to lie between 0.19 and 0.23 eV (*12*). As expected, the signal is nearly constant because the steady-state coverage of Xe on the 125 K surface is very small (*12*). No detectable signal was observed for exposures of Ag to He, Ne, Ar, or Kr, because their E_{ads} are less than the Schottky barrier.

To a first approximation, the time, t, dependent chemicurrent density may be written for a given species with a specific adsorption energy, E_{ads}, and incident kinetic energy, E_i, as a function of the total interaction rate, $r(t,T,E_i)$, of the adsorbates at the surface as $j = e_0 r(t,T,E_i) \varepsilon(E_{ex}) P_{na}(E_{ex},E_{ads},E_i)$, where e_0

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is the unit charge, T is the surface temperature, and $\varepsilon(E_{ex})$ is the detection probability of an excited electron possessing an excess energy, E_{ex}, above the Fermi level. The factor $P_{na}(E_{ex},E_{ads},E_i)$ denotes the product of the probability that an interaction by an adsorbate creates one or more mobile, energetic ("hot") electrons at an energy E_{ex} and the number of electrons produced per interaction. The value of $\varepsilon(E_{ex})$ depends on the excess energy and various intrinsic diode properties that include the probability of detecting secondary electrons created by scattering of hot electrons with high excess energies. The gas sensitivity of the Schottky diode sensor is given by the product $\gamma x \varepsilon P_{na}$, where, γ is the ratio of the total adsorption rate, r, and the incident flux, F, of adsorbates. We assume the predominant interaction to be adsorption $[\gamma(t = 0) \sim 1]$, either trapping-mediated or direct chemisorption; however, reactions between the incident beam and adsorbed species by way of an Eley-Rideal mechanism are possible and may be responsible for the temporally correlated O chemisorption observed from reactions of NO and NO_2 with adsorbed NO. The sensitivity (detected electrons per incident reactant) of an initially clean diode may be obtained from the maximum chemicurrent as $(\varepsilon P_{na})_{t=0} = j_{max}/e_0F$. The initial sensitivities for the adsorbates of Fig. 1 are 1.4×10^{-3} for NO_2, 1.8×10^{-4} for NO, 6.3×10^{-5} for H_2O, and 3.9×10^{-6} for Xe.

The transient diode sensitivities for exposures of a number of different adsorbates to clean Ag/Si diodes are shown (Fig. 2). As the coverage increases, the observed current decays are dependent on the specific interaction mechanisms and the relative rate coefficients for adsorption, reaction, and desorption (*4, 5*). We investigated the response to species that do not appreciably desorb at 125 K (Fig. 2A). Atomic O ($E_{ads} \sim 3.5$ eV) and atomic hydrogen ($E_{ads} \sim 2.5$ eV) interact by direct chemisorption and generate the largest number of detectable carriers we have observed to date, 9.1×10^{-3} and 2.4×10^{-3}, respectively. Benzene absorbs molecularly on Ag with significantly less energy ($E_{ads} \sim 0.5$ eV) (*13*), which is reflected in a greatly attenuated signal. The chemisorption energy of O_2 at 125 K is surface site–dependent with a maximum molecular E_{ads} of ~0.4 eV (*14*). A relatively weak signal and decay with increased coverage were observed (Fig. 2). Figure 2B shows the carrier detection efficiency from C_2H_6, C_2H_4, C_3H_8, CO_2, Xe, and N_2O. Low detection efficiencies and minimal signal decay were observed and were consistent with the relatively low E_{ads} and relatively rapid desorption rates of these species on Ag (*15–20*). Studies of C_2H_6 and C_2H_4 interactions with single-crystal Ag have measured adsorption energies of 0.25 for C_2H_6 (*15, 16*) and 0.33 eV for C_2H_4 (*17*). The signal from C_3H_8 decays slowly to a steady-state valve determined by the balance of adsorption and desorption at the surface temperature of 125 K. The peak desorption temperature reported from C_3H_8 on Ag(110) is 136 K (*18*) ($E_{ads} \sim 0.4$ eV). N_2O desorbs completely from Ag(111) at ~100 K (*19*), which was consistent with our observation of a constant signal at 125 K. CO_2 is also weakly bound on transition metals and has an E_{ads} of ~0.27 eV (*20*), which is approximately the height of our average Schottky barrier. A low-intensity constant-amplitude signal was observed when CO_2. For the different chemical species studied, the observed current transients

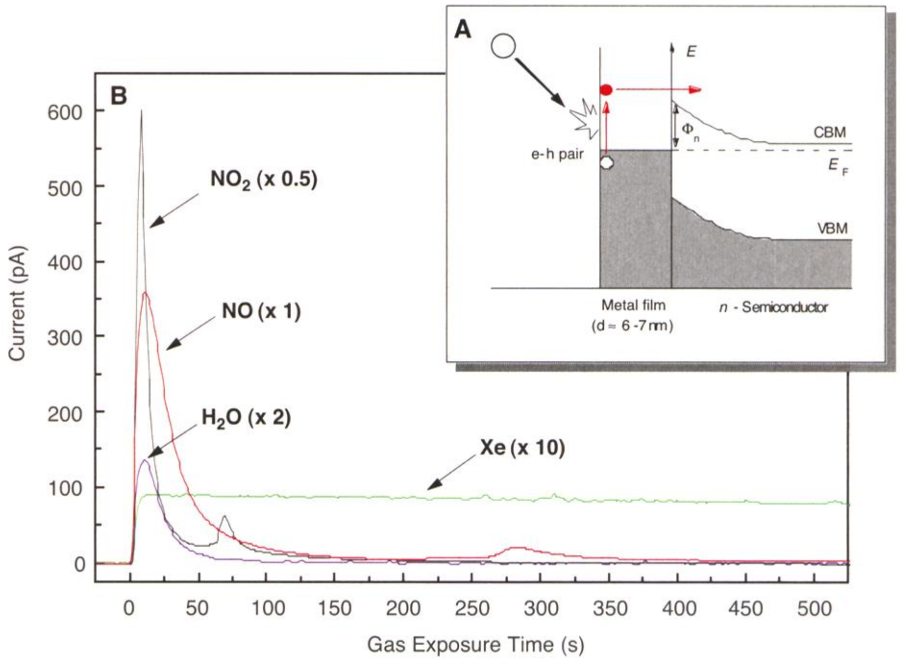

Fig. 1. (**A**) The energetics of electronic excitation during surface reaction with transport and capture of the excited charge carrier. (**B**) Chemical reaction–induced currents measured during exposure of atomically clean Ag/Si Schottky diode sensors at 125 ± 5 K to NO_2, NO, H_2O, and Xe. The beam fluxes ranged from approximately 2×10^{13} to 4×10^{13} cm^{-2} s^{-1}, and the thickness of the polycrystalline Ag films was 6 or 7 nm. Signals scaled (xX) to fit plot range.

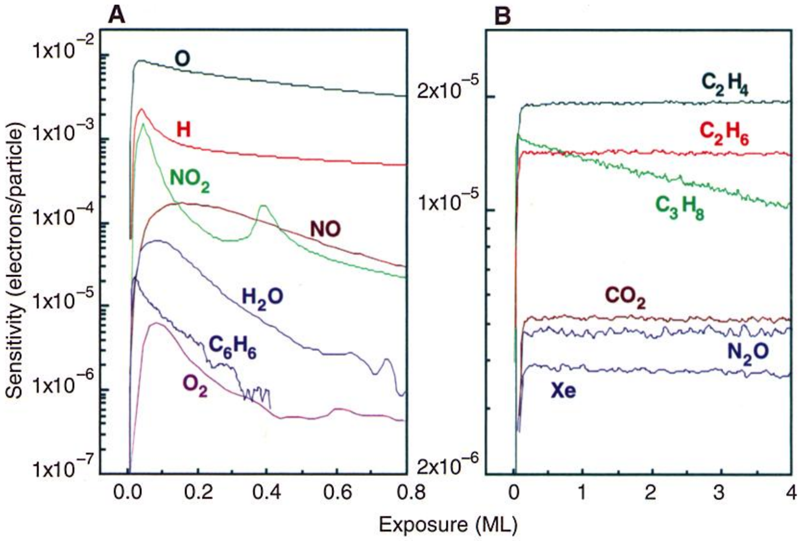

Fig. 2. Chemical reaction–induced currents measured from exposure of Ag/Si diodes at 125 ± 5 K to various atomic and molecular gases. The varying decay rates and apparent steady-state currents observed were a result of the different relative adsorption, reaction, and desorption rates. Reactant exposure is shown in terms of equivalent monolayers (ML) assuming a clean Ag(111) surface with 2.4×10^{15} sites/cm² and one site per adsorbate. For the rough polycrystalline Ag surfaces, the actual site density would be somewhat higher, and thus the exposure would be a lower limit. Species are shown with relatively strong (**A**) and weak (**B**) adsorption energies.

were consistent with their known mechanisms of adsorption. Error and uncertainty in our data are primarily systematic in nature because of several factors, including the uncertainties in the flux, film surface morphology, and inhomogeneities in the Schottky barrier height.

The initial sensitivities of Ag/Si Schottky diodes to electrons produced during adsorption, taken from the initial peak chemicurrent values, strongly correlate with the E_{ads} (compare in Fig. 3). For the various adsorbates studied, we observed a power law relation in the form, $(\varepsilon P_{na})_{t=0} \sim (E_{ads})^n$, where the exponent, n, was found to be ~2.7. The device sensitivity, εP_{na}, however, is the number of detected electrons per incident reactant. The number of hot electrons produced per gas-surface interaction is far greater than εP_{na} for two reasons. First, during transport from the film surface to the Schottky barrier, the ballistic electron current is attenuated by scattering that we have shown (*5*) to depend exponentially on the film thickness. For hot electrons with energies greater than the barrier height and less than a few electron volts, the attenuation length decreases strongly with increasing electron energy (*21*), and the probability of traversing the interface above the barrier without reflection is nearly unity. These transport effects will enter into the energy dependency of $\varepsilon(E_{ex})$ to increase P_{na}. Second, most theories predict that the process of nonadiabatic energy transfer will create electrons with a distribution of energies and trajectories relative to the barrier. Model calculations of the electron-hole pair energy distribution functions from adsorption are typically peaked just above the Fermi energy and monotonically decrease for higher excitation energies (*22*); i.e., most of the excited charge carriers are low energy and cannot traverse the Schottky barrier. The Schottky diodes act as a high-pass filter and detect only the "high-energy tail" of the excited charge carrier distribution.

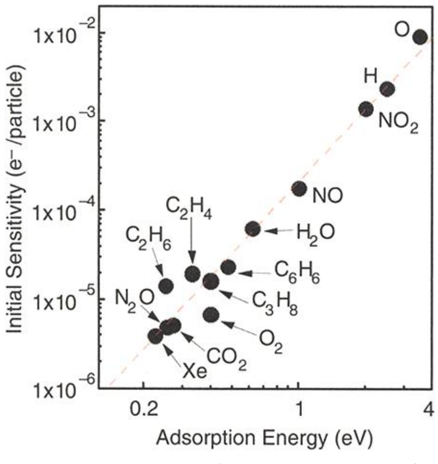

Fig. 3. Initial electron detection sensitivity for various gases of Ag/Si Schottky diodes as a function of E_{ads}. For N_2O, C_2H_6, and C_6H_6, no specific determination of the E_{ads} on Ag has been made, to our knowledge. An estimate of E_{ads} was made for N_2O from the reported desorption temperature (T_{des}) on Ag(111) (*22*) using the expression $E_{ads}(\mathrm{eV}) \sim 2.4 \times 10^{-3}\, T_{des}$. For C_2H_6 (*19*) and C_6H_6 (*17*), the E_{ads} on Ag were assumed to be approximately the same as on Au.

We compared sensitivity data for atomic O and NO measured previously using devices with a Schottky barrier, ϕ, of ~0.5 eV to the sensitivity on the lower barrier ($\phi \sim 0.2$ eV) devices from this study. There was no significant change for O in the peak sensitivity values of $(\varepsilon P_{na})_{O:\phi\sim0.5} \sim (\varepsilon P_{na})_{O:\phi\sim0.2} \sim 10^{-2}$; although for lower energy NO adsorption ($E_{ads} \sim 1$ eV), the ratio $(\varepsilon P_{na})_{NO:\phi\sim0.5}$: $(\varepsilon P_{na})_{NO:\phi\sim0.2}$ was approxiamtely 1:5. If we assume to first order that $\varepsilon \sim (\varepsilon P_{na})_O \sim 10^{-2}$, and if we assume a form of the electron-hole pair energy distribution function $P_{na}(E_{ex})$ derived by Schönhammer and Gunnarsson (*2*) with all excitations involving electrons at the Fermi level, fitting the distribution to the NO data gives a most probable electron energy, μ, of ~0.3 eV. The ratio of the integral of $E_{ex}P_{na}(E_{ex})$ to the E_{ads} suggests that approximately a quarter of the total E_{ads} is accounted for by hot electrons; phonon excitations would account for the remaining E_{ads}. Applying the same distribution function to the other species (taking $\mu \sim 0.3\, E_{ads}$), we calculated the fraction of the total electron-hole pairs produced with energies above the barrier to obtain an estimate of the total number of electrons produced per adsorbate required to give the number detected with our device. This estimate gave a range for P_{na} from ~1 for atomic O to ~0.06 for Xe. Quantitatively, these values depend strongly on the distribution function and parameters [e.g. $\mu(E_{ads})$], the inhomogeneity in the barrier height, and any modifications to the distribution from phonon creation; however, qualitatively the assertion that P_{na} is significantly higher than the observed value of εP_{na} remains valid. Direct single- and multiple-phonon excitations occur and will be an important energy dissipation pathway, particularly for energies below the Debye energy, E_D (for Ag, $E_D \sim 0.02$ eV), and for processes occurring slowly so that phonon cascades are probable. Nonetheless, our results are direct evidence of a relatively large number of electrons participating in the energy dissipation process during a variety of adsorption reactions.

Ongoing and previous work with different metals (*5*) (including Au, Pt, Pd, Cu, Ni, and Fe) and different semiconductors (GaAs and Ge) show that the phenomenon occurs for substrates other than Ag and that typically, for each adsorbing species, there is a distinctive combination of signal amplitude and kinetic behavior observable in the measured current. These observations suggest that electronic excitation with mobile hot electrons is a common feature of metal surface chemical reactions in which bonds are formed. One would also expect electronic excitations at liquid and solid phase interfaces with metals when bonds are formed, which would suggest an electronic means of energy dissipation in "friction." The chemoelectronic coupling suggests a new means of chemical sensing, in which the sensor is based on active charge carrier production rather than on passive variations in equilibrium thermodynamic quantities, such as resistivity or capacitance-based devices. Together with previous work in hot electron stimulated surface reactions, a unification of chemical rate processes and electronics is emerging that gives rise to a notion of "chemielectronics." Furthermore, if energetic e^-/h^+ pairs are routinely generated in surface-mediated reactions, these hot carriers have the potential to perform local chemistry not previously appreciated.

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