Nonlocal Dissociative Chemistry of Adsorbed Molecules Induced by Localized Electron Injection into Metal Surfaces

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We present a novel approach to surface chemistry studies using scanning tunneling microscopy (STM), where dissociation of molecules adsorbed on metal surfaces is induced nonlocally in a 10–100 nm radius around the STM tip by hot electrons that originate from the STM tip and transport on the surface. Nonlocal molecular excitation eliminates the influence of the STM tip on the outcome of the electron-induced chemical reaction. The spatial attenuation of the nonlocal reaction is used as a direct measure of hot-electron transport on the surface.

In photochemistry on metal surfaces, most chemical reactions are induced by hot electrons, i.e., electrons photoexcited above the Fermi level of the metal [1,2]. Scanning tunneling microscopy (STM) has proven to be a powerful method for direct analysis of electron-induced reactions on surfaces, because of its local electron injection and imaging capabilities [3]. Using STM one can analyze the products, kinetics, and intermediate states of a chemical reaction on the surface [4]. The majority of STM studies have focused on single-molecule chemistry, where the molecule located under the STM tip is locally excited by tunneling electrons [5–8]. An unresolved issue in such studies is the effect of the electric field of the STM tip and tip-molecule interactions on the local chemical reaction [9].

Here we show that tunneling electrons can induce dissociation of adsorbed molecules at a lateral distance of up to 100 nm from the STM tip. This occurs because injected hot electrons can propagate in the surface layer via surface resonances and inelastically scatter on adsorbed molecules inducing chemical changes. Diffusion of chlorine and germanium adatoms induced nonlocally by the tunneling current was previously observed on silicon surfaces [10,11], which have pronounced surface states and at least an order of magnitude longer lifetime of hot carriers compared to metal surfaces [12]. While nonlocal reactions of molecules adsorbed on metal surfaces were also reported in several cases [13,14], their hot-electron origin was not determined. Furthermore, in a recent report it was shown that large-scale chemical transformations can be caused by the electric field in the tunneling junction [14]. In this Letter, the nonlocal dissociation of CH_3SSCH_3 molecules on the Au(111) surface is shown to have unprecedented magnitude, and its hot-electron origin is quantitatively established. The effect is shown to be general for a number of molecules adsorbed on noble-metal surfaces. The nonlocal excitation eliminates tip artifacts since the tip and the adsorbed molecule are spatially separated. An additional merit of the nonlocal excitation is the ability to monitor the

hot-electron transport across the surface using the reaction yield as a measure of the hot-electron current.

The experiments were done using a commercial low-temperature STM (Omicron Nanotechnology) in ultrahigh vacuum. The Au(111), Cu(111), Cu(110), and Au(100) surfaces were prepared using Ar sputtering-annealing cycles. Adsorbate molecules were dosed onto metal surfaces from an effusive beam doser at a crystal temperature of <40 K to suppress thermally activated surface chemistry. No dissociation upon adsorption was observed for CH_3SSCH_3, C_6H_5SH, and CH_3SH molecules on the Au(111) surface (including elbows of the herringbone reconstruction) where most of the present analysis was carried out. Minor dissociation took place on single-atom step sites, but molecules in these regions are not considered here. The STM images of CH_3SSCH_3 molecules on Au(111) were acquired using a tungsten tip at $T = 5$ K, $V = 0.35$ V (sample positive), and $I = 0.1$ nA. Current pulses producing nonlocal chemistry were applied with the feedback engaged to surface regions unoccupied by adsorbate molecules.

Electron-induced dissociation of the CH_3SSCH_3 molecule on Au(111) [15] ruptures the S-S bond and produces two CH_3S fragments as seen in STM images before [Fig. 1(a)] and after [Fig. 1(b)] dissociation. To induce the dissociation reaction, the STM tip need not be positioned above the CH_3SSCH_3 molecule. As seen in Fig. 1(c), a pulse of tunneling current at a voltage exceeding 1.5 V causes nonlocal dissociation of the CH_3SSCH_3 molecules far from the tunneling junction. The efficiency of the reaction is dramatic: about 1000 molecules are dissociated by a single current pulse ($V = 2.5$ V, 3×10^9 electrons), with 100% dissociation found in a circular area of ~20 nm radius around the injection point. Using more intense pulses it is possible to dissociate molecules as far as 100 nm from the injection point.

Because of the large reaction yield, nonlocal dissociation of CH_3SSCH_3 is statistically reproducible for given STM tip and pulse conditions as seen in Fig. 1(d). The
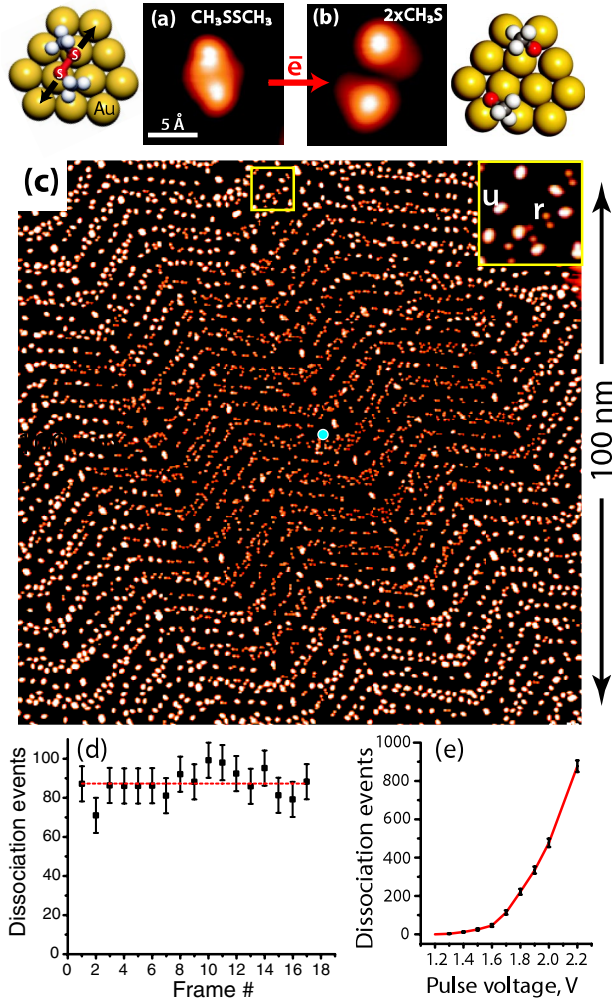
FIG. 1 (color online). STM images and structural models of (a) undissociated CH_3SSCH_3 molecule on the Au(111) surface and (b) products of its electron-induced dissociation (CH_3S). (c) STM image of nonlocal CH_3SSCH_3 dissociation induced by a single 2.5 V/1.0 nA/200 ms pulse at the (blue) point. The inset is a surface area (yellow square) located ~46 nm away from the pulse position. u marks unreacted and r marks reacted CH_3SSCH_3 molecules. (d) Total number of dissociation events per pulse obtained from 18 pulses of the same magnitude (1.8 V/0.350 nA/150 ms). The solid red line is the average number of events. (e) Total number of dissociation events per pulse (1.0 nA/200 ms) as a function of pulse voltage. The points are connected to guide the eye.

energy onset for the nonlocal dissociation of CH_3SSCH_3 on Au(111) is ~1.4 eV [sample positive, Fig. 1(e)], as measured from the total reaction yield as a function of pulse voltage. The relatively high energy suggests that the reaction proceeds via electronic excitation of CH_3SSCH_3 rather than vibrational excitation of the molecules in the ground electronic state [4]. This conclusion is supported by the observation of dissociative electron attachment to CH_3SSCH_3 molecules (adsorbed on ice) which cleaves the S-S bond [16]. Nonlocal dissociation of CH_3SSCH_3 was also observed on the Au(100), Cu(111), and Cu(110)

surfaces. In addition, nonlocal dissociation of the S-H bond in methanethiol (CH_3SH) and benzenethiol (C_6H_5SH) occurs on Cu(111) and Au(111) surfaces and the dissociation of the C-I bond in iodobenzene (C_6H_5I) occurs on Cu(111) and Cu(110) surfaces. The lateral extent and energy onset of the nonlocal reactions are different in each case, e.g., 0.8 eV for C_6H_5SH/Cu(111) and 3.5 eV for C_6H_5SH/Au(111). Since the energy onset is always higher (> 0.6 eV) than molecular vibrational energies, dissociative electron attachment is the likely reaction mechanism in all these cases.

We propose that the observed nonlocal chemistry is caused by hot electrons which are injected from the STM tip into the surface. Hot electrons propagate laterally causing dissociation of adsorbed molecules via dissociative electron attachment. Since the radius of the STM tip is typically 20–50 nm [17], two plausible alternative origins of the nonlocal chemistry are the electric field of the STM tip [14] and the field-emission current from random protrusions on the tip surface (microtips) near the tip apex. To rule out these alternatives, nanometer size clusters were created on the surface by a soft tip-crash [the cluster is ~1.2 nm high in Fig. 2(a)]. When the excitation pulse is applied on top of the cluster, the STM tip retracts by at least 1 nm [for Fig. 2(a)] away from the molecules adsorbed around the cluster, significantly reducing the electric field applied to the molecules and the possible field-emission current from random microtips. Nonetheless, Fig. 2(a) demonstrates that nonlocal dissociation is also caused by a current pulse on top of the cluster and its spatial extent is as large as when the same pulse is applied to the flat surface [Fig. 2(b)]. This experiment was reproduced for three different clusters [Fig. 2(c)] with only a 15%–30% variation in cluster/surface ratio of dissociation yield due to structural differences between the clusters and the STM tips.

The hot-electron origin of the nonlocal reaction was further confirmed from the statistical analysis of the radial distribution function of the dissociation events using a kinetic equation, $dP_r/dt = k(N_{0_r} - P_r)I_r^g$, which connects the rate of nonlocal reaction at radius r to the number of available molecules and the hot-electron current (I_r). Here, P_r is the number of dissociated molecules, N_{0_r} is the number of reactant molecules, k is the rate constant for the reaction, and g is the order of the reaction in electrons. A conceptually similar equation is used in the analysis of single-molecule chemistry [18], although the coverage dependence is not considered in the latter because only one molecule is excited at a time. It is further assumed that I_r is proportional to the tunneling current during the pulse (I_0), $I_r = I_0 f(r)$, where $f(r)$ is the attenuation function.

The value of g was determined from a series of nonlocal reaction measurements with a variable excitation current (I_0). For each electron pulse, the left part of the integral form of the rate equation, $-\ln(1 - P_r/N_{0_r}) = kt[I_0 f(r)]^g$, was evaluated as a function of radius r and then summed
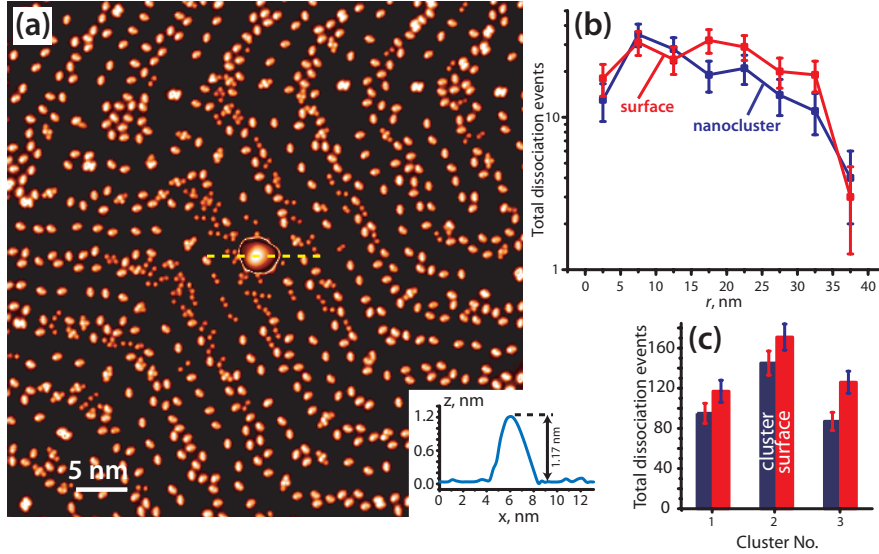
FIG. 2 (color online). (a) Nonlocal dissociation of CH_3SSCH_3 molecules from current pulse (1.8 V/0.5 nA/200 ms) on top of the metal cluster (inset is STM line scan of the cluster along the yellow dashed line). (b) Comparison of nonlocal reaction from a pulse on the cluster and on the flat Au(111) surface (1.8 V/0.5 nA/200 ms). (c) Total yield of nonlocal reaction from three pulses on different clusters compared to pulses of the same magnitude on the flat surface. Pulse conditions are 1.8 V/0.5 nA/200 ms for clusters 1 and 2, and 1.8 V/0.25 nA/250 ms for cluster 3.

over the radial extent of observed events:

$$-\sum_r \ln\left(1 - \frac{P_r}{N_{0_r}}\right) = ktI_0^g \sum_r [f(r)]^g. \quad (1)$$

The sum of attenuation terms $f(r)$ in Eq. (1) is not a function of I_0, because the average time interval between tunneling electrons is ~50 ps at 1 nA, which is much larger than the typical lifetime of hot electrons (20–40 fs) at the energy above 1.5 eV relative to the Fermi level [19]. We also chose the condition of constant total charge, $I_0 t = $ const, to prevent 100% dissociation in the scan range at large values of I_0. As seen in Fig. 3(a), g is close to unity. Both the observation of the nonlocal reaction in the experiment with the nanoclusters and the linear scaling of the nonlocal reaction rate with the excitation current ($g = 1$) support our hypothesis that the nonlocal chemistry is driven by the current of hot electrons injected from the STM tip.

As seen in Fig. 3(b), the attenuation function $f(r)$ beyond $r = 8$ nm is an exponential decay, $f(r) \propto e^{-r/\lambda_e}$ (the geometric factor $1/2\pi r$ was accounted for by summing all the dissociation events at a given radius, i.e., in the area $2\pi r \Delta r$). The decay length λ_e shows little dependence on the STM tip, the total charge of the hot-electron pulse (hence the range and total yield of nonlocal dissociation), and the energy of hot electrons (in the range of 1.8 to 2.2 V). The values of λ_e obtained in various experiments over several months were 5.4 ± 0.4, 5.4 ± 0.6, 5.2 ± 0.6 nm at $U = 1.8$ V; 6.5 ± 0.5, 5.6 ± 0.6 nm at $U = 2.0$ V; and 4.9 ± 0.4, 5.9 ± 0.9 nm at $U = 2.2$ V. Therefore λ_e must characterize the lateral attenuation of hot-electron current. If the hot-electron transport is ballistic, λ_e is proportional to the inelastic mean-free path of hot electrons (limited mainly by inelastic electron-electron scattering [20] at 1.8 V above E_f). We anticipate that nonlocal reactions will be a viable approach to study hot-electron transport on a metal surface in the presence of adsorbate

molecules which is complementary to the analysis of surface-state scattering on clean metal surfaces [21–23].

In this work the electronic states that carry hot-electron current in the surface layer cannot be rigorously assigned. Au(111) [24] and Cu(111) [25] surfaces have an unoccupied surface state (and the derivative surface resonance) in
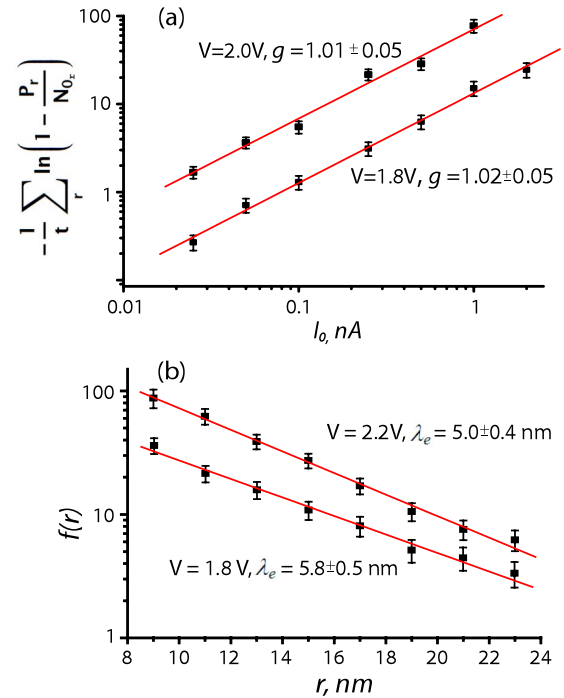

FIG. 3 (color online). (a) Linear scaling of nonlocal reaction rate with excitation current [Eq. (1)] from two experiments using pulses at 1.8 and 2.0 V. Each point on the log-log plot is an average of two measurements. Solid (red) lines are linear fits to the data. (b) Attenuation function of the nonlocal chemistry from two experiments using pulses at 1.8 V (average of 15 measurements) and 2.2 V (average of 5 measurements). Solid (red) lines are exponential decay fits to the data.

the $\bar{\Gamma}$-centered projected band gap at the energies of >1.5 eV above the Fermi level. However, on Cu(110) the lowest empty surface resonance in the $\bar{Y}$-centered band gap crosses the bulk bands at ~0.5 eV above the Fermi level [25,26] [and likely vanishes by analogy with Ag(110) [27]] although nonlocal dissociation of CH_3SH is observed at $E > 0.6$ eV (>1.0 eV for CH_3SSCH_3). On the (5×20) reconstructed Au(100) surface, no empty surface resonances below 4.0 V in the $\bar{X}$-centered band gap were found by photoemission [28,29]. Nonetheless, the nonlocal CH_3SSCH_3 dissociation on the Au(100) has an onset of ~1.3 V in our experiments. It is then possible that the bulk states at the edge of the projected band gap (which were shown to behave similarly to surface resonances [27]) may contribute to the hot-electron transport. Purely bulk states on any surface are unlikely to be involved, because of the large perpendicular momentum of the hot electron which will cause it to quickly leave the surface region [30,31].

Surface-resonance-mediated electronic excitation of adsorbed molecules makes nonlocal chemistry distinctly different from the local excitation under the STM tip, where electronic states of the tip directly couple to molecular resonances. In this regard nonlocal chemistry closely resembles surface photochemistry, where photogenerated hot carriers in the electronic states of the surface excite adsorbed molecules [32]. Nonlocal excitation also eliminates the effects of the STM tip on the chemical reaction by exciting molecules at a large distance from the tunneling junction. In our experiments, this is manifested in the high probability of conformation retention in the dissociation of CH_3SSCH_3 on the Au(111) surface [Figs. 1(a) and 1(b)]. The "*trans* conformation" of the reactant CH_3SSCH_3 molecule is retained in the geometrical arrangement of CH_3S products on the Au(111) surface [15] with a probability of $75 \pm 5\%$ (500 molecules studied) via the nonlocal excitation (pulse, 1.8 V/1 nA/100 ms) and with a much smaller probability of $10\% \pm 5\%$ (100 molecules studied) when the molecules are excited directly under the tip (pulse, 1.4 V/1 nA/100 ms). The high yield of conformation retention ($\sim65\%$) for local excitation is restored by decreasing the pulse current to 10 pA (increasing the tip-surface distance) [15], which implies that the reaction is locally influenced by the electric field or by tip-molecule interactions.

In summary, we have established that adsorbed molecules can be caused to dissociate at large distances (up to 100 nm) from the STM tip by hot electrons that are injected from the tip and transport laterally on the surface. The effect has been observed for several molecules and metal surfaces. This novel mode of molecular excitation provides unique opportunities to eliminate STM tip artifacts in the analysis of electron-induced chemical reactions on surfaces, to study hot-electron transport on surfaces in the presence of adsorbates, and to connect STM-induced chemistry to the photochemistry of adsorbed molecules.

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[1] X. Y. Zhu, Annu. Rev. Phys. Chem. **45**, 113 (1994).
[2] J. W. Gadzuk, Phys. Rev. Lett. **76**, 4234 (1996).
[3] J. K. Gimzewski, and C. Joachim, Science **283**, 1683 (1999).
[4] W. Ho, J. Chem. Phys. **117**, 11033 (2002).
[5] M. L. Bocquet, H. Lesnard, and N. Lorente, Phys. Rev. Lett. **96**, 096101 (2006).
[6] S. W. Hla, L. Bartels, G. Meyer, and K. H. Rieder, Phys. Rev. Lett. **85**, 2777 (2000).
[7] J. Henzl et al., Angew. Chem., Int. Ed. **45**, 603 (2006).
[8] M. Lastapis et al., Science **308**, 1000 (2005).
[9] A. J. Mayne, G. Dujardin, G. Comtet, and D. Riedel, Chem. Rev. **106**, 4355 (2006).
[10] Y. Nakamura, Y. Mera, and K. Maeda, Phys. Rev. Lett. **89**, 266805 (2002).
[11] R. Nouchi et al., Phys. Rev. Lett. **97**, 196101 (2006).
[12] J. R. Goldman and J. A. Prybyla, Phys. Rev. Lett. **72**, 1364 (1994).
[13] B. C. Stipe, M. A. Rezaei, and W. Ho, J. Chem. Phys. **107**, 6443 (1997).
[14] M. Alemani et al., J. Am. Chem. Soc. **128**, 14446 (2006).
[15] P. Maksymovych and J. T. Yates, Jr., J. Am. Chem. Soc. **128**, 10 642 (2006).
[16] H. Abdoul-Carime and L. Sanche, J. Phys. Chem. B **106**, 12 186 (2002).
[17] A. S. Lucier, H. Mortensen, Y. Sun, and P. Grutter, Phys. Rev. B **72**, 235420 (2005).
[18] B. V. Rao, K. Y. Kwon, A. Liu, and L. Bartels, Proc. Natl. Acad. Sci. U.S.A. **101**, 17 920 (2004).
[19] J. Cao et al., Phys. Rev. B **58**, 10 948 (1998).
[20] E. V. Chulkov et al., Chem. Rev. **106**, 4160 (2006).
[21] L. Burgi, O. Jeandupeux, H. Brune, and K. Kern, Phys. Rev. Lett. **82**, 4516 (1999).
[22] L. Vitali et al., Surf. Sci. **523**, L47 (2003).
[23] K. F. Braun and K. H. Rieder, Phys. Rev. Lett. **88**, 096801 (2002).
[24] D. P. Woodruff, W. A. Royer, and N. V. Smith, Phys. Rev. B **34**, 764 (1986).
[25] A. Goldmann, V. Dose, and G. Borstel, Phys. Rev. B **32**, 1971 (1985).
[26] P. Cortona and C. Sapet, Int. J. Quantum Chem., **99** 713 (2004).
[27] J. I. Pascual et al., Phys. Rev. Lett. **96**, 046801 (2006).
[28] F. Ciccacci, S. Derossi, A. Taglia, and S. Crampin, J. Phys. Condens. Matter **6**, 7227 (1994).
[29] F. J. Himpsel and J. E. Ortega, Phys. Rev. B **46**, 9719 (1992).
[30] K. Reuter et al., Phys. Rev. B **58**, 14 036 (1998).
[31] A. Schneider et al., Appl. Phys. A **66**, S161 (1998).
[32] C. D. Lindstrom and X. Y. Zhu, Chem. Rev. **106**, 4281 (2006).