Electronic Excitation and Dynamic Promotion of a Surface Reaction

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The mechanism of recombinative desorption of hydrogen from a Ru(0001) surface induced by femtosecond-laser excitation has been investigated and compared to thermally initiated desorption. For the laser-driven process, it is shown that hot substrate electrons mediate the reaction within a few hundred femtoseconds resulting in a huge isotope effect between H_2 and D_2 in the desorption yield. In mixed saturation coverages, this ratio crucially depends on the proportions of H and D. Deviations from second order desorption kinetics demonstrate that the recombination is dynamically promoted by excitation of neighboring, but nonreacting adatoms. A concentration dependent rate constant which accounts for the faster excitation of H versus D is proposed.

Chemical reactions involving species adsorbed on a metal surface are mediated through excitation of electrons and/or phonons of the substrate. Since thermal equilibration between these excitations occurs on a femtosecond (fs) to picosecond (ps) time scale, the rate normally may be described to a very good approximation within the framework of transition state theory [1] in terms of the temperature dependent rate constant and as a function of the surface concentrations. Rapid absorption of a fs-laser pulse by the conduction electrons of the substrate may, however, trigger the onset of a surface reaction before equilibration between the heat baths of electrons and phonons is reached, as has been exemplified in the reaction between O and CO adsorbed on a Ru(0001) surface yielding the release of CO_2 into the gas phase [2]. For adsorption on thin metal films with Schottky contact, it was recently demonstrated that nonadiabatic coupling to electron-hole pairs plays an important role in surface reactions and is not negligible even in low-energy processes in which phononic excitations are thought to dominate [3]. Hot electrons were proposed to routinely participate in substrate-mediated reactions contrary to the traditional picture of a thermal surface reaction, in which phonons solely drive the system over the reaction barrier in the electronic ground state.

Coadsorbed species on a metal substrate can modify the electronic structure and hence influence the surface reactivity. Altering the height of the reaction barrier in the electronic ground state and/or energetic shifts of the potential energy surface in electronically excited states are typical consequences. In the case of catalytic promotion (e.g., by alkali atoms), these *static* changes in the electronic potential energy landscape result in an enhanced reaction rate [4]. In this Letter, we report on *dynamic* promotion of a prototype surface reaction, $H_{ad} + H_{ad} \rightarrow H_{2,gas}$ on Ru(0001). Hydrogen recombination may be initiated thermally (i.e., under conditions of thermal equilibrium between all degrees of freedom), but if in-

duced by fs-laser excitation characteristic differences are observed: (i) The hydrogen molecules coming off the surface exhibit appreciable excess kinetic energy, (ii) there exists a large isotope effect between H and D (which is absent in the thermal reaction), and (iii) most remarkably, desorption of the heavier isotope (D_2) is facilitated by the presence of the lighter counterpart (H_{ad}) on the surface. This dynamic effect is attributed to the faster excitation of the lighter isotope. Its thereby initiated lateral displacement influences the energetics of the neighboring adspecies and thus promotes the desorption kinetics. In a more general sense, rate constants for a surface reaction $A + B \xrightarrow{k} AB$ may be reformulated as $k = k(C^*)$ with C^* being an excited, but not-reacting, coadsorbate as the results of this Letter demonstrate.

Hydrogen adsorbs dissociatively on Ru(0001) up to saturation [H-(1×1)] with occupation of threefold fcc sites [5]. In the present experiments, the Ru sample is mounted in an ultrahigh vacuum chamber (base pressure $< 1 \times 10^{-10}$ mbar) and can be temperature-controlled from 30 to 1530 K. Saturation of a pure H or D coverage is achieved by exposing the clean sample surface at 170 K to ~50 Langmuir H_2 or D_2, respectively [6]. Statistically mixed H:D coverages are obtained by first precovering the clean Ru surface with HD and subsequently saturating it with either of the pure isotopes. Thermal desorption is induced by resistively heating the sample (rate 1.5 K/s), while laser desorption is caused by fs pulses (800 nm, 130 fs, 2.2 mJ, ~60 J/m^2 absorbed yield-weighted fluence [7]). The desorbing molecules are detected by a quadrupole mass spectrometer, whereby the collection efficiency is greatly enhanced by a glass enclosure around the ionization region [8]. Details of the experimental setup can be found elsewhere [7].

Typical thermal desorption spectroscopy (TDS) data for H_2 and D_2 are reproduced in Fig. 1(a). Two characteristic maxima around 320 and 380 K are in accordance with previous reports [6,9] and are practically identical
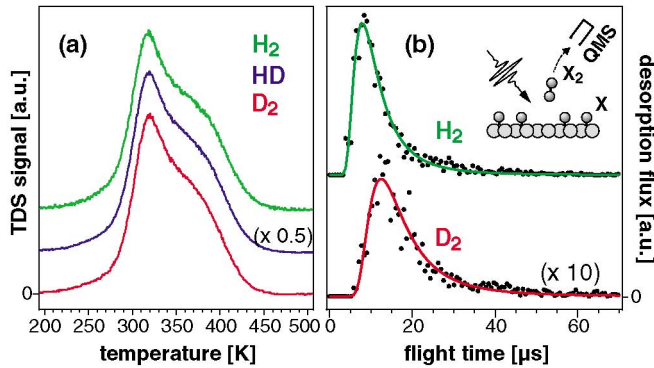
FIG. 1 (color). (a) TD spectra for H_2, HD, and D_2 from a saturation coverage of HD. Spectra are scaled according to detection sensitivity and offset for clarity. (b) The fs-laser induced TOF spectra for H_2 (offset) and D_2. Mean kinetic energies are obtained by fitting modified Maxwell-Boltzmann distributions (solid lines) to the experimental data. $E_{kin} = (2110 \pm 400)$ K and (1720 ± 290) K for H_2 and D_2, respectively.
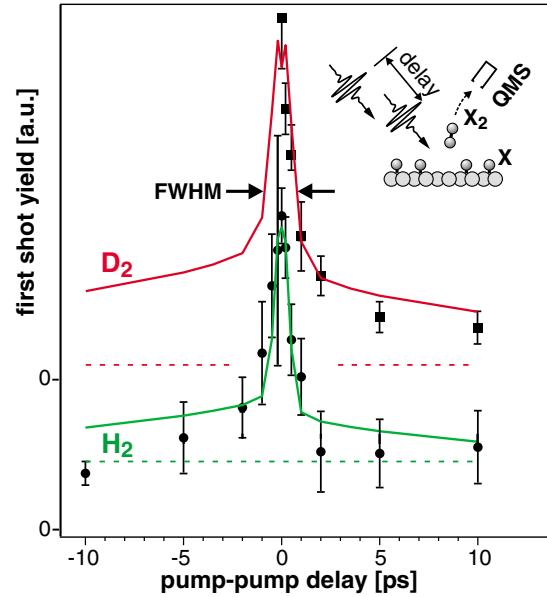

FIG. 2 (color). Two-pulse correlation (pulse intensity ratio 54:46) of the laser-induced desorption yield of hydrogen from Ru(0001). The yield of the first shot out of a series of laser pulses is shown as a function of the pulse-pulse delay (D_2 data offset). Dashed lines mark the overall yield of both individual pulses infinitely separated in time. Solid lines are obtained using the electronic friction model of Ref. [11] with a FWHM of 1.1 and 1.5 ps for H_2 and D_2, respectively. The dip at very short delays originates from the competition between the heat transport into the bulk and electron-phonon coupling [12].

for both H_2 and D_2. This indicates that there is no noticeable isotope effect in the thermal desorption kinetics, presumably because the zero-point energy differences are very similar in the initial and final states. Recombinative desorption initiated by absorption of a fs-laser pulse exhibits quite different characteristics: From the time-of-flight (TOF) spectrum as shown in Fig. 1(b), a mean translational energy of about 2000 K is derived for the desorbing H_2 and D_2 molecules, i.e., a much higher value than one would obtain from TDS. This indicates that after fs-laser excitation the hydrogen molecules leave the surface excited without complete equilibration with the heat bath of the solid.

Closer insight into the dynamics of this reaction pathway is obtained by two-pulse correlation (2PC) experiments [10]. Two equally intense fs-laser pulses are sent onto the Ru sample with variable time delay Δt. In Fig. 2, the resulting desorption yields for H_2 and D_2 from H-(1 × 1) and D-(1 × 1) surfaces, respectively, are plotted as a function of Δt. The narrow full width at half maximum (FWHM) of ~1 ps is a clear indication for the operation of the hot-electron mechanism, since only for pulse separations shorter than the electron-phonon equilibration time (~1 ps for Ru) the electron temperature is greatly enhanced due to the combined effect of both pulses. This in turn gives rise to a sharp peak in the 2PC of the H_2 and D_2 yield. In contrast, a phonon-mediated process proceeds on a much slower time scale of tens of picoseconds [2].

For theoretical modeling, the two-temperature model [13] in conjunction with the modified electronic friction model [11] accounting for the electron-mediated energy transfer from the Ru substrate to the H/D adsorbate is employed. In this model, the coupling time τ_{el} between substrate and adsorbate is the inverse of the friction coefficient and scales proportionally with the mass of the adsorbate. The solid lines in Fig. 2 fit the experimental data with a modified activation energy [14] of 1.35 eV and $\tau_{el} = 180$ fs and 360 fs for H_2 and D_2, respectively. As illustrated in Fig. 3(a) for an exemplary time delay of 1 ps, absorption of the first fs-light pulse causes a rapid rise of the electron temperature T_{el} which couples within less than 1 ps to the phonon temperature T_{ph}. If the second pulse is absorbed after Δt, the yield of both desorbing molecules H_2 and D_2 will be enhanced if full equilibration of T_{el} and T_{ph} has not yet been reached, underlining the observed narrow FWHM of the 2PC experiments.

The second striking difference of the laser-driven process to thermal desorption concerns the isotope effect: If the yields per laser shot from pure H and D adlayers, respectively, are compared with each other, a ratio of about 10($\pm$2):1 results [see scaling factor in Fig. 1(b)]. Unlike in phonon-mediated processes [15], distinct isotope effects in the reaction yield are characteristic for processes involving electronic excitation, e.g., in electron stimulated desorption [16] as well as in surface femtochemistry [2], and have to be attributed to the mass-dependent distance the system travels on the electronically excited state during its short lifetime [17]. The principle underlying this process is illustrated by Fig. 3(b). Absorption of light by the conduction electrons creates hot electrons above the Fermi level E_F. They rapidly equilibrate internally to an electron temperature T_{el}
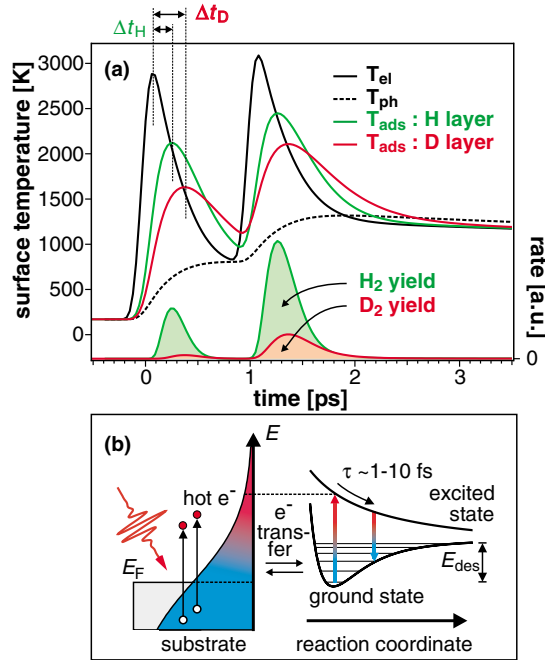
FIG. 3 (color). Energy transfer from substrate to adsorbate: (a) Based on the two-temperature model [13], the calculated time profiles of the electron and the phonon temperature T_{el} and T_{ph} at the substrate surface are plotted for two laser pulses with a pulse separation of $\Delta t = 1$ ps. Assuming a purely electron-mediated energy transfer [11], the adsorbate temperatures T_{ads} for an H and D saturation layer, respectively, result. In the lower section, the corresponding rates and their time integrals, the desorption yields, are displayed. (b) Illustration of the electronic processes after fs-laser excitation.

(within ≤ 100 fs [18]) and subsequently cool down by coupling to the lattice characterized by its phonon temperature T_{ph}. The distribution of the hot electrons is governed by T_{el} through Fermi-Dirac statistics. As a consequence, an adsorbate derived affinity level above E_F may become partially occupied, and the system is transferred to another electronically excited potential. The gradient on this potential initiates nuclear motion during the short lifetime (typically ≤ 10 fs [17]). Relaxation occurs by electron transfer back to the substrate, and thereby the system returns to the ground state potential. This electronically nonadiabatic process causes coupling between electronic and nuclear degrees of freedom [19] and is also denoted as electronic friction [11,20]. Its multiple repetition eventually enables the adsorbed species to take up enough energy to react and desorb from the surface (desorption induced by multiple electronic transitions [17]).

If the surface is saturated with hydrogen, but with a varying proportion of both isotopes H and D, i.e., constant (1×1) coverage, the total yields of H_2, D_2, and HD coming off in the TDS experiment should follow second order rate equations of the forms $d/dt[H_2] = k[H]^2$, $d/dt[D_2] = k[D]^2$, and $d/dt[HD] = 2k[H][D]$. These differential equations are coupled through the mass continu-

ities $d/dt[H] = -2d/dt[H_2] - d/dt[HD]$ and $d/dt[D] = -2d/dt[D_2] - d/dt[HD]$. It is assumed that there exists random mixing among both chemically identical adsorbates and both H_2 and D_2 desorb with the same (thermal) rate constant k which is justified by the TDS data in Fig. 1(a). Indeed, the experimental TDS yields show excellent agreement with theory [solid lines in Fig. 4(a)] and demonstrate that thermal desorption can be rationalized in terms of a simple bimolecular reaction.

The first-shot yields resulting from fs-pulse excitation are shown in Fig. 4(b). In contrast to the TDS data, now $\leq 5\%$ of the total coverage is released into the gas phase so that the data reflect the influence of the adsorbate composition on desorption from a fully covered surface to a good approximation [21]. The asymmetry in the laser-induced desorption yields is caused by the pronounced isotope effect between the pure adlayers already mentioned. Very intriguing discrepancies are found when one compares the experimental data with calculations [Fig. 5(a)] using the time-dependent rate constants $k[T_{ads}(t)]$ out of the friction model (see Fig. 3) in the rate equations introduced above [22]: the yields for D_2 are appreciably higher and those for H_2 lower than predicted. Because of the electronic nature of the energy transfer, the adsorbate temperatures T_{ads} for pure H and D adlayers follow T_{el} with a certain delay Δt_H and Δt_D of 180 and 330 fs, respectively [Fig. 3(a)]. $T_{ads}(t)$ for H clearly reaches its maximum before the respective T_{ads} for the heavier D, reflecting the different coupling times as derived from the electronic friction model. Consequently, energy transfer into the adsorbate occurs twice as fast for H as for D and hence the more rapidly excited H atoms will start earlier to be displaced from their equilibrium positions thereby also affecting (neighboring) D atoms [Fig. 5(b)] [23]. We propose that the resulting changes in the electronic structure lead to the enhancement of the recombinative desorption of D_2. One physical
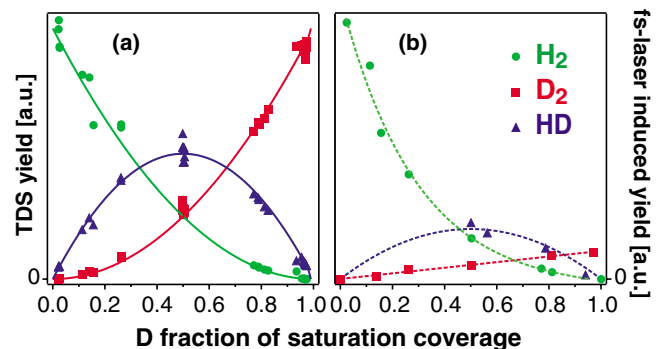

FIG. 4 (color). H_2, D_2, and HD desorption yield from a hydrogen-saturated Ru(0001) surface as a function of the D species concentration on the surface. (a) Thermal desorption by resistive heating. Solid lines are based on second order rate equations numerically integrated with the coupling continuity equations (see text). (b) Desorption induced by fs-laser excitation, reflecting the isotope effect of 10:1 between isotopically pure coverages. Dashed lines are guides to the eye.
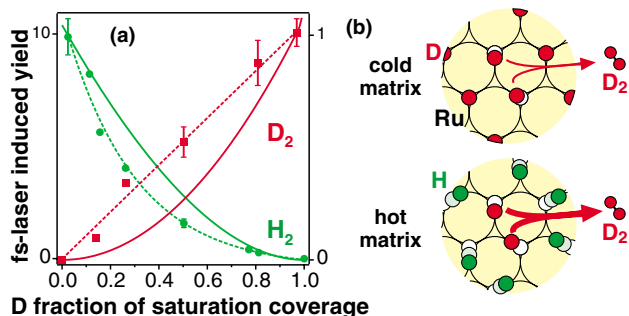
FIG. 5 (color). (a) Comparison of fs-laser induced H_2 and D_2 desorption yield with the outcome of second order rate equation calculations based on time-dependent rate constants (see text). (b) Top: In a cold matrix realized by a D surrounding, D_2 recombination occurs between two excited reactants. Bottom: The more rapid excitation of H atoms creates a hot matrix, in which the recombination of D_2 molecules is enhanced.

picture of the relevant microscopic motion would involve repulsive interactions in which H atoms give way to two D reactants. However, also nonlocal contributions to the promotion effect might play a role, as band structure changes induced even by low coverages in photoemission experiments from H on various metals indicate [24]. That the presence of neighboring H_{ad} species obviously enhances the D_2 recombination probability also applies to the H_2 formation despite the apparent reduction of the H_2 yield in the presence of a D surrounding [Fig. 5(a)]. Without the promotion effect for H atoms in an H surrounding, the isotope ratio between pure H and D coverages would have been smaller than the measured value of 10:1. Thus, the lighter isotope represents a dynamic promoter for the surface reaction of both D_2 and H_2 formation.

Our results imply that the rate constant k for the recombination reaction from mixed adlayers needs to be reformulated: k is no longer dependent only on a uniform adsorbate temperature $k = k(T_{ads})$, but rather is a function of the H:D proportion, i.e., the isotope concentrations [H] and [D]. Consequently, k might be rewritten as $k = k(T_{ads}^H, T_{ads}^D)$. This concept also holds for thermally initiated desorption since under equilibrium conditions $T_{ads}^H = T_{ads}^D$, describing the adsorbate system by a uniform parameter. However, even in the thermal case, the site fluctuations of neighboring adatoms will cause desorption preferentially in moments when the surrounding has created a favorable energy landscape. A crucial test for the promotion effect would be *ab initio* calculations for k solely accounting for both reactants compared to the experimental results reported here.

To summarize, our work on hydrogen recombination on Ru shows that femtosecond-laser excitation triggers an electron-mediated reaction pathway. The observed huge isotope effect is enhanced by a collective mechanism in which due to different energy coupling times the sur-

rounding of the reactants dynamically changes their reactivity. Although observed in a fs-laser induced reaction, dynamical promotion might be a common feature in surface chemistry, but cannot be resolved in thermal surface reactions due to equilibrium conditions.

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[21] Note that surface diffusion is widely suppressed in coverages at and near saturation due to blocking of the next nearest neighbor sites and hence is negligible.
[22] Successfully describing the substrate-adsorbate energy transfer, the friction model assumes equilibrium in the adsorbate subsystem with temperature T_{ads}. Hence, the use of equilibrium rate equations seems reasonable.
[23] Any competition effects, in which a fast H_2 desorption would reduce the reaction probability for HD formation and hence increase the D_2 yield, or changes in the electronic structure for the residual D share on the surface after an early departure of H_2 can be ruled out due to the low laser fluences applied in the experiments.
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