Diatomic Molecular Switches to Enable the Observation of Very-Low-Energy Vibrations

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Using low-temperature scanning tunneling microscopy and spectroscopy, we found that the coadsorption of atomic hydrogen to single transition-metal and rare-earth-metal atoms on a Ag(100) surface gives rise to surprising phenomena, a bias dependent switching from a large to a small apparent size of the diatomic molecules and a concomitant appearance of very low-energy vibrational features of 3 to 7 meV in the differential conductance spectra. These phenomena, which have until now escaped observation, may be of general relevance for low-temperature adsorption.

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The unique properties of scanning tunneling microscopy and spectroscopy to address an individual atom or a single molecule adsorbed on a surface have contributed considerably to our understanding of fundamental excitations and interactions at the atomic and molecular level. For example, taking advantage of inelastic electron tunneling (IET), spin-flip excitations of single magnetic adatoms [1] engineered in one-dimensional chains [2], luminescence [3,4], optical [5], and vibrational excitations of single molecules [6] have been successfully identified. Typically, these experiments are performed in ultrahigh vacuum (UHV) at temperatures below $T = 10$ K where the presence of hydrogen in the tunneling region may lead to surprising spectroscopic signatures, depending on the adsorbate concentration and on the tunneling parameters. Gupta *et al.* [7] observed on a Cu(111) surface differential conductance (dI/dV) spectra ranging from those reminiscent of an energy gap in a superconductor to ones with negative differential resistance features, characteristic for vibrational excitations of an adsorbed molecule on a surface [8]. These findings call for a clarification of the role of hydrogen in low-temperature adsorption.

In this Letter, we show that the coadsorption of atomic hydrogen to transition-metal (Cr) and rare-earth-metal (La, Ce) atoms deposited on a Ag(100) surface leads to intriguing changes of (i) the apparent height of the molecules and of (ii) their differential conductance (dI/dV) spectra. The metal-monohydride molecules can be switched between two states characterized by the presence or absence of a depletion in the observed spectra around the Fermi energy. As this characteristic dip is also observed for LaH, where the $4f$ orbitals are empty, an interpretation in terms of a Kondo resonance [9–11] is excluded. In contrast, the physical origin of this novel spectroscopic feature lies in low-energy vibrational excitations of the molecule.

The experiments were performed in a low-temperature scanning tunneling microscope (STM) in UHV at temperatures of $T = 4.9$ K [12]. Ce, La, and Cr atoms were thermally evaporated from pure metal ingots wound in a tungsten filament and deposited onto a well-prepared Ag(100) surface. A cut PtIr wire was used as the STM tip. Bias voltages V_T refer to the sample voltage with respect to the tip. All STM images were obtained in constant-current mode. Local scanning tunneling spectroscopy was performed with the lock-in technique by modulating the bias voltage with a sinusoidal signal ($V_{\mathrm{mod}} = 1$ mV peak to peak) under open feedback loop conditions.

In Fig. 1(a), obtained on Ag(100) with a Ce adatom concentration of 5×10^{-4} monolayer (ML) at a bias voltage of $V_T = -100$ mV, two different adsorbate species are clearly distinguishable. While about 50% of the objects on the surface are stable, the remaining ones display a "fuzziness" during the horizontal tip scan. Figure 1(b) illustrates the bias voltage dependent imaging. During scanning at tunneling voltages V_T between -90 and $+120$ mV the unstable adsorbates B are imaged as large protrusions of typically 210 ± 10 pm apparent height, only slightly smaller than the stable ones A of about 230 ± 10 pm height, determined from an analysis of 700 adsorbates. By contrast, scanning at bias voltages below $V_T = -90$ mV or at $120 < V_T < 200$ mV reveals several reversible transitions of the object from a large apparent height of 210 ± 10 pm to a small one of 95 ± 10 pm and vice versa. The switching object spontaneously returns back to its large state once the tip is removed during scanning, as is clearly visible in Fig. 1(b). Scanning at bias voltages above 200 mV images the object in its large state. The instability in the line scan indicates small lateral displacements of the adsorbate under the tip. The switching to the small state is found for both bias polarities, indicating that the electrostatic interaction between tip and adsorbate creates an induced dipole [13]. However, the effect is not symmetric as at positive bias voltages larger than 200 mV the adsorbate returns to its large state. Therefore, also at least quadrupolar electrostatic interactions have to be present. Data from different Ag(100) samples with varying Ce coverages ($\leq$0.001 ML) and different tips (PtIr, W) show that between 1%–50% of all adsorbates are switchable, while the remaining ones are stable. Ce and La adsorbates

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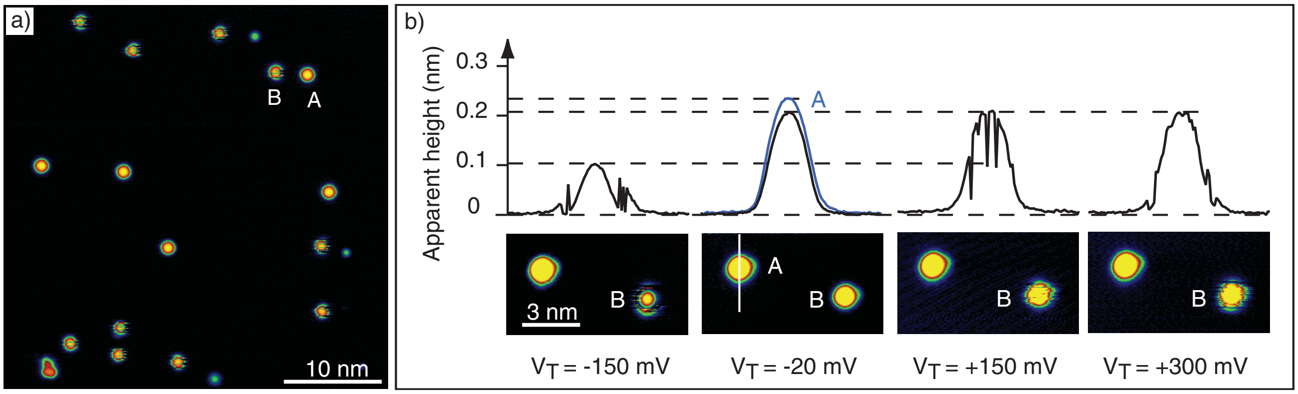

FIG. 1 (color). (a) STM image of a 5×10^{-4} monolayer (ML) Ce on Ag(100) at a temperature of 4.9 K revealing two different adsorbate species at the surface, a stable one A and an unstable switching object B. Scanning is horizontally line by line from bottom to top [(a),(b)]. Image size 40×40 nm^2, $V_T = -100$ mV, $I_T = 50$ pA. (b) Cross sections (as indicated by the vertical white line in the topography at $V_T = -20$ mV) and STM topographies of the two objects A and B at different bias voltages, showing the switching behavior in the apparent height of the object B.

show similar switching characteristics, Cr adsorbates typically switch at bias voltages of 300 mV.

In order to identify the chemical nature of the adsorbates we performed many evaporation cycles with the hot tungsten filament. We found that the number of switchable objects decreases to less than 1% after numerous outgassing and deposition cycles accompanied by a concomitant decrease of the hydrogen partial pressure as detected by mass spectroscopy. This finding points to the presence of hydrogen on the sample. In addition, STM revealed a number of depressions on the bare Ag(100) surface, characteristic of atomic hydrogen adsorption [14–16]. Additional experimental evidence for the presence of hydrogen on the sample is obtained from the following observations. By applying short positive voltage pulses (4 V, 50 ms) to the adsorbates, the unstable adsorbates are transformed into stable objects, pointing towards a tip-induced detachment of hydrogen [17,18]. Moreover, a switching object can be laterally displaced by several nanometers indicating molecular bonding between Ce and H. Consequently, the origin of the observed surprising switching phenomenon of the adsorbates is rationalized as follows. Atomic hydrogen coadsorbs (in the gas phase, by dissociative adsorption at the metal adatom sites, or by tip-induced diffusion in the presence of the electric field between tip and sample [13,19]) at the Ce, La, or Cr atoms. This hydrogen coadsorption distinguishes the switchable objects from the stable ones. The former are identified as metal-monohydride molecules (MH) and the latter as bare metal adatoms. The intriguing switching behavior at a threshold bias voltage indicates a flipping between two characteristic conformations of the molecule on the surface induced by the electric field in the STM junction [8,13,20,21].

The STM image in Fig. 2(a) shows a close-up of such an unstable, flipping CeH molecule B recorded at a bias voltage of $V_T = -100$ mV. The small and the large state of the molecule are clearly visible. The voltage dependent switching of the molecule is shown in Fig. 2(b) which displays typical distance-bias voltage $z(V_T)$ curves recorded on top of a stable Ce adatom (A) and on a switching CeH molecule (B) in constant-current mode, i.e., under closed feedback loop conditions. At a specific bias voltage of about -100 mV an abrupt vertical tip displacement of about 0.1 nm towards the sample is observed, reflecting the transition of the molecule from its large to its small state.

A careful inspection of high-resolution images reveals that the molecule in its small state is always at the same position on the surface when switched from large to small. However, as shown in Fig. 2(c), after a switching event, the center of the molecule in its large state is found displaced by about 0.1 nm (Ag lattice constant 0.289 nm) as compared to its former position in its large state. Four different positions of the molecule in its large state are observed on the Ag(100) surface which hints at the geometrical arrangement of the CeH molecule on Ag(100) as proposed in Fig. 2(d). Here, the hydrogen atom is supposed to occupy a fourfold hollow site and the CeH molecule is lying on the surface. The small state is assumed to correspond to a conformation where the molecular axis is perpendicular to the surface, a configuration stabilized by the tip. However, once the tip is removed, the molecule returns to its large state, for which four equivalent orientations on the surface are observed, as sketched in Fig. 2(d) [22]. Once switched to the small state, the molecule remains in this state even at reduced absolute tunneling voltage below the switching voltage of ≈100 mV as long as the tip is maintained above the molecule. Evidently, in addition to the electric field, a van der Waals force is acting between tip and molecule. This characteristic behavior allows us to obtain spectroscopic data of the molecule in its two states.

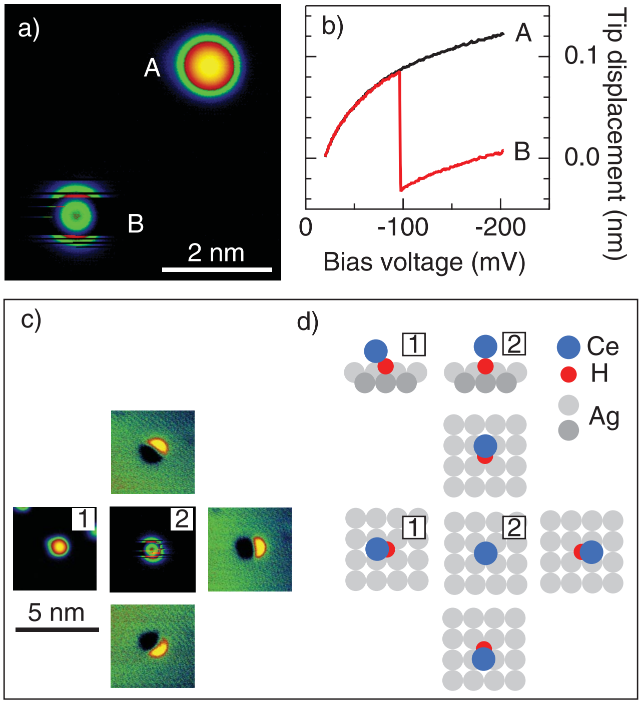

FIG. 2 (color). (a) STM topography of a switching object B and a nonswitching one A recorded at $V_T = -100$ mV, $I_T = 100$ pA. Image size 5.7×5.7 nm^2. (b) Constant-current spectroscopy $z(V_T)$ on a nonswitching adsorbate A and a switching one B. The vertical tip displacement at $V_T \cong -100$ mV bias voltage corresponds to an apparent height difference of 0.1 nm. (c) One switching molecule, observed in its small state (2) at $V_T = -100$ mV and in its large state (1, left) at $V_T = -20$ mV. The three other equivalent large configurations are revealed by displaying the height differences with respect to configuration (1). (d) Ball model (top and side views) showing the geometry of the CeH molecule adsorbed on Ag(100) in its small (2) and large (1) state.

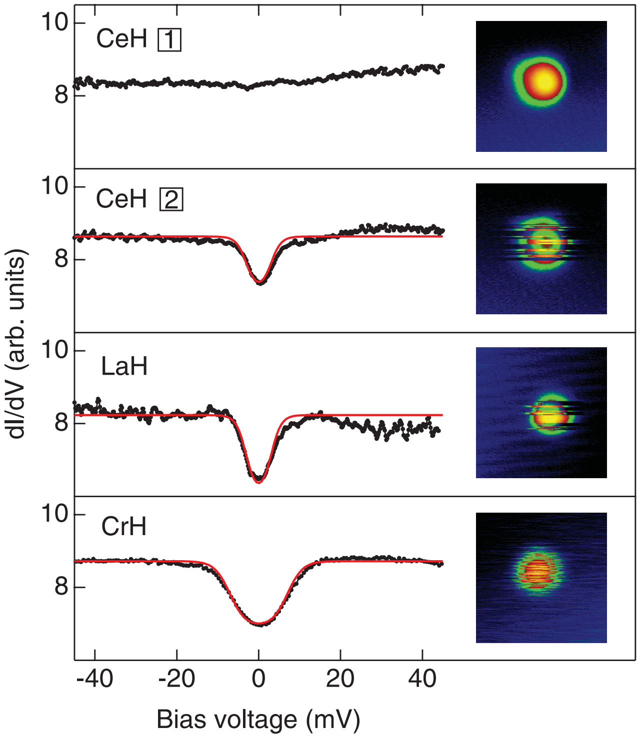

FIG. 3 (color). dI/dV spectra (black) and STM topographies of metal-monohydrides. CeH in its large (1) and small (2) state, as well as LaH and CrH in their small state recorded at $T = 4.9$ K. Tunneling spectroscopy parameters $V_{\mathrm{mod}} = 1$ mV, $I_T = 500$ pA. Simulation of the data (red) using Eq. (1) yields an excitation energy $E_i \approx 3$ meV for CeH and LaH and ≈ 7 meV for CrH.

If the tip is placed above the CeH molecule in its large state, the measured differential conductance dI/dV is rather featureless and constant around the Fermi energy E_F as indicated in Fig. 3 (1). By contrast, if the dI/dV spectrum is taken on the same molecule after being switched to the small state, a pronounced depletion of about 20% around E_F, with a full width at half maximum of ≈ 6 meV, is observed [Fig. 3 (2), (black)]. Similar symmetric dips around E_F are observed for LaH and CrH molecules in their small state [Fig. 3 (black)]. As this dip is also present for LaH, which bears no occupied $4f$ states, an interpretation of this feature in terms of a Kondo resonance has to be discarded. Consequently, the observed spectral features are identified as vibrational excitations. Measurements with varying tunneling resistances give essentially identical results, indicating an inelastic tunneling process in the nonsaturated regime [7].

The dI/dV spectrum for such an IET process can be expressed as [7,23–25]

$$\left.\frac{dI_T}{dV}\right|_{V_T} = \sigma_e + \sigma_i\left[F\left(\frac{-eV_T + E_i}{k_BT}\right) + F\left(\frac{eV_T + E_i}{k_BT}\right)\right], \tag{1}$$

where σ_e and σ_i denote the elastic and inelastic linear conductance, respectively, E_i is the excitation energy, and F is a function defined by $F(x) = [1 + (x - 1) \times \exp(x)]/[\exp(x) - 1]^2$. The spectral line shape shows a steplike increase of width $5.4k_BT$ in the conductivity at excitation energies $\pm E_i$ with respect to E_F. A simulation of the data with Eq. (1) yields good agreement between experiment and model as shown in Fig. 3 (red). Consequently, we identify this prominent spectral feature as a vibrational mode of ≈ 3 and ≈ 7 meV excitation energy for the CeH (LaH) and CrH molecules, respectively.

Spin-flip excitations, as observed recently for single Mn atoms on an ultrathin oxide layer [1], have to be excluded in the present case where the adsorbates are in direct contact with a metallic surface. It is interesting to note that the vibrational excitation energy for CeH and CrH molecules scales roughly with the inverse square root of the atomic masses, confirming the vibrational origin of the observed spectral feature [26]. The fact that the vibrational excitation is only observed when the metal-monohydride molecules are in the small state can be attributed to two factors: (i) The local electronic structure for the two molecular conformations is different in order to selectively allow for the excitation of vibrational mode of specific symmetry. (ii) The large conductance drop when passing from large to small apparent height of the molecule is accompanied by a corresponding large increase of the ratio between inelastic and elastic contributions to the current making these excitations measurable [28].

Typical internal vibrational modes for free CrH and LaH molecules are in the range of 200 meV [29,30]. Furthermore, e.g., for single Co adatoms on a Cu single crystal surface the vertical stretch mode is predicted to have an energy of 33 meV [27]. Consequently, these modes cannot be responsible for the low-energy vibrations detected in the present experiment. However, very low-energy vibrational modes have been observed, e.g., for CO molecules and for Co adatoms on Cu surfaces in an energy range between 3 and 6 meV. They have been assigned to external frustrated translational modes, where the molecule or atom vibrates parallel to the surface [20,27,31]. Therefore, we tentatively identify the observed inelastic vibrational excitation for the MH molecules with a frustrated translational mode on the Ag(100) surface.

To summarize, we observed a peculiar switching phenomenon for CeH, LaH, and CrH molecules on a silver single crystal surface characterized by bias dependent different apparent heights of the individual molecules and the concomitant appearance of a very low-energy vibrational feature in the differential conductance spectra. By choosing characteristic bias voltages, this vibrational mode is deliberately turned on or off. These results show how hydrogen coadsorption decisively alters the electronic and vibrational properties of adsorbates. They provide a striking example in the emerging field of nanotechnology for the controlled engineering of physical and chemical properties at the single molecule level.

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