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Bistable hysteresis and resistance switching in hydrogen-gold junctions

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Current-voltage characteristics of H_2-Au molecular junctions exhibit intriguing steps around a characteristic voltage of $V_s \approx 40$ mV. Surprisingly, we find that a hysteresis is connected to these steps with a typical time scale >10 ms. This time constant scales linearly with the power dissipated in the junction beyond an off-set power $P_s = IV_s$. We propose that the hysteresis is related to vibrational heating of both the molecule in the junction and a set of surrounding hydrogen molecules. Remarkably, by stretching the junction the hysteresis' characteristic time becomes $>$days. We demonstrate that reliable switchable devices can be built from such junctions.

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The central idea behind molecular electronics is that novel devices can be created using intelligently designed functional molecules. The simplest example is a molecular junction that exhibits conductance switching. Chemists have synthesized various types of bistable molecules, many of which have subsequently been applied in devices.[1–5] Surprisingly, however, conductance switching has also been observed in junctions that incorporate passive molecules only.[6–9] Understanding the fascinating physics behind the latter phenomenon may lead to a novel design philosophy of switchable molecular devices. Here, we present detailed transport studies on H_2-Au molecular junctions. We demonstrate that if $I(V)$ curves are taken by fast data acquisition, hysteretic behavior is observed. Moreover, we can manipulate our junctions such that the hysteresis' characteristic time scale grows from ~10 ms to >days. The resulting H_2-Au junctions are arguably the smallest switchable devices around. The physics behind these fascinating phenomena forms the main subject of this Rapid Communication.

Molecular junctions incorporating hydrogen molecules have a number of remarkable properties.[10–14] Perhaps most striking is that differential conductance (dI/dV) curves exhibit sharp features at a well-defined voltage V_s.[11–14] In Fig. 1, we show two typical measurements for a H_2-Au contact. In one case, two sharp peaks are observed [Fig. 1(a)], whereas in the other, two dips are seen [Fig. 1(b)]. Both curves are symmetric with respect to voltage. Remarkably, the dip in Fig. 1(b) is so deep that the differential conductance around $V_s = \pm 43$ mV becomes negative. Recently, Thijssen and Halbritter *et al.* measured curves similar to Figs. 1(a) and 1(b) and put forward a two-level model.[11,12] The two levels (1 and 2), most likely representing different geometries of the H_2-Au contact, give rise to two specific conductance values (G_1, G_2).[15] Hence, if transitions between level 1 and level 2 are induced at $V = V_s$, the conductance changes discontinuously from G_1 to an average of G_1 and G_2 (the weighing being dependent on the degeneracy of the levels[12]). This naturally results in a dip (if $G_1 > G_2$) or peak (if $G_1 < G_2$) in dI/dV, or analogously, in a step down or up in an $I(V)$ curve. The latter is illustrated by the lowest $I(V)$ characteristic presented in Fig. 1(c). In both models proposed, a double potential well is assumed to describe the two-level system [schematized in Fig. 1(d)), inset]. However, there is disagreement on the question how a transition between the levels occurs. Halbritter *et al.* related V_s to the energy difference between the two levels. Furthermore, they explained the negative differential conductance by proposing that level 2 is highly degenerate. In contrast, Thijssen *et al.* proposed that a transition is only possible if a molecular vibration is excited with high enough energy $\hbar\omega_1$ to assist a jump over the barrier. Hence, they conclude that $V_s = \hbar\omega_1 / e$, a statement for which they provide significant experimental evidence. Regardless of the exact model, however, the transition between states 1 and 2 is anticipated to be fast around

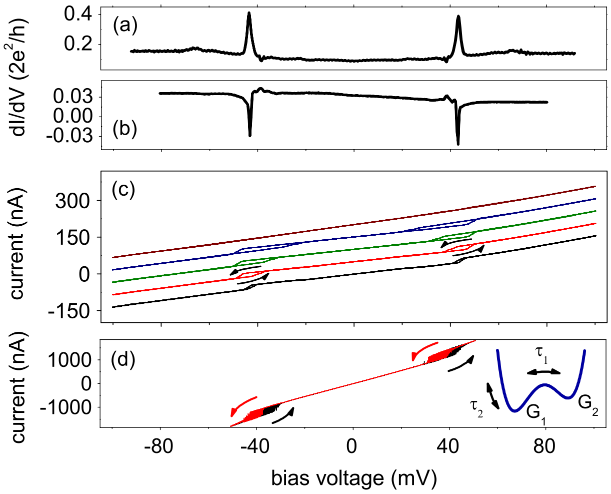

FIG. 1. (Color online) (a) and (b) Examples showing (a) peaks or (b) dips in dI/dV around ≈43 mV, measured on a H_2-Au contact (at 5 K). Note that (b) features a negative differential conductance. (c) $I(V)$ curves measured with varying sweep rates. The lower curve, measured in 10 s, corresponds to curves such as (a). However, for faster voltage sweeps, a hysteresis shows up around V_s. Sweeping times are 10, 1, 0.5, 0.33, and 0.1 s. For clarity, the traces are shifted vertically. (d) $I(V)$ curve showing both hysteresis and two-level fluctuations around V_s (voltage swept in 1s). Inset: double-well potential for the two-level model. We associate the fast switching between the two wells to time scale τ_1, and the slower changes in the potential landscape to τ_2.

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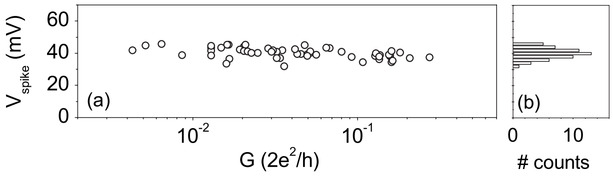

FIG. 2. (a) Position of the conductance peak/dip for 56 different contacts as a function of its zero-bias conductance. (b) Histogram of all data points. On average, $V_s = 40 \pm 3$ mV.

V_s, with time scales <1 ns, determined by tunneling or electron-phonon interaction. The results we present here, strongly contradict this expectation. In Fig. 1(c), we show $I(V)$ curves taken with various sweeping times. When slowly ramping V, one obtains the lower curve discussed above. However, when sweeping faster than 1 s per curve, a pronounced hysteresis appears around $V = V_s$. In other words, there is a macroscopic time scale connected to the system's return from the high conductance state to the low one. Moreover, for even faster voltage sweeps, ≥ 10 Hz, the system does not have enough time to relax back to state 1; it keeps the "high" conductance value for all V. Not only does this not agree with the two-level models, it also rules out the possibility that the steps in the $I(V)$'s are due to resonant tunneling. Hence, this intriguing hysteresis forms the central item of this study.

To obtain stable molecular junctions, we employ mechanically controllable break junctions.[16] Basically, a gold wire is broken in cryogenic vacuum (at ≈ 5 K), and the electrode tips are sharpened by a "training" procedure.[17] Subsequently, a small volume of H_2 (99.999% pure) is introduced and the junction is opened with ≈ 5 pm/s.[18] Meanwhile, $I(V)$ curves are recorded by sweeping V between -90 and 90 mV at ≈ 1 Hz. After several minutes, nonlinear $I(V)$ curves are observed with pronounced conductance steps.[11,12] During this procedure, we do not observe a jump out of contact. In total, we have used six break junctions on which 56 different H_2-Au contacts were studied. To obtain geometrically different H_2-Au junctions for one single device, we use the following procedure. First, the H_2-Au junction is broken, resulting in a jump out of contact. Then, the electrodes are pushed back into contact to conductance values $>10G_0$ (where $G_0 = 2e^2/h$). Finally, the gentle pulling process is started again until a new H_2-Au contact forms. To connect to previous work, we have first investigated the $I(V)$ curves of all these junctions at low-voltage scan rates. In Fig. 2(a) we present a statistical analysis of the on-set voltage V_s. Interestingly, V_s is positioned around 40 meV, rather independent of the conductance of the contact. Indeed, the zero-bias conductances show a broad variation between 0.003 and 0.3 G_0. Since we did not observe a jump out of contact while creating the junctions, this may point to chain formation as reported in Ref. 19. These authors found conductance values in the same range as observed here. In Fig. 2(b), we present a histogram of all V_s values. The average position is $V_s = 40 \pm 3$ mV. This is in good agreement with Thijssen *et al.*, who found $V_s = 42 \pm 2$ mV.[11] As explained above, they relate V_s to a H_2 phonon, which induces transitions between levels 1 and 2. Experimentally, they provide two pieces of evidence. First, they show that V_s shifts down by a factor $\approx \sqrt{2}$ when H_2 is replaced by D_2 (deuterium). Second, they show that upon pulling a junction, a step down in a dI/dV curve can evolve into a peak. Since a step in dI/dV is related to the excitation of a phonon,[20,21] this confirms their assertion. We have performed similar pulling experiments. In some cases, peaks in dI/dV grew larger. In other cases, they would virtually disappear, leaving a step as the dominant feature. This confirms the result by Thijssen.

As we increase the scan velocity of our $I(V)$ scans, a hysteresis develops around V_s [Fig. 1(c)]. Generally, we observe a smooth transition from one conductance state to the other. However, this is not always the case. The $I(V)$ scan in Fig. 1(d) for example, shows pronounced two-level fluctuations (TLFs) in combination with hysteresis. A comparison of Figs. 1(c) and 1(d) leads to a number of important observations. First, the hysteresis is not an artifact of our electronics: TLFs much faster than the time scale of the hysteresis are easily observed. Second, the occurrence of TLFs confirms a two-level model. Halbritter *et al.* could not resolve the actual TLFs. Also in our case, most curves show an apparently smooth step around V_s. This is due to the TLF frequency exceeding the bandwidth of the electronics (≈ 50 kHz). Third, we see that the TLF amplitude around V_S is approximately equal to the difference between the "low" and "high" conductance states far away from V_s. This indicates that for $V \gg V_s$, the system is in state 2 most of the time. Hence, state 2 is either relatively stable or highly degenerate.[12] Finally, we deduce from Fig. 1(d) that despite continuous communication between both levels (through the TLFs), the hysteresis is still present. This suggests that the exact shape of the double potential well (at $V \approx V_s$) differs for the upward and downward voltage scans. We deduce that there are two time scales in our system: a time τ_1 corresponding to fast switching between states (TLFs) and $\tau_2 > \tau_1$ connected to changes in the effective potential landscape, resulting in hysteresis.

To gain more insight in τ_2, we have recorded response times using well-defined voltage pulses. An example is given in Fig. 3(a). First, V is set to a value $V_{high} > V_s$, i.e., beyond the conductance step. The system's conductance is "high." After 1 s, long enough to reach equilibrium, the voltage is instantly dropped to a value $V_{low} < V_s$ (in this case 20 mV). Interestingly, the current responds to this decrease within 20 μs, consistent with our bandwidth. However, the *conductance* I/V does not. It is still "high" after 20 μs. Only after 10 ms, it starts to drop to a lower value. We define τ_2 as the time in which the conductance drops halfway [dotted line in Fig. 3(b)]. Remarkably, we find larger τ_2 for higher V_{high} [see Fig. 3(b)], which implies that τ_2 depends on the history of the junction. We have systematically investigated τ_2 vs V_{high} for four different contacts, as depicted in Fig. 3(c).[22] Clearly, τ_2 increases more than linearly with V_{high}, with an onset around 40 meV. In fact, if we plot τ_2 as a function of $I \cdot (V_{high} - V_s)$ we find a linear relation for all four samples [see Fig. 3(d)]. Hence, there is a direct connection between τ_2 and the power IV_{high} that was being dissipated before the voltage step, corrected for an onset value $P_s = IV_s$. From this interesting result, we deduce that heating effects (multiple phonon excitations) are at the basis of the hysteresis. The

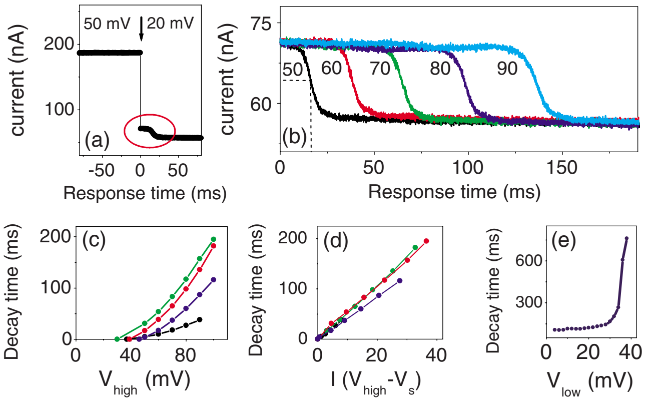

FIG. 3. (Color online) (a) Pulse response. At $t=0$, the voltage is instantly dropped from a high voltage ($V_{high}>V_s$), to a low voltage ($V_{low}<V_s$). Here, V_{high} (V_{low}) is 50 mV (20 mV). Right after the voltage drop, the conductance is still in the high conductance state. (b) Response for different initial voltages. V_{high} is systematically varied between 50 (first curve) and 90 mV (last curve), while V_{low} is 20 mV. The decay time τ_2 is defined as the time where the conductance has dropped halfway (16 ms for $V_{high}=50$ mV). (c) Decay times as a function of V_{high}, for four different contacts ($V_{low}=20$ mV). The contacts have a conductance of, from lower to upper curve, 0.015, 0.044, 0.048 and 0.058 G_0 (at 50 mV). (d) Decay times as a function of dissipated power during the voltage pulse, corrected for an onset value $P_s=IV_s$ (same contacts as in c). (e) Decay times as a function of V_{low}. V_{high} was set to 80 mV and for this contact $V_s=39$ mV.

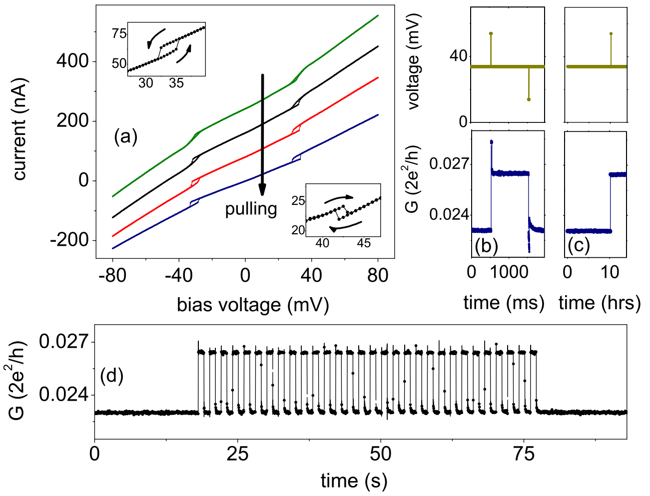

FIG. 4. (Color online) (a) $I(V)$ sweeps while pulling the electrodes (voltage is swept in 1 min). After stretching 2 ± 0.3 Å, a time-independent hysteresis appears. For clarity, the curves are shifted vertically. Insets: two other examples of contacts showing time-independent hysteresis. (b) Hydrogen switch. Upper graph: voltage used to control the switch. On top of an offset voltage (here 34 mV), the voltage is pulsed with +20 and −20 mV (duration is 20 ms). Lower graph: Pulse response. After each pulse, the system switches. (c) Stability of the hydrogen switch. After 10 h, the voltage is pulsed by +20 mV (20 ms) to switch to G_2. After 14 h, the measurement is stopped. d) Multiple switching events. The pulse height is ±4 mV, on top of a dc voltage of 34 mV (pulse duration is 20 ms).

fact that $V_s=40$ mV serves as a threshold in all cases points to the pivotal role of a hydrogen phonon in this process.[11] A second experiment that demonstrates this connection is shown in Fig. 3(e). This measurement is similar to that in Fig. 3(b). However, now V_{high} is kept constant at 80 mV, whereas V_{low} is systematically varied. We find that τ_2 increases dramatically as V_{low} approaches V_s.

Remarkably, when slowly stretching the contact, a special type of hysteresis appears for the majority of the junctions. In general, a contact is stretched in steps of 10 pm while for each position an $I(V)$ curve is measured (in 1 min). Figure 4(a) shows four $I(V)$'s with 50 pm intervals. The upper curve is measured right after the H_2-Au contact is formed. With further stretching a hysteresis appears, which is most pronounced after 2 Å (lower curve). Interestingly, this type of hysteresis does not show any time dependence, contrasting the data above. Therefore, we can use it as a stable memory element. For this, we first apply an offset voltage $V=V_s$. Subsequently, we switch conductance by applying positive (low $G\rightarrow$high G) or negative voltage pulses (v.v.). This is demonstrated in Fig. 4(b). The switch is remarkably stable in time. Even after 14 h, no degradation is observed [see Fig. 4(c)]. Furthermore, no deterioration is seen after multiple switching events [see Fig. 4(d)]. We have performed over 5000 switching events and saw no changes to the sample. Hence, we have created a switchable molecular device from the smallest molecule nature provides.

To discuss our observations, we first return to Fig. 3. Here we concluded that heating, i.e., electron-phonon excitation, plays a pivotal role in the hysteresis. Furthermore, the molecular phonons are crucial in this process. We never observed heating effects on bare gold electrodes, which is consistent with the relatively low dissipation in our junctions (cf. Ref. 23). Recently, Galperin *et al.* and Chen theoretically studied the temperature of molecular junctions under a bias voltage.[24,25] It is not trivial, however, to define a temperature for a single molecule. Galperin *et al.* approach this problem as follows. First, they assume that an external phonon bath is weakly coupled to the active mode of the molecule in the junction. Then, they calculate the ensuing heat flux between mode and bath. The bath temperature at which the heat flux vanishes is finally assigned to the molecular junction. For H_2 junctions, a temperature increase ~100 K was predicted, exactly when the voltage reaches the phonon energy $eV=\hbar\omega$.[24,25] From this, one might naively expect a hysteresis between upward and downward $I(V)$ scans. Going up in V, the molecule is "cold" and in state 1; coming down, the molecule is "hot," i.e., in a combination of states 1 and 2. However, it is highly unlikely that a single molecule will remain excited on time scales as large as $\tau_2>10$ ms. For the most likely relaxation mechanism, electron-phonon coupling, typical time scales are <1 ns, depending on the vibration mode.[26] We propose that there is a larger phonon bath that preserves the energy for a relatively long time (cf. Galperin). A good candidate is formed by the large set of H_2 molecules that likely surround the actual molecule in the junction. At $V>V_s$, these molecules will be excited by efficient phonon-phonon coupling from the junction outwards. After V is dropped below V_s, it will take a relatively long time before this bath (and the molecule in the junction) is at the base temperature again. It may well be that heating of surrounding H_2 molecules actually induces a phase transition, although this is not essential to explain Figs. 1–3. In fact, we have only observed current steps at experimental temperatures below ≈ 20 K. A phase transition has been proposed by Gupta and Temirov *et al.* to explain nonlinear *IV* curves.[13,14] Such a transition could indeed explain the time-independent hysteresis observed in Fig. 4. Upon a phase transition, the hydrogen phonon energy will most likely change. If it assumes a lower value ω_2 than before (ω_1), the hydrogen molecule(s) will still be excited if the voltage drops below V_s, provided that $\omega_2 < eV < \omega_1$. This situation may be quasipermanent, since the system is continuously excited. Only when V is decreased further, a transition back is expected. Our work may thus represent the first experimental case in which molecular heating is directly distinguished in a single junction.[24,25]

In summary, we demonstrate that the presence of H_2 in a Au junction leads to two-level fluctuations, steps in $I(V)$ curves and hysteresis. Moreover, by carefully stretching the junctions, a reversible and stable molecular switch can be created. Interestingly, similar features have been reported for a large variety of molecular junctions, with molecules ranging from larger organic molecules to CO.[6–8,11,27,28] Since such switching effects are general phenomena in molecular electronics, there may be one basic mechanism behind them. In parallel, our work stresses the requirement to work in a hydrogen-free environment if one focuses on a different molecular system. Finally, we note that the steps in $I(V)$ curves (explained by a two-level model) may easily be confused with resonant tunneling. To distinguish the two, fast $I(V)$ scanning is an efficient tool since resonant tunneling should not lead to hysteresis.

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