Effect of metal-molecule contact on electron-vibration interaction in single hydrogen molecule junction

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The effect of the strength of metal-molecule contact on electron-vibration interaction was investigated for the single hydrogen molecule bridging between Cu electrodes and Pt electrodes. For the single hydrogen/Pt junctions, conductance suppression caused by electron-vibration interaction was observed only for the junction with a conductance value above 0.5 $G_0(G_0 = 2e^2/h)$, which corresponded with the prediction of the one-level model in the symmetric coupling of the molecule to metal electrodes. In contrast, conductance suppression was also observed for the single hydrogen/Cu junctions with a conductance value below 0.5 G_0, which could be explained by a decrease in the interaction between the hydrogen molecule and the Cu electrodes.

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I. INTRODUCTION

Electron transport through single molecule junctions is of scientific and technological interest, and one of the current topics in this research field is electron-vibration interaction[1]. Electron-vibration interaction relates to molecule motion and the chemical reaction induced by an electronic current, and local heating of the molecule junction is the key issue in developing reliable single molecule devices[2,3]. It also relates to the vibration spectroscopy of the single molecule junctions, such as point contact spectroscopy (PCS) and inelastic electron tunneling spectroscopy (IETS), which are powerful techniques used to characterize the single molecule junction[4–8]. PCS and IETS are similar measurements of current through the single molecule junction as a function of bias voltage. Electron-vibration interaction increases the junction conductance (IETS) in the tunneling regime and decreases junction conductance (PCS) in the contact regime. The increase and decrease in conductance are explained by forward scattering and backscattering of electrons that lose energy to a vibration mode[1].

Electron-vibration interaction in the single molecule junction has been investigated by theoretical calculation using the one-level model[7,8]. Paulsson *et al.* showed that the conductance change by the excitation of molecular vibration depends on the conductance of the single molecule junction and symmetry of the coupling of the molecule to metal electrodes. In the case of symmetric coupling, conductance is increased or decreased for the single molecule junction having a conductance below or above 0.5 G_0 ($G_0 = 2e^2/h$), respectively. The transition conductance between the increase and decrease in conductance decreases with the asymmetry of the coupling of the molecule to metal electrodes[7]. Shimazaki *et al.* showed that the conductance change by excitation of molecular vibration depends on the energy difference between metal and molecule orbitals and the strength of the coupling of the molecule to metal electrodes[8]. Oren *et al.* experimentally investigated the transition between PCS and IETS for H_2O/Pt junctions, in which electrons were transported mainly through a single channel. They showed that the transition conductance between PCS and IETS was around 0.5 G_0 (Ref. 5).

These previous studies indicated that the strength and symmetry of the coupling of the molecule to metal electrodes plays a decisive role in determining the conductance change by the excitation of molecular vibration. However, this issue has not been addressed experimentally. In the present study, we investigate electron-vibration interaction for the single hydrogen molecule bridging Cu and Pt electrodes. The interaction between hydrogen and the metal electrodes is large for Pt electrodes and small for Cu electrodes[9]. The current-voltage characteristics of hydrogen/Pt and hydrogen/Cu junctions were investigated by considering the strength and symmetry of the coupling of the hydrogen molecule to metal electrodes.

II. EXPERIMENT

The measurements were performed using a mechanically controllable break junction (MCBJ) technique (see Ref. 10 for a detailed description). A notched Cu or Pt wire (0.1 mm in diameter, 10 mm in length) was fixed with epoxy adhesive (Stycast 2850FT) on top of a bending beam and mounted in a three-point bending configuration inside a vacuum chamber. In an ultrahigh vacuum (UHV) at 10 K, the metal wire was mechanically broken by bending the substrate. The bending could be relaxed to form atomic-sized contacts between the wire ends by using a piezoelement for fine adjustment. Hydrogen was admitted to the contacts via a capillary. DC two-point voltage-biased conductance was measured during the breaking process under an applied bias voltage ranging from 20 to 300 mV. AC voltage bias conductance measurements were performed using a standard lock-in technique. The conductance was recorded for the fixed contact configuration using an AC modulation of 1 mV amplitude and 7.777 kHz frequency while slowly ramping the DC bias between −100 and +100 mV. The experiments were performed for 11 and 5 independent samples for Pt and Cu, respectively.

III. RESULTS AND DISCUSSION

Figure 1 shows the typical conductance traces and conductance histograms of the Pt contacts before and after admitting hydrogen. The stretch length was the displacement

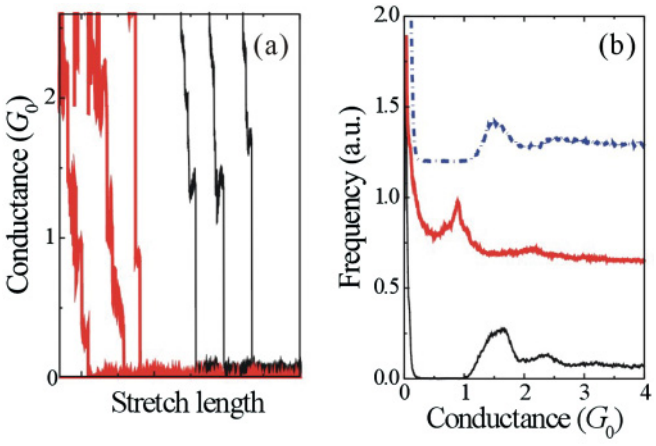

FIG. 1. (Color online) (a) Conductance traces and (b) conductance histograms of Pt contacts before (black thin curve) and after (red thick curve, blue dot-dashed curve) the introduction of hydrogen. The bias voltage was 300 mV (black), 200 mV (red), and 300 mV (blue). The intensity of the conductance histograms was normalized with the number of the conductance traces. The conductance histogram was obtained from 1000 conductance traces of breaking Pt contacts. The bin size was 0.004 G_0.

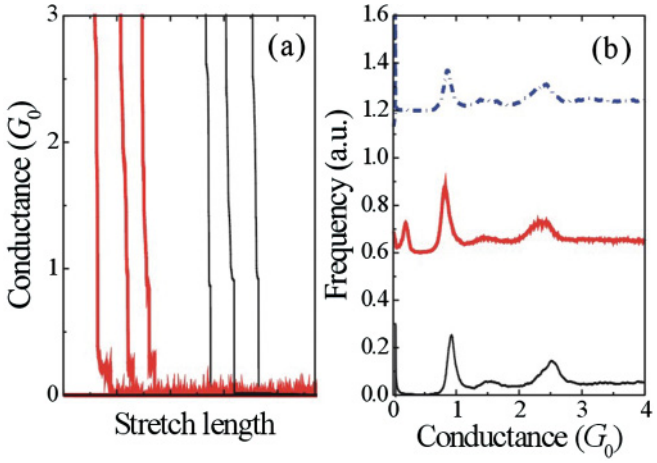

FIG. 2. (Color online) (a) Conductance traces and (b) conductance histograms of Cu contacts before (black thin curve) and after (red thick curve, blue dot-dashed curve) the introduction of hydrogen. The bias voltage was 200 mV (black), 20 mV (red), and 200 mV (blue). The intensity of the conductance histograms was normalized with the number of the conductance traces. The conductance histogram was obtained from 1000 conductance traces of breaking Cu contacts. The bin size was 0.004 G_0.

of the distance between the Pt electrode stem parts, which were fixed with epoxy adhesive. Before admitting hydrogen, the conductance decreased in a stepwise fashion and the corresponding conductance histogram showed a peak at 1.5 G_0, which corresponded to the clean Pt atomic contact[6]. After admitting hydrogen, a plateau near 1 G_0 was frequently observed and the corresponding histogram showed a sharp 1 G_0 peak accompanied by a low conductance tail. The 1 G_0 plateau and peak corresponded to the single hydrogen molecule bridge between clean Pt electrodes, in which the hydrogen bond axis was parallel to the transport direction[6]. For larger bias voltages above 300 mV, the conductance traces and histogram were recovered to those of clean Pt. For a larger bias voltage, the hydrogen molecule desorbed from the Pt contact owing to joule heating, which leads to the clean Pt contacts. The obtained conductance behavior corresponded with the previously reported one[6,11–13]. Figure 2 shows the typical conductance traces and conductance histograms of the Cu contacts before and after admitting hydrogen. After admitting hydrogen, a plateau near 0.2 G_0 was frequently observed, and the corresponding histogram showed a sharp 0.2 G_0 peak together with a clear 1 G_0 peak, which corresponded to the Cu atomic contacts. No plateaus or features were observed in the conductance traces or histograms below 0.1 G_0. Therefore, the conductance of the last plateau of 0.2 G_0 in the conductance trace and the peak in the conductance histogram correspond to the conductance of the single hydrogen molecule bridging between the Cu electrodes, as is the case with the single-molecule Au-H_2-Au contacts[14]. The conductance traces and histogram were recovered to those of clean Cu for larger bias voltages above 200 mV. The bias voltage dependence on the conductance behavior of Pt and Cu contacts in a hydrogen environment indicates that the interaction between hydrogen and metal contacts was larger for Pt than Cu.

The dI/dV curves were measured as a function of voltage across the single molecule junction where the electrodes' separation was fixed. Before measuring the dI/dV curves, we waited until the conductance of the junction was stabilized. Figure 3 shows examples of dI/dV and d^2I/dV^2 curves for the single hydrogen/Pt molecule junction taken at zero-bias conductance ranging from 0.3–1.2 G_0. The shape of the spectra varied with the single molecule junction. The steps in the dI/dV curves indicated the onset of a vibration excitation at these voltages. While Fig. 3(a) shows a decrease in the differential conductance, Figs. 3(b) and 3(c) show an increase in differential conductance. Clear symmetric peaks or dips were observed in their derivative. The increase in conductance (step up) is explained by the opening of an additional tunneling channel for electrons that lose energy to a vibration mode. The decrease in conductance (step down) is explained by the backscattering of electrons that lose energy to a vibration mode, as discussed in the Introduction[1,5–8]. Figure 4 shows the examples of the dI/dV curves for the single hydrogen/Cu junctions taken at zero-bias conductance ranging from 0.01–0.06 G_0. While Fig. 4(a) shows a decrease in differential conductance, Figs. 4(b) and 4(c) show increases. The single hydrogen/Cu junctions with a conductance above 0.1 G_0 was unstable. The conductance of the single hydrogen/Cu junctions decreased to less than 0.1 G_0 for most of the junctions during waiting for the stabilization of the junction.

To discuss the shape of the dI/dV curves, around 70 dI/dV curves with a step up or step down were collected for the single hydrogen/Pt and hydrogen/Cu junctions with zero-bias conductances of 0.01 $G_0 \sim 1.2$ G_0 (Ref. 15). Figure 5 shows the distribution of dI/dV curves with step ups and step downs according to their conductances of the single hydrogen/Pt and hydrogen/Cu junctions. In the single hydrogen/Pt junction, curves with a step up were observed below 0.5 G_0, and both curves with step up and down were observed above 0.5 G_0. In the single hydrogen/Cu junctions, curves with a step up were frequently observed throughout the

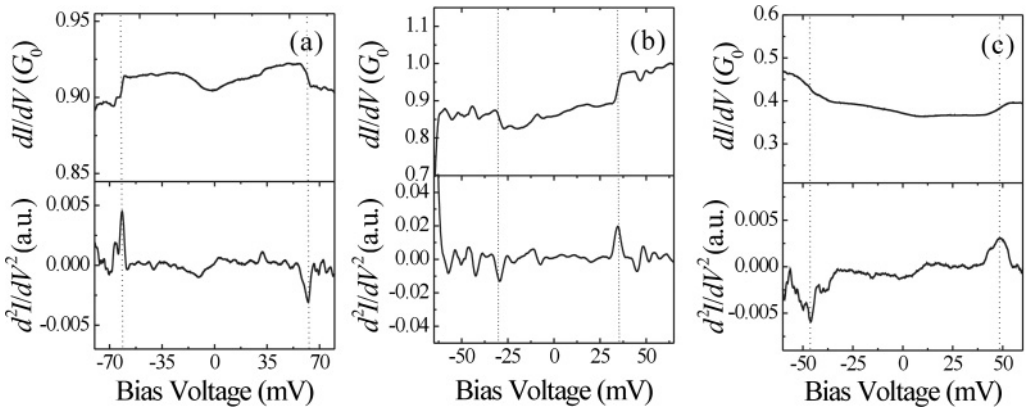

FIG. 3. Example of dI/dV (top) and d^2I/dV^2 (bottom) curves for the single hydrogen/Pt molecule junctions taken at zero bias conductance of (a) 0.9 G_0, (b) 0.9 G_0, and (c) 0.4 G_0.

entire conductance regime. It should be noted that curves with a step down were observed for the junctions with a conductance smaller than 0.5 G_0. For comparison, the experimental results for the single hydrogen/Au junctions are shown in Fig. 5. The distribution was similar to that for the single hydrogen/Cu junctions. Curves with a step up were frequently observed throughout the entire conductance regime. Curves with a step down were observed for the junctions with a conductance smaller than 0.5 G_0.

Here, we briefly comment on the low conductance value of the single hydrogen/Cu molecule junction in which the dI/dV curves were measured. The conductance histogram showed a peak around 0.2 G_0, indicating that the formation of the molecule junction showed a conductance of 0.2 G_0. However, this structure was unstable. It was difficult to keep this structure for 1 minute to measure the dI/dV curves. The conductance of the single hydrogen/Cu junctions decreased to less than 0.1 G_0 for most of the junctions during waiting for the stabilization of the junction. The dI/dV curves were measured for the molecule junction showing a conductance below 0.1 G_0 in most cases. On the other hand, the conductance traces (histogram) were measured during the stretching of the contact and the metal electrodes deformed via inelastic structural transformation during this time. The transformation preferentially occurred in the direction of the close-packed (111) plane for Cu fcc metal[10], leading to the formation of the molecule junction having a certain atomic configuration of 0.2 G_0. This structure is the metastable structure and eventually transforms into the most energetically stable structure. This transformation takes some time, and thus, the most energetically stable structure is not formed during the stretching of the contact. It is possible for the molecule junction to break without being in its most energetically stable structure, so the conductance histogram did not show a peak below 0.1 G_0. On the other hand, the molecule junction generally transformed into the most energetically stable structure and showed a conductance below 0.1 G_0 when we stopped stretching the contact. Most of the dI/dV curves were then measured for the molecule junctions showing a conductance below 0.1 G_0. The instability of the molecule junctions showing a conductance above 0.1 G_0 were also observed for the single hydrogen/Au junctions. The conductance of the single hydrogen/Au junctions decreased to less than 0.1 G_0 for most of the junctions during the wait for the stabilization of the junction.

The strength of the interaction between metal and hydrogen was evaluated based on the shape of the dI/dV curves. Figure 6 shows the dI/dV curves for the single hydrogen/Cu junction taken at a zero-bias conductance below 0.3 G_0 (Ref.

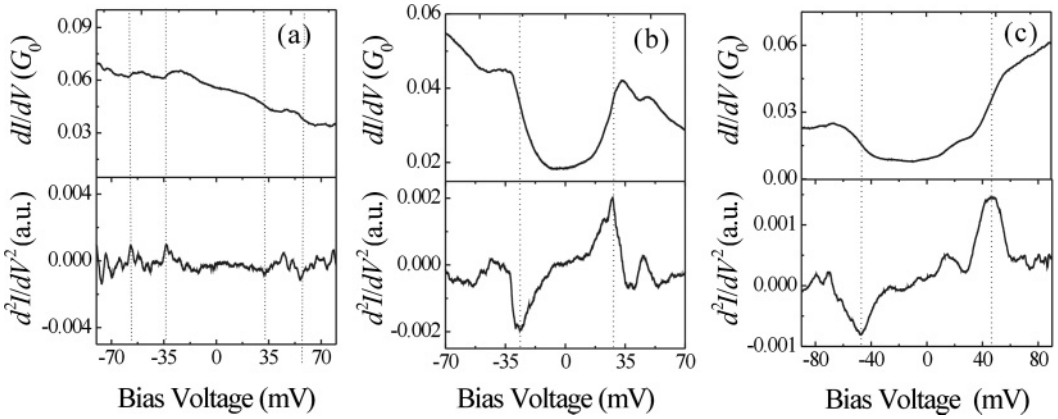

FIG. 4. Example of dI/dV (top) and d^2I/dV^2 (bottom) curves for the single hydrogen/Cu molecule junctions taken at zero bias conductance of (a) 0.06 G_0, (b) 0.02 G_0, and (c) 0.01 G_0.

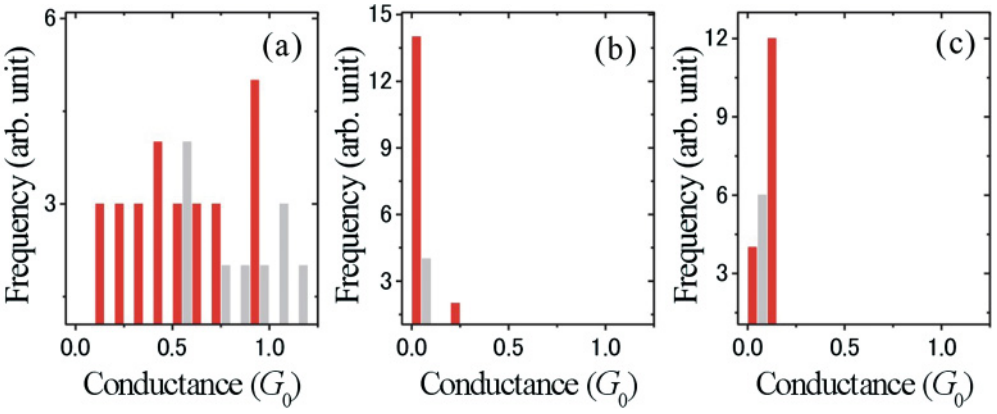

FIG. 5. (Color online) Histogram of step up (red) and step down (gray) features in dI/dV curves for the (a) single hydrogen/Pt, (b) hydrogen/Cu, and (c) hydrogen/Au molecule junction as a function of zero-bias conductance of the single molecule junction.

15). Symmetric peaks were observed in the dI/dV curves. The peak in these curves is explained by the abrupt switching between two slightly different local geometric configurations induced by the excitation of vibration[14,16]. Three types of spectra ("normal," "peak," and "nonsymmetric") were observed in the dI/dV curves. The first "normal" spectrum (Figs. 3, 4) showed clear symmetric peaks in the d^2I/dV^2 curves. The second "peak" spectrum showed symmetric peaks in the dI/dV curves, and the third "nonsymmetric" spectrum did not show any symmetric features in either the dI/dV or d^2I/dV^2 curves. The third "nonsymmetric" spectra were most frequently observed for the hydrogen/Pt, hydrogen/Cu and hydrogen/Au junctions. There was a clear difference of the distribution of spectra among the hydrogen/metal junctions. The relative ratio of percentage of "peak" to "normal" was 0.27 for the hydrogen/Pt junction, 2.3 for the hydrogen/Cu junction, 2.9 for the hydrogen/Au junction, respectively. The abrupt switching between the two different local geometric configurations hardly occurred for the molecule junction, in which a molecule strongly bound to metal electrodes. The high probability of the appearance of peaks in the dI/dV curves for the hydrogen/Cu and hydrogen/Au junctions indicated that the interaction between hydrogen and Cu or Au electrodes was weaker than that of the Pt electrodes.

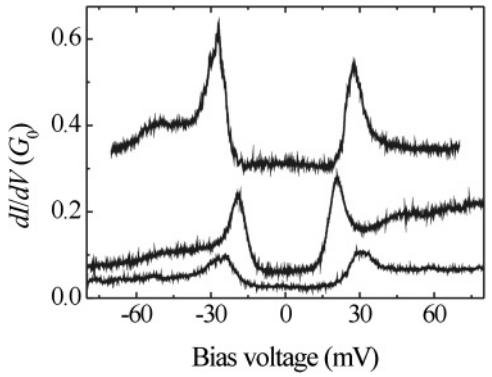

FIG. 6. Example of dI/dV curves for the single hydrogen/Cu molecule junctions taken at zero bias conductance of 0.05 G_0, 0.1 G_0, and 0.3 G_0.

When a hydrogen molecule bridges between metal electrodes, electrons transport through the bonding or antibonding molecular orbitals modulated by the metal electrodes. Since these orbitals are not degenerate and energetically well separated, only one orbital contributes to the electron transport through the hydrogen molecule bridge. This fact was supported by previous studies[12]. Therefore, a one-level model can be applied to the hydrogen/Pt, hydrogen/Cu, and hydrogen/Au junctions[7]. The one-level model couples a single electronic level to two electronic leads and a localized vibration. For this model, the maximal transmission is $T_{\max} = 4\alpha/(1+\alpha)^2$, where α is the ratio of the coupling to the two leads. The crossover from a decrease to an increase in conductance is given by the 1/2 rule (i.e., $T_{\text{crossover}} = T_{\max}/2$, Ref. 7). Backscattering dominates the high-transmitting system, leading to a decrease in the conductance, while forward scattering leads to an increase in the low-transmitting case. In the case of the symmetric coupling of the molecule to both metal leads, this model predicts an increase in conductance below a transmission probability of $T_{\text{crossover}} = 0.5$ and a decrease in conductance above this value.

The bias voltage dependence of the conductance histogram and the shape of the dI/dV curves indicate that the hydrogen molecule is strongly bound to the Pt electrodes while the hydrogen molecule is weakly bound to the Cu and Au electrodes. In the case of the hydrogen/Pt junction, the hydrogen molecule is strongly bound to the Pt electrodes due to the effective hybridization of the metal and molecular orbital. The degree of hybridization of the orbitals is not altered by the slight change in the atomic configuration of the interface due to the effective hybridization of the orbitals. The coupling of the molecule to the metal electrodes depends on the degree of hybridization of the orbitals, and thus, the difference in the coupling between the right and left electrodes is relatively small, leading to symmetric coupling ($\alpha = 1$). The dI/dV curves with a step down were observed only above 0.5 G_0 for the single hydrogen/Pt junctions. In the case of the hydrogen/Cu molecule and hydrogen/Au molecule junctions, the hybridization between metal and molecular orbitals is weak. The degree of hybridization of the orbitals is drastically altered by the change in the atomic configuration of the interface. The difference in the coupling between the right

and left electrodes is relatively large, leading to asymmetric coupling (small α). The crossover conductance between the increase and decrease in conductance decreases from 0.5 G_0 for the molecule junction with small α. Therefore, the dI/dV curves with a step down were observed below 0.5 G_0 for the single hydrogen/Cu and hydrogen/Au molecule junctions.

Here, we discuss the reason why the dI/dV curves with a step up were observed for the single hydrogen/Pt junctions above 0.5 G_0. Previous experimental and theoretical studies showed the formation of two stable atomic configurations: a bridging configuration (BC) in which the hydrogen bond axis is parallel to the transport direction, and a perpendicular configuration (PC) in which the hydrogen bond axis is perpendicular to the transport direction[17]. The conductance of the hydrogen molecule junction with BC and PC are 1 G_0 and 2 G_0, respectively. The number of the conduction channels is more than 1 for the single hydrogen molecule junction with PC. The effect of hydrogen incorporation into the stem part of the metal electrodes was investigated for the single hydrogen molecule junction with Pd electrodes, where Pd was the platinum group metal[18]. The incorporation of hydrogen into the stem part of the Pd electrodes did not change the main features of the transmission spectra while the magnitude of the total transmission coefficients reduced. The pressure-composition isotherms (PCT) measurements for the Pt nanoparticles showed that hydrogen can be adsorbed inside the Pt nanoparticles[19]. Therefore, the conductance of the single hydrogen molecule junction with PC could be reduced below 1 G_0 when hydrogen is adsorbed or incorporated into the stem part of the Pt electrodes. The number of the conduction channel is still more than 1 for these contacts, and thus, the one-level model cannot be applied to these junctions. The dI/dV curves with a step up were observed for the single hydrogen/Pt junctions above 0.5 G_0.

IV. CONCLUSION

We have investigated dI/dV curves for the single hydrogen/Cu and hydrogen/Pt junctions at low temperatures (10 K). In the single hydrogen/Pt molecule junction, curves with a step up were observed below 0.5 G_0, and both curves with a step up and step down were observed above 0.5 G_0. In the single hydrogen/Cu molecule junctions, curves with a step up were frequently observed in the whole conductance regime, and the dI/dV curves with a step down were also observed. The shapes of the dI/dV curves were discussed based on the one-level model and strength of the interaction between the hydrogen molecule and metal electrodes. The interactions between the hydrogen molecule and metal electrodes were investigated by the bias voltage dependence of the conductance histograms and the shapes of the dI/dV curves. The interaction of the hydrogen molecule to the Pt electrodes was larger than that of the Cu electrodes. The appearance of the dI/dV curves with a step down for the junction with a conductance smaller than 0.5 G_0 could be explained by a decrease in the symmetry of the coupling of the hydrogen molecule to the two leads, which is due to weak interaction.

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