

Atomic motion in H₂ and D₂ single-molecule junctions induced by phonon excitationManabu Kiguchi,^{1,2,*} Tomoka Nakazumi,^{1,*} Kunio Hashimoto,¹ and Kei Murakoshi¹¹*Division of Chemistry, Graduate School of Science, Hokkaido University, N10W8, Kita, Sapporo 060-0810, Japan*²*PRESTO, Japan Science and Technology Agency, N10W8, Kita, Sapporo 060-0810, Japan*

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We have investigated Au atomic contacts in H₂ and D₂ environment by conductance measurement and dI/dV spectroscopy. A single H₂ or D₂ molecule was found to bridge Au electrodes. In the case of the Au/H₂/Au junction, symmetric peaks were observed in dI/dV spectra while they were not observed for the Au/D₂/Au junction. The shape of the peaks in dI/dV spectra originated from the structural change in the single-molecule junction induced by the phonon excitation. The structural change could occur only for the Au/H₂/Au junction. The difference in the two single-molecule junctions could be explained by larger zero-point energy of Au-H₂ vibration mode than that in the Au/D₂/Au junction.

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I. INTRODUCTION

Nanojunctions using single molecules have attracted wide attention in recent year.^{1,2} In order to investigate the atomic-scale single-molecular junctions, it is important to characterize a single-molecule bridging between metal electrodes using some spectroscopic measurements. As for the spectroscopy of the single-molecule junctions, point-contact spectroscopy (PCS),^{3–5} inelastic tunneling spectroscopy (IETS),^{6–10} and action spectroscopy have been investigated for the single-molecule junctions.¹¹ In these spectroscopies, electron current through the single-molecule junction is measured as a function of bias voltage. In the IETS and PCS, spectrum is obtained as an inelastic-scattering event of electrons with sufficient energy to excite certain vibration mode. The vibration energy is determined from the bias voltage in which conductance of the single-molecule junction abruptly changes. The difference between PCS and IETS is operating conductance regime. IETS operates in low-conductance regime ($G \ll 1G_0$, where $G_0 = 2e^2/h$) while PCS operates in conductance regime close to $1G_0$.^{5,12,13} The PCS and IETS have been applied for various single-molecule junctions with H₂, C₆₀, benzene, and alkane dithiol.^{3–10}

Action spectroscopy of the single-molecule junction was a recently developed technique to detect the vibration modes of the single-molecule junctions.¹¹ The action spectroscopy observes the abrupt conductance change (peak in dI/dV spectra) originated from the structural change in the single-molecule junction induced by the phonon excitation. The energy of the peak provides the vibration energy of the single-molecular junction. The action spectroscopy of the single-molecular junction was applied for the single-molecular junctions with H₂, O₂, and CO.¹¹ In the case of single molecules adsorbed on metal surfaces, the action spectroscopy has some advantage compared to IETS.^{14–16} It can detect the vibration modes which could not be detected by IETS. In addition, action spectroscopy can be applied for the system in which IETS signal is too weak to detect since the signal of the action spectra is much larger than that of IETS. The action spectroscopy has been applied for various molecules on metal substrates. On the other hand, there is little study of the action spectroscopy of the single-molecular junction, and

thus, the character of this spectroscopy is not clear up to now. It is important to investigate the characters of the action spectroscopy of the single-molecular junction. In the present study, the action spectroscopy has been performed for the Au atomic contact in H₂ and D₂ environment. This system has been already investigated by the conductance measurement, dI/dV spectra, and theoretical calculation by other groups.^{17–20} However, IETS or PCS of this system has not been obtained up to now, and the energy of the vibration mode was not fixed yet. The structure of the Au atomic contact in H₂ environment was not defined. In the present study, the atomic configuration of the Au atomic contact in H₂ and D₂ environment was investigated by the conductance measurement and action spectroscopy. Here it should be noticed that hydrogen has large zero-point energy due to its small mass. Since the action spectroscopy detects the structural change in the single-molecular junctions induced by the phonon excitation, it provides the information of the atomic motion of the single-molecular junction. The effect of the zero-point motion on the atomic-scale structural change in the single-molecule junction could be revealed by the action spectroscopy. In the present study, we have investigated the effect of the zero-point motion on the atomic motion of the single-molecular junction by investigation of the action spectroscopy of the Au atomic contacts in H₂ and D₂ environment.

II. EXPERIMENT

The measurements have been performed using the mechanically controllable break junction technique (see Ref. 2 for a detailed description). A notched Au wire (0.1 mm in diameter and 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 ultrahigh vacuum at 4 K, the Au wire was broken by mechanical bending of the substrate, and clean fracture surfaces were exposed. The bending could be relaxed to form atomic-sized contacts between the wire ends using a piezoelement for fine adjustment. H₂ or D₂ gas was admitted to the contacts via a capillary. dc two-point voltage-biased conductance measurements were performed by apply-

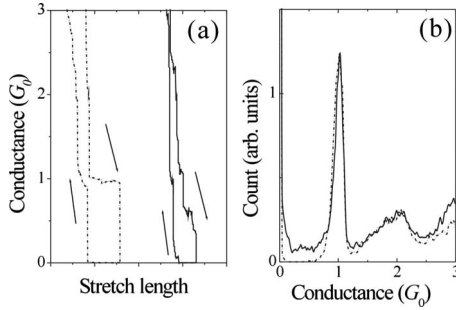


FIG. 1. (a) Conductance trace and (b) conductance histogram of Au contacts before (dotted line) and after (line) introduction of H_2 at the bias voltage of 100 mV.

ing a bias voltage in the range from 10 to 300 mV. Every statistical data set was built from a large number (over 3000) of individual digitized conductance traces. ac voltage-bias conductance measurements were performed using a standard lock-in technique. The conductance was recorded for fixed contact configuration using an ac modulation of 1 mV amplitude and a frequency of 7.777 kHz while slowly ramping the dc bias between -100 and $+100$ mV.

III. RESULTS AND DISCUSSION

Figure 1 shows typical conductance traces and histograms for Au contacts before and after introduction of H_2 . The stretch length was the displacement of the distance between the stem parts of the Au electrodes which were fixed on the substrate. Before introduction of H_2 , conductance decreased in a stepwise fashion, with each step occurring at integer multiples of G_0 . The corresponding conductance histograms showed a peak near $1G_0$, which corresponded to a clean Au atomic contact. After introduction of H_2 , the conductance decreased multistepwise fashion below $1G_0$. The widths of the multiple steps were not well defined and showed various value less than $1G_0$. The corresponding conductance histogram showed a broad feature below $1G_0$. The appearance of steps and features below $1G_0$ agreed with the previously reported results.¹⁷ Here, it should be noticed that the return conductance traces showed the steps around $0.05-0.5G_0$, before making large contacts. The certain atomic configurations showing conductance values below $1G_0$ would be formed in both breaking and making contacts.

The differential conductance (dI/dV) spectra were measured for the Au atomic contact in H_2 environment at a conductance value of $0.05-0.5G_0$. Three types of dI/dV spectra were observed, as shown in Fig. 2. The first “normal” spectrum [Fig. 2(a)] showed an increase in the differential conductance symmetrically around 45 meV, and clear symmetric peaks were observed in the second derivative (d^2I/dV^2). The second “peak” spectrum [Fig. 2(b)] showed symmetrical peaks and the third “nonsymmetric” spectrum [Fig. 2(c)] did not show any symmetric features. The third nonsymmetric spectra were most frequently observed for the Au contact in H_2 and D_2 environment. The increase in conductance observed for the normal spectra could be explained by the phonon excitation at the single-molecular junction.^{3-9,12,13} The

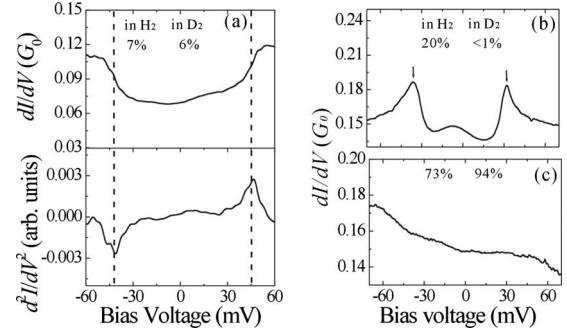


FIG. 2. Schematic dI/dV spectra of Au contacts in H_2 environment: (a) normal, (b) peak, and (c) nonsymmetric feature-type spectra. The percentage of the normal-, peak-, and nonsymmetric-type dI/dV spectra for single Au/ H_2 /Au and Au/ D_2 /Au junctions is shown in the figure. The number of the total dI/dV spectra was 200.

single-channel model predicts conductance enhancement below a transmission probability of 0.5 and suppression of conductance above this. In the present study, the spectra were measured for the junction having zero-bias conductance below $0.5G_0$. The increase in the conductance agreed with the theoretical prediction. In the single-molecular junction having low conductance, an additional tunneling channel for electrons was opened, when the bias voltage was increased and crossed the threshold for excitation of a vibration mode. This opening of the new channel resulted in a sudden increase in the differential conductance at the threshold voltage. Here, it should be noticed that dI/dV spectra of the Au atomic contacts in H_2 environment has not been obtained before.^{10,17,18} In the present study, we could measure the vibration spectra of this system by measuring the carefully prepared sample. The peak observed in the peak spectra could be explained by the abrupt switching between two slightly different local geometric configurations induced by the phonon excitation.¹¹ Action spectroscopy observes these peaks to determine the energy of the vibration mode. The nonsymmetric feature in the nonsymmetric spectra could be explained by interference of electron waves which scatter on defects or impurities close to the contact.^{2,3} Since the distribution of the defects or impurities and shape of the left and right electrodes would be different from each other, that is, nonsymmetric, the nonsymmetric feature could appear in the spectra. The conductance fluctuation is most enhanced for the contact showing a conductance value around $0.5G_0$, if the conductance channel is a single channel.² Therefore, the nonsymmetric spectra were most frequently observed for the Au contact in H_2 and D_2 environment showing conductance of $0.05-0.5G_0$.

In order to determine the vibration energy from action spectra, 122 differential conductance spectra showing peaks in dI/dV spectra were collected for junctions having conductance of $0.05-0.5G_0$. Figure 3(b) shows the distribution of vibration energy. The broad features were observed around 33 and 66 meV. The two modes were also observed for the normal dI/dV spectra. Since the phonon energy of the Au atomic contact is around 10–20 meV,² the observed vibration modes would be the vibration modes of the bonding between Au and hydrogen. The distribution of the vibration energy

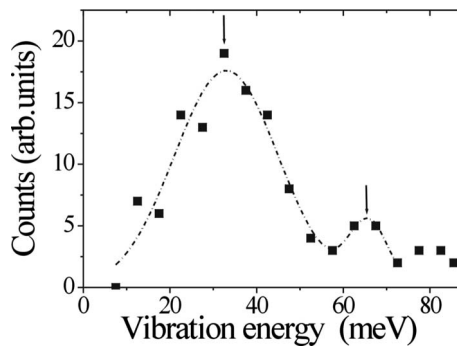


FIG. 3. Distribution of phonon energy for the Au/H₂/Au junctions obtained from the action spectroscopy of the single-molecule junction.

could not be defined for the Au contact in D₂ environment due to the difficulty in obtaining the peak spectra.

The structure of the Au atomic contact in H₂ environment is discussed based on the present experimental results and previously reported theoretical calculation result.^{19,20} After introduction of H₂, the Au contact showed a conductance value below $1G_0$. The vibration modes between Au and hydrogen were observed around 33 and 66 meV in the action spectra. The interaction between Au atomic contact with H atom or H₂ molecule have been investigated by density-functional theory calculation.¹⁹ H atom and H₂ molecule were stably incorporated into the Au atomic contact. Because of the incorporation of hydrogen into the contact, the conductance of the Au atomic contact decreased from $1G_0$ to $0.6-0.01G_0$, depending on the atomic configuration of the contact. The decrease in conductance was possibly due to scattering or interference of conducting electrons in the contact. No preferential atomic configurations were found for the hydrogen-incorporated Au atomic contact. Although there was no clear difference in conductance between the Au atomic contact with a single H atom and H₂ molecule, there was clear difference in the vibration energy between two contacts.²⁰ The Au atomic contact with a H atom showed the vibration mode around 150–220 meV corresponding to the vibration of the H atom along the contact axis. Comparatively, the Au atomic contact with a H₂ molecule showed two transverse modes of the H₂ molecule around 25–150 meV, in addition to the internal H₂ stretching mode around 180–250 meV. These experimental and theoretical calculation results indicated that a H₂ molecule bridged Au electrodes in the present experimental condition. The formation of the Au/H₂/Au junction was supported by the conductance trace. In the return conductance trace, the conductance jumped to a conductance value of $0.05-0.5G_0$. Before making the contact, H₂ molecules would adsorb on Au electrodes without dissociation. In making the contact, a single H₂ molecule would probably bridge Au electrodes in the initial stage. The vibration mode was also observed around 30–50 meV for the contact having conductance of $0.05-0.5G_0$, which was formed in making the contact. The close agreement in conductance and vibration energy supported that the atomic contact (conductance: $0.05-0.5G_0$ and vibration energy: $30\sim 50$ meV) formed in breaking the contact would be similar to that in making the contact, and that a single H₂ mol-

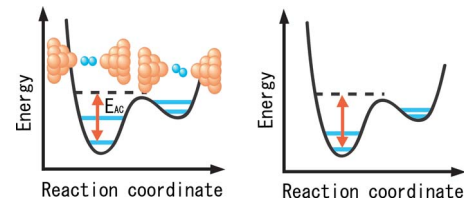


FIG. 4. (Color online) Potential-energy surface of Au/H₂/Au and Au/D₂/Au junctions.

ecule would bridge Au electrodes. Now, the Au atomic contact in H₂ environment was well characterized by the conductance measurement, action spectra of the single-molecule junction, and theoretical calculation. Briefly, the effect of surrounding hydrogen molecules on the Au/H₂/Au junction is discussed. In the present experimental condition, hydrogen molecules would adsorb on the Au/H₂/Au junction. Since the interaction between the hydrogen molecule and the hydrogen molecule in the Au/H₂/Au junction would be small, the conductance and vibration energy of the Au/H₂/Au junction would be insensitive to the presence of the surrounding hydrogen.

Next, dI/dV spectra of the Au/H₂/Au and Au/D₂/Au junctions were discussed. Three types of spectra (normal, peak, and nonsymmetric) were observed in dI/dV spectra. There was clear difference of the distribution of spectra between the Au/H₂/Au and Au/D₂/Au junctions. The percentage of the normal, peak, and nonsymmetric spectra were 7%, 20%, and 73% for the Au/H₂/Au junction, and 6%, <1%, and 94% for the Au/D₂/Au junction, respectively. The peak spectra (action spectra) were frequently observed for the Au/H₂/Au junction while they were not observed for the Au/D₂/Au junction.

The peak in the dI/dV spectra is discussed using a model of vibrationally induced two level systems (see Fig. 4).¹¹ In this model, the potential curve of the molecular junction is represented as the double-well potential with ground states Ψ_1 and metastable Ψ_2 in the two energy minima. The two energy minima are separated by the activation barrier (E_{AC}). The molecular junction could be vibrationally excited by the conduction electron. If the junction is fully excited, the junction with ground state Ψ_1 could overcome the activation barrier, and change into the junction with metastable Ψ_2 , which leads to the abrupt change in conductance (peak in the dI/dV spectra). The Ψ_1 and Ψ_2 states have slightly different local geometrical configurations, such as adsorption site of a H₂ molecule to Au electrodes, molecule tilt angle, and configuration of the Au electrodes. Appearance of the peak spectra only for the Au/H₂/Au junction indicated that the structural change could occur only for the Au/H₂/Au junction.

The difference between the two single-molecule junctions is discussed by considering the zero-point energy of the single-molecular junction. Since a H₂ molecule has half the mass of a D₂ molecule, the energy of Au-H₂ vibration mode and zero-point motion would be larger than those for D₂. On the other hand, the potential curve would be the same for both single-molecular junctions.¹⁵ Therefore, E_{AC} would be smaller for the Au/H₂/Au junction than that for the Au/D₂/Au junction. The structural change could, thus, eas-

ily occur for the Au/H₂/Au junction due to smaller E_{AC} . The difference in the dI/dV spectra between the Au/H₂/Au and Au/D₂/Au junctions could be also explained by the number of the excitation process. If E_{AC} was larger than the energy of the Au-H₂ (D₂) vibration mode, the system should be excited into the states with higher vibrational quanta in a ladder climbing manner in order to overcome activation barrier for the structural change.¹⁵ In the multiple excitation process, the excitation of the system would be getting harder with the number of the excitation process. The number of the excitation process to overcome the activation barrier would be smaller for the Au/H₂/Au junction than that for the Au/D₂/Au junction due to the larger energy of the Au-H₂ vibration mode. Therefore, the structural change could easily occur for the Au/H₂/Au junction. The above discussion was supported by the previously reported result.¹¹ Thijssen *et al.* reported that the peak spectra were observed for the Au contact in both H₂ and D₂ environment. They observed the peak spectra for the junction having a conductance value around $1G_0$. In the present study, the dI/dV spectra were taken for the junction having a conductance value below $1G_0$ (around $0.05-0.5G_0$). It is because the clear difference in the conductance histogram between clean Au contact and Au contact in hydrogen environment was observed in the conductance regime around $0.05-0.5G_0$, and thus, the interaction between Au atomic contact and hydrogen was clear for the contact showing conductance around $0.05-0.5G_0$. The peak spectra could not be observed for the Au/D₂/Au junction. In the case of the vibrational heating mechanism, the reaction rate (R) per electron can be represented as $R \propto I^n$, where I and n are the current and the order of the reaction.¹⁵ The reaction

rate shows nonlinear power-law dependence on current. The structural change would occur for the Au/D₂/Au junction having a high-conductance value while it would not occur for those having a low-conductance value. These experimental results suggested that the structural change in the Au/D₂/Au junction would be the multiple excitation process.

IV. CONCLUSIONS

The formation of the single Au/H₂/Au and Au/D₂/Au junctions was revealed by the conductance measurement and action spectroscopy. In the dI/dV spectra, symmetric peaks were observed for the Au/H₂/Au junction while symmetric peaks were not observed for the Au/D₂/Au junction. The peaks in the dI/dV spectra originated from the structural change induced by the phonon excitation. In the case of the Au/H₂/Au junction, the structural change induced by the phonon excitation could easily occur because the activation energy for the structural change and the number of excitation process would be small due to the large zero-point energy and large energy of the Au-H₂ vibration mode.

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