MEASUREMENT OF THE CONDUCTANCE OF A HYDROGEN MOLECULE

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Recent years have shown steady progress in research towards molecular electronics [1, 2] where molecules have been investigated as switches [3, 4, 5], diodes [6], and electronic mixers [7]. In much of the previous work a Scanning Tunnelling Microscope was employed to address an individual molecule. As this arrangement does not provide long-term stability, more recently metal-molecule-metal links have been made using break junction devices [8, 9, 10]. However, it has been difficult to establish unambiguously that a single molecule forms the contact [11]. Here, we show that a single H_2 molecule can form a stable bridge between Pt electrodes. In contrast to results for other organic molecules, the bridge has a nearly perfect conductance of one quantum unit, carried by a single channel. The H_2-bridge provides a simple test system and a fundamental step towards understanding transport properties of single-molecule devices.

In this work we employ a mechanically controllable break junction [12, 13] at low temperatures (4.2 K) to produce pure metallic contacts of atomic size. The inset in Fig. 1 shows a typical conductance curve for a clean Pt contact[1] that is recorded while gradually decreasing the contact size by ramping up the piezovoltage (black curve). The conductance is expressed in terms of the quantum unit, $G_0 = 2e^2/h$, with e the electron charge and h Planck's constant. The jumps in the conductance are the result of sudden atomic rearrangements in response to the applied strain [14]. After the conductance has dropped to a value corresponding to a single atom, which for Pt is in the range 1.2–2.3 G_0, the contact suddenly breaks. In order to extract the common features in these conductance curves the data of a large series of conductance curves are collected into a conductance histogram. The main panel in Fig. 1 shows such a histogram for Pt contacts (black). It is dominated by a large peak at 1.4–1.8 G_0, which represents the range of conductance values for contacts having a single atom in cross section (for a recent review see Ref. [15]). The histogram drops sharply to zero for lower conductance values, as is typically found for Pt contacts in absence of adsorbates and impurities. Remarkably, the character of the conductance curves and the shape of the resulting histogram change dramatically when a small quantity of hydrogen gas is admitted to the vacuum pot (grey curves). The critical amount is difficult to establish since most hydrogen is expected to condense on the walls of the container,[2] but the results are not very sensitive to the precise quantity. The peak at the position characteristic for Pt disappears and a large weight is added in the entire range below that value. On top of this background a distinct peak close to 1 G_0 is found, which grows for larger currents through the contact, while the background is suppressed. For still larger bias voltages, above 200 mV, we recover the histogram for clean Pt. The low-conductance tail and the peak at 1 G_0 reappear upon lowering the bias again. The bias dependence of the histograms is attributed to local heating by the current. For moderate bias the weakly bound physisorbed H_2 is evaporated, and only above 200 mV the chemically bonded hydrogen molecules are removed from the Pt surface.

We concentrate now on the remarkable fact that in the presence of hydrogen there appears to be a frequently occurring stable configuration that has a conductance of nearly unity, an example of which is shown in the inset of Fig. 1, and which is responsible for the sharp peak just below 1 G_0 in the histogram. We can select this configuration by recording conductance traces of the type shown in the inset, and stop the motion of the electrodes as soon as we find a plateau at 1 G_0. In order to investigate the structure of the contact on this plateau we use point contact spectroscopy (PCS). PCS was originally developed by Yanson [16, 17] for contacts that are large compared to the atomic scale. One measures the differential conductance, $G_d = dI/dV$, as a function of the dc bias voltage. The electrons in the contact are accelerated to an excess energy eV. When this energy reaches that of the main phonon modes of the metal inelastic scattering results in an enhanced probability for the electrons to scatter back through the contact, which is seen as a drop in G_d. Recently, this principle has been applied to single-atom metallic contacts and

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[1] We concentrate on results obtained for Pt wires, but conductance histograms suggest similar behaviour for Pd.

[2] The equilibrium H_2 gas pressure at a temperature of 4.2 K is about 10^{-6} mbar.
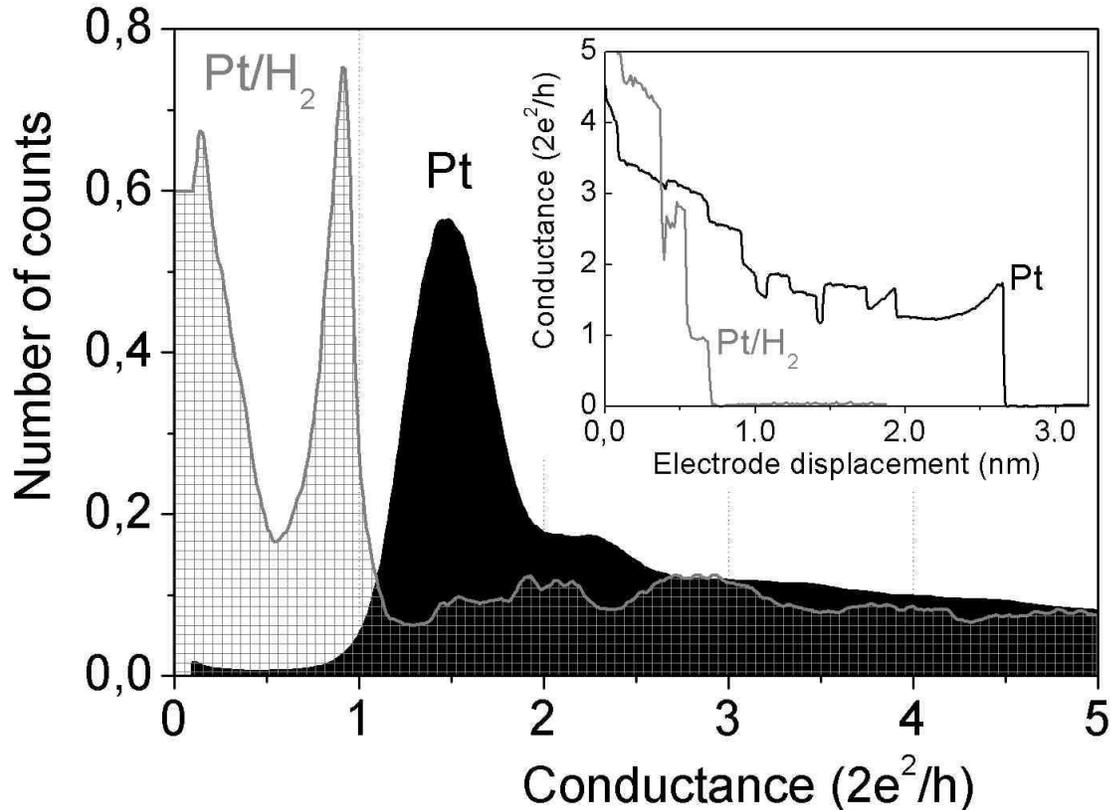
FIG. 1: Conductance curves and histograms for clean Pt, and Pt in a H_2 atmosphere. The inset shows a conductance curve for clean Pt (black) at $4.2\,K$ recorded with a bias voltage of $10\,mV$, before admitting H_2 gas into the system. About $10\,000$ similar curves are used to build the conductance histogram shown in the main panel (black), which has been normalized by the area under the curve. After introducing hydrogen gas the conductance curves change qualitatively as illustrated by the grey curve in the inset, recorded at $100\,mV$. This is most clearly brought out by the conductance histogram (grey; recorded with $140\,mV$ bias). Briefly the mechanically controllable break junction technique works as follows: Starting with a macroscopic metal wire a notch is formed by incision with a knife. The samples are mounted inside a vacuum container and pumped to a pressure below $5 \cdot 10^{-7}\,mbar$. Next, the system is cooled to $4.2\,K$ in order to attain a cryogenic vacuum. After cooling, the sample wire is broken at the notch by bending of the substrate onto which it has been fixed. The clean, freshly exposed fracture surfaces are then brought back into contact by slightly relaxing the bending. With the use of a piezoelectric element the displacement of the two electrodes can be finely adjusted to form a stable contact of atomic size. A thick copper finger provides thermal contact to the sample inside the container.

chains of atoms [18, 19], and a theoretical description for localised vibration modes in quantum point contacts has been developed [20, 21]. Vibration modes for individual molecules have been observed before, using inelastic electron tunnelling spectroscopy (IETS) in a low-temperature STM [22]. Although the principle is similar, the conductance increases at the vibration energy in IETS, while it decreases in PCS. Experimentally, a great advantage is the short data acquisition time for a spectrum in our experiment, $10\,s$ compared to 1–$10\,h$ for IETS [22]. This is attributed mainly to a lower shot noise level as result of the lower resistance of the junction, and due to the quantum suppression of shot noise for a single-channel contact [23]; the lower junction impedance also allows us to work at a higher modulation frequency.

Fig. 2 shows the differential conductance and its derivative taken at a $1\,G_0$-plateau for the Pt/H_2 system. We find a pronounced single resonance at about $63.5\,mV$, symmetrically for both voltage polarities. The energy is much higher than the typical phonon modes for metals, which are found between 5 and $25\,mV$ [24]. The width of the resonance is about $14\,mV$ and is much larger than expected from the thermal and instrumental broadening. A similar large
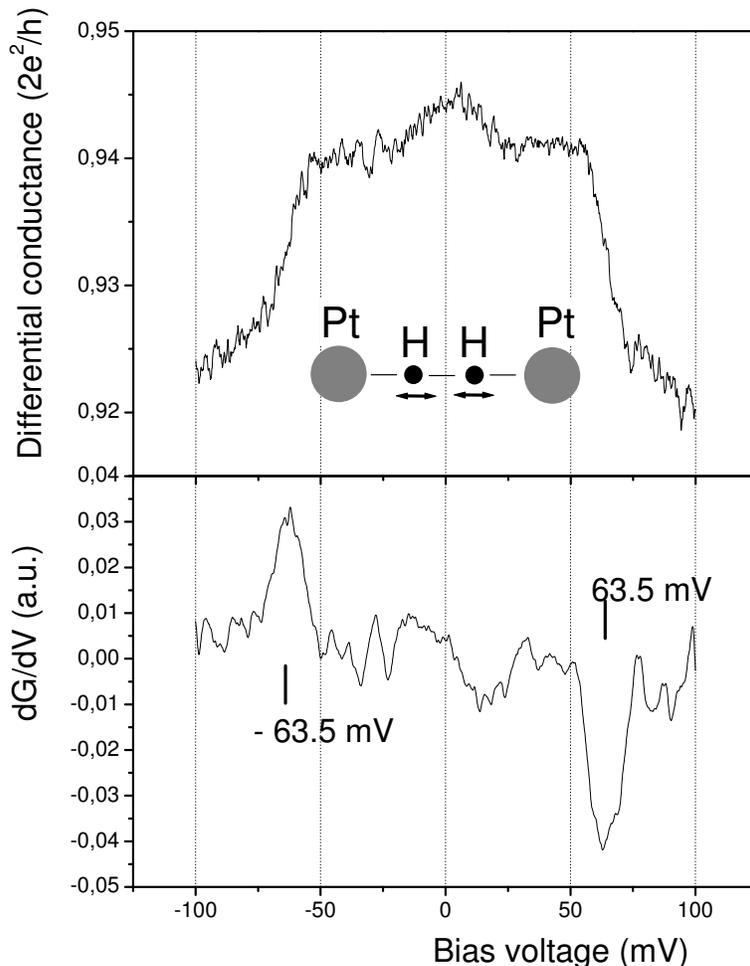
FIG. 2: Differential conductance (top) and its derivative (bottom) for a Pt/H_2 contact taken at a conductance plateau close to $1\,G_0$. The differential conductance is recorded by a lock-in amplifier using a modulation amplitude between 0.88 and $1.5\,\mathrm{mV_{rms}}$ at $7\,\mathrm{kHz}$ and a time constant of $10\,\mathrm{ms}$, and the derivative is numerically calculated. A full spectrum is recorded in $10\,\mathrm{s}$.

'intrinsic width' has been observed in IETS [22] and it probably results from the short lifetime of the molecular vibration excitations due to the strong coupling to the metal. We observe a modest variation in the position of the main signal between different experiments, which is likely due to variations in the bonding configuration of the hydrogen to the Pt electrodes. The frequencies obtained from 23 spectra for Pt/H_2 are shown by the open circles in Fig. 3, having a mean value of $64\,\mathrm{mV}$ and a standard deviation of $4\,\mathrm{mV}$.

In order to test the interpretation of the observed resonance we repeated the experiment using the isotopes D_2, and HD. From 23 spectra for Pt/D_2 we obtain a distribution of energies shown by open squares in Fig. 3, being centred at $47\,\mathrm{mV}$, while 20 spectra obtained for Pt/HD (bullets) are found to be centred at $51\,\mathrm{mV}$. The inset to Fig. 3 shows the same distributions with energies scaled by the expected ratios for the vibration energies $\omega_{H_2}/\omega_{D_2} \sim \sqrt{m_{D_2}/m_{H_2}} = \sqrt{2} \simeq 1.414$, and $\omega_{H_2}/\omega_{HD} \sim \sqrt{m_{HD}/m_{H_2}} = \sqrt{3/2} \simeq 1.225$, confirming our interpretation of the conduction through a hydrogen molecule. Note in particular that this excludes the possibility of conductance through a hydrogen *atom*, since this would have resulted in a two-peak distribution of frequencies for HD.

Experimental information on the number of conductance modes can be obtained from the fluctuations in $G_\mathrm{d}(V)$ as a function of voltage by measuring their root-mean square amplitude σ_{GV} following the method described in Ref. 25. For a contact with a single conductance channel with transmission probability $T < 1$ the dominant contribution to the fluctuations results from interference of partial waves reflected at the contact itself and those reflected on defects nearby. The wavelength of the electrons changes as a function of the bias voltage, producing random variations in the interference and thus in the conductance. For $T = 1$ the reflection at the contact vanishes resulting in a suppression of the fluctuations. Fig. 4 shows that the peak in the conductance histogram at $0.95\,G_0$ coincides with a pronounced minimum in σ_{GV}. From the finite value of at the minimum [25] we extract a value for the transmission
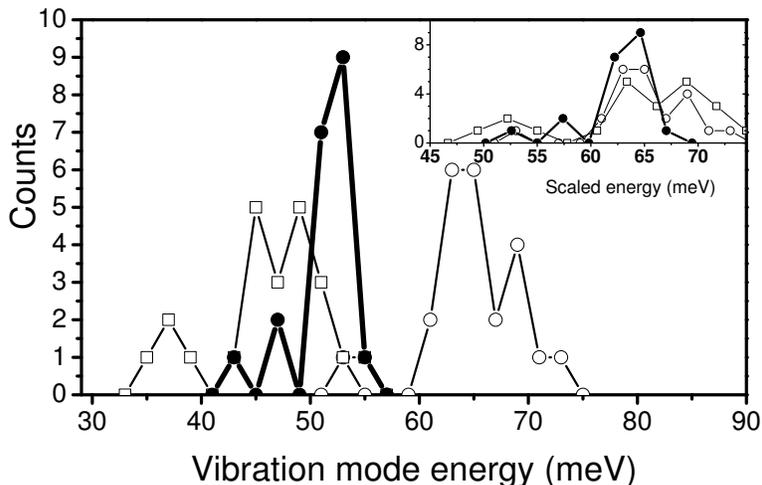
FIG. 3: Vibration mode energies obtained from point contact spectra similar to that shown in Fig. 2, for Pt/H$_2$ (○), Pt/D$_2$ (□), and for Pt/HD (●). The vertical scale shows the number of spectra with energies within a bin size of 2 meV. The inset shows the same data with the energy axis scaled by the factors expected for the isotope shifts of the hydrogen molecule, $\omega_{H_2}/\omega_{D_2} \sim \sqrt{m_{D_2}/m_{H_2}} = \sqrt{2} \simeq 1.414$ (□), and $\omega_{H_2}/\omega_{HD} \sim \sqrt{m_{HD}/m_{H_2}} = \sqrt{3/2} \simeq 1.225$ (●).

$T = 0.97 \pm 0.01$, confirming that the conductance through the molecule is almost entirely carried by one channel. This finding also excludes other configurations for which the conductance would be carried through several parallel channels and confirms that we have only a single molecule.

Hydrogen is known to bind strongly to a Pt surface, and Pt surfaces catalyse hydrogen dissociation. Little is known about the catalytic activity of this system at 4.2 K, but it is likely that a small energy barrier is present that prevents H$_2$ dissociation under these conditions. In the experiment we cannot rule out the formation of contacts with atomic hydrogen, but the ones that we have been able to fully analyse have a molecular bridge. We have verified the stability of the H$_2$-bridge configuration using density functional calculations employing the Gaussian 98 program [26] with the SDD relativistic effective core basis set [27] and the B3LYP functional [28]. Calculations were performed starting with a linear chain of four Pt atoms, and the results were verified to be insensitive to adding more atoms to the length of the Pt chain. Performing first-principles molecular dynamics we find that a H$_2$ molecule bonded to the side of a Pt chain spontaneously moves as a whole into the chain when the bonds between the Pt atoms are being stretched. The energy gain is 2.0 eV, as compared to free H$_2$ and two Pt$_2$ chain fragments at infinity. The binding energy of the Pt atoms in the chain is 2.75 eV per bond. H$_2$ will therefore never move spontaneously into the chain but first requires an external force to stretch a Pt-Pt bond, which is a way to supply chemical energy to a single bond. In order to obtain the longitudinal vibrational modes of H$_2$ in a Pt chain, we have explicitly calculated the potential energy curves. For the center of mass motion of H$_2$ we obtain an excitation energy of 61.5 meV, using equilibrium bond distances in a linear arrangement of 0.08 nm and 0.21 nm for H-H and Pt-H, respectively. This vibration mode fits very closely the observed excitation energy. The internal vibration mode of H$_2$ is too high in energy ($\sim$ 430 meV) to be observed in the experiment since the contact becomes unstable at bias voltages above about 200 mV.

The conductance of the hydrogen bridge was calculated using a model of a chain of Pt-H-H-Pt, sandwiched between two jellium bulk electrodes. We refer to Ref. 29 for more details on the computation method. For the equilibrium bond distances we find a conductance of 0.9 G_0, in close agreement with experiment. We have not attempted to obtain the eigenchannel decomposition of the conductance.

The conduction through the molecule involves mainly the H$_2$ antibonding states, but the hybridisation with the Pt metal states is strong enough to largely fill the HOMO-LUMO gap. It is surprising that the closed-shell configuration of H$_2$ permits such strong bonding with Pt, while the molecular character is largely conserved. The latter is evidenced by the calculated H-H bond distance, which is close to that of the free molecule, and the fact that in the simulations upon further stretching the bridge finally breaks at the Pt-H bond. A Pt one-atom contact is expected to have five conductance channels due to the partially occupied d-orbitals. It appears that the insertion of a hydrogen molecule has the effect of filtering out a single one from these five channels, with nearly perfect transmission.

It will be interesting to attempt to extend our technique to more complex molecules with built-in functional groups. Although most organic molecules are expected to have a conductance many orders of magnitude below the quantum unit, our experiments confirm [30] that full transmission of a single channel is possible when the coupling to the leads is sufficiently strong. Very recently two groups have demonstrated conductance through single metalorganic molecules
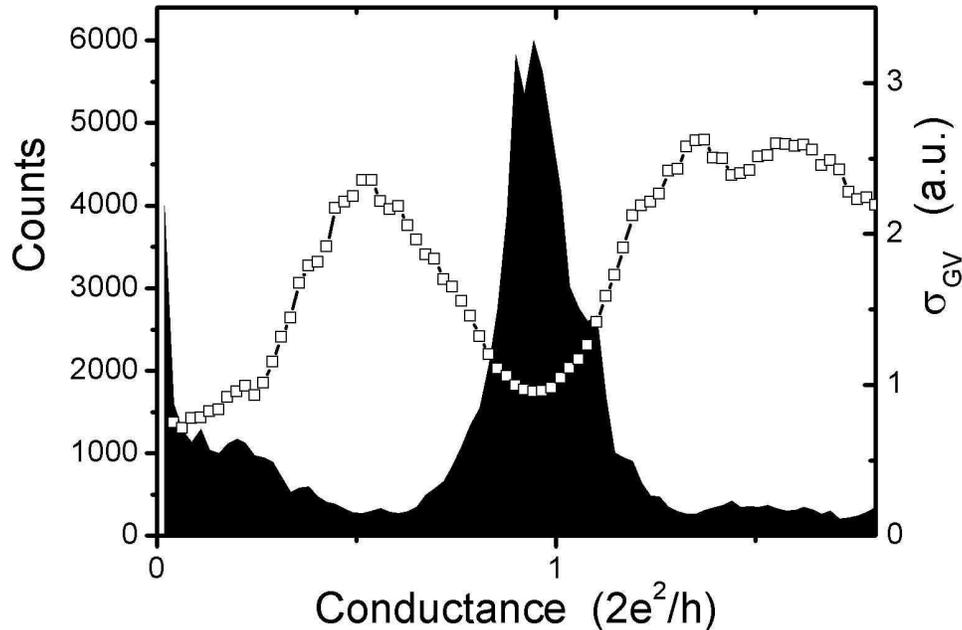
FIG. 4: Conductance histogram (black, left axis) and rms amplitude of the conductance fluctuations ($\square$, right axis) for a Pt/H_2 sample obtained using 2000 cycles of contact breaking. The conductance and its derivative were measured with two parallel lock-in amplifiers, detecting the frequencies f and $2f$, with 140 mV bias voltage and 20 mV modulation amplitude. The derivative signal is used to calculate the average of the conductance fluctuations, σ_{GV}, and each of the points is obtained from the data belonging to one bin of the histogram.

[31, 32], for which the charge-state of the metal ions could even be controlled by a gate electrode. In stead of using mechanical adjustment of the contact size as in our experiments the size of the metal contacts to the molecule was reduced exploiting electromigration. This further illustrates that we are rapidly developing the tools to study and control electron transport at single-molecule level.

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