Electron transport through single gold atoms and hydrogen molecules switching on the atomic scale
Trouwborst, Marius Leendert

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Chapter 5

Molecular heating in hydrogen-gold junctions

Abstract
In this chapter, we present conductance measurements on hydrogen-gold junctions. By fast data acquisition, a strong hysteretic behavior is observed, starting exactly at the hydrogen vibration frequency. We show that this is related to a substantial heating effect, triggered by vibrational excitations of the hydrogen molecule. Hence, our results give new insights in the influence of molecular vibrations on the conductance properties of molecular junctions.

5.1 Introduction
One of the most important issues in molecular electronics is the coupling between the molecule and the metallic electrode. The coupling does not only determine the conductance of the molecular system, but also the local temperature of the system. Theoretical studies have shown that molecules could heat up by several hundreds of Kelvin, under bias voltages below 1 V (see for example Ref. [1]). Only recently this has been confirmed experimentally on C60 molecules. These molecules can thermally degrade when brought into resonance by a bias voltage [2].

In this chapter we present an experimental study of heat dissipation in a system where molecular hydrogen is contacted between two gold electrodes. By first

This chapter is based on Ref. 3 on p. 147
vibrationally exciting the molecules, and subsequently measuring the response
time for releasing this vibrational energy, interesting effects appear. Surprisingly,
response times of 200 ms are observed, for the system to return to equilibrium.
These relatively large response times are explained by a substantial heating ef-
fect, triggered by inelastic excitations of the hydrogen molecules. We will start,
however, with a short overview on the vibrational spectra of molecules, contacted
in between two electrodes.

Figure 5.1: Differential conductance spectra on a single deuterium molecule,
contacted by platinum electrodes. The electrodes were moved apart 0.1 Å and 0.2
Å in figure (b) and (c) respectively, as compared to figure (a). In all figures, the
step in conductance can be observed, around the hydrogen vibration frequency. In
figure (b), an extra feature occurs, a spike in dI/dV. Measurement is taken at 4.2
K by Thijssen et al, Ref. 4.

5.2 Literature: vibrational spectra of molecules

5.2.1 Spikes in the differential conductance

As first shown by Smit et al, the vibration mode of a single hydrogen molecule
can be clearly observed by point contact spectroscopy [3]. When the applied
voltage is equal to $\hbar \omega$ (where $\omega$ is the vibration frequency), the reflectivity of the
contacts is enhanced, leading to a step down in the differential conductance [16].
An example is given in Fig. 5.1(a), showing a decrease in dI/dV around 40 meV
(measurement by Thijssen et al) [4]. However, at the same time, another effect
can show up, leading to a spike in dI/dV (as shown in Fig. 5.1(b)). We emphasize
that this effect can be much larger than the conductance step (> 100% versus typically <5 % for PCS), and can result in a peak or dip feature in the differential conductance. These anomalies are the key ingredient of our experiments.

Interestingly, the spikes are observed on a large variety of molecular systems. For example, peaks or dips in dI/dV have been reported on STM and MCBJ systems, with Au, Ag, Pt, Ni, NiAl, or Cu as the metallic contact. Also, the anomalies have been observed on a large number of molecules, like O2, C2H2, CO, H2O, H2, D2 and pyrrolidine molecules [5, 6, 7, 9]. An example is shown in Fig. 5.2, where a pyrrolidine molecule (C4H8NH) on a copper [001] surface is measured with a STM. A strong dip in dI/dV was observed around 400 mV, which was ascribed to the vibration energy of the molecule; when the hydrogen atoms in the molecule are substituted for deuterium, the energy of the vibration decreases, as expected by the higher mass of D2 (lower graph). This relation has also been observed by Thijssen et al. For H2 on gold, the spikes were always observed around 41 meV, while for D2 the spikes were found around 29 meV (as shown in Fig. 5.4(a)). This $\sqrt{2}$ difference is exactly as expected, since the vibration frequency scales with the mass by $\sqrt{k/m}$. Furthermore, spikes can only be observed for certain vibration modes. In the case of H2 and D2, only the transversal vibration mode shows the anomalies, and no spikes are observed for the longitudinal modes [4]. Finally, two other examples from Thijssen et al, are the measurements on Co-Pt and Au – H2, as shown in Fig. 5.3. We note that for both systems, both dips and peaks are observed, depending on the contact.

![Figure 5.2: Upper graph: dI/dV spectrum, taken with an STM, for a pyrrolidine molecule on a Cu[001] surface, taken at 7 K. Lower graph: Spectrum taken on a similar molecule, where the hydrogen is substituted with Deuterium. Note that the spectra are obtained by averaging over > 100 scans, which also averages out the fluctuations around the dip in conductance. Picture from Ref. 7.](image-url)
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Figure 5.3: Upper graph: $dI/dV$ spectrum of a CO molecule, contacted with Pt electrodes. Lower graph: $dI/dV$ spectrum of an Au$-\text{H}_2$ contact. Both figures are measured with a MCBJ at $\approx 4.2K$. Picture from Ref. 5.

Figure 5.4: (a) Histogram, as measured by Thijsen et al, on the position of the spike, for different contacts. For hydrogen, the average position is 41 meV, and when the measurements are repeated on $\text{D}_2$, the position is shifted to 29 meV. This is exactly a $\sqrt{2}$ difference, as expected by the mass ratio. Picture from Ref. 4. (b) Position of spikes, as measured by us, on 6 different samples. The average voltage is 40.5 mV. Clearly, the average position of the peak is equal to the $\text{H}_2$ vibration frequency (41 meV).

To summarize the observations, we describe the four characteristic features of the spectroscopic anomalies. First, the position of the peak is equal to the position of the (regular) conductance step. This shows that the spike is related to molecular vibrations. A second observation is the increase of electrical noise, at the conductance spike. Third, the observed features can be a peak or a dip in the conductance. And finally, the appearance of the peak strongly depends on
the exact morphology of the contact, and on the distance between the electrodes (as shown in Fig. 5.1).

5.2.2 Literature: proposed explanation for the spectroscopic anomalies

Although the exact mechanism which drives the anomalies is not yet understood, in the past years, a number of models were suggested to fit the corresponding data \[4, 6, 9\]. For all models, a two level system is suggested, which explains the increase in noise around the conductance spike. The idea is as follows: When the molecule is vibrationally excited, the molecular energy increases, resulting in a larger spatial freedom of the molecule. Hence, it can hop to a neighboring (lattice) position. Since this second position can have a higher or lower conductance than the first position (at \(V < V_{\text{M}}\)), a peak or dip can be observed in the differential conductance respectively. Furthermore, the cross-over between these two conductance levels can be gradual, when assuming that the molecule hops back and forth in between the two levels. This then results in an apparently smooth transition, when the hopping process is faster than the bandwidth of the electronics. Finally, we note that, even though the two level models can fit the data, the exact physical origin of the relaxation rates (from one level to the other) is not yet understood.

5.3 Experimental details

For our measurements, we focus on the spikes in \(dI/dV\), on \(H_2 - Au\) chains. The procedure is as follows: First, the break junction is opened in cryogenic vacuum, at 4.2 K, and the electrode tips are ”trained” (see chapter 4). Subsequently, high purity hydrogen gas (99.999 %) is introduced into a space of \(\approx 1 \text{ cm}^3\) volume (at a pressure of \(\approx 1 \text{ mbar}\)). This space has two valves; 1 connected to the hydrogen vessel and pump, and one valve connected to the insert. Hence, after repeatedly flushing the space with hydrogen gas, the content of the space is brought into the insert. This ensures us to have only a small number of molecules (<1 \(\mu\text{mol}\)) in the chamber. Next, we wait for one hour for the hydrogen molecules to cool down. Subsequently, the junction is closed and slowly opened again to stimulate the formation of \(H_2 - Au\) chains (the pulling is done with a speed of \(\approx 5 \text{ pm/s}\)). Meanwhile, IV curves are recorded, real time, by sweeping the voltage using a triangular waveform of 1 Hz (amplitude is in between 90 and 100 mV). Hence,
steps in the IV curves can be easily recognized, giving enough time to stop the pulling of the electrodes, and to start characterizing the contact. Two examples are plotted in Fig. 5.5, showing a peak and dip feature around 40 mV. For a statistical analysis on many different contacts the wires are broken, subsequently brought into contact again (to conductance values of $> 5 G_0$), before starting the pulling process over again. In total, we have measured 56 different contacts, on 6 different samples. From all the measurements, we collected the position of the spikes into a histogram, as shown in Fig. 5.4. The average position of the peaks is 40.5 mV, which is the typical value for the hydrogen vibration frequency (around 41 mV, as shown in Fig. 5.4(a)). The zero bias conductance of the contacts varied in between 0.001 and $1 G_0$, which are typical conductance values for $H_2 – Au$ chains [11] (see Fig. 5.6). Furthermore, most of the measurements ($\approx 85\%$) showed a peak in conductance, at $eV = \hbar \omega$, while the rest showed a dip feature.

Figure 5.5: Two examples of spikes in the IETS spectra, measured on a $H_2 – Au$ contact (relatively slow measurement). Both the current as the differential conductance are plotted, which are measured simultaneously. Note the negative differential conductance for the right plot. Dwell time is 500 ms, $V_{ac} = 0.5$ mV, step size is 0.5 mV. Temperature is $\approx 4$ K.

5.4 Hysteresis effects in $Au – H_2$ junctions

5.4.1 Hysteresis in IV measurements

Let us now return to Fig. 5.5. Clearly, the observed spikes in dI/dV have a much larger amplitude than the regular vibrational steps in dI/dV (typically
5.4 Hysteresis effects in Au – H$_2$ junctions

Figure 5.6: Position of the spikes as a function of zero bias conductance of the contact (in total, 56 different contacts are measured).

$\geq 200\%$ versus $\leq 5\%$). To measure the small steps in $dI/dV$, one uses a standard lock-in technique, to average out any electrical noise. However, this technique needs a relatively long averaging time for each data point. In contrast, the dips and peaks have a much larger amplitude, and can already be observed from the IV measurements. This makes it possible to acquire the data directly by IV measurements, using a much faster data acquisition. Hence, we have the unique opportunity to investigate the decay times of vibrational excitations of single molecules.

A typical example of such a measurement is shown in Fig. 5.7. Here, the current is recorded, while sweeping the voltage with different time scales. Surprisingly, we find that time plays an important role in the conductance spikes. For the lower trace, measured over 10 s (0.1 Hz), no hysteresis is observed. However, when sweeping the voltage faster, a hysteresis effect shows up, exactly at the vibration frequency. In other words, the system needs time to fall down from the upper to the lower conductance state. Remarkably, when the voltage is swept even faster, in 100 ms (10 Hz), the system has not enough time to relax to the lower conductance state, and stays in the upper state. These unexpected results are the main focus of this chapter.

We emphasize that the hysteresis effect is not an artifact of our electronics. This is simply shown by the fact that the system responds immediately at the turning points (at $V = \pm 100$ mV), and the observation of two level fluctuations (as will be shown in section 5.6). Finally, we stress that the method of fast data acquisition has not been used before on these measurements, which explains that we are the first to observe the hysteresis effect. Even the lower curve, showing almost no hysteresis and measured with 0.1 Hz, is recorded faster than typically used for PCS measurements (for PCS, one uses acquisition rates of minimum 20
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s (0.05 Hz) for a full trace) [5].

**Figure 5.7:** Hysteresis while sweeping the voltage with 0.1 Hz (lower curve), 1 Hz, 2 Hz, 3 Hz and 10 Hz (upper curve). For clarity, the upper traces are shifted by 50 nA each. Sample rate is 10,000 data points per second, with an averaging time of 100 µs for each data point. Temperature is \(\approx 4\) K. Each trace consists of 3 voltage sweeps, showing the perfect reproducibility.

**Figure 5.8:** Response of pulsing the voltage around the conductance step. At \(t=0\), the voltage is dropped from an initial voltage \((V_{\text{high}} > V_{\text{th}})\), to a low voltage \((V_{\text{low}} < V_{\text{th}})\). For this measurement, \(V_{\text{low}}\) is constant and is set to 20 mV. The initial voltage is 50 mV (first curve), 60, 70, 80 and 90 mV (last curve).
5.4.2 Pulse response

To further investigate the hysteresis, we use voltage pulses to record the response times. An example of such a measurement is shown in Fig. 5.8. Here, the voltage was set to a certain voltage above the anomaly, defined as $V_{\text{high}}$. The conductance is now in the upper state. After 1 second, long enough to reach equilibrium, the voltage was instantly dropped to a certain voltage below the anomaly, in this case 20 mV (defined as $V_{\text{low}}$). Meanwhile, the conductance is measured, as a function of time. Let us first consider the trace with $V_{\text{high}} = 50$ mV. The time scale is defined as the time after the voltage drop (to $V = V_{\text{low}}$). Clearly, the system does not respond immediately. Only after about 10 ms, the conductance starts to drop to the lower state. This relatively large hysteresis time is an indication of an heating effect close to the contact. Remarkably, when these measurements are repeated for different initial voltages, strong differences are observed in the response time. This occurs even though the initial voltage is well above the vibration frequency.

To compare the effect for different contacts and initial voltages, the typical decay times were measured. This decay time is defined as the time where the conductance has dropped halfway (as depicted by the dotted line, which gives a decay time of 16 ms). We have plotted these decay times, for 4 different contacts, as shown in Fig. 5.9(a). Clearly, the process has an onset around 40 meV and the decay times strongly increase at higher voltages. Apparently, a heating process is initiated around the vibration frequency of the hydrogen molecule. This effect is even more pronounced in Fig. 5.9(b). Here, the results are shown on a similar measurement. However, now $V_{\text{high}}$ is constant, and $V_{\text{low}}$ is systematically varied. Close to the vibration frequency, the response time increases dramatically. Apparently, the observed heating effect is somewhat broadened towards lower voltages. Here, we note the similarity of the two plots 5.9(b) and 5.4(b). Both curves have approximately the same broadening around 40 mV.

Let us now focus on the relation between the decay times and applied bias voltage (as depicted in Fig. 5.9(a)). Actually, since the exact conductance value varies for each data point, also the injected current differs for each voltage pulse. Hence, to compare the data, one could divide the decay times by the total injected current. This result is given in Fig. 5.10(a). Interestingly, the decay times, corrected for the injected current, have a linear relation with the applied voltage. Moreover, the origin of the linear relation is equal to the position of the spectroscopic anomaly (and so the energy of the vibration mode). Thus, when taking into account the different vibration energies of each contact, one can plot the
Figure 5.9: (a) Decay times as a function of the initial voltage, for 4 different contacts ($V_{\text{low}} = 20$ 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). (b) Decay times as a function of the final voltage. The initial voltage, $V_{\text{high}}$, was set to 80 mV. For this sample, the spike in $dI/dV$ occurred at 39 meV.

Figure 5.10: (a) Decay times, divided by the total injected current during the pulse, including linear fits (Same data as in Fig. 5.9(a)). (b) Same data as in Fig. 5.9(a), but now divided by $I \cdot (V - \hbar \omega / e)$.
decay times divided by the relation $I \cdot (V - \hbar \omega/e)$. This results in an almost constant decay, independent of the conductance of the contact (varying in between $0.015 \, G_0$ and $0.058 \, G_0$), or the energy of the vibration mode (between 30 and 46 meV) (see Fig. 5.10(b)). This important result can be used for understanding the observed hysteretic behavior of the hydrogen-gold junctions, and will be further discussed in section 5.6.

### 5.5 Temperature dependency of the conductance spikes

In the previous section, we suggested a heating effect to explain the observed hysteresis. To investigate the relation with the bath temperature (temperature of the electrodes), the temperature of the insert was varied systematically. This was done by slowly lifting the insert above the helium level, thereby warming up the entire insert. The result is plotted in Fig. 5.11. Surprisingly, the position of the anomaly shifts towards higher voltages, with increasing temperature (up to 80 mV at 8 K.). A similar effect was observed by Kubatkin et al, on C60 molecules in between gold electrodes [10]. Here, a step in the current was measured, which shifted from 40 mV (at 4 K) to 90 mV (at 8 K). Cooling down from 4 K to 2 K did not change the position of the step. Instead, the position of the step saturated close to 40 mV. Since their results are similar to ours, and hydrogen can easily show up as an impurity, we suggest that their data could also be related to molecular hydrogen.

We emphasize that it is difficult to draw conclusions from the observed temperature dependency. When raising the temperature, many different effects occur, like electron and phonon heating of the gold electrodes, a strong increase of partial pressure of the hydrogen, and decreasing electrode separation. Nevertheless, it is interesting that the shape of the hysteresis is not effected by the temperature. Finally, we note the similarity between our observations and the STM experiments by Gupta et al [6]. Here, a step in current was observed for $H_2$ on a Cu surface, which shifted towards higher voltages when increasing the hydrogen pressure in the system. However, it is difficult to separate the two effects of hydrogen pressure and electrode temperature. Especially in an STM setup, high gas pressures can cause a strong thermal coupling between the STM tip and other (room temperature) parts of the cryostat. This can result in a higher temperature of the STM tip, in comparison with the surface temperature.
**Figure 5.11:** IV measurements on a hydrogen gold junction, as a function of temperature. By heating the system to 8 K (middle curve), the step in current shifts towards higher voltages. When cooling down again, the anomaly returns to its initial value. For clarity, the curves are shifted with 20 nA each, relative to the middle curve. We estimate the measurement error for the temperature to be 2 K, due to uncertainties for the thermal coupling between sample and insert. Measurement is done by sweeping the voltage with 1 Hz and a sample rate of 10kS/s, with an averaging time of 100 µs for each data point.

**Figure 5.12:** Example of IV measurement, showing the origin of the peak structure. Measurement taken with 0.6 Hz (lower curve), 1 Hz and 1.4 Hz (upper curve) (curves are shifted 500 µA each for clarity). At faster voltage sweeps, clear two level fluctuations appear when decreasing the voltage. Inset: zoom in of the upper curve.
5.6 Discussion of the experimental results

In section 5.4, we showed that the IV characteristics of $H_2 - Au$ junctions have a strong hysteretic behavior, at voltages above the vibration energy of the hydrogen molecule. Apparently, at $V \geq \hbar \omega/e$, a large amount of energy is put into the system, which needs a ms time scale to flow away into the electrodes. This observation is consistent with a heating effect. To quantify the observed hysteresis, we recorded the decay times for the system to return to equilibrium, as a function of the applied voltage. We found that the decay times are proportional to $I \cdot (V - \hbar \omega/e)$, where $\hbar \omega$ is the vibration energy of the molecule. Since $I$ is proportional to $V$, by $G$, the relation can be rewritten as $G \cdot (V - \hbar \omega/e) \cdot V$. Furthermore, the number of electrons which are inelastically scattered is proportional to $G \cdot (V - \hbar \omega/e)$. This suggest that the decay times are proportional to the number of inelastically scattered electrons times the energy of each electron. However, a basic analysis of Inelastic Electron Tunneling Spectroscopy (IETS), would result in an energy of the inelastic electrons equal to $\hbar \omega$. Hence, a more advanced theoretical analysis is needed, for understanding the observed relation for the decay times. In this context, we note that we did not take into account any cooling effects. Since the molecular system is in equilibrium at the end of the voltage pulse, both heating and cooling effects should be taken into account.

To make it even more intriguing, we note here that the heating is related to a much faster two level process (as also proposed by others, and introduced in section 5.2). Even though most of the measurements show a smooth transition around $V_{h\omega}$, an exceptional measurement is plotted in Fig. 5.12. When the voltage is swept relatively slow (lower curve), a smooth transition can be observed around 36 mV, with hysteresis. However, when sweeping faster as for the upper curve (resulting in less heating), two level fluctuations appear when going down in voltage. These two level fluctuations are also observed in measurements where the hydrogen is not contacted, but separated by a tunnel barrier (as will be shown in chapter 7). In the next section, we discuss two possible mechanisms which could give a qualitative explanation of our observations: a heating effect of the gold electrodes, or phonon heating of the hydrogen molecule(s).
5.7 Possible mechanisms

5.7.1 Heating of the electrodes

One could suggest that the observed current step is triggered by a critical temperature of the electrodes. In fact, the temperature of the gold lattice is expected to increase at high current densities. This was shown experimentally by Kolesnychenko et al [12]. Here, it was observed that the metal electrodes expand under large current densities (at power dissipations above 1 µW). When suddenly dropping the current, the electrodes cool down with a millisecond time scale (as shown on W break junctions). These relatively long cooling times were attributed to heating of the entire electrodes.

Nevertheless, we claim that electrode heating can not be the (main) responsible mechanism for our observations. The first argument is that the power dissipation during our measurements is relatively small (in the order of 10 nW). As shown by Kolesnychenko et al, any increase in electrode temperature can be observed directly by thermal expansion of the electrodes. For this purpose, we have performed reference measurements on bare gold tunnel junctions. In agreement with Ref. [12], the conductance of the tunnel junctions did not rigorously change for power dissipations up to 100 nW. Hence, the tunnel distance did not decrease by more than 1 pm. When we assume a heating length of 1 µm and a thermal expansion coefficient of $10^{-5} \, \text{K}^{-1}$, an electrode expansion of 1 pm would coincide with a temperature increase of only 0.1 K. Clearly, this can not explain our observations.

The second argument is that the current step is always positioned around 40 mV, independent on the current density through the contact (see Fig. 5.6). This is also shown in Fig. 5.13, where IV measurements are plotted for different stretching configurations of the contact. Although the current density increases by more than 200%, the position of the step in current hardly changes. This proofs that the anomaly is not triggered at some critical electrode temperature. Furthermore, the temperature profile is not expected to change dramatically when an extra inelastic path opens (like the hydrogen vibration mode). Only a small number of electrons will be scattered inelastically ($\approx 5\%$). Hence, the total current will only slightly increase. Finally, the phonon coupling between a hydrogen molecule and the gold atoms is expected to be negligible (due to the large mass difference between the different atoms) [15]. Moreover, even in the hypothetical case of large phonon coupling, the temperature profile will only change locally. In
this case, the inelastic current would be dissipated close to the molecules, instead of within an distance equal to the inelastic mean free path (which is in the order of 200 nm). The heat conduction over such a small distance is expected to be a fast process. Especially at temperatures below 20K, where the thermal diffusivity of metals is orders of magnitude higher than at room temperature [12]. Thus, the cooling times are expected much faster than the observed ms decay time. To conclude, we claim that the observed heating effect can not be explained by an increase in temperature of the electrodes.

![Graph](image)

**Figure 5.13:** Example of IV measurements, while stretching the junction. Although the zero bias conductance increases by more than a factor of 2, the position of the step in current changes only by 5% (from 41 to 43 mV). Hence, the vibration frequency is rather independent on the conductance of the junction. The voltage is swept with 1 Hz, and the junction is stretched relative to the lower curve, by 0.4 Å (middle curve) and 0.8 Å (upper curve).

### 5.7.2 Molecular heating by vibrational excitations

In the previous section we discussed that the observed heating effect must be directly related to the hydrogen molecules. Therefore, we start with a discussion on the number of molecules which are involved in the heating process. In this context, we emphasize that the two level system is always observed around the hydrogen vibration frequency of 40 mV (independent on the sample, hydrogen exposure or conductance of the contact). This can not be explained by some critical energy of a much larger system. Instead, the critical voltage of 40 mV suggests that a small number of molecules (possibly even a single molecule) is responsible for the switching. Another indication for a small number of molecules
is that we have also measured IV curves with 2 or 3 current steps, each with their own onset voltages (but close to 40 mV).

On the other hand, we have observed extremely long decay times of more than 100 ms. While the lifetime of a vibrational excitation of a $H_2$ molecule on a metal surface is expected smaller than 1 ns. This indicates a large number of molecules.

Therefore, we suggest the following model. Let us assume a hydrogen molecule contacted between two electrodes, and that this system is surrounded by many other hydrogen molecules. When applying a bias voltage equal to $\hbar \Omega/e$, inelastic excitations will cause a vibration of the hydrogen molecule. Interestingly, this can result in a strong temperature increase of the molecule, exactly at a voltage $\hbar \omega/e$ (as shown in Fig. 5.14) [1, 8]. Subsequently, the molecule can release its vibrational energy by creating an electron hole pair, or by phonon coupling to the environment. As mentioned before, the phonon coupling between a hydrogen molecule and the gold electrodes is negligible, due to the large mass difference between $H_2$ and Au [15]. In contrast, the phonon coupling between identical molecules is expected to be a highly efficient process. Interestingly, this could result in heating of the entire cluster of hydrogen molecules. When now decreasing the bias voltage below the vibration energy, the entire cluster has to cool down. This thermal process could explain the observed decay times of typically 100 ms.

The process described above could even suggest a phase transition of a small cluster of molecules [6, 19]). In fact, the temperature during our measurements ($\approx 4K$) is close to the melting point of molecular hydrogen (14K). Moreover, the two level system disappears at temperatures above 25K, which is equal to the desorption temperature of hydrogen (as observed experimentally). Thus, it is very well possible that (part of) the cluster of hydrogen molecules undergoes a phase transition, by heating of the cluster. This heating effect could be triggered by inelastic excitations of the molecules.

So let us discuss such a phase change in more detail. Obviously, there are two possible phase transitions. At voltages above $\hbar \Omega/e$ a transition could occur towards the liquid phase or a transition towards the gas phase. In the second case, the molecules would evaporate from the electrodes. However, there are indications that the gas phase is not reached during our experiments. First of all, we have observed that the contacts are not stable at much higher voltages. At voltages above 150 mV, the contacts show irreversible changes in the conductance. Since these changes are not observed for bare gold electrodes, the hydrogen molecules are expected to be still adsorbed on the electrodes (at voltages below 150 mV).
A second indication is formed by the reproducibility of the hysteresis and the relation of the decay times with bias voltage (as depicted in Fig. 5.10(a)). If the molecules would evaporate, the decay times would be given by some typical diffusion time for the molecules to return to the electrodes. This diffusion time would be independent on the initial voltage, something which is not observed. To conclude, we suggest that the observed heating process is probably related to a phase transition of the hydrogen molecules, from the solid phase to a liquid phase. To return to the solid phase (at voltages below $\hbar \Omega/e$), the entire cluster of hydrogen molecules has to cool down. This can be a time consuming process, thereby explaining the observed hysteresis effect.

Figure 5.14: Calculated molecular temperature, as a function of voltage over a molecular junction. For the modeling, one molecular level is included (at 2 eV above the Fermi energy), and 1 vibrational level at 0.2 eV. The temperature of the leads is set to 100 K. Note the sudden increase in temperature at voltages just above the vibration energy (see inset). Fig. from Ref. 1.

5.7.3 Comparison with STM experiments

As already discussed in the introduction, spikes in dI/dV have also been observed in STM experiments by Gupta et al and, more recently, by Temirov et al [6, 19]. Here, hydrogen gas was admitted into a STM chamber, with a pressure around $10^{-8}$ mbar (leading to a much higher hydrogen exposure compared to our experiments). Interestingly, in contrast to our break junction experiments, the spikes already occurred at voltages of 10 mV. This difference in onset voltages could be explained by the experimental differences. For example, for our break junction experiments, the molecules are contacted in between the electrodes. In contrast, for the STM experiments, the electrodes are separated by a tunnel.
gap, where the surface and STM tip are covered by the molecules. Hence, it is possible that for the STM measurements, the two level system starts by heating of an entire cluster. Indeed, the phonon excitation energy of a small cluster of molecules can be as low as 10 meV [20]. Moreover, when considering a phase transition of the molecules, one would expect a strong relation with the hydrogen pressure in the system (especially for larger hydrogen exposures). This could result in a broad range of onset voltages for the two level system. We will return to this discussion in chapter 7, where we present experiments similar to the STM measurements.

### 5.7.4 Proposed two level system

In this section, we speculate about an alternative explanation for the two level system. This is done with the help of the measurement plotted in Fig. 5.15. Here, a $H_2$-Au contact is characterized by slowly pulling the electrodes. At first, two different conductance levels are observed, above and below $eV = \hbar \omega$. However, by stretching the junction, the system is left in the high conductance state, even at zero bias voltage. Thus, the change in conductance can be triggered in two ways, by vibrational heating or by stretching of the electrodes. This behavior is consistent with a spatial change of the molecule. Let us focus on a contact like the one drawn in Fig. 5.16(a). For simplicity, we assume a single molecule, although more molecules are expected in the vicinity of the contact. The molecule is connected to two gold electrodes, in a configuration perpendicular to the direction of the current flow. However, when stretching the electrodes, the hydrogen molecule will change to a parallel configuration (as drawn in Fig. 5.16(b)). As shown by DFT calculations by Barnett et al, this configuration indeed has a higher conductance [11, 21]. One can argue that this second configuration can also be reached by vibrational excitation of the molecule. For example, when considering the so called hindered rotation mode, the molecule has the tendency to rotate from the perpendicular towards the parallel configuration. At sufficient vibrational energy, this could result in a spatial change of the molecule, from a perpendicular to a parallel configuration. Furthermore, as shown by Barnett et al, the energy difference between the two states strongly depends on the stretching of the contact. And finally, the long decay times could then be explained by the weak phonon coupling between the light molecule and the much heavier gold atoms. Hence, cooling down of the molecule could be a relatively slow process.
Figure 5.15: Example of step in the current, while pulling the electrodes. When stretching the junction, the step disappears and the junction is left in the same conductance state as the level at higher bias, before stretching. Note that the zero bias conductance increases, while stretching the junction. This can be characteristic for a Au – H$_2$ chain [11]. In total, the junction is stretched 0.7 Å. The voltage is swept by 1 Hz.

Figure 5.16: Schematic model for the proposed two level system, showing the molecule at low voltage (a), and when vibrationally excited (b). In the initial state, the molecule is contacted in a configuration perpendicular to the direction of the current flow. In contrast, when the molecule is vibrationally excited, the molecular energy increases, possibly leading to a change from contact (a) to contact (b). The same change in configuration is expected when stretching the electrodes. Note that much more molecules could participate in the process.
5.8 Conclusions

To conclude, we have investigated the vibration spectra of hydrogen molecules, contacted in between gold electrodes. By fast data acquisition, a large hysteretic behavior is observed, starting exactly at the hydrogen vibration frequency. Large hysteresis times up to 200 ms were observed, for the system to return to equilibrium. Our observations are an indication of a substantial heating effect of the hydrogen molecule(s), due to inelastic electron scattering. In detail, the hysteresis times were found to have a linear relation with $I \cdot (V - \frac{\hbar \omega}{e})$, where $\omega$ is the vibration frequency of the hydrogen molecule. To understand this relation, and the relatively large hysteresis times, a more advanced theoretical model is needed. Possibly, the heating effect can be explained by a phase transition of a cluster of molecules near the contact, due to the efficient phonon coupling between identical molecules.

Finally, we emphasize the following: the observed peaks in dI/dV (related to molecular vibrations) are very similar to the ones one can observe when bringing a molecule into resonance. Both features start at a certain voltage, can be symmetric in the voltage and can have identical amplitudes. Hence, when the energies of the vibration modes and molecular levels are unknown, it is difficult to separate or identify the two different mechanisms.

5.9 Future experiments

It is an intriguing result that the position of the conductance spike shifts upwards with increasing temperature (Fig. 5.11). It is unclear why this shift occurs. To investigate a shift in vibration frequency, we propose the following experiment. As plotted in Fig. 5.10(a), the vibration frequency can be measured indirectly by extrapolating the response times. By repeating the measurement (of the decay times) at higher temperatures, one can investigate whether the vibration frequency changes with temperature.

A second experiment we propose, is to repeat the fast IV measurements on other (organic) molecules. It is well known that the conductance of an organic molecule changes when brought into resonance [22, 23]. At the same time, it is expected that the molecular temperature strongly increases when a molecular level starts to participate (as shown in Fig. 5.14). Hence, it is possible that also for these molecular systems, millisecond decay times can be observed. We are
aware of one example from literature, also showing ms decay times. This was observed for the so called BPDN-DT switch [24]. The IV characteristics of this molecular switch were found to be strongly dependent on the measurement speed (at 100K).

References