Molecular electronics: controlled manipulation, noise and graphene architecture

Tewari, S.

6. Two-level fluctuations in molecular junctions

Conductance measurements in single-molecule junctions (SMJs) are on many occasions accompanied by inelastic spectroscopy and shot-noise measurements in order to obtain information about different vibration modes (or vibrons) and channels involved in the transport respectively. We have extended the single-molecule shot-noise measurements, which were previously performed at low bias, to high bias and we have studied the effects of these vibrons on shot noise for a Deuterium (D_2) molecule between Pt leads. We report here three important findings from these measurements. First, we find in our noise measurements that at the vibron energies of the molecule, a two-level fluctuation (TLF) is excited in the junction. Second, we show that in the presence of this TLF, a form of enhanced noise spectroscopy can be performed to detect inelastic electron-vibron interactions, by studying the third derivative of the noise ($\mathrm{d}^3 S_I/\mathrm{d}V^3$). This is possible because TLFs are insensitive to elastic scattering of electrons from defects, which nevertheless leave their signature in the usual inelastic electron tunnelling spectroscopy (IETS) measurements. Third, we also report here the detection of a step-up in conductance for the Pt-D_2-Pt junction due to inelastic interactions. As the zero-bias conductance of these contacts lies close to 1 G_0, so the occurrence of step-up in conductance goes against the usual electron back-scattering picture. However, this can be explained as a consequence of the coupling of d-orbital of Pt contacts with the usual s-orbital taking part in transport.

The work is done in collaboration with - Carlos Sabater and Jan M. van Ruitenbeek
Huygens-Kamerlingh Onnes Laboratorium, Universiteit Leiden, The Netherlands.

6.1 Introduction

Single molecule conductance measurements are possible now from nearly three decades. Soon after the first single molecule experiment[1], researchers started to explore the other degrees of freedom, for example, the effect of molecular vibrations[2,3] on electronic transport and shot-noise measurements[4]. The study of molecular vibrations using charge transport measurements helped to further strengthen the claim of contacting single molecules and the study of low-bias shot noise provides information about the number of channels involved in the charge transport. The vibration measurements are also compared frequently with other single molecule vibration measurement techniques like surface enhanced Raman or infra-red spectroscopy. Important to note is that in all these measurements of the vibrations of a single molecule the molecule remains connected to metallic leads, the coupling to which influences the vibration frequency and the nature of the modes. In this chapter, we will refer to a vibration mode of the molecule as a vibron and the vibrations in the bulk metallic lead as phonons.

The vibration measurements done by studying charge transport through a single molecule depend strongly on the electron-vibron (e-vib) coupling strength. For stronger coupling between electrons and vibrons, the electrons could have large transit times on the molecule and this could even polarize the molecule. This is seen as polaron formation and the transport in this regime is incoherent hopping transport[5]. In the other limit, for weak electron-vibron coupling the traversal time for an electron to cross the molecule is much smaller than the oscillation period of with the vibron modes of the molecule. Conversely, this electron-vibron coupling strength determines how quick the excited vibrons in the molecule pass their energy back to the electrons and consequently to the metallic bath, where the electrons loose their energy. On applying a bias $V \geq \hbar\omega/e$ across the molecule, the electrons crossing the molecule loose part of their energy to emit/excite a vibron of the molecule. This is visible in the differential conductance as a small step-change, at least for simple coherent off-resonant transmission and for weak electron-vibron coupling.

6.2 Literature review

The first measurements aimed at studying such electron-vibron interaction on single molecules[2] were done for electrons crossing a single acetylene (C_2H_2) molecule absorbed on a Cu(100) surface. A step-up or increase in conductance at a voltage equal to $\hbar\omega/e$ (the energy of a vibron associated with the molecule) was recorded. This measurement was done in tunneling mode (with transmission, $T << 1$) using a scanning tunneling microscope (STM) and the increase in conductance at energy $\hbar\omega$ was attributed to the opening of a second inelastic channel. In another measurement done

[1] M. A. Reed et al. In: *Science* 278 (1997), p. 252.
[2] B. C. Stipe et al. In: *Science* 280 (1998), p. 1732.
[3] Nicolás Agraït et al. In: *Phys. Rev. Lett.* 88 (2002), p. 216803.
[4] D. Djukic and J. M. van Ruitenbeek. In: *Nano Letters* 6 (2006), p. 789.
[5] Juan Carlos Cuevas and Elke Scheer. Molecular electronics : an introduction to theory and experiment. New Jersey [u.a.] : World Scientific, 2010.

on single H_2 molecule attached between two Pt leads[6,7], a step-down or decrease in the molecular conductance was recorded. This measurement was done in point contact mode with transmission (T) close to unity. A similar decrease in conductance is also recorded in mono-atomic chains made of gold atoms[3,8], where the transport is again ballistic. For these contacts with high transmission ($T \approx 1$), backscattering of electrons due to unavailability of empty states in the forward direction is considered to be a reason for the decrease in conductance.

To study the crossover between the two transport regimes, from the low transmission ($T << 1$) where the conductance shows a step-up to the high transmission regime ($T \approx 1$) where the conductance shows a step-down, a single vibron model in the weak electron-vibron coupling regime[5] is developed. Using this single-vibron model it can be shown that other than the elastic and inelastic (due to vibron emission or absorption) contribution, there also exists a contribution due to interference between direct elastic transport and a two-step process involving virtual emission and absorption of a vibron. It is called an 'elastic correction' as the energy is conserved here and depending on whether this interference is constructive or destructive the forward or the back scattering probability is enhanced, thus giving a positive or a negative contribution to the conductance respectively. The model further suggests that for symmetric contacts, that have the same scattering rates to the left (Γ_L) and right electrodes (Γ_R), the sign of the inelastic signals lies exactly at transmission $T = 1/2$[9]. Important to point out is that the assumption of same scattering rates to the two electrodes is not always true, for example in the tunneling case, the scattering rates on two sides are very different and so this cross-over point depends in reality on the asymmetry of the contact[10] defined as $\alpha = \Gamma_R/\Gamma_L$.

This crossover between the step-up and step-down regime has been also observed in experiments[11,12]. Contrary to the above, Kristensen *et al*.[13] have shown through first-principles calculations that the transverse vibration mode of a H_2 molecule in a Pt-H_2-Pt junction can also cause a step-up in conductance even when a single channel is involved in the transport and the transmission is close to 1. The reason behind the increase in conductance was investigated by a scattering theory calculation showing that due to transverse vibration of the molecule, d-orbitals of the Pt-leads start to couple with the s-orbital, and thus also begins to take part in transport. The authors have not observed such an increase in case of a Au-H_2-Au system, where no such d-orbital is present in the leads. Figure 6.1 taken from Kristensen *et al*.[13] shows such a step-up in conductance. This is a surprising result as from the single channel single vibron-mode model explained above, one expects the step-up in conductance to occur only at transmission much smaller than unity. And also in experiments done for Pt-H_2-Pt or Pt-D_2-Pt systems such increase in conductance has not been reported[4,6,7]. However, these steps are very small, around 1% of the conductance

[6] R. H. M. Smit et al. In: *Nature* 419 (2002), p. 906.
[7] D. Djukic et al. In: *Phys. Rev. B* 71 (2005), p. 161402.
[8] Nicolás Agraït et al. In: *Chemical physics* 281 (2002), p. 231.
[9] Magnus Paulsson et al. In: *Phys. Rev. B* 72 (2005), p. 201101.
[10] Magnus Paulsson et al. In: *Phys. Rev. Lett.* 100 (2008), p. 226604.
[11] O. Tal et al. In: *Phys. Rev. Lett.* 100 (2008), p. 196804.
[12] W. H. A. Thijssen et al. In: *New Journal of Physics* 10 (2008), p. 033005.
[13] I. S. Kristensen et al. In: *Phys. Rev. B* 79 (2009), p. 235411.

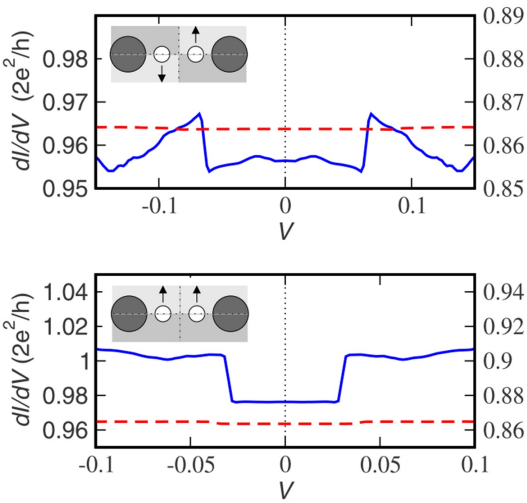


Figure 6.1: First-principles calculations from Kristensen *et al*.[13] showing differential conductance of the Pt-H_2-Pt (solid blue line) and Au-H_2-Au (dashed red line) junctions when scattering on a single transverse vibrational mode. The top figure shows a hindered rotations mode and the bottom figure shows a transverse center of mass mode.

values, and could be very difficult to detect, especially when we have oscillations in the conductance due to elastic scattering through defects[14–16].

Another interesting excitations that lies at energies close to vibrational energies of a molecule is the excitation of two-level fluctuations in the molecule. Thijssen *et al*.[17] have discussed in an experimental study, the effect of such two-level fluctuations on molecular conductance. They have reported measurement on different molecules (including also H_2 and D_2 molecules) and shown that in many occasions sharp spikes in the differential conductance are seen at energies close to a vibrational mode of the molecule. They explain these using a vibrationally induced two-level system which they call 'VITLS', where excitation of a vibron could change the molecular conformation between the leads which could change consequently the conductance and thus will be observed as a spike. Figure 6.2 shows one of their results. They have further shown that the strength of the observed spike in conductance for Pt-D_2-Pt system depends also on the stretching of the junction and could be suppressed completely once full stretched with the maximum in amplitude occurring somewhere at an intermediate stretch. They have also reported for the Pt-D_2-Pt system that the two-level fluctuation is excited only at energies close to the transverse mode of vibration. Similar peaks in the $\mathrm{d}I/\mathrm{d}V$ signals in Au-H_2-Au junctions, have also been observed by other[18] groups. Such two-level fluctuations are also reported in an STM

[14] B. Ludoph et al. In: *Phys. Rev. Lett.* 82 (1999), p. 1530.
[15] B. Ludoph and J M van Ruitenbeek. In: *Physical Review B* 61 (2000), p. 2273.
[16] C. Untiedt et al. In: *Phys. Rev. B* 62 (2000), p. 9962.
[17] W. H. A. Thijssen et al. In: *Phys. Rev. Lett.* 97 (2006), p. 226806.
[18] Manabu Kiguchi et al. In: *Phys. Rev. B* 81 (2010), p. 045420.

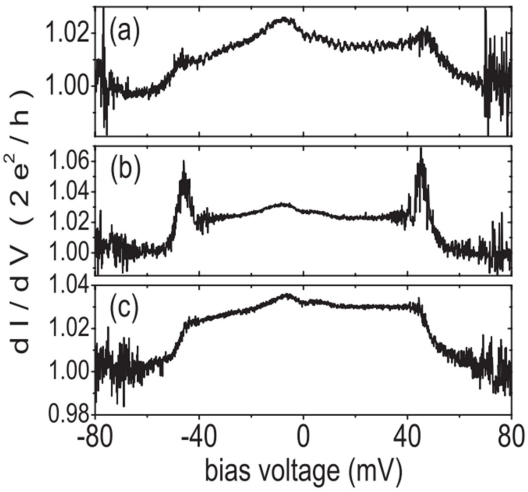


Figure 6.2: Differential conductance spectra for a Pt-D_2-Pt junction taken from Thijssen *et al*.[17]. (a-c) are spectra taken at different stretched states of the molecule. Vibration induced spikes are visible clearly at the shoulder positions.

configuration[19] for H_2 molecules over a Cu(111) surface.

In this chapter, we report a study performed on the Pt-D_2-Pt system to further explore the vibrational effects described above. We have done high-bias shot-noise measurements along with the usual differential conductance at energies where a vibron in D_2 molecule between Pt leads is excited. Previously, shot noise measurements were only performed at low bias values[4,20] to obtain information about the number of channels involved in the transport (at zero bias). We show here that, be it rarely, but we were able to detect in our measurements a step-up in conductance at energies close to the transverse vibrational mode for Pt-D_2-Pt junctions with conductance close to 1 G_0, as predicted by Kristensen *et al*.[13]. Most of the other conductance measurements show the usual step-down feature in conductance and almost all of our conductance measurements are smooth and do not have spikes-like features which were earlier attributed to two-level fluctuations[17]. Having said this, using our shot-noise measurement we have also detected the emergence of non-white noise spectra close to the energies corresponding to the vibration energy of the molecule. This is also the case with junctions which have shown a clean usual step-down or decrease in conductance at the vibrational energies. This challenges our understanding, both in qualitative and quantitative terms, of these IETS or PCS differential conductance signals and suggests that a model coupling vibration excitations and TLF could be more generally applicable in molecular junctions.

[19] J. A. Gupta et al. In: *Phys. Rev. B* 71 (2005), p. 115416.
[20] Regev Ben-Zvi et al. In: *ACS Nano* 7 (2013), p. 11147.

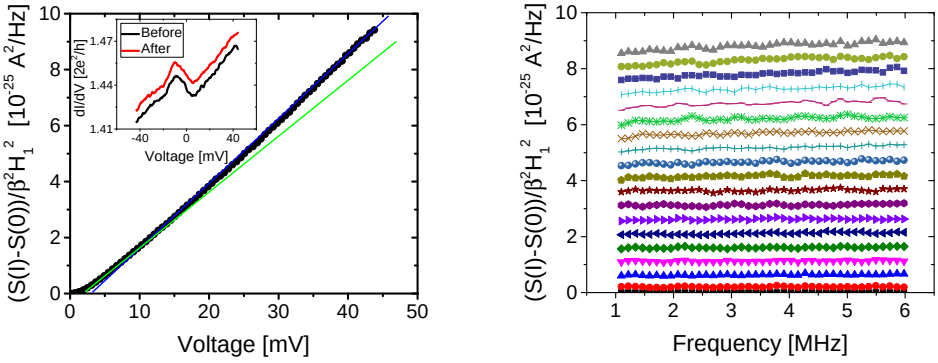
6.3 Experimental setup

To study shot noise at energies where the vibration modes of the single molecules are present, one has to fight with the notorious 1/f noise which scales with the square of the applied bias voltage. We have developed recently[21] a new high-bias shot-noise measurement setup which works in MHz regime and can be useful in studying such molecular systems. We have also demonstrated earlier using this setup shot-noise measurements up to 800 mV on a single Au-atomic point contact (see chapter 5) and have shown how at such high bias, the elastic and inelastic part of the transport, due to energy and voltage dependence of transmission can give highly non-linear shot noise. A schematic of the setup is shown in Figure 5.1 in the previous chapter. The setup is mounted on a cryogenic dipstick to do measurements at liquid He temperature. The gas molecules are deposited using a capillary tubing which goes all the way from a gas reservoir on the top to a break-junction sample mounted at the bottom. Noise measurements are done using a cross-correlation technique for which we have connected two cryogenic amplifiers in parallel at a short distance (approximately 1 cm) from the sample followed by two parallel room temperature amplifiers. For fast measurements of the noise, while still recording all the spectra at each applied bias voltage, we have incorporated a field programmable gate array (FPGA) in the spectrum analyzer. Conductance measurements are done by means of a lock-in amplifier using an input AC modulation signal of few mV amplitude over the sample and 677 Hz frequency. The details of the system and its benefits are discussed in chapter 4[21].

6.4 Measurements on a D_2 molecule

Single molecule measurements in general (not specific to D_2 molecule) are more likely to become affected by two-level fluctuations (TLF) than purely metallic atomic contacts. Such TLF are attributed to the switching between two (or more) conformational states with similar energy separated by a small barrier[17]. These TLF can also occur in metallic point contacts and atomic chains. There they can be attributed to changes in position of a defect in the leads, close to the point contact. Harder materials like Pt are more subjected to such TLF as compared to Au[21]. Here, we have taken special care to avoid such TLF in the Pt leads by pre-annealing the break-junction notched wire in a separate UHV setup (10^{-9} mbar) for 3-4 hours at 300°C. After this, we mounted carefully the sample back in the dipstick for pumping and cool down. Such a pre-annealing step is essential as we don't want the noise coming from TLF of the leads to affect our molecule noise measurement. For clean deposition of the molecules, the capillary was baked before cool down at high vacuum (10^{-6} mbar) and several flushing cycles with clean D_2 gas were done prior to breaking the Pt wire. For clean operation, the Pt wire is broken only when the system is cold and the sample is at cryogenic vacuum. Next, conductance and noise measurements of clean Pt were performed to check the cleanliness of the contact and also to train[22] the junction prior to molecule deposition. Figure 6.3 shows white noise spectra recorded (after the pre-annealing step) on a clean Pt atomic contact up to 4.9 μA current. This experiment shows the benefit of measuring shot noise at the MHz frequency range,

[21] Sumit Tewari et al. In: *Review of Scientific Instruments* 88 (2017), p. 093903.
[22] C. Sabater et al. In: *Phys. Rev. Lett.* 108 (2012), p. 205502.



(a) (b)

Figure 6.3: (a) shot-noise measurements on a clean Pt atomic contact up to 44 mV bias which for the zero bias conductance of the contact is equivalent to 4.9 μA current. The inset shows the differential conductance of the contact taken before (black) and after (red) the shot-noise measurements. Two linear fits (blue and green) to the shot noise data intercepts at the phonon frequency of the Pt junction which is around 10 mV. (b) White noise spectra recorded by our FPGA based spectrum analyser demonstrating the absence of 1/f noise and two-level fluctuations.

as we don't have any detectable 1/f noise signal in our measurements. The spectra also confirm that there are no two-level fluctuations initiated in the clean Pt junctions. The procedure that we follow in our measurement is to perform differential conductance measurements of the junction two times: before and after the shot-noise measurement series. This helps in confirming the stability of the junction during the noise measurements. A kink or a linear deviation in the shot-noise data can be seen in Figure 6.3 (a) which corresponds to the phonon frequency of the Pt junction which is around 10 mV. The rounding at the low bias ($\leq$ 2 mV) is due to submerging of the shot noise in the thermal noise background at the measurement temperature of 5 K.

6.4.1 Step down in junction conductance

While depositing the molecules, Pt contact forming and rupture traces are continuously monitored. It is known from previous conductance measurements for this system that a D_2 molecule attached between Pt leads gives rise to a last conductance plateaus at 1 G_0. So, once we started seeing such 1 G_0 plateaus appearing, we stop the deposition. Once the D_2 molecule is stable between the Pt leads, point contact spectroscopy or $\mathrm{d}I/\mathrm{d}V$ measurements of such a junction are known to show a step-down or decrease of conductance due to inelastic interaction with the vibron of the molecule. This we also found in our experiments (see Figure 6.4 (a) and (c)) in agreement with the literature[4,6,7].

Next, we perform high-bias shot noise measurements on this junction. In Figure 6.4(b) we show the corresponding shot-noise measurement results. Initially, at low bias the shot noise shows a linear increase (shown with black solid symbols) and then approximately at the point where a vibrational mode is excited giving a step-

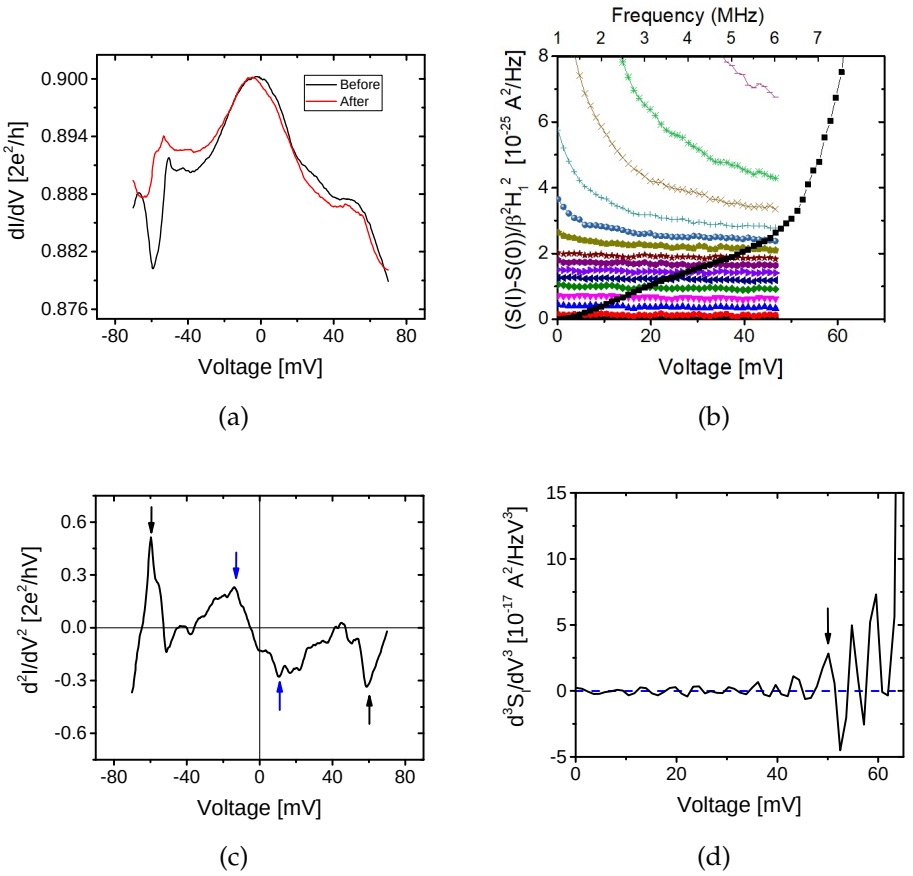


Figure 6.4: (a) A step-down in conductance for a Pt-D_2-Pt junction taken before (black) and after (red) the noise measurement. The left shoulder of the dI/dV spectrum shows a signature of two-level fluctuation similar to Thijssen *et al.*[17]. (b) High-bias shot-noise measurements (black) taken up to 60 mV bias (i. e. 4.2 μA for G(0V)=0.9 G_0). The noise spectra (in color and axis along the top) are shown from 1 to 6 MHz frequency. (c) Usual IETS spectrum of the junction showing the vibrational modes of the molecule (black arrows) and of the Pt leads (blue arrows). (d) The IENS-3 spectrum showing positions of inelastic interactions giving rise to two-level fluctuations in the molecule. The first peak marked with a black arrow, points towards a vibrational mode excitation of the molecule, while the other peaks correspond to inelastic interactions due to more complex atomic-scale dynamics occurring as the applied bias is increased further.

down in the conductance, we see a non-linear increase in the noise. We repeated this measurement for different stretching states of the molecular junction, which changes the vibrational energy[4], and we found that the locations where the shot-noise starts to deviate from linearity also changes accordingly. As we record the

spectral information of the noise, we see in Figure 6.4 (b) that the place where the noise starts to show a non-linear deviation, the spectra (taken between 1 to 6 MHz frequency) are no longer white. The detection of these non-white spectra suggests that two-level fluctuations are excited by the vibrons[1]. In the absence of such spectral information, one would be tempted to attribute this non-linear increase in shot noise to a non-equilibrium increase in population[23–26] of the vibrons due to their larger relaxation time. As mentioned in the last chapter elastic scattering through defects could also add to the non-linearities in the shot noise. But as our conductance values are not very close to 1 G_0, we expect to have very small of such contribution.

6.4.2 Inelastic electron noise spectroscopy (IENS)

The two-level fluctuations (TLF) mentioned above can, in fact, be used constructively. As described earlier, TLF are due to jumps of the system between two resistive configurations separated by an energy barrier. An inelastic interaction between an electron and a vibron can shift the molecule from one resistive configuration to other. TLF will not occur due to elastic interactions as there is no energy transfer. The sensitivity of two-level fluctuations to inelastic interactions and not to the elastic scattering of electron waves makes their detection via noise into a new tool for spectroscopy. Use of shot noise as a tool for spectroscopy has been shown previously as well with the name of inelastic electron noise spectroscopy (IENS)[24]. By studying inelastic interactions in Au atomic point contacts, deviations from the linear $2eIF$ relation for shot noise has been demonstrated. As the deviations were also linear, a plot of $\mathrm{d}^2S_\mathrm{I}/\mathrm{d}V^2$ as a function of bias forms an IENS spectrum and shows peaks at the positions of the kinks in noise. IENS is similar to inelastic electron tunnelling spectroscopy (IETS), where inelastic effects will be visible as peaks in $\mathrm{d}^2S_\mathrm{I}/\mathrm{d}V^2$ spectra or IETS spectra. The IETS and IENS spectra are directly affected also by the elastic interactions as a result of quantum interference. On the contrary, two-level fluctuations (TLF) increase as the square of the input current or applied bias, similar to 1/f noise. Thus, the $\mathrm{d}^3S_\mathrm{I}/\mathrm{d}V^3$ of the measured noise (S_I) should show peaks corresponding to the TLF excited by inelastic interactions. We call this inelastic electron noise spectroscopy-3 (IENS-3). IENS-3 holds a unique benefit over IENS and IETS because of the insensitivity of TLF to elastic scattering, this new mode of noise spectroscopy can give distinctly clear peaks due to inelastic interactions leading to TLF. To make the third-order derivative of the noise data, we used a commercial OriginPro software which does the 3^{rd} order derivative using a numerical differentiation technique starting from the raw noise data. It is important to take care of the boundaries while doing higher order numerical derivatives. A third-order derivative computed at a voltage bias value relies on the noise values on the two

[1] It is also possible that there are multiple two-level fluctuations excited by the vibrons giving a 1/f noise spectra, but this we cannot confirm with our setup as we cannot measure the full spectra up to the DC level.

[23] Loah A. Stevens et al. In: *Journal of Physics: Condensed Matter* 28 (2016), p. 495303.
[24] Manohar Kumar. PhD thesis. Leiden Institute of Physics (LION), Leiden University, 2012.
[25] Tomá Novotný et al. In: *Phys. Rev. B* 84 (2011), p. 113107.
[26] D. F. Urban et al. In: *Phys. Rev. B* 82 (2010), p. 121414.

adjacent voltage data points on either side.[2] In all the $\mathrm{d}^3S_\mathrm{I}/\mathrm{d}V^3$ spectra presented in this chapter, the derivatives are shown up to a voltage bias where we have more than two data points after it.

Figure 6.5 shows a first example of the benefit of IENS-3 over IETS. Here one can see that the peaks in the IETS spectrum (Figure 6.5 (b)) due to inelastic scattering (in this example at +50 mV) are of similar amplitude as other structure that could be coming from elastic quantum interference effects. On the contrary, in the IENS-3 spectrum, the first peak (marked with an arrow) corresponds to the excitation of a TLF due to inelastic effects. This peak marks clearly the position of the vibration mode energy of the molecule and the spectrum is not affected by the background conductance fluctuations. As we keep increasing further the applied voltage bias, more complex atomic-scale dynamics can lead to other peaks and structures in the IENS-3 spectrum.

Some more examples for comparison between IETS and IENS-3 structures are shown in the Figure 6.5, 6.6 and 6.7. Here again one can see that IENS-3 shows clear peaks marking the position of inelastic interactions which could excite TLF. Important to note is that IENS will detect only those inelastic interactions which lead to two-level fluctuations. This probably explains why in the first example shown in Figure 6.7, the IETS spectrum shows the position of the vibration mode of the Pt metallic leads at a low bias of around 10 mV, while there is no signature in the corresponding IENS-3 spectrum shown in Figure 6.7 (d).

6.5 Inelastic tunneling versus two-level fluctuations?

Interesting to note is that all the examples shown in this chapter have no signature of two-level fluctuations in the $\mathrm{d}I/\mathrm{d}V$ measurements. The two-level fluctuations mentioned above can easily be on the time scale of tens of microseconds or smaller making them inaccessible in our AC conductance measurement, performed with a modulation frequency of 667 Hz and a bandwidth of 1 Hz, or less. Depending on the duty cycle[3] of these fluctuations, the measured conductance could be anywhere between the two conductance states. Thus when a two-level fluctuation (TLF) is excited, one would see a step (increase or decrease) in the differential conductance[4] which is different in its physical interpretation from the step due to usual inelastic back-scattering process. Moreover, changes in conductance due to TLF, also occurring at the vibrational energy of the molecule, will then be added to the usual step increase or decrease in conductance you expect from the inelastic effects.

Consequently, this questions the way we study the inelastic scattering in single molecules as these TLF are not included in the theory used for interpreting measured differential conductance for inelastic effects.

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[2] $f'''(x_i) = \frac{f(x_{i+2})-2f(x_{i+1})+2f(x_{i-1})-f(x_{i-2})}{2h^3}$
Here, $h = \Delta x$ = step-size.

[3] Duty-cycle defines the percentage of time the contact stays in high or low conductance states

[4] There will be a peak (or a dip) followed by a step in the differential conductance due to the excitation of the two-level fluctuations.

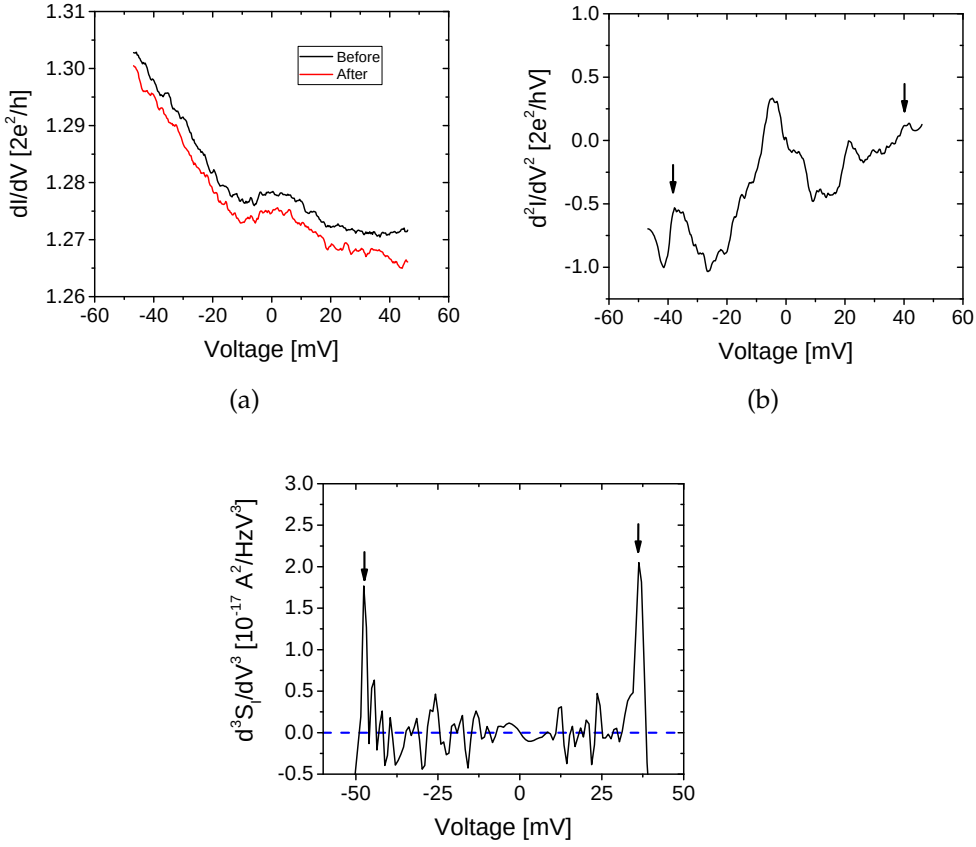

Figure 6.5: (a) Differential conductance for a Pt-D_2-Pt junction taken before (black) and after (red) the noise measurement. (b) Usual IETS spectrum of the junction showing the vibrational modes of the molecule (black arrows) with other equally large peaks possibly due to quantum interference of electron waves. (d) The IENS-3 spectrum showing enhanced peaks corresponding to the positions of the inelastic interactions giving rise to two-level fluctuations in the molecule. The first peak marked with a black arrow points towards a vibrational mode excitation of the molecule. Here the noise measurement is done both for positive and negative voltage bias.

6.5.1 Step-up in junction conductance close to 1 G_0

We report here the possible detection of a step-up or increase in conductance of a Pt-D_2-Pt junction. This has been predicted by Kristensen *et al.*[13] who suggested it as an outcome of coupling of the d-orbital with the usual s-orbital of Pt leads during a transverse hindered rotation mode of vibration. It goes against the conventional norm where contacts with conductance close to 1 G_0 should always have a step-down in conductance (as shown in Figure 6.4) due to back-scattering of electrons. Figure

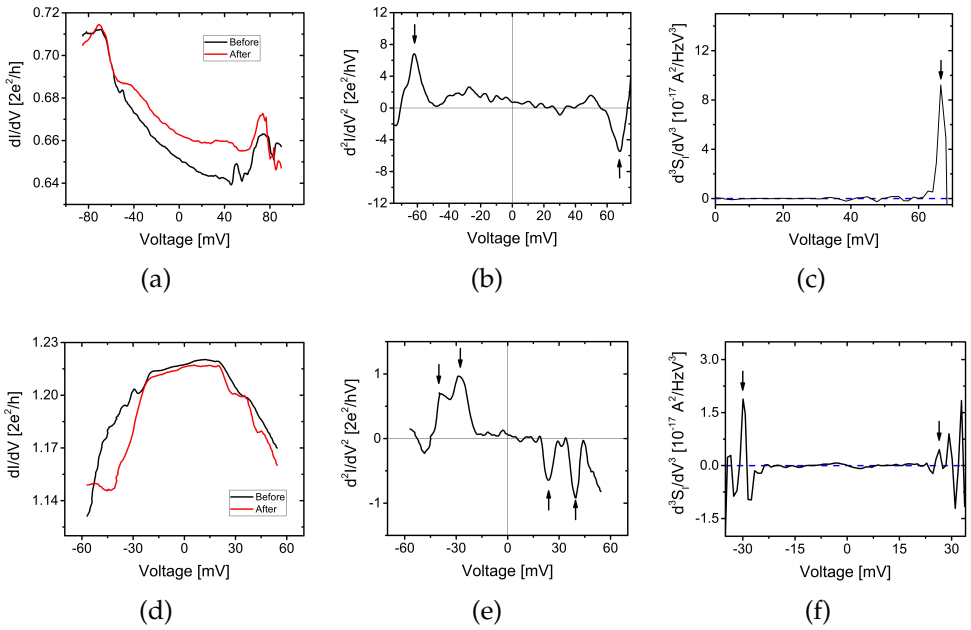

Figure 6.6: Junction 1: (a) Differential conductance for a Pt-D_2-Pt junction taken before (black) and after (red) the noise measurement. (b) Usual IETS spectrum of the junction showing the vibrational modes of the molecule (black arrows). (c) The IENS-3 spectrum showing an enhanced peak corresponding to the position of a vibrational mode of the molecule. Increasing the bias further, marks positions of other inelastic interactions (not shown here) corresponding to more complex atomic-scale dynamics. Here the noise measurement is performed for only positive bias. Junction 2: d) Differential conductance showing a step-down taken before (black) and after (red) the noise measurement. (e) Usual IETS spectrum of the junction showing the vibrational modes of the junction (black arrows). (f) The IENS-3 spectrum showing enhanced peaks corresponding to the positions of inelastic interactions. The first peak marked with a black arrow corresponds to the excitation of a vibrational mode of the molecule. Here the noise measurement is performed for negative to positive bias.

6.7 (a) shows an example of step-up in conductance for a Pt-D_2-Pt junction. In fact, it is similar to Figure 6.7, where now the conductance has been flipped upside down. Again it can be seen that the IETS spectrum in Figure 6.7 (b) shows two peaks with the lowest likely due to a Pt-Pt vibration mode and the higher associated with a Pt-D_2-Pt vibration mode.

Elastic scattering of electronic waves through defects could also cause features that resembles like a step-up in conductance. This possibility cannot be dismissed just by looking at the dI/dV an IETS spectra. However, as for these contacts, the zero-bias conductance is sufficiently far from 1 G_0, so the elastic scattering of electronic waves (discussed in chapter 5) will cause a negligible effect on the linear shot-noise spectra. Thus, the IENS-3 peaks (shown in Figure 6.7 (c)) will pinpoint the inelastic

interactions with certainty. The first peak (marked with the black arrow) although small, should correspond to the excitation of a vibron in the molecule which triggers a TLF. This suggests that the step-up in conductance shown in Figure 6.7 (a) is occurring at a vibration energy of the D_2 molecule between the Pt leads and thus is less likely to be an outcome of a background conductance oscillations caused by elastic scattering.

The example shown in Figure 6.7 (d-f) does not fit in either step-up or step-down picture. We see here that the differential conductance first rises to a particular value and then decreases. This, however, holds similarity to the hindered rotation mode studied using first-principles calculations by Kristensen *et al*.[13] and shown in the top graph in Figure 6.1. The IETS spectrum of this differential conductance, showing step-up followed by the decrease in conductance, will have a peak followed immediately by a dip. A peak in the IETS spectrum usually points towards a step-up in the conductance, while a dip towards a step-down. The IETS spectra for our data (shown in Figure 6.7 (e)) also shows such a dip around 45 mV. Similar to the previous example we calculated the IENS-3 spectrum shown in Figure 6.7 (f). This shows a TLF excitation and so a vibration mode presence already around 30 mV bias. Important to note here is that in the IENS-3 spectra one cannot differentiate between step-up and down in conductance as the TLF triggered by a vibration excitation will always increase the noise. But we do see that the first vibration mode excited in the molecule leaves an IENS-3 peak pointing towards a triggered TLF around 30 mV, which is far from the dip seen in the IETS spectrum. In fact, around 30 mV there is a small peak in the IETS, which might be due to the first step-up in conductance, which is rounded by a conductance oscillations background.

In comparison to what was studied by Kristensen *et al*. , the energy of vibration is different in both the examples shown in Figure 6.7. Possible reasons for it could be different stretched state[4] of the molecule and/or different binding configurations to the leads. We encountered such step-up rarely as compared to the usual step-down behaviour show in the Figure 6.4. This observation does not resolve the discrepancy between theory and experiment, but it shows that the sign observed in the calculations is not fully excluded by the experiment.

6.6 Conclusion

In this chapter, we report using our newly built high-frequency setup[21], high-bias shot-noise measurements to study inelastic electron-vibron interaction for the Pt-D_2-Pt system. A pre-annealed Pt metallic contact is used to avoid unwanted two-level fluctuations in the leads. After that, doing high-bias shot-noise measurements on the Pt-D_2-Pt system, we show that at the energies where a vibrational mode or vibron of the molecule exists the noise changes character. It develops frequency dependence characteristic of TLF. Further, we propose that an enhanced noise spectroscopy can be done using these TLF, by studying the third derivative of the noise signal ($\mathrm{d}^3S_I/\mathrm{d}V^3$). We call this inelastic electron noise spectroscopy-3 (IENS-3). We have shown using several examples how IENS-3 spectrum can possibly detect inelastic scattering processes more precisely than usual IETS spectrum. Moreover, there is no signature of these two-level fluctuations (TLF) in the $\mathrm{d}I/\mathrm{d}V$ measurements. Depending on the duty cycle of the TLF, a step-up or down (after a peak or dip) in the measured conductance can occur at the vibrational energies of the molecule. This change in conductance adds to the usual inelastic back-scattering signal of electrons. Hence, it

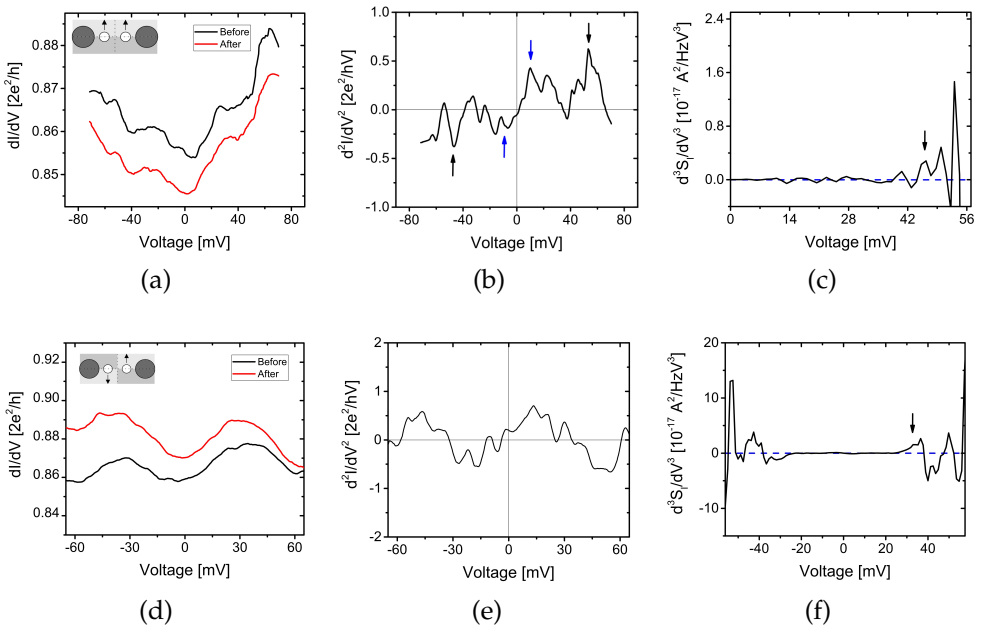

Figure 6.7: Junction 1: (a) Differential conductance for a Pt-D_2-Pt junction showing a step-up or increase in conductance. (b) IETS spectrum of the junction showing multiple peaks, including the vibrational modes of the molecule (black arrows) and that of the leads (blue arrows). (c) The IENS-3 spectrum showing enhanced peaks corresponding to the positions of inelastic interactions (black arrow). Here the noise measurement is performed for only positive bias. Junction 2: d) Differential conductance showing a step-up taken before (black) and after (red) the noise measurement. This is similar to hindered rotation mode shown in Figure6.1. (e) Usual IETS spectrum of the junction showing weak detection of the vibrational modes of the junction (black arrows). (f) The IENS-3 spectrum showing enhanced peak corresponding to the positions of inelastic interactions (black arrow). Here the noise measurement is performed for negative to positive bias.

questions our usual interpretation of the differential conductance measurements in the context of electron-vibron interaction in single-molecule junctions.

In addition, we report detection of a step-up or increase in differential conductance in a few of our Pt-D_2-Pt junctions. This increase is in contrast to the conventional picture where a junction with conduction close to 1 G_0 shows a step-down or decrease in conductance due to back-scattering of electrons. This increase has been attributed to the coupling of the d-orbital of Pt junction to its usual s-orbital[13], under a transverse rotational mode of vibration.