Journal Name

ARTICLE TYPE

Cite this: DOI: 00.0000/xxxxxxxxxx

Supplementary Information: Identification of vibration modes in single-molecule junctions by strong inelastic signals in noise†

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1 Calculation of the third order derivative of the noise

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 adjacent voltage data points on either side.

$$f'''(x_i) = \frac{f(x_{i+2}) - 2f(x_{i+1}) + 2f(x_{i-1}) - f(x_{i-2})}{2h^3} \quad (1)$$

Here, $h = \Delta x =$ step-size. In all the $\mathrm{d}^3 S_\mathrm{I}/\mathrm{d}V^3$ spectra presented in this article, the derivatives are shown up to a voltage bias where we have more than two data points after it.

2 Inelastic tunneling versus two-level fluctuations?

To understand the origin of the steps in conductance due to TLFs, we provide a simple example shown in Fig. 1. Here Fig. 1 (a) shows two linear IVs (red and blue) which corresponds to the two conductance states (G1 and G2) between which the junction is fluctuating. Once the applied voltage hits the vibron energy a TLF is initiated and the current will start to jump between the two conductance states (G1 and G2). As the bias is increased further the size of these jumps in current will increase. These jumps can easily be on the time scale of tens of microseconds or smaller making them inaccessible in the AC conductance measurement, performed with relatively slow modulation frequency (for example in our case it is of 667 Hz and a bandwidth of 1 Hz, or less). Depending on the duty cycle of these fluctuations, the measured conductance could be anywhere between the two conductance states (G_{eff}). Thus when a two-level fluctuation (TLF) is excited, one would see a step (increase or decrease) in the differential conductance as shown in Fig. 1 (b), 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. As the peaks preceding the step in the conductance due to TLFs may or may not be resolved in the experimental differential conductance data, it is hard to tell seeing a step in IETS signal whether it is coming from the inelastic interactions or the TLFs.

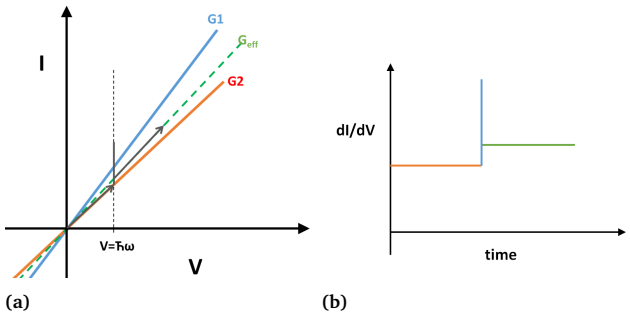

Fig. 1 (a) Linear IV curve models showing two conductance states G1 (blue), G2 (red) and an effective conductance G_{eff} (green dashed line). (b)Differential conductance trace vs time, showing that once a vibron is excited, there will be a spike in the conductance followed by a change in conductance to G_{eff}.

3 Step-up in junction conductance close to 1 G_0

For junctions having a single conductance channel and a transmission close to 1 the inelastic signals in the differential conductance show up as a small step downward. In exceptional cases we have detected a step-up, or increase in conductance of a Pt-D_2-Pt junction. This would seem consistent with first-principle calculations by Kristensen *et al.*[1], who suggested it is an outcome of coupling of the d-orbital with the usual s-orbital of Pt leads during a transverse hindered rotation mode of vibration. Fig. 3 (a) shows an example of step-up in conductance for a Pt-D_2-Pt junction. In fact,

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it is similar to Fig. 3 (in the main text), where now the conductance has been flipped upside down. Again it can be seen that the IETS spectrum in Fig. 3 (b) shows two peaks with the lower one likely due to a Pt-Pt vibration mode and the higher associated with a Pt-D_2-Pt vibration mode.

We caution that 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 and IETS spectra. For shot noise, however, however, as for these contacts the zero-bias conductance is sufficiently far from 1 G_0, so the elastic scattering of electronic waves[2] will cause a negligible effect on the linear shot-noise spectra. Thus, the IENS-3 peaks (shown in Fig.3 (c)) will pinpoint the inelastic interactions more easily. 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 Fig. 3 (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 Fig. 3 (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 holds similarity to the hindered rotation mode studied using first-principles calculations by Kristensen *et al.*[1] and shown in the top graph in Figure 2. 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 Fig. 3 (e)) also shows such a dip around 45 mV. Similar to the previous example we calculated the IENS-3 spectrum shown in Fig. 3 (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 Fig. 3. Possible reasons for it could be different stretched state[3] 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 Fig. 3(a) of the main text. 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.

4 Other examples of IENS-3 measurements

Figure 4 has two more examples, showing the measurement of the IENS-3 signals for both polarity of bias voltages. Again you can see here a TLF is excited in both the cases at the vibron energy of the junction leading to peaks in the IENS-3 measurements.

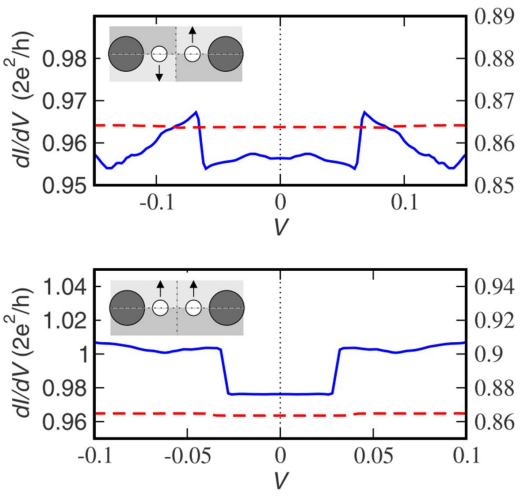

Fig. 2 First-principles calculations from Kristensen *et al.*[1] showing differential conductance of the Pt-H_2-Pt (solid blue line) and Au-H_2-Au (dashed red line) junctions when scattering on a single transverse vibrational mode. The top figure shows a hindered rotations mode and the bottom figure shows a transverse center of mass mode. (Figure reproduced from Kristensen *et al.*[1])

Notes and references

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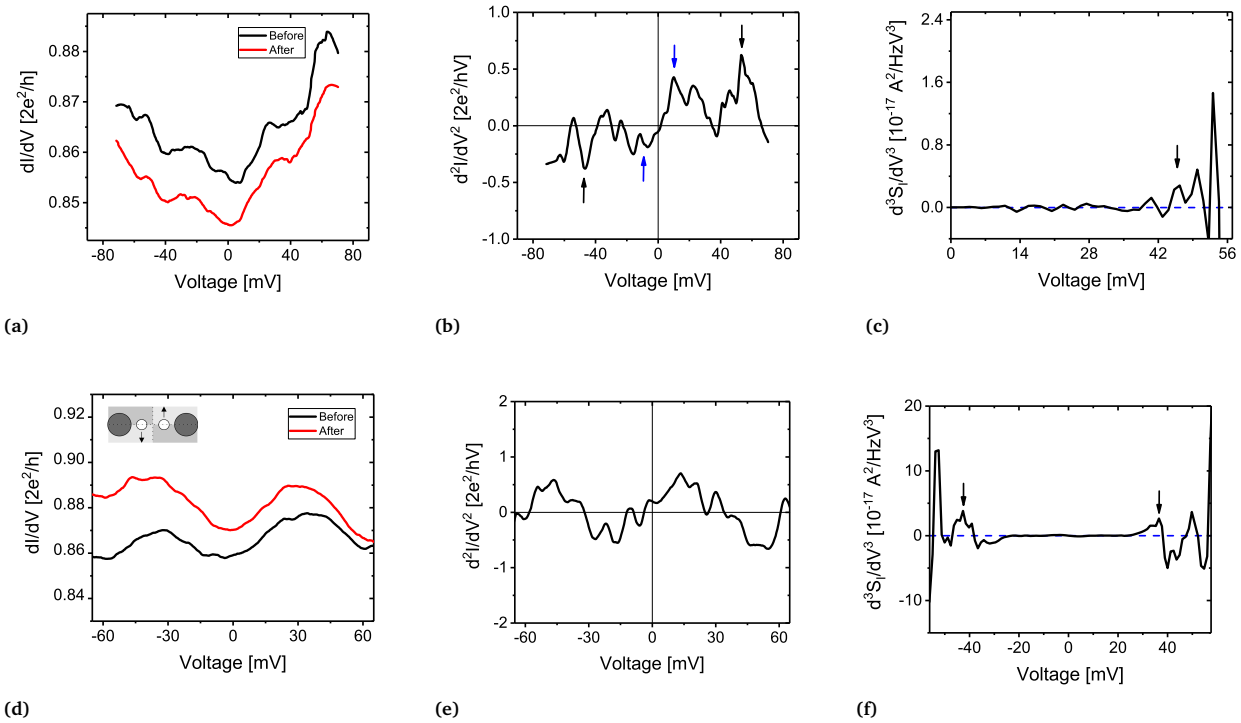

Fig. 3 Junction 3: (a) Differential conductance for a Pt-D_2-Pt junction showing a step-up or increase in conductance. (b) IETS spectrum of the junction showing multiple peaks, including the vibrational modes of the molecule (black arrows) and that of the leads (blue arrows). (c) The IENS-3 spectrum showing enhanced peaks corresponding to the positions of inelastic interactions (black arrow). Here the noise measurement is performed for only positive bias. Junction 4: 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 Fig.2. (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.

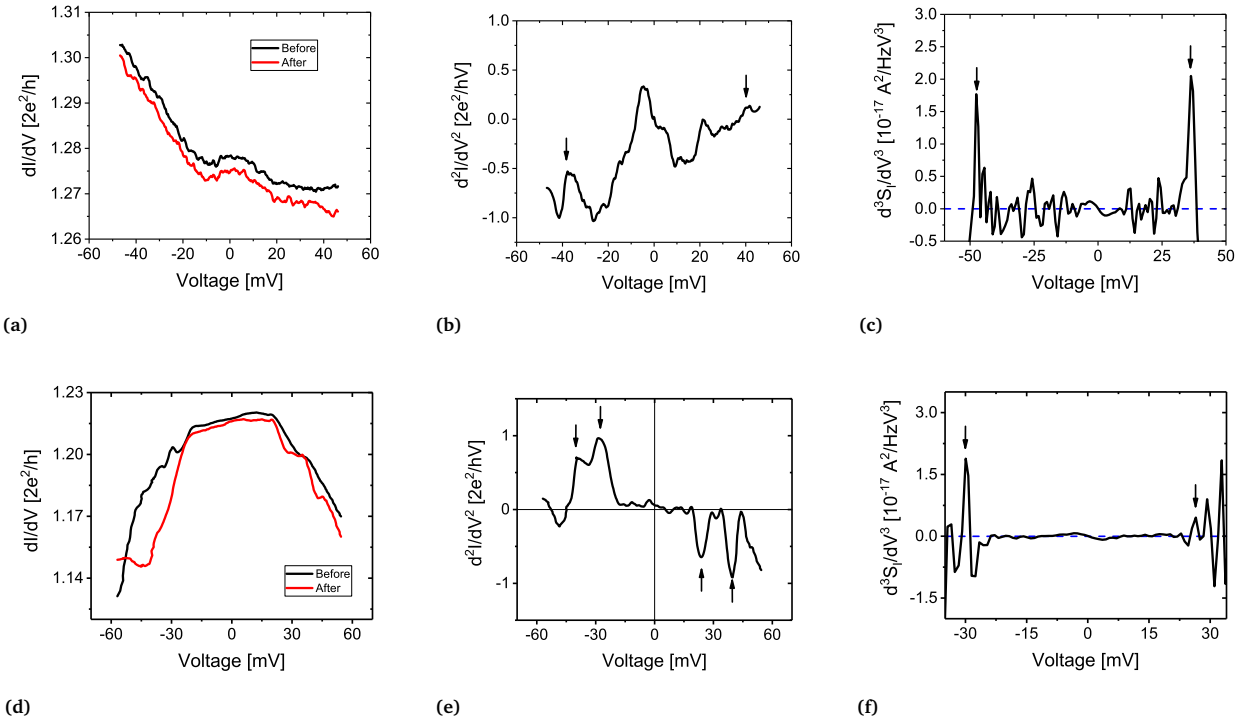

Fig. 4 Other Examples. Junction 5: (a) Differential conductance for a Pt-D_2-Pt junction taken before (black) and after (red) the noise measurement. (b) Usual IETS spectrum of the junction showing the vibrational modes of the molecule (black arrows). (c) The IENS-3 spectrum showing an enhanced peak corresponding 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 6: 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.