# SI for "Identification of vibrational signatures from short chains of interlinked molecule-nanoparticle junctions obtained by inelastic electron tunnelling spectroscopy "

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# I. DETAILS OF THE AB-INITIO CALCULATION OF MOLECULAR VIBRATIONS AND INELASTIC SPECTRA OF ODT BETWEEN TWO AU ELECTRODES

The theoretical calculations were performed using previously reported methods (Jafri *et al.*, 2010; Prasongkit *et al.*, 2010). Using the density functional theory (DFT) based code SIESTA(Soler *et al.*, 2002), the ODT adsorption structures were first optimized between two Au(111) surfaces and followed by phonon calculations. The IETS was calculated in the lowest order expansion (LOE) method (Paulsson *et al.*, 2006) where TranSIESTA (Brandbyge *et al.*, 2002) is used to calculate the elastic electron transport which is combined with the electron-phonon (e-ph) couplings in Inelastica(Frederiksen *et al.*, 2007) to calculate the inelastic response. All calculations were performed using the local-density approximation (LDA) for the exchange correlation potential, core electrons were modeled with Troullier–Martins soft norm-conserving pseudopotentials (Troullier and Martins, 1991) and the valence electrons were a single-zeta polarized (SZP) were used(Junquera *et al.*, 2001). To apply LOE the system needs to have a weak e-ph coupling and the density of states close to Fermi energy should vary slowly. This can be justified by the transmission spectra in Fig. S1 which has no sharp peaks close to the Fermi energy, hence the conductance is almost bias independent. It has also been shown that less then 3% of the electrons undergo inelastic scattering for alkanethiols(Okabayashi *et al.*, 2008).

The calculated IETS for the ODT molecule sandwiched between two gold surfaces are shown in Fig. S2 together with the most important vibrations modes influencing the current. These modes are  $E_{\nu 1} \sim 40$  meV (Au-S stretch),  $E_{\nu 2} \sim 80$  meV (C-S stretch),  $E_{\nu 3} \sim 110$  meV (CH<sub>2</sub> twist),  $E_{\nu 4} \sim 122$  meV and  $E_{\nu 5} \sim 142$  meV (two different modes of C-C stretch)

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Figure S1: Zero-bias transmission for ODT molecule sandwiched between two gold electrodes



Figure S2: (a) Inelastic spectra  $(d^2I/dV^2)$  for a ODT molecule between gold electrodes. (b)-(f) The five vibration modes with most influence on the current. Au-S stretch, C-S stretch, CH2 twist and two different C-C stretch

### **II. MODEL OF CARRIER TRANSPORT THROUGH THE MOLECULAR JUNCTIONS**

#### A. Model of the set-up and charge current

We assume that the molecules function only as vibrating tunnel barriers with no electronic level that take an active part in the conduction. We therefore propose to employ the model

$$\mathcal{H} = \mathcal{H}_{L/R} + \mathcal{H}_{NP} + \mathcal{H}_T,\tag{1}$$

where  $\mathcal{H}_{\chi} = \sum_{\mathbf{k}\sigma \in \chi} \varepsilon_{\mathbf{k}} c_{\mathbf{k}\sigma}^{\dagger} c_{\mathbf{k}\sigma}$  is the free electron like electronic structure for the electrode  $\chi = L, R$ . Here, an electron with energy is created (annihilated) in the state  $|\mathbf{k}\sigma\rangle$  at the energy  $\varepsilon_{\mathbf{k}}$  and spin  $\sigma = \uparrow, \downarrow$  by  $c_{\mathbf{k}\sigma}^{\dagger}$  ( $c_{\mathbf{k}\sigma}$ ). Further, the Hamiltonian  $\mathcal{H}_{\mathrm{NP}} = \sum_{m\sigma} \varepsilon_m d_{m\sigma}^{\dagger} d_{m\sigma} + \sum_m U_m n_m \uparrow n_{m\downarrow}$  denotes the electrons in the nano particles (NPs), where electrons are created (annihilated) in the state  $|m\sigma\rangle$  with energy  $\varepsilon_m$  by  $d_{m\sigma}^{\dagger} (d_{m\sigma})$ . The coupling between the metallic components via the molecules are described by the tunneling contribution  $\mathcal{H}_T$ . This Hamiltonian contains both the elastic and inelastic contributions to the tunneling, where we have introduced

$$\mathcal{H}_{\rm el}^{(\chi)} = \sum_{\mathbf{k}m\sigma} v_{\mathbf{k}m} c_{\mathbf{k}\sigma}^{\dagger} d_{m\sigma} + H.c., \tag{2}$$

$$\mathcal{H}_{\rm el}^{\rm (NP)} = \sum_{mm'\sigma} v_{mm'} d_{m\sigma}^{\dagger} d_{m'\sigma} + H.c., \tag{3}$$

$$\mathcal{H}_{\text{inel}}^{(\chi)} = \sum_{\mathbf{k}m\sigma l} v_{\mathbf{k}m} \lambda_l (b_l + b_l^{\dagger}) c_{\mathbf{k}\sigma}^{\dagger} d_{m\sigma} + H.c., \tag{4}$$

$$\mathcal{H}_{\text{inel}}^{(\text{NP})} = \sum_{mm'\sigma l} v_{mm'} \lambda_l (b_l + b_l^{\dagger}) d_{m\sigma}^{\dagger} d_{m'\sigma} + H.c.,$$
(5)

where the first two terms describe the elastic tunneling between an electrode and a NP, and between two NPs, respectively, whereas the last two terms describe the corresponding vibration assisted tunneling.

Using standard (non-equilibrium) methods we write the elastic tunneling current through an arbitrary molecule as

$$I_{\rm el} = 2e \sum_{ij\sigma} |v_{ij}|^2 \int \frac{G_{i\sigma}^{>}(\omega)G_{j\sigma}^{<}(\omega') - G_{i\sigma}^{<}(\omega)G_{j\sigma}^{>}(\omega')}{\omega - \omega' + eV + i\delta} \frac{d\omega}{2\pi} \frac{d\omega'}{2\pi},\tag{6}$$

where the indices i (j) denotes the metallic contact to the left (right) of the molecule. The contact may either an electrode ( $\mathcal{H}_{(\chi)}$ ) or an NP ( $\mathcal{H}_{(NP)}$ ). The lesser (greater) Green function (GF)  $G_{i\sigma}^{<(>)}(\omega)$  describe the electronic structure in contact i, and V denotes the bias voltage across the junction. We can assume stationary conditions since there are no time-dependent external fields acting on the system.

The GF for the electrons in the electrodes can be written  $g_{\mathbf{p}\sigma}^{</>}(\omega) = (\pm i)2\pi f(\pm \omega)\delta(\omega - \varepsilon_{\mathbf{p}})$ , where f(x) is the Fermi distribution function. For the NPs we have to consider the charging energy  $U_m$ . For simplicity though, we calculate the NP GF in the atomic limit. This will give an inclusion of the charging, or activation, energy present in the NP. The atomic limit is a reasonable approximation considering that the NPs are well separated from one another and from the electrodes, and since the molecules between in the system merely act as potential barriers, let be vibrating, between the metallic parts. Under those assumptions we can write the GF for the NP

$$G_{m\sigma}^{}(\omega) = (\pm i)2\pi f(\pm \omega)[\langle 1 - n_{m\bar{\sigma}}\rangle\delta(\omega - \varepsilon_m) + \langle n_{m\bar{\sigma}}\rangle\delta(\omega - \varepsilon_m - U_m)],\tag{7}$$

where the occupation number  $\langle n_{m\sigma} \rangle$  is calculated through the equation

$$\langle n_{m\sigma} \rangle = (-i) \int G_{m\sigma}^{<}(\omega) \frac{d\omega}{2\pi} = f(\varepsilon_m) - \langle n_{m\bar{\sigma}} \rangle [f(\varepsilon_m) - f(\varepsilon_m + U_m)], \tag{8}$$

leading to

$$\langle n_m \rangle = \frac{f(\varepsilon_m)}{1 + f(\varepsilon_m) - f(\varepsilon_m + U_m)}.$$
(9)

under the spin-degenerate conditions (giving  $\langle n_{m\sigma} \rangle = \langle n_m \rangle$ ). Expressing the NPs in terms of the GF  $G_m$  reflects that the Coulomb repulsion in the NPs is not completely screened out, thus, the electrons are not completely free. Calculating the state occupations according to the formula in Eq. (9) is a result of correlated states in the NPs.

Using the GFs for the electrodes and the NPs, we can write the elastic current between an electrode and NP as

$$I_{\rm el}^{\chi 1}(V) = 2e\Gamma_{\chi} \int \left( f(\omega) - f(\omega + eV) \right) \left( 1 - \langle n_1(\omega + eV) \rangle + \langle n_1(\omega - U_1 + eV) \rangle \right) d\omega, \tag{10}$$

where  $\Gamma_{\chi} = 2\pi |v|^2 \rho_{\chi} \rho_{\text{NP}}$  defines the coupling between the electrode and the NP in terms of the densities of electron states  $\rho_{\chi}$  and  $\rho_{\text{NP}}$  and the tunneling rate v. The expression is obtained under the assumption that the density of electron states in the NP is continuous and slowly varying with energy.

By the same token we write the elastic current between two NPs according to

$$I_{el}^{12}(V) = 2e\Gamma \int \left\{ \left( f(\omega) - f(\omega + eV) \right) \langle 1 - n_1(\omega) \rangle \left( \langle 1 - n_2(\omega + eV) \rangle + \langle n_2(\omega - U_2 + eV) \rangle \right) + \left( f(\omega + U_1) - f(\omega + U_1 + eV) \right) \langle n_1(\omega + U_1) \rangle \left( \langle 1 - n_2(\omega + U_1 + eV) \rangle + \langle n_2(\omega + U_1 - U_2 + eV) \right) d\omega$$
(11)

From this expression we observe similar features as we did above, however, here the assumption of correlated states in the NPs make an impact on the electrons both tunneling out from an NP as well as into an NP.

The vibration assisted tunneling can be expressed in quite a similar fashion, that is, we have

$$I_{\rm inel} = -2e \operatorname{Re} \sum_{ijl\sigma} \lambda_l^2 |v_{ij}|^2 \int \frac{G_{i\sigma}^<(\omega) G_{j\sigma}^>(\omega') \mathcal{D}_l^>(\omega'') - G_{i\sigma}^>(\omega) G_{j\sigma}^<(\omega') \mathcal{D}_l^<(\omega'')}{\omega - \omega' - \omega'' + eV + i\delta} \frac{d\omega}{2\pi} \frac{d\omega'}{2\pi} \frac{d\omega''}{2\pi}.$$
 (12)

Here, the GF for the vibrations,  $\mathcal{D}_{l}^{</>}$  is given by

$$\mathcal{D}_{l}^{}(\omega) = (-i)2\pi [n_{B}(\omega_{l})\delta(\omega \mp \omega_{l}) + \{1 + n_{B}(\omega_{l})\}\delta(\omega \pm \omega_{l})],$$
(13)

where  $n_B(x)$  is the Bose distribution function. The currents of interest are, thus, given by

$$I_{\text{inel}}^{\chi 1}(V) = 2e\Gamma_{\chi} \sum_{l,s=\pm 1} \lambda_l^2 \int \left\{ n_B(\omega_l) \left( f(\omega) - f(\omega - s\omega_l + eV) \right) \left( \langle 1 - n_1(\omega - s\omega_l + eV) \rangle + \langle n_1(\omega - U_1 - s\omega_l + eV) \rangle \right) + sf(s\omega) f(-s[\omega + eV] + \omega_l) \left( \langle 1 - n_1(\omega - s\omega_l + eV) \rangle + \langle n_1(\omega - U_1 - s\omega_l + eV) \rangle \right) \right\} d\omega,$$

$$(14a)$$

$$\begin{split} I_{\rm inel}^{12}(V) = & 2e\Gamma \sum_{l,s\pm 1} \lambda_l^2 \int \bigg\{ n_B(\omega_l) \Big( f(\omega) - f(\omega - \omega_l + eV) \Big) \langle 1 - n_1(\omega) \rangle \\ & \times \Big( \langle 1 - n_2(\omega - s\omega_l + eV) \rangle + \langle n_2(\omega - U_2 - s\omega_l + eV) \rangle \Big) \\ & + n_B(\omega_l) \Big( f(\omega + U_1) - f(\omega + U_1 - s\omega_l + eV) \Big) \langle n_1(\omega + U_1) \rangle \\ & \times \Big( \langle 1 - n_2(\omega + U_1 - s\omega_l + eV) \rangle + \langle n_2(\omega + U_1 - U_2 - s\omega_l + eV) \rangle \Big) \\ & + sf(s\omega) f(-s[\omega + eV] + \omega_l) \langle 1 - n_1(\omega) \rangle \\ & \times \Big( \langle 1 - n_2(\omega - s\omega_l + eV) \rangle + \langle n_2(\omega - U_2 - s\omega_l + eV) \rangle \Big) \\ & + sf(s[\omega + U_1]) f(-s[\omega + eV] - U_1 + \omega_l) \langle n_1(\omega) \rangle \\ & \times \Big( \langle 1 - n_2(\omega + U_1 - s\omega_l + eV) \rangle + \langle n_2(\omega + U_1 - U_2 - s\omega_l + eV) \rangle \Big) \bigg\} d\omega. \quad (14b) \end{split}$$

For the calculations we have assumed that the NPs have equal charging energies, i.e.  $U_m = U$ , reflecting equivalent NPs. We observe that there is an interplay between the inelastic modes and the charging energies, which will be reflected in the transport curves.

#### B. Current through a chain

Consider a chain of N molecules and N-1 NPs and let the end molecules be connected to one electrode each, see Fig. 3 (a) in the paper. Let the current through the chain be denoted by  $I_N$  and let the current through each junction be denoted by  $I_n$ . From classical circuit theory it is known that the current of resistances in series is connected to the total current by

$$\frac{1}{I_N} = \frac{1}{N} \sum_n \frac{1}{I_n},\tag{15}$$

from which we write the total current  $I_N$  in terms of the currents  $I_n$  through each tunnel junction n as  $I_N = N(\sum_n 1/I_n)^{-1}$ .

For chains in parallel, the currents through the individual channels can simply be added according to  $I_{\text{tot}} = \sum_{N} a_N I_N$ , where the coefficients  $a_N$  describe the number of N-junctions chains. Those coefficients are determined using least square fitting, i.e. minimizing the function  $Q = \sum_{N} (a_N I_N - I_{\text{exp}})^2$ , where  $I_{\text{exp}}$  is the experimental current.

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