Electron-Phonon Interactions in Single Octanedithiol Molecular Junctions

Supporting Information

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Power dissipation in a single molecule junction:

In the main text we discuss the possibility of fitting the conductance changes in a molecular junction due to phonon modes using a simplified model.[1, 2] This model will allow us to extract some useful information about the damping of phonon modes, and allow us to compare the conductance changes in different molecular junctions in a straightforward manner. In Figure S1a, we show the results of the fitting including broadening due to the use of a lock-in amplifier for measuring the first-derivative. However, in addition to fitting the conductance curve, the fitting parameters also provide a framework for determining the power dissipated in the molecule by each phonon mode:

$$I = \frac{e^2}{\pi\hbar^2}\tau V + \frac{1-2\tau}{4}\pi\sum_{\lambda} I_{sym}\frac{\gamma_{eh\lambda}}{\omega_{\lambda}} \tag{1}$$

$$I_{sym} = \frac{e}{\pi\hbar}\left(2eVn_{\lambda} + \frac{\hbar\omega_{\lambda}-eV}{e^{\frac{\hbar\omega_{\lambda}-eV}{kT}}-1} - \frac{\hbar\omega_{\lambda}+eV}{e^{\frac{\hbar\omega_{\lambda}-eV}{kT}}-1}\right) \tag{2}$$

$$P = \sum_{\lambda}\left[\gamma_{eh\lambda}\hbar\omega_{\lambda}\left(n_B - n_{\lambda}\right) + \frac{\gamma_{eh\lambda}\pi}{4\omega_{\lambda}}\mathcal{P}\right] \tag{3}$$

$$\mathcal{P} = \frac{\hbar\omega_\lambda}{\pi\hbar}\frac{\left[\cosh\left(\frac{eV}{kT}\right)-1\right]\coth\left(\frac{\hbar\omega_\lambda}{2kT}\right)\hbar\omega_\lambda - eV\sinh\left(\frac{eV}{kT}\right)}{\cosh\left(\frac{\hbar\omega}{kT}\right)-\cosh\left(\frac{eV}{kT}\right)} \qquad (4)$$

In these equations τ is the transmission probability, n_λ is the bias dependent phonon occupation number including non-equilibrium heating,[6, 44] k is the Boltzmann constant, T is the temperature, $\hbar$ is the Plank constant, n_B is the Bose-Einstein distribution, ω is the phonon mode frequency, V is the applied bias, and γ_{eh} and γ_d are the electron-hole and external phonon damping rates. Equations 1 and 2 are described in the main text, and equations 3 and 4 give the power dissipated by the phonon modes. The occupation probability must be determined for each phonon mode in order to perform the fitting. The occupation is found by solving a simple rate equation for the steady state case:

$$\dot{n}_\lambda = \frac{P}{\hbar\omega} + \gamma_d[n_B(\hbar\omega) - n_\lambda] \qquad (5)$$

Since at steady state there should be no change in the phonon occupation, this equation is set to zero to solve for n_λ. Solving this equation results in an expression for n_λ that increases linearly once the phonon mode energy is surpassed by the applied bias. It should be noted that this assumption necessarily requires that if γ_d=0, then P must also equal zero. However, in order to achieve an acceptable fit of the experimental data, γ_d must be included in the fitting parameters, yielding a nonzero power term for the molecular device. This is a reasonable result since we previously observed local heating behavior in octanedithiol molecular junctions.[3, 4] Using the fitting parameters defined in the main text (τ=4.05x10^{-5}, $\hbar\omega/e$=17, 51, and 93mV, γ_{eh}=3.6x10^7, 2.5x10^7, and 1.4x10^8 s^{-1}, and γ_d =15γ_{eh}, 5γ_{eh}, and 1γ_{eh} for each of the three modes respectively) results in a total molecular power dissipation of 0.42 pW at 150 mV. The total power dissipated

by the system is 76 pW at this bias. Clearly, the power dissipated by the molecule is a small fraction of the total power dissipated, the results are shown in Figure S1.

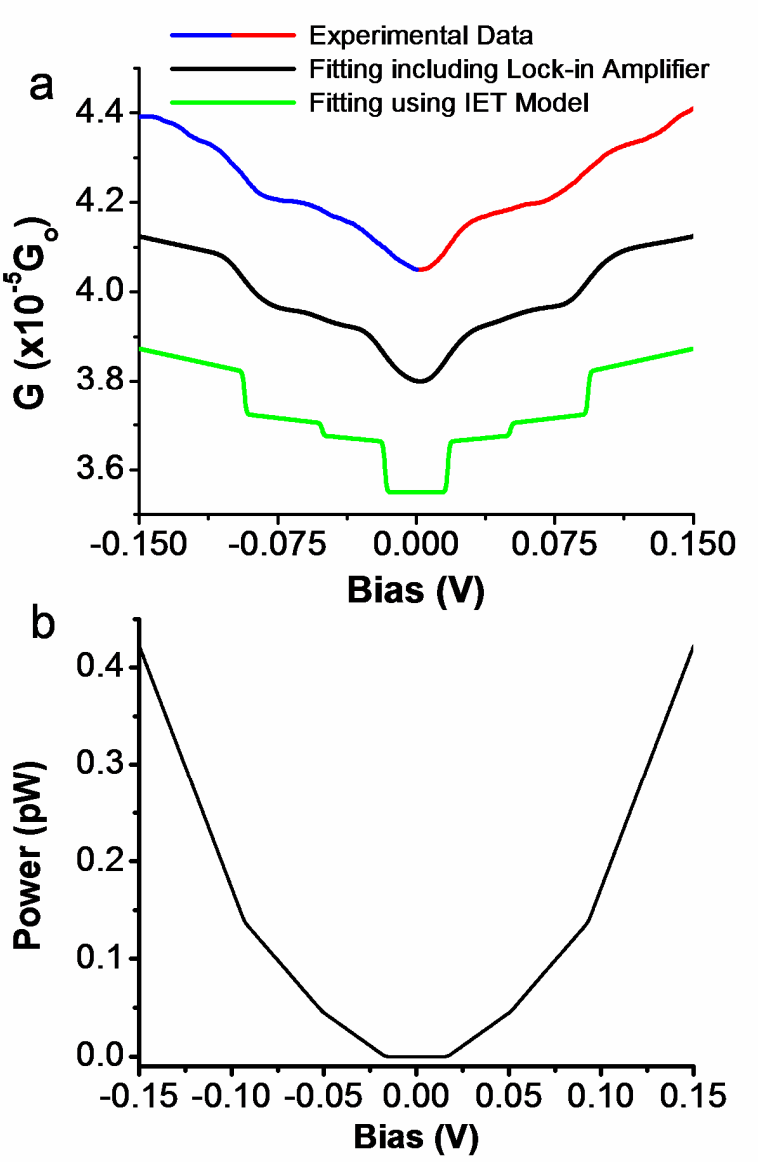

Figure S1. a) Reproduces Figure 3a from the text and shows explicitly the effect of including the lock-in amplifier in the model. The red and blue curve is the experimental data, and the black curve is the fitted curve including the broadening from the lock-in amplifier, and the green curve is the fitting without including the lock-in amplifier. b) demonstrates the power dissipated in the molecular junction as a function of the bias. Clearly, as each mode is activated, an additional slope in the power dissipation occurs.

References:

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2. Frederiksen, T.; Paulsson, M.; Brandbyge, M.; Jauho, A. P., Inelastic Transport Theory from First Principles: Methodology and Application to Nanoscale Devices. *Phys. Rev. B: Condens. Matter* 2007, 75.
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