Supporting information for: A Self Energy Model of Dephasing in Molecular Junctions

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Dephasing Correction in a Metabenzene Junction

We applied the dephasing model to a metabenzene junction, a minimal molecular system which exhibits a strong suppresion of the transmission in the middle of the HOMO-LUMO gap due to quantum interference (QI) between the frontier orbitals. The chemical structure of the junction and the corresponding transmission curve are shown in Figure S1.

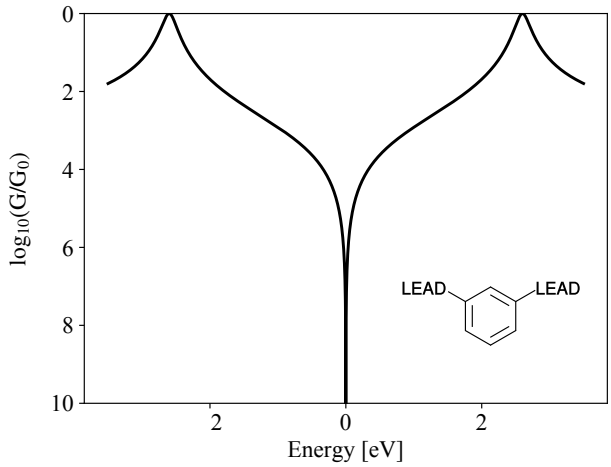

Figure S1: Chemical structure (inset) of the metabenzene junction and conductance calculated in MO basis.

We choose this system as the QI effect on the transmission is qualitatively similar to the case of anthraquinone (AQ) and results from previous authors are available for direct comparison. The QI feature is well captured with both a minimal two sites and a Hückel Tight Binding (TB) model. In the two sites model the interference is given by a stub-like effect: one site is coupled to both leads and to a second site acting as a resonator. The corresponding Hamiltonian and the coupling with the leads (in wide band approximation) are defined as:

$$H = \begin{pmatrix} 0 & -t \\ -t & 0 \end{pmatrix} \tag{1}$$

$$\Gamma_{L,R} = \begin{pmatrix} v & 0 \\ 0 & 0 \end{pmatrix} \tag{2}$$

We choose values in order to fit the calculation from Markussen and Thygesen:[S1] $t = 2.6$eV and $v = 0.2$eV. The authors calculate the current in presence of electron-phonon interaction by including an inelastic SCBA model. In the following we will compare with their results.

In a TB representation, the hopping matrix is the same as in the two sites model, but the coupling with the leads is applied on the meta substitution, as pictured in the inset of Figure S1. We calculate the current by introducing temperature in two different ways: through the thermal broadening in the leads only (coherent current) and through the combined effect of thermal broadening and dephasing self energy (incoherent current). We use the terms "coherent" and "incoherent" to avoid confusion with the use of the expression "elastic current" in the reference[S1] to define the current obtained by Landauer formula for a non-interacting system. This definition is misleading in the context of our work, as the contribution from the interacting system (captured by the dephasing model) is elastic as well, but can not be included at the level of Landauer formula.

The SCBA inelastic calculation is assuming a single-phonon bath with energy $\hbar\omega = 0.073$eV and coupling (in the two sites basis):

$$M = \begin{pmatrix} m & m \\ m & m \end{pmatrix} \tag{3}$$

where $m = 0.060$eV. We choose the value of dephasing coupling which reproduces the inelastic calculation better at room temperature and calculate the current-temperature char-

acteristics for a Fermi energy ε_F at the QI transmission dip and a bias $\Delta V = 0.1$V. The calculation is done for both the two sites and TB model. The result is shown in Figure S2.

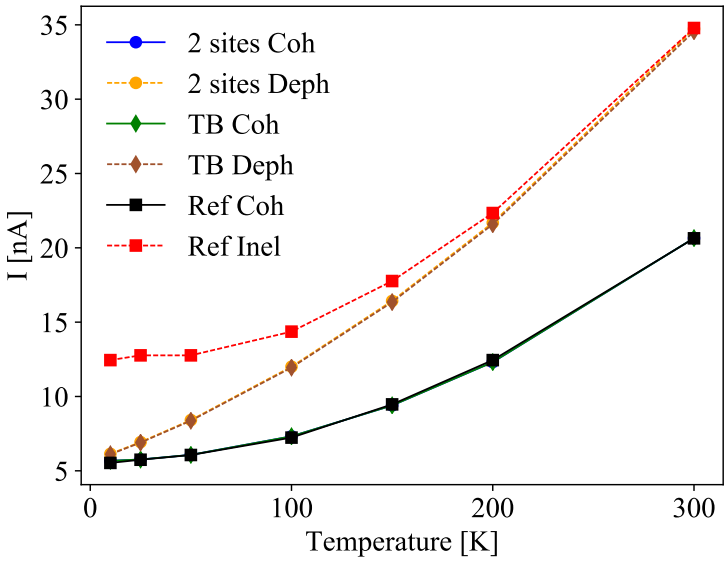

Figure S2: Current-temperature plot for the metabenzene junction at a bias $\Delta V = 0.1$V. In the legend "Coh" and "Deph" refer to the coherent current and to the incoherent current with the dephasing self energy for the two sites and TB model. The reference data includes the coherent current ("Ref Coh") and the incoherent current with the inelastic SCBA Self energy ("Ref Inel"). Reference data is extracted from the work of Markussen and Thygesen[S1] (Figure 5a in reference).

The coherent curves for the two sites and TB model and the reference data are completely overlapped, assuring that the choice of parameters for the non-interacting system is consistent. The dephasing coupling in the two sites model has been chosen as $\gamma = k_B T \times 0.08$eV, to reproduce the value of inelastic current at room temperature. The value of the coupling for the TB representation is set as $\gamma = 3k_B T \times 0.24$eV. The factor 3 arises from the ratio between the Hückel TB and the two sites model basis consistently to the arguments in the body of the paper. The curves for the two different representations are overlapped and almost indistinguishable, verifying that the scaling of the dephasing parameter works as expected. We can evaluate the electron-phonon coupling energy for this model as $2m^2/(\hbar\omega) = 0.1$eV. The value is close to the fitting quantity for the two sites model, even though not identical. We may attribute the quantitative difference to different factors: we are enforcing locality

of the oscillators and the high occupation limit approximation is quantitatively wrong in this case, therefore the difference from the expected γ is probably compensating for those approximations.

The inelastic and the dephasing model are quite close to each other for sufficiently large temperatures (> 150K), consistently with the underlying physical assumptions. The results obviously differ completely at lower temperatures. The inelastic model can successfully capture the opening of additional conduction channel when $\Delta V > \hbar\omega$ while all the low temperature physics is ignored in the dephasing model.

References

(S1) Markussen, T.; Thygesen, K. S. Temperature Effects on Quantum Interference in Molecular Junctions. *Phys. Rev. B* **2014**, *89*, 085420.