Strong Overtones Modes in Inelastic Electron Tunneling Spectroscopy with Cross-Conjugated Molecules: A Prediction from Theory

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Supplementary Materials

Calculating IETS

The starting point for calculating IETS is the famous Meir-Wingreen equation.\textsuperscript{1}

\[ I(V) = \frac{2e}{h} \int_{-\infty}^{\infty} Tr[\Sigma_{L}^{\leq}(E)G^{\geq}(E) - \Sigma_{L}^{\geq}(E)G^{\leq}(E)]dE \]  

The in-(out-)scattering of the contacts is simply,

\[ \Sigma_{L(R)}^{\leq}(E) = if_{L(R)}\Gamma_{L(R)}, \]  

\[ \Sigma_{L(R)}^{\geq}(E) = -i(1 - f_{L(R)})\Gamma_{L(R)}, \]  

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where \( f_{L(R)} \) is the Fermi function of the left and right contact and \( \Gamma_{L,R} \) is the coupling to the electrodes. \( G^{<}(\gamma) \) satisfy the Keldysh-Kadanoff-Baym-equation

\[
G^{<}(\gamma) = G^r(\gamma)(\Sigma^L + \Sigma^R + \Sigma^\text{ph})G^a(\gamma)
\]

With the retarded (advanced) greens functions defined in the usual way

\[
G^{r(a)}(\gamma) = [(\gamma \pm i\eta)S_D - H_D - \Sigma_L - \Sigma_R]^{-1}
\]

Here, \( S_D \) and \( H_D \) are the overlap and the Hamiltonian of the device region respectively and \( \eta \) is a positive infinitesimal.

The energy dependence of the self-energy is neglected (wide-band approximation), which is a reasonable approximation since the density of states for gold is quite flat near the Fermi energy.

The last term in 4 introduces the electron-phonon interactions within the First-Order Born approximation.

\[
\Sigma^\text{ph}(\gamma) = \sum_q \frac{i}{2\pi} \int_{-\infty}^{\infty} \alpha_q G^{<}(\gamma)(\gamma - \gamma')\alpha_q D^{<}(\gamma) d\gamma,
\]

where the \( \alpha_q \) is the electron-phonon coupling matrix for normal mode \( q \).

\[
\alpha_q = \frac{\partial H}{\partial Q_q} - \frac{\partial S}{\partial Q_q}S^{-1}H - HS^{-1}\frac{\partial S}{\partial Q_q}
\]

The non-orthogonality of the basis is reflected by the presence of the overlap matrix \( S \). The free-phonons greens function, \( D^{<}_0 \), is

\[
D^{<}_0(\gamma) = -2\pi i[(N_q + 1)\delta(\gamma \pm \omega_q) + N_q\delta(\gamma \mp \omega_q)]
\]
Assuming the zero temperature limit and that the phonons are in thermodynamic equilibrium with a bath, i.e. $N_q \to 0$, $\Sigma_{\text{ph}}$ can be written as

$$
\Sigma_{\text{ph}}^{<}(E) \approx \sum_q \frac{i}{2\pi} \alpha_q G^{<}(E - \omega_q) \alpha_q
$$

$\Sigma_{\text{ph}}$ couples to the current via the $\alpha_q$’s and the out-going energy is then downshifted by the energy of the phonon mode $\omega_q$.

To obtain the current with inelastic effects included, it is necessary to solve the equation

$$
I(V) = \frac{2e}{h} \int_{-\infty}^{\infty} I(E) dE
$$

where the presence of inelastic effects in $I(E)$ gives rise to additional terms beyond the Landauer term.

$$
I(E) = \frac{2e}{h} (T(f_L - f_R) + T_{\text{inc}})
$$

Here $T$ is the elastic Landauer term, $f_{L/R}$ are the Fermi functions of the left/right electrode and all inelastic effects are collected in the $T_{\text{inc}}$ term. The inelastic effects can be obtained by solving iteratively the kinetic equation and the Meir-Wingreen equation to an arbitrary order. Each iteration will allow for a higher order process, i.e. the first order term allows for 1 scattering event (fundamental process) and the second order term allow for 2 scattering events (overtone process) etc. The current is then given by

$$
\int_{-\infty}^{\infty} I(E) dE = I_{0\text{th Order}} + \sum_q \Theta(E - \omega_q) I_{1\text{st Order}}^q + \sum_{qq'} \Theta(E - \omega_q - \omega_{q'}) I_{2\text{nd Order}}^{qq'} + \text{higher order terms}...
$$

where $\Theta(x)$ is the Heaviside step function. In the present study three iterations are performed, which essentially corresponds to the full self-consistent Born approximation. Expanding equations 9, 4 and 1 to second order, retaining only the emissive terms which contribute to the inelastic current (i.e. in-scattering through the left contact and out-scattering
through the right contact) and separating the terms into zeroth, first and second order processes the following equations for the zeroth, first and second order scattering processes are obtained.

0th order: \[ I_{coh}^{L \rightarrow R}(V) = \frac{2e}{h} \int_{-\infty}^{\infty} T_{L \rightarrow R}^{L \rightarrow R}(f_L - f_R)(E)dE = \frac{2e}{h} \int_{-\infty}^{\infty} Tr[T_L G^r T_R G^a](f_L - f_R)dE \]

1st order: \[ I_{inc}^{L \rightarrow R}(V) = \frac{2e}{h} \sum_q \int_{\mu_L+\omega_q}^{\mu_L} T_{1st\ order}^{L \rightarrow R}(E)dE = \frac{2e}{h} \sum_q \int_{\mu_R+\omega_q}^{\mu_L} Tr[A_L \alpha_q A_R^\dagger \alpha_q]dE \]

2nd order: \[ I_{inc}^{L \rightarrow R}(V) = \frac{2e}{h} \sum_{qq'} \int_{\mu_L+\omega_q+\omega_{q'}}^{\mu_L} T_{2nd\ order}^{L \rightarrow R}(E)dE \]

\[ = \frac{2e}{h} \sum_{qq'} \int_{\mu_L+\omega_q+\omega_{q'}}^{\mu_L} Tr[A_L \alpha_q G^r-\alpha_{q'} A_R^\dagger \alpha_{q'} G^a-\alpha_q]dE \]

The zeroth order term is simply the elastic (Landauer) transmission, except that the Greens functions are renormalized by the electron-phonon self-energy.

The - signs indicate that the energy has been shifted by an energy quanta \( \omega_q \) and the transmission channels, \( A_{L(R)} \), for the left and right electrodes are given by

\[ A_L = G^a T_L G^r \quad (16) \]
\[ A_R = G^r T_R G^a \quad (17) \]

Equations 14 and 15 give rise to what we will designate the "inelastic" transmission functions, \( T_{nth\ order}^{L \rightarrow R} \). The equations are straightforwardly interpreted as the processes described in equations 1 and 2 of the main text respectively.

Similar to previous studies,\(^3,4\) we approximate

\[ \frac{d^2I}{dV^2} \approx \frac{dI(E)}{dE} \quad (18) \]
which ignores the bias dependence of the electron-phonon couplings, the self energies and molecular structure. All of which are assumed to be small.

Block diagonalizing the matrices $A, \alpha_q$ and $G^{r/a}$ gives insight into the chemical properties of the inelastic channels and the coupling to the electrodes. Utilizing the symmetry of the molecules (Cs in this case), it is possible to assign a symmetry property to all of these terms. This allows for the interpretation that the elastic channels transport through the $\pi$ or $\sigma$ system of the molecule. However, since the electron-phonon coupling matrix is included twice in the expression, the sub matrices in the block-diagonalized matrices are not completely independent of each other. This gives rise to cross-terms which are excluded from the calculation causing the symmetry resolved IETS to differ quantitatively from the regular IETS. The qualitative picture remains clear, however.
The symmetry resolved IETS

Figure 1: The symmetry resolved IETS of CC (top left), LC (top right), MB (bottom left) and PB (bottom right). Resolving the total scattering into symmetry components allows for the analysis of the different scattering processes. It is found that for the most of the peaks only one scattering process is responsible for the whole mode. For the asymmetrical modes the two complementary processes $\pi$ to $\sigma$, and $\sigma$ to $\pi$ is behind the asymmetric fundamental modes. Symmetrical processes are shown in blue ($\pi$ to $\pi$) and green ($\sigma$ to $\sigma$), and asymmetrical processes are shown in red ($\pi(\sigma)$ to $\sigma(\pi)$)

Control Calculations

In figure 2, the calculated IET spectra for CC are shown for a range of electrode sizes. The first two numbers denote the number of atoms in the plane perpendicular to the flow of current, and the third number denotes the number of layers in each electrode.
Figure 2: **IETS of CC while varying the size of the Au clusters included in the calculation.** First two numbers indicate the number of atoms in the supercell in the plane perpendicular to the current flow, and the final number indicate the number of Au layers.

Below (Figure 3), is the IET spectrum of CC calculated for various Au-S distances.
Figure 3: IETS of CC while varying the Au-S distance. The insets show the corresponding transmission. The main quantitative change is the appearance of the C-C triple bond stretch at $\sim 0.27\text{eV}$ when the distance gets small. It is seen that the transmission of the $\sigma$ system dominates the transmission when the Au-S distance becomes small. The overall appearance of the IET spectrum is generally not very dependent Au-S distance in the vicinity of the calculated equilibrium Au-S distance. The Au-S distance variation after the geometry optimization is small so that the main difference when decreasing the distance between the electrodes is to squeeze the molecule. The Au-S distance in the absence of one electrode was found to be $\sim 2.64\text{Å}$.
Below (Figure 4), we show that the first and second Born approximation essentially corresponds to a fully self-consistent Born calculation.

Figure 4: The calculated IET spectra of CC and LC with various numbers of born iterations. The calculation is essentially converged after one iteration for linearly conjugated molecules, whereas for cross-conjugated molecules another iteration is needed to get the overtones. Further iterations adds only small features which are most likely well below the experimental detection limit.
Electron-phonon coupling matrices

The electron-phonon coupling matrices for the asymmetric and the symmetric vibrational mode for \textit{CC} are shown in tables 1 and 2. The orbitals in the molecule are shown schematically in figure 5.

Table 1: The electron-phonon coupling matrix for the asymmetrical vibrational mode which gives rise to an overtone in the IETS for \textit{CC}.

\[
\begin{array}{ccccccccc}
\text{C1-SP2-1} & 0 & 0 & 0 & 0 & 0 & 0 & -0.018 & 0 & 0 \\
\text{C1-SP2-2} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
\text{C1-SP2-3} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
\text{C1-}\pi & 0.0 & 0.0 & 0.0 & 0.0 & 0.018 & 0.0 & 0.0 & 0.0 & 0.0 \\
\text{C2-SP2-1} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
\text{C2-SP2-2} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0.021 & 0.0 \\
\text{C2-SP2-3} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0.021 & 0.0 \\
\text{C2-}\pi & -0.018 & 0.0 & 0.0 & 0.0 & 0.021 & 0.021 & 0.0 & -0.037 & -0.037 \\
\text{H} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -0.037 & 0.0 \\
\text{H} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -0.037 & 0.0 \\
\end{array}
\]

The electron-phonon coupling matrix for the symmetric vibrational mode for \textit{CC}.

Table 2: The electron-phonon coupling matrix for the symmetric vibrational mode for \textit{CC}.

\[
\begin{array}{ccccccccc}
\text{C1-SP2-1} & -0.077 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
\text{C1-SP2-2} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
\text{C1-SP2-3} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
\text{C1-}\pi & 0 & 0 & 0 & -0.001 & 0 & 0 & 0 & 0.01 & 0.0 \\
\text{C2-SP2-1} & 0.086 & 0 & 0 & 0 & -0.077 & 0 & 0 & 0 & 0 \\
\text{C2-SP2-2} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
\text{C2-SP2-3} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
\text{C2-}\pi & 0 & 0 & 0 & 0.01 & 0 & 0 & 0 & -0.001 & 0.0 \\
\text{H} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
\text{H} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
\end{array}
\]

The electron-phonon coupling matrix elements used for \textit{LC} are identical to the ones shown above, however the matrix is changed to reflect the differing topology.
Orthogonalization and transformation of the gDFTB matrices into an orthonomal sp2 basis

A unitary transformation of the atomic orbitals was performed to orient the orbitals correctly relative to each other.
Then the sub-blocks of the matrices corresponding to each atom, were linearly combined into an sp2 basis in the following way.

\[
|SP2-1\rangle = \frac{1}{\sqrt{3}}(|s\rangle + \sqrt{2}|p_x\rangle)
\]

(19)

\[
|SP2-2\rangle = \frac{1}{\sqrt{3}}(|s\rangle - \frac{1}{\sqrt{2}}|p_x\rangle + \sqrt{\frac{2}{3}}|p_y\rangle)
\]

(20)

\[
|SP2-3\rangle = \frac{1}{\sqrt{3}}(|s\rangle - \frac{1}{\sqrt{2}}|p_x\rangle - \sqrt{\frac{2}{3}}|p_y\rangle)
\]

(21)

Where the three different resulting SP2 hybrid orbitals correspond to the three orbitals around the carbons atoms in figure 5. In this way, the coupling between the atoms and the electrodes was concentrated on a single \(\pi\) and a single \(\sigma\) orbital. The Hamiltonians and electron-phonon coupling matrices were then orthogonalized by the Löwdin orthogonalization method

\[
M_{orthogonal} = S^{-1/2}M_{non-orthogonal}S^{1/2}
\]

(23)

where \(S\) is the overlap matrix.

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