Incoherent tunneling and heat dissipation in molecular bridges

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1. Abstract
Simulated IV characteristics and inelastic electron tunneling spectra of octanedithiol chemisorbed on gold electrodes are presented. The geometric and electronic structure is obtained from calculations based on a density functional scheme. A non-equilibrium Green’s function formalism is employed to deal with the transport aspect of the problem. Both the IV and the calculated spectra show good agreement with experimental results and suggest further details in the assignment and characterization of such spectra.

Keywords: Molecular electronics, Incoherent tunneling, electron-phonon scattering, IETS.

2. Introduction
The field of molecular electronics is steadily progressing as new experimental breakthroughs are achieved. Conduction through single molecules can now be routinely obtained by several groups, particularly in break-junctions configurations. Fingerprints of molecular species can unequivocally be detected in tunneling experiments by using inelastic tunneling spectroscopy (IETS). Such technique not only provide conclusive evidence that electrons are really tunneling through the molecular bridges \cite{1, 2}, but could provide in future a valuable characterization tool providing useful information about the interface structure, morphology and molecular geometry. As such information is not directly available, theoretical simulations will be necessary in order to interpret the measured IETS spectra. The assignment and interpretation of the spectra are not without difficulties. The spectra are usually assigned with the help of IR, Raman and HREELS results for monolayers of the molecule in question, or even isolated molecules. However, the interaction with the substrate and the absence of definite selection rules means that IETS may exhibit markedly different spectra from these other techniques and the characteristics of these spectra are difficult to predict.

recently there has been considerable theoretical work done in relation to IETS \cite{3, 4, 5, 6}. The most theoretically advanced approaches have been applied to model systems while many
of the earlier approaches made significant approximations in order to treat real molecules with ease.

Recently, a sophisticated theoretical method was applied to varying length alkane thiols to give results which reproduced experimentally observed odd-even effects with varying chain length [7].

In this paper we present IETS results derived from coherent and incoherent tunneling currents calculated using the non-equilibrium Green’s function formalism for octanedithiol chemisorbed on gold.

These results are a simple extension of a method previously developed [8, 9] which described incoherent electron-phonon scattering in these molecules. We investigate the correspondence between the experimental and theoretical IETS spectra.

Despite the apparent simplicity, simulating realistic metal-molecule-metal junctions represent a big theoretical challenge. Highly accurate quantum chemical methods are far too computationally expensive to treat the very large clusters required to simulate realistic electrodes (hundreds of atoms). On the other hand, semi-empirical methods are often unable to catch the real behavior of molecular systems between electrodes.

In this work we present the development of a code used to describe partially coherent current in molecular devices. Non-equilibrium Greens function formalism (NEGF) has been implemented on a underling density functional tight binding (DFTB) code which provides the one-particle Hamiltonian, derived from DFT calculations. The strength of such code is its ability to describe large systems (many hundreds of atoms) reaching an accuracy often comparable to DFT, whilst avoiding the cost of full DFT implementations. Within this code the molecular vibrations and frequencies are computed. The system Hamiltonian also provides the electron/vibration interaction matrices.

By means of simplifying assumptions we have implemented an efficient code which is able to handle the interaction with a large number of vibrational modes in realistic molecular structures. We present simulated IETS characteristics within self-consistent Born approximation for realistic molecules and compare to recent experiments. Our simulations not only reproduce the main features of the experimental results but also suggest the assignment of experimentally observed peaks that were not explained through conventional spectroscopic data available for isolated molecules and have been attributed to impurities.

3. The DFTB Hamiltonian
The electronic system is described via a single-particle tight-binding Hamiltonian derived from Density functional theory (DFTB) [10, 11]. The method has been fully reviewed for instance in [12, 13] and has been recently extended to the non-equilibrium Green’s function (NEGF) approach [14, 15].

The scheme allows to treat contacts and molecules at equal footing and the computation of the tunneling current in a fully self-consistent manner with the open boundary and non-equilibrium conditions encountered in transport problems.

4. Electron-phonon scattering
While the electrons cross the molecule, they interact with its ionic degrees of freedom and can suffer inelastic scattering events corresponding to the adsorption or emission of phonons. In the present context we assume that the gold ions do not move, henceforth the electron-phonon scattering within the leads is neglected.

In order to study the electron-phonon coupling we expand the TB Hamiltonian to first order in the atomic displacements [8]. The electron-phonon Hamiltonian can be written as:
\[ H_{el-ph} = \sum_{q,\mu,\nu} \gamma_{\mu \nu}^q c_{\mu}^+ c_{\nu} [a_{q}^+ + a_{q}] \]  

(1)

where \( c_{\mu}^+ \) and \( c_{\nu} \) are, respectively, the creation and annihilation operators of one electron in the local basis, \( a_{q}^+ \) and \( a_{q} \) are the creation and annihilation operators of phonon quanta in the vibrational mode \( q \), and

\[ \gamma_{\mu \nu}^q = \sqrt{\hbar \omega_q M_q} \sum_\alpha \left[ \frac{\partial H_{\mu \nu}}{\partial R_\alpha} - \sum_{\sigma,\lambda} \frac{\partial S_{\mu \sigma}}{\partial R_\alpha} S_{\sigma \lambda}^{-1} H_{\lambda \nu} - \sum_{\sigma,\lambda} H_{\mu \lambda} S_{\lambda \sigma}^{-1} \frac{\partial S_{\sigma \nu}}{\partial R_\alpha} \right] e_{\alpha}^q \]  

(2)

are the electron-phonon coupling matrices. \( M_q \) are the atomic masses, \( \omega_q \) the mode frequencies and \( e_{\alpha}^q \) are the normalized atomic displacements for each mode. The non-orthogonality of the basis set is reflected by the presence of the overlap matrix, \( S_{\mu \nu} \), and its derivative with respect to the ionic positions, \( R_\alpha \).

The Hamiltonians of the decoupled mode oscillators are quantized in the usual way, by making use of the standard relationships between the position operator and the Bose field operator. Within the NEGF formalism the relevant quantities are the correlation functions, \( G^< \) and \( G^> \), representing the electron and hole density respectively. The technicalities of the theory are mathematically rather involved and we refer the reader to specialized reviews which can be found, for example, in Ref. [16] or the introductory book by Datta [17]. The relevant phonon self-energy is evaluated within the first order Born approximation, expressed as

\[ \Sigma_{el-ph}^{<,>}(\omega) = i \sum_q \gamma_q^2 \int \frac{d\omega'}{2\pi} G^{<,>}(\omega - \omega') D_{0,q}^{<,>}(\omega') \]  

(3)

where the \( D_{0,q}^{<,>}(\omega) \) are the correlation functions related to the vibrational modes, assumed Einstein oscillators in thermal equilibrium with a bath,

\[ D_{0,q}^{<,>}(\omega) = -2\pi i \left( (N_q + 1) \delta(\omega - \omega_q) + N_q \delta(\omega + \omega_q) \right) . \]  

(4)

In principle the phonon-bath interactions can be included explicitly by solving an additional kinetic equation, an approach that might be relevant in studying heat dissipations in molecular junctions. To first approximation the effect of phonon-bath interactions could be included as a Lorentzian broadening of the \( \delta \)-functions corresponding to a finite phonon lifetime owing to decay into other phonons or electron-hole pairs. Such effects are neglected in the present work. The current flowing, for instance, from the left contact across the molecule is computed using a generalized version of the Landauer formula, valid also for non-equilibrium conditions and in particular when sources of incoherent scattering are present.

\[ I = \frac{2e}{h} \int \text{Tr}[\Sigma_L^>(\omega)G^>(\omega) - \Sigma_L^<(\omega)G^<\omega)]d\omega \]  

(5)

where \( \Sigma_L^<(>\) represents the in-scattering of electrons (holes) from the left contact of the device into the molecule.

The IETS spectrum is formally defined as the second derivative of \( I \) vs \( V \). As such spectra are obtained at very low temperature (usually 4.2 K) only phonon emission is possible. When the applied bias matches a phonon frequency an additional channel of tunneling assisted by phonon emission opens up. This corresponds to a barely visible kink in the I-V characteristics, but it can be amplified as a peak in the second derivative.
To obtain our spectrum we calculate the current at $T=0$, generally given by

$$I(V) = \int_{\mu_L-eV}^{\mu_L} i(\omega; V) d\omega,$$

(6)

where $i(\omega; V) = \frac{2}{\hbar} Tr[...]$ as from equation (5), whose dependence on $V$ comes from the Green’s functions. In the limit of small applied bias such dependence can be neglected, giving a simpler expression for the second derivative as $d^2I/dV^2 = e di(V; V = 0)/dV$. This approximation neglects the voltage dependence of the electronic structure, however this is assumed to be minimal at low voltages. The dependence of the geometry and vibrational structure on voltage is neglected in any case, so the full calculation of $I(V)$ would not improve this aspect.

5. Results

The geometry of the molecule in the junction is determined in two steps. First, an optimized geometry is obtained for octanethiol chemisorbed through the terminal sulfur to a single Au(111) surface. Periodic boundary conditions are used, however the chemisorbed molecules were sufficiently far apart to be considered isolated (p(5x5) unit cell). The geometry for the full electrode-molecule-electrode system was then generated by symmetrizing about a point of inversion between the C4-C5 bond to give octanedithiol bound to two co-facial Au(111). We have chosen a hcp bonding site for the octanedithiol molecule as reported to be a minimum for the molecule bonded to a gold surface.

In Figure 1 the computed conductance and the I-V characteristics of such system are reported. The theoretical curve is also compared to recent experimental results [18, 1] obtained by measuring the current through a SAM assembled within a nanopore. Assuming that the SAM assembled on the gold (111) surface in a $\sqrt{3} \times \sqrt{3}$ hexagonal lattice, from the measured nanopore diameter of 45 nm, we can estimate that approximately 10,000 molecules are sampled in parallel. Accordingly, the experimental measurements are scaled by a factor $10^{-4}$ in order to compare with our calculations. The order of magnitude of the tunneling current is predicted very well.

It has been shown previously that gDFTB reproduces, to a reasonable extent, experimentally observed vibrational frequencies for octanedithiol chemisorbed on Au [8]. In the case of a molecule bound to two metallic electrodes the vibrational modes of the molecule are somewhat more complicated than the previous analysis might suggest. In fact the electrodes produce a significant perturbation in the character of the molecule and as a consequence the vibrational modes associated with the extremities of the molecule differ in frequency from modes of the same character associated with the central region. For example, the C-H symmetric stretching modes occur at different frequencies for the modes associated with the central region (0.368 eV) and the extremities (0.348 eV). This is reflected in the calculated IETS spectra for octanedithiol, shown in Figure 2 with the peaks assigned as shown in Table 1. Unlike IETS, the spectroscopies used to assign IETS spectra of octanedithiol (IR, Raman, HREELS) all have specific selection rules. It has been observed previously that in IETS spectra both IR-active modes and Raman-active modes can be seen as well as additional modes, although not all IR-active modes and Raman-active modes may be seen. This complex relationship between what is observed in IETS and what is observed in other spectroscopic techniques means that for a system of the complexity of octanedithiol a complete assignment of the IETS spectra from IR, Raman and HREELS is difficult to achieve. For instance, in the experimental IETS spectra for octanedithiol [1] there were a number of unknown peaks attributed to Si3N4 impurities.

Indeed, according to our calculations, relevant signal from molecular modes in the high frequency range (above 2000 cm$^{-1}$) should not be expected. On the other hand, peaks 1, 2 and 5, nicely correspond to observed, but not clearly assigned, features. These are low frequency modes (Table 1), the first of which can be described as a rigid out-of-plane oscillation of the...
four central CH$_2$-groups, the second as a rigid and symmetric out-of-plane oscillation of the two C-C-C-S backbones. The fifth mode is associated to the longitudinal oscillation of the CH$_2$-CH$_2$ subunit pairs.

Another interesting result of our simulations is related to the possibility of applying the method to different bonding sites and different molecular geometries. As shown in Figure 3, the IETS proves to be a sensitive technique to different adsorption geometry. Different spectra for hcp and top bonding sites have been compared. It can be seen as the two spectra, although quite similar in the main aspects, are different in details in many important regions, especially between 1000-1700 cm$^{-1}$ where the main C-C-C stretching modes are located. This represent an important proof of concept.

6. Power emitted
A relevant quantity is the amount of power dissipated in the molecule due to inelastic phonon emission, which can be obtained by considering the virtual contact current, as discussed for instance in Ref. [17]. The power dissipated is given by the net rate of energy transferred to the molecule and can be easily calculated by

$$W = \frac{2}{\hbar} \int_{-\infty}^{+\infty} \omega \text{Tr}[\Sigma_{ph}^{\geq}(\omega)G^{\leq}(\omega) - \Sigma_{ph}^{\leq}(\omega)G^{\geq}(\omega)]d\omega.$$  (7)

This quantity is the so-called virtual contact current, simply representing the total current scattered from its original energy to a new one after phonon emission (or absorption). This process can be associated to the concept of a phase-breaking contact, similar to the Buttiker probes, which absorb electrons at a given energy (negative I$_{ph}(E)$) and emit them at another energy (positive I$_{ph}(E)$). The net virtual current should be zero, for current conservation. Figure 4 represents the virtual contact current for this system. The energy interval with a negative current corresponds to electrons incoming into the virtual contact, where positive current corresponds to electrons outgoing from the virtual contact. A net electron flux from higher to lower energies is evident from Figure 4. Most of the power is emitted in the C-C stretching modes, for which we have computed an average of 10 pW per mode. C-S and S-Au modes adsorb approximately 8 pW. The total power emitted in the molecule under this simple stationary model is 0.16 nWatt at the applied bias of 2.0 V, rising with an approximately linear behavior. A more realistic model taking into account the non-equilibrium (and non-thermal) phonon population resulting from the balance of joule heating and heat dissipation into the reservoirs is currently under development.

7. Conclusions
Our method provide a useful tool to simulate I-V characteristic for molecular device in tunneling regime. The NEGF permits also to address problems related to the inelastic aspect of the transport in such small system. Moreover the possibility to describe, small details as IETS spectra represents a great advantage, especially because the IETS spectra bares an important fingerprint of the molecule and its contact geometry with the electrodes.

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Figure 1. *IV characteristic for the octandithiol. Dots are experimental data and the continuous line is our simulation.*
Figure 2. Simulation of the IETS for the octanedithiol (hcp bonding site). Numbers for peaks are related to modes of vibration in table 1.

Figure 3. Comparison between IETS simulations for octanedithiol on gold surface in two different bonding sites: hcp and top.
Table 1. Principal peaks in IETS spectrum.

| Peak | Voltage (V) | mode                          |
|------|-------------|-------------------------------|
| 1    | 0.008       | S-C-C out-of-plane wag        |
| 2    | 0.017       | S-C-C out-of-plane wag        |
| 3    | 0.033       | Au - S stretch                |
| 4    | 0.044       | S-C-C scissor                 |
| 5    | 0.060       | C-C-C scissor                 |
| 6    | 0.083       | C-S stretch                   |
| 7    | 0.111       | CH2 in-plane rock (extremities) |
| 8    | 0.121       | CH2 in-plane rock (central)   |
| 9    | 0.135       | CH2 in-plane rock (central)   |
| 10   | 0.150       | CH2 in-plane rock (all)       |
| 11   | 0.157       | C-C stretch                   |
| 12   | 0.164       | C-C stretch                   |
| 13   | 0.180       | CH2 scissor (extremities)     |
| 14   | 0.196       | CH2 scissor (central)         |
| 15   | 0.212       | CH2 out-of-plane wag (all)    |
| 16   | 0.217       | CH2 out-of-plane wag (all)    |
| 17   | 0.348       | C-H stretch sym (extremities) |

Figure 4. Virtual contact current. Negative contribution corresponds to in-current and positive to out-current. The figure evidences a net transfer of electron energy.