# First-Principles Simulations of Inelastic Electron Tunneling Spectroscopy of Molecular Junctions

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## Abstract

A generalized Green's function theory is developed to simulate the inelastic electron tunneling spectroscopy (IETS) of molecular junctions. It has been applied to a realistic molecular junction with an octanedithiolate embedded between two gold contacts in combination with the hybrid density functional theory calculations. The calculated spectra are in excellent agreement with recent experimental results. Strong temperature dependence of the experimental IETS spectra is also reproduced. It is shown that the IETS is extremely sensitive to the intra-molecular conformation and to the molecule-metal contact geometry.

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Inelastic electron tunneling spectroscopy (IETS) has been recently applied to the molecular junctions[1, 2, 3]. The measured spectra show well-resolved vibronic structures corresponding to certain vibrational normal modes of the molecule. It helps to understand the vibronic coupling between the charge carriers and nuclear motion of molecule. The IETS has also been found to be sensitive to the experimental setups, for instance, distinct difference has been revealed between the spectra of alkanethiol molecular junctions measured by Kushmerick et al. [1] and Wang et al.[2]. It is therefore expected that the IETS can be used as a tool to identify the geometrical structures of the molecule-metal interface, an important factor in the design and characterization of molecular devices. The basic theory of IETS has been known for many years[4]. Its extension to the molecular wires[5, 6], atomic metal wires[7] and molecular junctions[5, 8, 9], however, has just appeared in the literature very recently, partly motived by the success of the experiments. The theoretical modellings are generally based on the Green's function theory at different levels, and have contributed to many fundamental understandings of the inelastic electron tunneling processes inside a molecular/atomic junction. However, none of the theoretical studies has been able to make realistic comparisons with the experimental spectra.

In this letter we present a new computational scheme based on our early developed quantum chemical approach for electron transport in molecular junction[10]. The vibronic coupling is introduced by expanding the electronic wavefunction along different vibrational normal modes. We have applied this new method to the gold-octanedithiolate-gold junction. The electronic structures and vibrational modes are calculated using the hybrid density functional theory (DFT). The simulated spectra are in excellent agreement with the experimental ones. Our computational scheme can be easily applied to other systems. Theoretical simulations are extremely useful for assigning the experimental spectra and to reveal many detailed informations that are not accessible in the experiments.

Our approach is also based on the Green's function formalism. We divide the molecular device into three parts, source, drain and extended molecule, as shown in Figure 1. The source and drain are described by an effective mass approximation (EMA), while the extended molecule is treated with the hybrid density functional theory. The extended molecule is in equilibrium with the source and drain through the line up of their effective Fermi level. This approach is proved to lead to very good descriptions for the experimental results[10]. The current density for the three-dimensional electrodes along the molcular axis $z$ is given

as[10]

$$i_{SD} = \frac{em^*k_B\mathrm{T}}{\hbar^3} \int_0^\infty \ln \frac{1 + \exp(\frac{E_f + eV_D - E_z}{k_B\mathrm{T}})}{1 + \exp(\frac{E_f - E}{k_B\mathrm{T}})} |T(V_D, Q)|^2 n^S n^D \mathrm{d}E_z \tag{1}$$

where $n^S$ and $n^D$ are the density of states (DOS) of the source and drain, respectively. $E_f$ is the Fermi energy, and T is the device working temperature. $V_D$ is the external voltage. The transition matrix element from the source to the drain, $T(V_D, Q)T(V_D, Q)$, is dependent on the vibronal motion, $Q$, and can be written as[10]

$$T(V_D, Q) = \sum_J \sum_K V_{JS}(Q) V_{DK}(Q) \sum_\eta \frac{\langle J(Q) \mid \eta(Q) \rangle \langle \eta(Q) \mid K(Q) \rangle}{z_\eta(Q) - \varepsilon_\eta(Q)} \tag{2}$$

where $J$ and $K$ run over all atomic sites of the molecule, which are denoted as 1,2,...,N, site 1 and $N$ are two end sites of molecule that connect with two electron reservoirs. $V_{JS}$ ($V_{DK}$) represents the coupling between atomic site $J$ ($K$) and reservoirs S (D). Orbital $\mid \eta \rangle$ is the eigenstate of the Hamiltonian ($H_f$) of a finite system that consists of the molecule sandwiched between two clusters of metal atoms: $H_f \mid \eta \rangle = \varepsilon_\eta \mid \eta \rangle$. The product of two overlap matrix elements $\langle J \mid \eta \rangle \langle \eta \mid K \rangle$ represents the delocalization of orbital $\mid \eta \rangle$. Here parameter $z_\eta$ is a complex variable, $z_\eta = E_\eta + i\Gamma_\eta^{JK}$, where $E_\eta$ is the energy related to the external bias and Fermi level, at which the scattering process is observed. $\Gamma_\eta^{JK}$ is the escape rate which is determined by the Fermi Golden rule

$$\Gamma_\eta^{JK}(Q) = \pi n^S V_{JS}^2(Q) \mid \langle J(Q) \mid \eta(Q) \rangle \mid^2 + \pi n^D V_{DK}^2(Q) \mid \langle \eta(Q) \mid K(Q) \rangle \mid^2 \tag{3}$$

All the key parameters are obtained from the calculations of the finite metal-molecule cluster. The use of the finite system allows us easily including the vibronic coupling since the description of vibronic coupling in a molecular system has long been established. The nuclear motion dependent wavefunction can be expanded along the vibrational normal mode using a Taylor expansion. The IETS experiment is often done at electronic off-resonant region. The adiabatic harmonic approximation can thus be applied, therefore, only the first derivative like $\frac{\partial \Psi(Q)}{\partial Q_a}$ needs to be considered, where $Q_a$ is the vibrational normal mode $a$ of the extended molecule. The working formula we have used for IETS calculations follows the same principle as the one given by Troisi, Ratner, and Nitzan[5].

We have calculated an octanedithiolate, $SC_8H_{16}S$, embedded between two gold electrodes through S-Au bonds. The extended molecule consists of two gold trimers bonded with an

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octanedithiolate molecule. The gold trimers were tested in two basic conformations - a triangle and a linear chain, see Figure 1. For the triangle configuration, the sulfur atom is placed above the the middle of the triangle, resembling the hollow site of a Au(111) surface. Geometry optimization and electronic structure calculations have been carried out for the extended molecules of different configurations at hybrid DFT B3LYP level [11] using Gaussian03 program package with the LanL2DZ basis set [12]. In the case of the triangle configuration, two different schemes have been used for the geometry optimization. The first geometry is obtained by optimizing octanedithiol in gas phase and then replace the terminal hydrogens with the gold contacts without further optimization (Tr1). The second geometry is obtained by optimizing the first geometry with the same fixed gold and sulfur distance (Tr2), which is also the approach for the chain configuration (Ch1). The S-Au distance in all calculations is fixed to 2.853 Å. The QCME program[13] has been employed for all the IETS calculations.

The calculated IETS of the octanedithiolate junction with the triangle gold trimers are shown in Figure 2, together with the experimental spectrum of Wang et al. at temperature 4.2 K [2]. One can clearly see that the calculated result for Tr1 configuration is in excellent agreement with the experiment. The calculations do not only reproduce all the major spectral features observed in the experiment, but also provide very detailed features that are smeared out by the background due to the encasing $Si_3N_4$ marked with stars [2]. Both theory and experiment shows that the intensity of the vibronic feature follows the order: $\nu$(C-C) (131mV) > $\gamma$(CH$_2$) (155mV) > $\delta$(CH$_2$) (185mV). It should also be mentioned that theory and experiment agrees well for the current-voltage characteristics (I-V) which are determined mainly by the elastic scattering, see the inserts of the Figure 2 (A) and (B).

The IETS calculated with the Tr2 configuration, Figure 2 (C), shows also very rich structures. However, its spectral profiles are quite different from those obtained from the Tr1 configuration, as well as the experiment of Wang et al[2]. For instance, the spectral peak at 155 mV ($\gamma$(CH$_2$) mode) has the largest intensity, instead of the mode of $\nu$(C-C) at 131 mV. The Tr1 and the Tr2 configurations have the same Au-S bondings, but slightly different intra-molecular conformations. The sensitivity of the IETS with respect to the molecular geometry is really high. It can thus be concluded that the molecular geometry and contact configuration of the device in the experiment of Wang et al[2] is very close to our Tr1 configuration.

The calculated temperature dependence of the IETS of the Tr1 configuration is shown in Fig.3 together with the experimental results of Wang et al[2]. The agreement between the theory and the experiment is more than satisfactory. The evolution of the spectral bands upon the increase of the temperature is the same for both the experiment and the calculation. As an example, in both cases, the peak for mode $\delta(CH_2)$ at 185 mV disappears at 35K, and the peak for mode $\gamma(CH_2)$ at 155 mV becomes invisible at 50K. Our simulations indicate that the observed temperature dependence is mainly due to the changes of the Fermi distribution.

In Table I, the assignments of the vibronic bands observed in theoretical and experimental spectra are shown. It can be seen that the vibrational frequencies given by the B3LYP calculations are in very good agreement with the experiments. Our computational scheme also allows to calculate the spectral linewidth directly, which is determined by the orbital characters and molecule-metal bonding, see Eq. 3. The calculated full width at half maximum (FWHM) for the spectral profile of mode $\nu(C\text{-}C)$ at 132 mV is found to be around 4.3 meV, in good agreement with the experimental result of 3.73±0.98 meV[2]. However, it is also noticed that such a band is attributed from several modes of the same character with vibration frequencies 1012, 1038, 1061, 1069, 1084, 1090, 1097, and 1100 cm$^{-1}$, respectively, covering a range of 11.0 meV. The overlapping between different vibration modes makes it impossible to determine the actual intrinsic lindwidth of the spectral profile from a single vibration mode.

We have calculated the IETS of the gold chain configuration (Ch1), shown in Figure 4(B), to examine the dependence of the IETS on the molecule-metal bonding structure. Indeed, the IETS of Ch1 shows a distinct difference in spectral intensity distribution from those of the Tr1 and the Tr2 configurations. The spectral peak of mode $\delta(CH_2)$ at 382 mV has become the absolute dominate feature in the spectrum. Furthermore, the intensities of different spectral features follow the order of $\nu(C\text{-}C)$ (132 mV) $< \gamma(CH_2)$ (172 mV) $< \delta(CH_2)$ (382 mV), completely different from the results of the Tr1 and the Tr2 configurations. The Au-S bonding structure of the Ch1 configuration differs from that of the Tr1 and the Tr2, resulting a noticeable difference in their spectral profiles for the mode $\nu(Au\text{-}S)$ around 40 mV. The changes in molecular conformations seems to be the major cause for the large difference in the spectral intensity distributions of two devices. It is found that the molecule in the Ch1 configuration is twisted around the otherwise linearly oriented molecular back-bone in

the Tr1 configuration. It is interesting to note that the spectrum of the Ch1 configuration resembles the experimental IETS of an alkanemonothiol molecule, $HS(CH_2)_8H$ (C11)[1], quite well, as clearly demonstrated in Figure 4. The molecule-metal bonding structure of the C11 is very different from that of octanedithiol. Such a difference should be reflected by the spectral profiles of the Au-S modes at the low energy region. The large difference in the experimental spectral intensity distribution [1, 2] related to the molecular vibration modes implies that the molecular conformations in two experimental setups is very different. The molecular back-bone of the octanedithiolate junction in the device of Wang et al.[2] should be linear, while it is slightly twisted for the C11 in the device of Kushmerick et al[1].

In conclusion, we have proposed a new computational scheme that is capable of describing the IETS of molecular junctions with unprecedented accuracy. Our first-principles calculations provide reliable assignments for the experimental spectra and reveal important details that are not accessible in the experiment. We have also demonstrated that the IETS is a powerful characterization tool for molecular devices.

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TABLE I: Assignments of the vibrational modes observed in the IETS of the octanedithiolate junction. The calculated peak positions (in meV), the full width at half maxmimum (FWHM) of a single spectral line (in meV), the beginning and the ending of a spectral band (in cm$^{-1}$), and the total width of the band $\Delta$ (in meV) are given. The experimental results of Wang et al. [2] are also listed for comparison.

| Mode | Peak(meV) | | | Band | | |
|---|---|---|---|---|---|---|
| | Exp.[a] | Cal. | FWHM | begin | end | $\Delta$ |
| $\delta(CH_2)$ | – | 12 | 5.3 | 93 | 138 | 5.4 |
| $\nu(Au\text{-}S)$ | 34 | 28 | 4.8 | 228 | 250 | 2.7 |
| | – | 44 | 4.2 | 335 | 353 | 2.3 |
| | – | 57 | 3.3 | 453 | 474 | 2.6 |
| $\nu(C\text{-}S)$ | 79 | 79 | 2.2 | 639 | 652 | 1.6 |
| $\delta(CH_2)$ | – | 95 | 5.1 | 742 | 783 | 1.7 |
| | 104 | 104 | 1.1 | 841 | 841 | 0.0 |
| | – | 114 | 1.1 | 917 | 917 | 0.0 |
| | – | 124 | – | 991 | 998 | 1.0 |
| $\nu(C\text{-}C)$ | 132 | 132 | 4.3 | 1012 | 1100 | 11.0 |
| $\gamma(CH_2)$ | 159 | 155 | 13.9 | 1225 | 1402 | 22.0 |
| $\delta(CH_2)$ | 180 | 185 | 7.2 | 1484 | 1536 | 6.4 |
| $\nu(CH_2)$ | 354 | 379 | 8.4 | 3012 | 3146 | 17.0 |

[a] Ref. [2]

FIG. 1: Structures of the gold-octanedithiol-gold junctions with triangle (A) and chain (B) local contacts.

FIG. 2: Inelastic electron tunneling spectrum of the octanedithiol junction from (A) experiment[2], (B) calculation for the Tr1 configuration and (C) calculation for the Tr2 configuration. The I-V curves are given in the inserts of (A) and (B). The working temperature is 4.2 K.

FIG. 3: Temperature dependent IETS of the octanedithiolate junction from (A) experiment[2], and (B) calculation for the Tr1 configuration. The intensity is in arbitrary unit.

FIG. 4: Inelastic electron tunneling spectroscopy from (A) experiment for C11 monothiol [1] and (B) calculation for the Ch1 configuration. The working temperature is 4.2 K.