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Modeling the inelastic electron tunneling spectra of molecular wire junctions

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A method to predict inelastic electron tunneling (IET) spectra is proposed. Standard quantum chemical techniques are adapted to compute the Green's function derivatives with respect to the normal vibrational coordinates, used to calculate the intensities of the IET peak for each vibration. The agreement between the computed spectra and the experimental measurements presented by Kushmerick *et al.* [Nano Lett. **4**, 639 (2004)] is very good, and helps in understanding the electron-vibration coupling in these systems.

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When electrons tunnel through a low-temperature metal-molecule-metal junction, a small fraction of them, interacting with the nuclear motion of the molecule, excite one or more molecular vibrational levels, losing the equivalent amount of energy. A signature of this *inelastic electron tunneling* (IET) channel can be found in a plot of d^2I/dV^2 versus V (I is the current and V the applied bias) which shows peaks for biases corresponding to the vibrational levels of the molecule. Although the first IET spectra on bulk materials date back to the 1960s,[1] measurements at a single-molecule level (with a scanning tunneling microscope tip) were pioneered by Ho and co-workers only a few years ago.[2,3] Very recently, several different groups provided IET measurements of metal-molecule-metal interfaces relevant to molecular electronics.[4–6] The quality, reproducibility, and richness of information that these measurements provide suggest that this technique could soon become a standard way to characterize molecular junctions. However, the information contained in an IET spectrum can be useful only in the presence of a predictive model that allows its univocal assignment. Unlike other vibrational spectra (ir, Raman) there are not easily accessible computational methods to predict IET spectra, and selection rules are not known for this spectroscopy. We propose in this paper a model to interpret IET spectra of molecular junctions from simple quantum chemical density functional theory calculations, and we compare the results with the recent measurements by Kushmerick and co-workers.[4]

The vibronic interaction between the tunneling electron and the intervening molecular media was considered by several authors using different formalisms.[7–12] IET spectra are measured at low temperature ($kT \ll \hbar\omega$), very low bias ($V \sim \hbar\omega/e$), and with the Fermi levels of the electrodes far from resonance with the molecular level. In these conditions charging and polaron formation on the molecular wire can be neglected, the electrode can be assumed to be in equilibrium, and the *elastic* component of the conductance can be written as[13]

$$g^{el}(E) = g_c \,\mathrm{Tr}[\mathbf{\Gamma}^L(E)\mathbf{G}(E)\mathbf{\Gamma}^R(E)\mathbf{G}(E)^+], \tag{1}$$

where g_c is the quantum conductance ($2e^2/h$), and $\mathbf{\Gamma}^L$ and $\mathbf{\Gamma}^R$ are twice the imaginary part of the self-energy matrices associated with the interaction of the molecular subsystem with the left and right electrodes. $\mathbf{G}$ is the matrix representation of the Green's function operator $G(E)=(E-H-i\varepsilon)^{-1}_{\varepsilon\to 0+}$. H is any electronic Hamiltonian describing the molecule and the electrodes (it is dependent on the nuclear positions).

The elastic contribution to the current is

$$I^{el} = \int_{-\infty}^{+\infty} \frac{g^{el}(E)}{e}[f_L(E) - f_R(E)]dE, \tag{2}$$

where f_L and f_R are the Fermi functions of the left and right electrodes, modified according to the external potential Φ applied to the electrode [$f=f(E-e\Phi)$].

The interaction of the tunneling electron with the vibrational levels can be treated easily at the perturbative level, allowing the exchange of a *single* vibrational quantum of energy per tunneling electron and assuming that the molecule is in its ground vibrational state (low-temperature limit).[12] The Green's function matrix elements are parametrically dependent on the set of normal modes $\{Q_\alpha\}$ and their dependence can be expanded in a Taylor series around the equilibrium position $\{Q_\alpha\}=0$ (we use dimensionless coordinates)

$$G_{ij}(E,\{Q\}) \cong G_{ij}(E,0) + \sum_\alpha \left(\frac{\partial G_{ij}(E,\{Q_\alpha\})}{\partial Q_\alpha}\right)Q_\alpha. \tag{3}$$

The matrix $\mathbf{G}^\alpha$, with $G^\alpha_{ij}=\sqrt{2}/2[\partial G_{ij}(E_F,\{Q_\alpha\})/\partial Q_\alpha]_{Q_\alpha=0}$, quantifies the importance of the inelastic channel involving the vibrational mode α. Each vibrational mode α could contribute to the IET spectrum (d^2I/dV^2 versus V) with a peak centered at $V=\hbar\omega_\alpha/e$ (or $-\hbar\omega_\alpha/e$) and the peak area W_α is given by[12]

$$W_\alpha = g_c \,\mathrm{Tr}[\mathbf{\Gamma}^L(E_F)\mathbf{G}^\alpha(E_F)\mathbf{\Gamma}^R(E_F)\mathbf{G}^\alpha(E_F)^+]. \tag{4}$$

This method can be easily generalized to account for molecules initially in an excited vibrational state or with anharmonic modes. This formalism is essentially based on a perturbative approach and it is therefore valid for small electron-phonon coupling and in the limit of electrodes in quasiequilibrium (the usual case in IETS spectroscopy).[14] More sophisticated and computationally demanding methods based on the nonequilibrium Green's function formalism appeared recently.[15] Examples of phenomena that can be captured only by a nonequilibrium formalism are discussed in Ref. 15.

The direct evaluation of Eq. (4) is not very helpful for rationalization of the IET spectra. First, the intensity of each peak in the IET spectra depends on too many matrix elements and it is also affected by the details of the molecule-metal interaction (determined by $\mathbf{\Gamma}^L$ and $\mathbf{\Gamma}^R$). Moreover, the evaluation of $\mathbf{\Gamma}^L$ and $\mathbf{\Gamma}^R$ is demanding and requires a preliminary investigation of the interface geometry to be carried out on a case-by-case basis.

An extremely useful simplification allows the interpretation of IET spectra in term of a single matrix element per vibrational mode, analogous to what is found for infrared or Raman spectra. With a modest loss of predictive capability it is possible to simulate the features of the spectrum that are solely dependent on the molecule, factorizing out the effect of the metal-molecule interface. We assume that there is a single orbital on each end of the molecule strongly coupled both with the electrode and with the rest of the molecule and through which the interelectrode current flows. We refer to the two orbitals interacting with the left and right electrodes as *gateway* orbitals. Denoting with λ and ρ these gateway orbitals localized at the two ends of the molecule and coupled to the left and right electrodes, the elastic and inelastic components (for one mode) of the conductance can be written simply as

$$g^{el}(E_F) = g_c\Gamma^L(E_F)\Gamma^R(E_F)|G_{\lambda\rho}(E_F)|^2, \tag{5}$$

$$g^{inel}_{\alpha}(E_F) = g_c\Gamma^L(E_F)\Gamma^R(E_F)|G^{\alpha}_{\lambda\rho}(E_F)|^2. \tag{6}$$

Very often the experimental IET spectra are presented as plots of the ratio $(d^2I/dV^2)/(dI/dV)$ versus the applied bias V.[4] When this is done the IET peak due to the vibrational mode α and centered at $V=\hbar\omega_\alpha/e$ has intensity R_α given by the ratio

$$R_\alpha(E_F) = |G^{\alpha}_{\lambda\rho}(E_F)|^2/|G_{\lambda\rho}(E_F)|^2. \tag{7}$$

Within the validity of this approximation, the relative intensity of each peak that could potentially give a signal in an IET measurement is proportional to the square of a single matrix element $[|G^{\alpha}_{\lambda\rho}(E_F)|^2]$, as in common vibrational spectroscopies. We note that the effect of the Γ matrices has been completely factorized out in Eq. (7).[16] The approximation leading to Eq. (7) is valid if (i) the localized (atomic) orbitals interact mostly with their neighbors (tight-binding approximation) and (ii) there is a single principal channel for the tunneling electron (see below for the applicability of this approximation to our systems). The exact value of the Fermi energy is not known and it can be considered a parameter of the simulation. The "intrinsic" linewidth that could be derived by this model (of the order of kT/e with $T<10$ K) is much smaller than the experimental width (ca. 200 cm^{-1}) because the molecular vibrational levels are broadened by the interaction with the phonons and electronic levels of the electrodes.

We considered the simulation of three chemical systems where the molecular wire is connected to each electrode through a sulfur-gold bond (see Fig. 1): (i) oligo-phenylene-ethynylene (OPE), (ii) oligo-phenylene-vinylene (OPV), and (iii) 1-7 heptane dithiolate (HDT). The selected systems allow a direct comparison with the measurements by Kushmerick *et al.*[4] We built model compounds where the S—Au bond present in the molecular junction is substituted by the S—H bond. Geometry optimizations, frequencies, and

TABLE I. Predicted intensity and frequency of the most important peaks in the IET spectra for the three considered systems. In all three cases only the frequencies with intensity larger than a threshold are reported. The threshold is set to 1/200 the intensity of the most intense peak. The scaled frequencies are reported in wave numbers (cm^{-1}). The intensity [R_α from Eq. (7)] is given multiplied by 10 000.

OPE		OPV		HDT	
Frequency	Intensity	Frequency	Intensity	Frequency	Intensity
133.1	14	118.5	13	172.5	13
391.3	17	388.3	21	440.4	10
581.0	8	564.9	11	707.0	17
733.6	3	989.5	3	978.4	10
1073.3	83	1079.3	74	1023.5	55
1113.8	60	1164.0	125	1081.3	9
1176.7	21	1175.7	20	1223.7	6
1582.0	234	1187.6	2	1366.0	33
2211.4	282	1322.4	48	1456.0	1
		1330.3	6	1461.0	7
		1404.4	9	1466.6	5
		1534.8	43	2900.8	2
		1578.2	386	2909.2	1
		1633.8	49	2923.7	4
		1634.0	9		

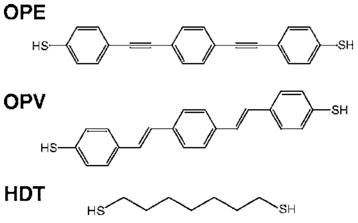

FIG. 1. The three molecules (OPE, OPV, HDT) whose IET spectra are studied in this paper.

Green's function evaluation for these compounds were performed at the B3LYP/6-31G* level[17] (the computed frequencies are scaled by the recommended factor[18] of 0.961). The vibrations that could be assigned to the stretching and bending combinations of the S—H bonds (not present in the real system) are excluded from the list of normal modes. After selecting the two gateway orbitals [λ and ρ of Eq. (8)] for each model compound (see below), we computed numerically the Green's function derivative $G^{\alpha}_{\lambda\rho} = \sqrt{2}/2[\partial G_{\lambda\rho}(E_F,\{Q_\alpha\})/\partial Q_\alpha]_{Q_\alpha=0}$ with respect to each normal mode.

With this approach one cannot predict the features of the IET spectrum arising from the vibrations localized at the interface (e.g., from the S—Au bond). However, through a systematic study and comparison between theory and experiment one can use this method to separate the portion of the spectrum that is typical of the molecule and the portion deriving from the interface. For the first two considered systems (OPE and OPV) the gateway orbitals were selected to be the $3p_z$ orbitals on the two sulfur atoms connected with the gold electrodes (the z axis is perpendicular to the plane of the molecule). In fact, in planar conjugated systems the coupling between the two ends of the molecules is mediated by the π orbitals (the other orbitals give a contribution several orders of magnitude lower). The tunneling through saturated molecules such as HDT is mediated instead mainly by the bonding (σ) and antibonding (σ^*) orbitals of the C—C bonds. We therefore selected the gateway orbitals for the dithiolalkane to be the $3s$ orbitals on the sulfur atoms.

The appropriate E_F for such molecular junctions is not known accurately. However, it is clear form several theoretical analyses[13] and from the comparison with metal bulk and molecular gas phase properties that E_F is between the highest occupied (HOMO) and lowest unoccupied (LUMO) molecular orbitals and generally lies closer to the HOMO. We report calculations done assuming $E_F=-0.14$ a.u. for all three considered systems, corresponding to 12 070, 10 315, and 20 630 cm^{-1} above the gas phase HOMO of OPE, OPV, and HDT. The calculation was repeated for $E_F=-0.16$, -0.12, and -0.10 a.u. and only minor changes were observed in the computed spectrum, leading us to the conclusion that the exact determination of E_F is not crucial for understanding the IET spectra, so long as E_F is sufficiently far from the molecular levels. We have not tried a best fitting of E_F.

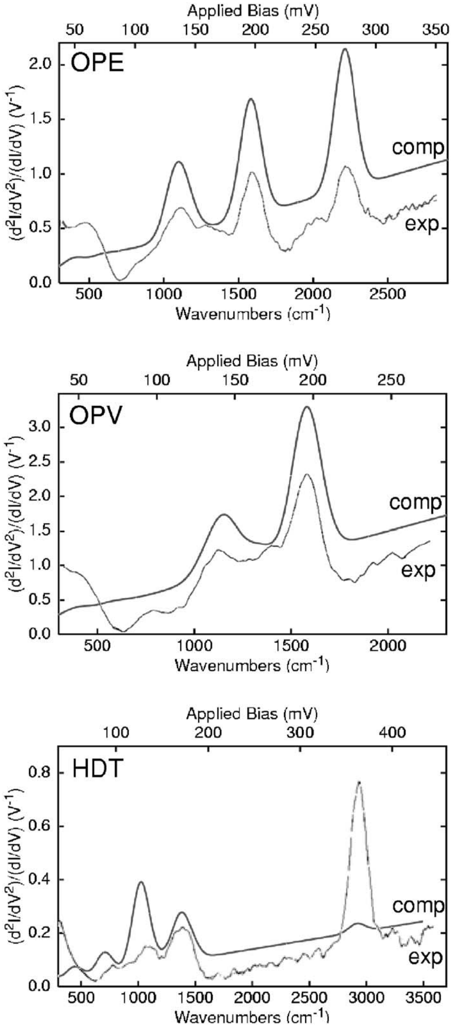

FIG. 2. Comparison between computed and experimental IET spectra for the molecules OPE, OPV, and HDT. An arbitrary baseline is added to the computed spectra (Table I). The vertical scale reflects the intensity of the computed spectra while the experimental plots (from Ref. 4) are scaled, respectively, by factors of 0.94, 2.22, and 0.30.

Table I collects, for the three investigated systems, the vibrational modes that show non-negligible activity in the IET spectrum. The intensity of each mode is computed according to Eq. (7). From these data, the simulated IET spectra are built adding a Gaussian broadening of 200 cm^{-1} to each peak and compared with the experimental measurements (Fig. 2). A vast majority of the vibrational transitions are inactive and the IET spectrum can be very well simulated including fewer than ten modes for molecules of this size. Selection rules are used in more well-established spectroscopies to determine *a priori*, exploiting the symmetry properties of the wave function, what transitions are allowed or forbidden. Our approach is entirely numerical, i.e., we computed the intensity for *all* vibrational modes and, in the absence of a better theoretical treatment, we obtained a short list of "allowed" transitions.

The experimental IET spectrum of OPE shows three main bands that are very well reproduced by our simulation [Fig. 2(a)]. Four intense modes account for the observed spectrum. The higher-frequency signal (2211 cm^{-1}) is due to the symmetric stretching of the C—C triple bond, the peak at 1582 cm^{-1} is due to C—C double-bond stretching, while

C—C—C bending motions localized on the aromatic rings give the largest contribution to the peak computed at $\sim$1100 cm^{-1}. The simulated IET spectrum of OPV [Fig. 2(b)] is similar except for the missing peak due to the triple bond. Minor features of the experimental OPV spectrum (shoulders at $\sim$1400 and $\sim$750 cm^{-1}) are not reproduced by our simulation but further joint experimental and computational investigations could clarify if these signals are due to interfacial vibrations that are not included in our model. In Figure 2(c) we compare the IET spectrum of HDT with the experimental measurements relative to undecane thiolate (a longer alkane with one end terminated by a —CH$_3$ instead of a —S—Au bond). The large peak measured at $\sim$2950 cm^{-1} is due to the —CH$_3$ stretching modes that are missing in our model. Good agreement with the experiment is found in the low-frequency region of the spectrum where three vibrations dominate the observed features between 600 and 1500 cm^{-1}.

The overall agreement for the three systems is very encouraging. Even more reassuring is the agreement between the computed and experimental *absolute values* of the intensity for the individual peaks in the IET spectrum. For example, the predicted integrated intensity of the peak at 2211 cm^{-1} of the OPE molecule is 0.0282, while the area underneath the experimental peak is ca. 0.024. This agreement confirms that our model correctly captures the essential physics of the inelastic electron tunneling through molecular junctions.

We show in this paper that it is possible to predict the inelastic electron tunneling spectrum of molecular junctions using standard quantum chemical calculations. The possibility of assigning easily an IET spectrum increases the usefulness of the technique, applicable in principle to characterize *all* molecular junctions. Straightforward improvements of the method include the adoption of larger model systems (considering several surface metal atoms) to describe also the interfacial vibrations and the explicit inclusion of the interfacial effects on the electronic structure of the molecular wire.

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[16] In the same spirit that led to Eq. (5) (only two orbitals coupled to the wires) the self-energy matrices ($\mathbf{\Sigma}^L$ and $\mathbf{\Sigma}^R$) have only one non-null element (namely, $\Sigma^L_{\lambda\lambda}$ and $\Sigma^R_{\rho\rho}$). They appear in the $G_{\lambda\rho}$ matrix element as a factor $(E-E_\lambda-\Sigma^L_{\lambda\lambda})^{-1}(E-E_\rho-\Sigma^R_{\rho\rho})^{-1}$ independent by the nuclear coordinates and that cancels out in the computation of R_α.

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