

Tracing electronic pathways in molecules by using inelastic tunneling spectroscopy

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Using inelastic electron tunneling spectroscopy (IETS) to measure the vibronic structure of nonequilibrium molecular transport, aided by a quantitative interpretation scheme based on Green's function-density functional theory methods, we are able to characterize the actual pathways that the electrons traverse when moving through a molecule in a molecular transport junction. We show that the IETS observations directly index electron tunneling pathways along the given normal coordinates of the molecule. One can then interpret the maxima in the IETS spectrum in terms of the specific paths that the electrons follow as they traverse the molecular junction. Therefore, IETS measurements not only prove (by the appearance of molecular vibrational frequencies in the spectrum) that the tunneling charges, in fact, pass through the molecule, but also can be used to determine the transport pathways and how they change with the geometry and placement of molecules in junctions.

molecular electronics | molecular junctions | molecular transport

The electron-transfer process is crucial in chemistry, materials science, condensed matter physics, and electrical engineering. Although it is always modeled either explicitly or implicitly by pathways (how electrons actually move within the molecule), there is as yet no direct measurement or observation of such pathways. The pathways idea has been present in physical organic chemistry for years in connection with reaction mechanisms and has been widely used in the interpretation of electron tunneling pathways in proteins (1), but no distinct observations have been made. The absence of direct measurement of pathways is because the measurements are usually made starting with an equilibrium structure, exciting quickly (optical spectroscopy), and then observing the new perturbed structure. Although it is instructive to observe these initial and final states, they are static snapshots and cannot capture the dynamics of the electron-transport process. In molecular transport junctions, where current is moving continuously through the molecule, the nonequilibrium inelastic electron tunneling spectroscopy (IETS) probe permits direct observation of how different modes modulate the transport and, therefore, can be used to deduce actual pathways.

It is well established that tunneling electrons can lose energy through excitation of a molecular vibrational level contained within the tunnel junction (2–5). The threshold for such excitation is $eV = \hbar\omega$ where V is the bias voltage and $\hbar\omega$ is the energy of the molecular vibration. Peaks in d^2I/dV^2 versus V , or more commonly the normalized quantity $(d^2I/dV^2)/(dI/dV)$ versus V , correspond to molecular vibrations. IETS has become quite popular in the field of molecular electronics over the last 3 years (6–9) and has distinguished itself as a unique spectroscopic probe of molecular junctions. Because an IET spectrum is acquired directly from the measured transport characteristics (Fig. 1), the only added experimental requirement is the ability to cool the junction. From comparison between experiments and computations (10–17), IETS is useful for characterizing numerous aspects of molecular junctions such as the actual presence of

the molecule, information on the nature of the interfaces (18), the orientation of the molecule (19), and some symmetry aspects of the junction (20, 21).

In the current contribution, we investigate how the inelastic signatures provide information about the actual pathways followed by the tunneling electron. Only vibrations that involve atoms lying along favorable tunneling pathways are active in IETS (because only these motions modulate the electron transport). If we can obtain good assignment of the IET spectrum, it should be possible (at least for medium-sized molecules) to reconstruct the path followed by the tunneling electrons, always remembering that the tunneling path actually comprises the atomic orbitals that describe the electronic motion rather than the position of the atomic nuclei themselves.

Computational Approach

The IETS is due to electron/vibration interaction in the transport junction. The general problem is a complicated one, and when the charge injection gap ΔE_G is small (of order Γ , the decay rate of an electron from the molecule to the electrode, also often called the spectral density), strong vibronic coupling in the injection region can lead to switching, hysteresis, activation, heating, reaction, and dephasing behavior (22–27). But for most simple organics with Au electrodes, the injection gap ΔE_G is large (more than ≈ 1 eV) for small applied voltage ($V \leq 0.4$ V) so that the Landauer–Buttiker contact time is smaller than a vibrational period and, thus, vibronic coupling is a weak effect (28). This is the Landauer–Imry regime, in which transport occurs by a coherent tunneling process. The simplest interpretation of an IET spectrum is then based on the perturbation theory because in this regime (coherent tunneling limit and very far in energy from electronic resonances), one can expand the low-voltage transmission of a molecular junction in terms of a normal coordinate analysis. The formal analysis and development of the perturbation theory approach to IETS is presented elsewhere (29), along with comparisons with experiment for several molecules (10) demonstrating its remarkable accuracy for predicting the peak positions and intensities in the IET spectrum (the actual line shapes are a more difficult problem) (30). This approach is complementary to, and generally simpler than, other theoretical treatments of molecular IETS; it is well justified only in the Landauer–Imry tunneling regime discussed above.

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Abbreviations: IET, inelastic electron tunneling; IETS, IET spectroscopy.

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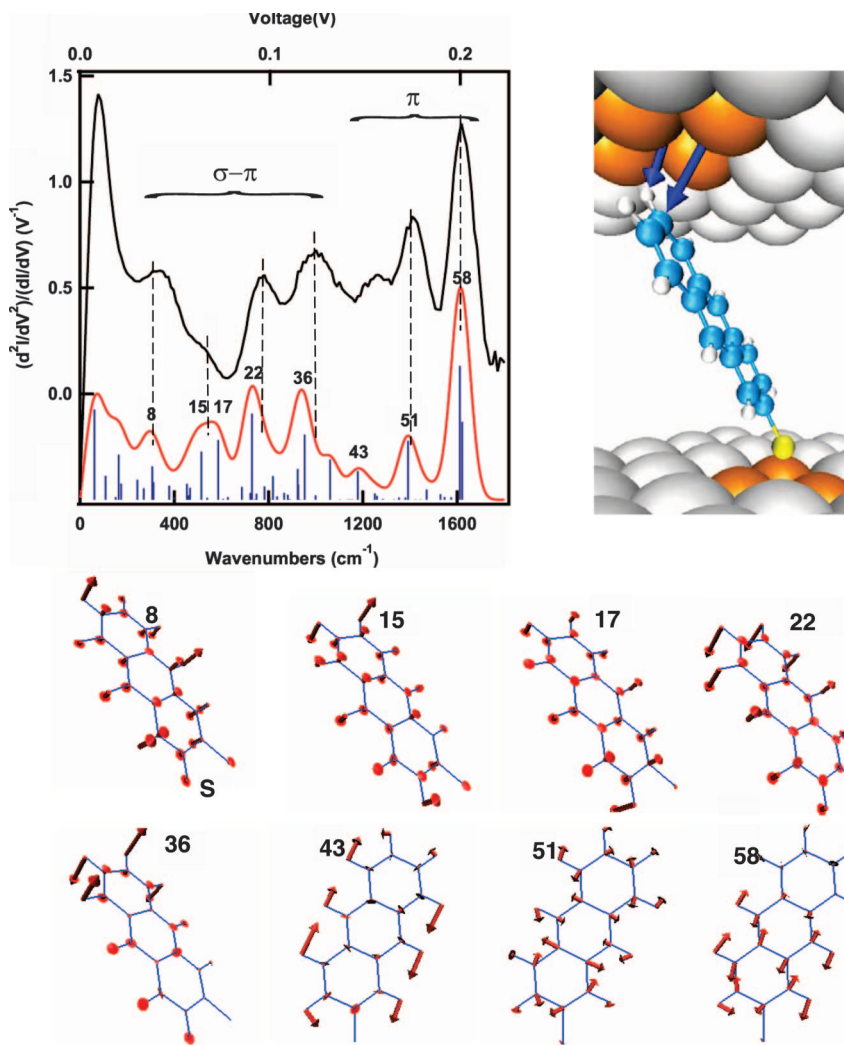


Fig. 2. IET spectra of an anthracene thiol junction. Experimental (black) and computed spectra (red) of the anthracene (1) junction. Labels refer to the normal modes of the molecule computed in the absence of metal and numbered from the lowest energy vibration. Further computational details are given in ref. 13 and supporting information (SI) Tables 1 and 2. The observed normal modes belong to two groups: out-of-plane modes that favor the intercommunication between the σ and π tunneling channels and in-plane C—C stretches that modulate the main π -type tunneling channel. The molecules couple to the electrode through the s orbital of the hydrogen and the p_z orbital of the carbon. However, in the first case, only if the C—H bond bends out of plane can the electron follow the most favorable tunneling path across the molecule.

near 950 cm^{-1} , and by the C—S stretching peak near 650 cm^{-1} . The C—H stretching vibration at $\approx 2,900\text{ cm}^{-1}$ observed for alkyl junctions is likely because of tunneling between the electrode and carbon backbone as will be discussed below (5, 8). For conjugated molecules, the primary inelastic signature is from C=C and C≡C stretching modes as well as phenyl ring deformations associated with the π channel (5, 9). Propensity rules based on symmetry further limit the number of modes that might contribute to the signal (13).

The junctions we discuss here contain more complex molecular structures (1 and 2 in Fig. 1*b*), for which tunneling may be expected to occur through a combination of σ and π channels, and where the tunneling electron excites vibrations that are localized to specific portions of the molecule. Both σ and π channels are important to the two molecules for differing reasons. In 1, it is a consequence of weak coupling at the nonbonded electrode, and in 2, it is a direct result of the chemical structure.

Pathways for Electron Tunneling

Anthracene Thiol. For molecular junctions formed from Au electrodes and a monolayer of 1, the direct chemical linkage to one

metal electrode, through the thiolate interaction, gives a large spectral density and strong coupling in contrast with the other metal–molecule interface, where only a physical contact between the terminal hydrogen and electrode occurs (32). There is no strong chemical interaction at this nonbonding contact and, therefore, there are only weak spectral density and minimal mixing of electronic states. At the nonbonding interface, one expects the strongest electrode–molecule coupling to occur between the hydrogen s orbital, oriented toward the electrode, and the electrode itself. However, because one expects the most favorable tunneling pathway through the molecule to involve π orbitals in the anthracene fragment, which are electronically decoupled from the hydrogen s orbitals, the tunneling electrons might prefer to bypass the hydrogen atom and tunnel directly between the molecular π system and the electrode. This suggestion is directly supported by the IET spectrum shown in Fig. 2. The excellent correspondence between the computed and experimental spectrum for this junction enables us to analyze the individual vibrations that make up the IET spectrum, and from this derive information on the path of the tunneling charge carrier. In the high-energy range ($1,100$ – $1,600\text{ cm}^{-1}$), the sym-

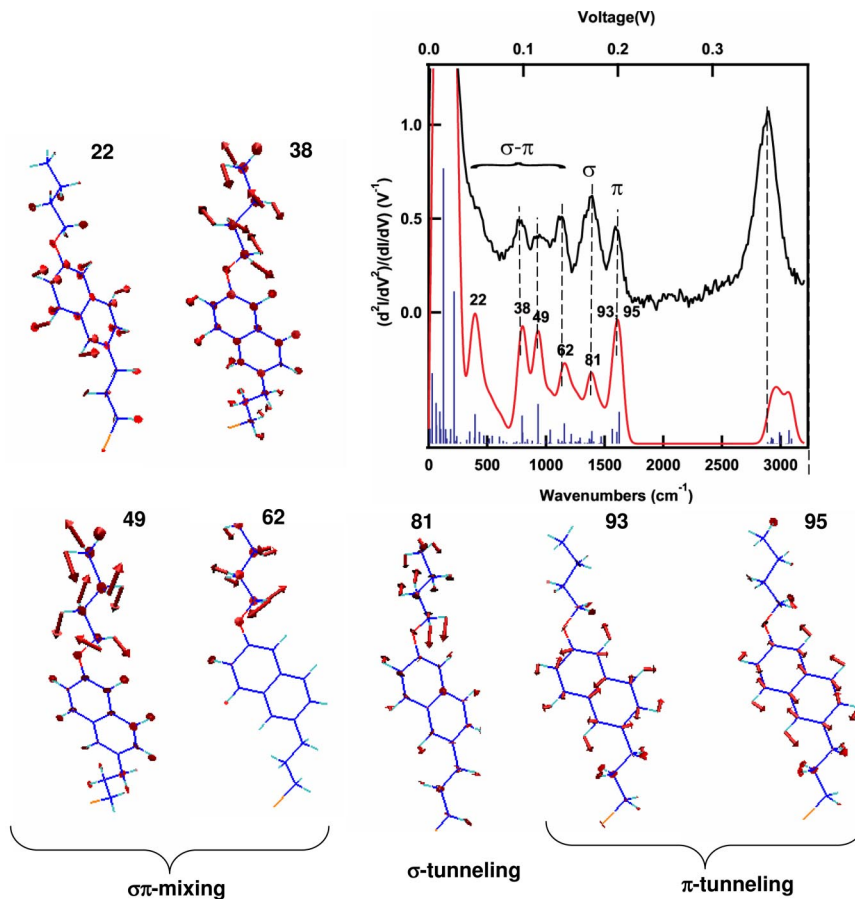


Fig. 3. IET spectra of a naphthyl ether junction. Experimental and computed spectra of **2**; a set of IETS-active normal modes are shown. The low frequency modes are antisymmetric with respect to the symmetry plane of the molecule and they connect the σ and π tunneling channels (where the naphthalene and the alkyl fragments come into contact). Mode at $1,350\text{ cm}^{-1}$ is associated with σ tunneling through the alkyl fragment, whereas the modes at $1,600\text{ cm}^{-1}$ are in-plane C—C stretching modes modulating the π -type tunneling through the naphthalene (the C—H stretching modes $\approx 2,900\text{ cm}^{-1}$ are similar to those observed in simple alkane monothiulates).

metric combination of C—C stretches (modes 51 and 58) dominates the spectrum. These vibrational modes are expected for π tunneling paths because they derive from electrons that tunnel from the electrode directly into the π system without passing through the σ orbitals of the terminal hydrogen atoms.

In the energy range below $1,100\text{ cm}^{-1}$, the active normal modes (i.e., 15, 17, 22, and 36) have the common characteristic that they all contain an out-of-plane displacement of hydrogen atoms that are closer to the nonbonding molecule–electrode contact. These interfacial out-of-plane motions facilitate molecule–electrode coupling because they enable σ – π mixing: the electron initially tunnels into the hydrogen σ orbital and then is vibronically coupled to the molecular π system.

Alkyl Naphthyl Ether Thiol. A more complicated situation arises in the naphthalene ether structure (**2**). Such molecular structures have been suggested as potential molecular diodes because they consist of a pseudoquantum dot (the aromatic naphthalene core) spaced asymmetrically between the electrodes by alkyl tails (33). Although our (low-voltage) study of this and related molecular structures has not found any diode-like properties, the complex electronic structure of **2** provides an interesting system for probing σ – π mixing. In **2**, the electron is forced to tunnel into the orbitals of the C—C-saturated alkyl chain on either end of the molecule, although the favorable tunneling across the central naphthyl fragment must involve localized π orbitals.

Our fully assigned IET spectrum (Fig. 3) again demonstrates

very good agreement between theory and experiment, permitting us to attribute with confidence the observed signals to the depicted normal modes and to deconstruct the tunneling pathway. Three classes of vibrational modes are identified in the 300 – $1,700\text{ cm}^{-1}$ range. First, vibrations of the σ tunneling channel (mode 81, wagging) correlate well with the signal obtained for simple alkanes near $1,350\text{ cm}^{-1}$. Second, vibrations that modulate tunneling through the π orbitals of the naphthalene core; these are almost totally symmetric modes responsible for the peak at $1,600\text{ cm}^{-1}$ (modes 93 and 95) and can be related to the hypothetical IETS on naphthalene itself. Third, vibrations near 800 and $1,200\text{ cm}^{-1}$ are modes 49 and 62, which allow the interchange between σ and π channels, corresponding to out-of-plane twisting motions of the CH_2 on the alkyls or out-of-plane vibrations of the naphthalene fragment. Vibrations in the first two categories are derived from the two independent portions of the molecule, whereas the third category describes the interaction between the two otherwise orthogonal tunneling channels. In particular, mode 62 is a twisting of the alkyl group that would be absent in the alkane thiolate. It is made important in **2** because of the required symmetry mixing of σ and π orbitals along the pathway. Together, the three types of vibrations provide a fingerprint of the actual σ – π – σ tunneling pathway that occurs in the molecular junction. The signal at $\approx 2,900\text{ cm}^{-1}$, commonly found in alkane thiolates IETS, is less molecule-specific, and it is because of the C—H stretching vibration encountered by the electron tunneling between the gold and the alkylic portion of the molecule.

In addition to providing information on the tunneling pathways in these two molecules of interest, the observations hint at the additivity/transferability of IETS. That is, IETS can probe the molecular type (conjugated or saturated) but is also sensitive to internal interfaces that can force a change in the tunneling mechanism. In **1**, most of the distinctive peaks come from vibrations localized at the interface between the molecule and the electrode, where π orbitals are coupled by out-of-plane vibrations to the σ orbitals of the molecule that are, in turn, effectively coupled to the gold electrode. For **2**, the interface is within the molecule itself: vibrations that favor the σ - π mixing in the vicinity of the contact between the naphthalene and the alkyl tail are the most characteristic signals in this molecule.

We believe that this IETS analysis is a remarkable demonstration of the ability of transport measurements to clarify the actual transport pathways that electrons take in passing through molecular junctions under nonequilibrium conditions. Although the perturbative model used here is expected to fail near

electronic resonances, it works well for ordinary small organics where the coherent, electronically elastic Landauer-Imry regime characterizes the fundamental transport mechanism. Using standard molecular density-functional-theory calculation (the B3LYP correlation functional method and 6-31G* basis) schemes, we can fit the IETS quantitatively. This assignment, in turn, allows vibrational-normal coordinate-coupling analysis and, hence, an interpretative mapping of the actual transport pathway. As such, this combination of theory and experiment can be used to further our understanding of the geometries, chemistries, and transport mechanisms in the molecular junctions that are of interest in much of molecular electronics.

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