Molecular nanowires in which a single molecule bonds chemically to two metal electrodes and forms a stable electrically conducting bridge between them have been studied intensively for more than a decade. However, the experimental determination of the bonding geometry between the molecule and electrodes has remained elusive. Here we demonstrate by means of \textit{ab initio} calculations that inelastic tunneling spectroscopy (IETS) can determine these geometries. We identify the bonding geometries at the gold–sulfur interfaces of propanedithiolate molecules bridging gold electrodes that give rise to the specific IETS signatures that were observed in recent experiments. 

We focus on inelastic tunneling processes that are sensitive to the structure of the gold–sulfur interfaces, i.e., those that involve excitation of vibrational modes with strong amplitudes on the sulfur atoms. Therefore, it is necessary to calculate accurate equilibrium geometries and also the frequencies and atomic displacements from equilibrium for the whole system, including both the molecule and the gold electrodes. We do this by performing \textit{ab initio} DFT calculations for extended molecules consisting of the PDT molecule and two finite clusters of gold atoms that the molecule connects, relaxing this entire structure. By carrying out systematic DFT studies of extended molecules with gold clusters of different sizes (up to 13 gold atoms per cluster) we establish that our conclusions are independent of the cluster size for the larger clusters that we study and, thus, are applicable to molecules bridging the nanoscale tips of experimentally realized macroscopic gold electrodes.

We found extended molecules whose sulfur atoms bond to the gold clusters over bridge sites to have lower energies than those with top site bonding by at least 0.76 eV. Extended molecules for which DFT geometry relaxations were started with the sulfur atoms over hollow sites on the surfaces of close packed gold clusters invariably relaxed to bridge bonding site geometries. While we found it possible to generate examples of relaxed extended molecules with each sulfur atom bonding to three gold atoms (i.e., hollow site bonding) the structures of the gold clusters near these bonding sites were much more open than that of a fcc gold crystal. The energies of these structures were also higher than those of either bridge or top site bonded extended molecules. Because of the much greater

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fragility and higher energies of hollow site bonded structures relative to bridge and top site bonding we will focus primarily on bridge and top site bonding but will revisit hollow site bonding near the end of this paper.

After identifying the normal modes of the extended molecule that have the largest vibrational amplitudes on the sulfur atoms and calculating the frequencies of those modes as is outlined above, we determine which of these modes has the strongest IETS intensity, i.e., it gives rise to the largest conductance step height as the bias voltage applied across the extended molecule is varied.

We calculate the IETS intensities perturbatively in the spirit of an approach proposed by Troisi et al.9 who transformed the problem of calculating IETS intensities into an elastic scattering problem. However, we formulate our IETS intensities explicitly in terms of elastic electron transmission amplitudes \( t_{ji}^{tel} \) through the molecular wire. We find the height \( \delta g_\alpha \) of the conductance step due to the emission of phonons of vibrational mode \( \alpha \) to be

\[
\delta g_\alpha = \frac{e^2}{2\pi \hbar \omega_\alpha} \lim_{A \to 0} \sum_{ij} \frac{v_j}{v_i} \left| t_{ji}^{tel}(i|A_{\alpha\alpha}|0) \right|^2 ,
\]  

(1)

at low temperatures. Here \( t_{ji}^{tel}(0|0) \) is the elastic electron transmission amplitude through the molecular wire in its equilibrium geometry from state \( i \) with velocity \( v_i \) in the electron source to state \( j \) with velocity \( v_j \) in the electron drain. \( d_{\alpha\alpha} \) represents the displacements from their equilibrium positions of the atoms \( n \) of the extended molecule in normal mode \( \alpha \) normalized so that \( \sum_n m_n d_{\alpha n}^2 = \delta_{\alpha',\alpha} \) where \( m_n \) is the mass of atom \( n \). \( \omega_\alpha \) is the frequency of mode \( \alpha \). \( t_{ji}^{tel}(i|A_{\alpha\alpha}|0) \) is the elastic electron transmission amplitude through the molecular wire with each atom \( n \) displaced from its equilibrium position by \( A_{\alpha n} \) where \( A \) is a small parameter. Our formal derivation of Eq. (1) will be presented elsewhere; here we point out that Eq. (1) is plausible intuitively in a similar way to the result of Troisi et al.9 Eq. (1) states that in the leading order of perturbation theory the scattering amplitude for inelastic transmission of an electron through the molecular wire is proportional to the change in the elastic amplitude for transmission through the wire if its atoms are displaced from their equilibrium positions as they are when vibrational mode \( \alpha \) is excited.

In our evaluation of \( t_{ji}^{tel} \) in Eq. (1) the coupling of the extended molecule to the macroscopic electron reservoirs was treated as in previous work10,11 by attaching a large number of semi-infinite quasi-one-dimensional ideal leads to the valence orbitals of the outer gold atoms of the extended molecule. The transmission amplitudes \( t_{ji}^{tel} \) were then found by solving the Lippmann–Schwinger equation:

\[
|\Psi\rangle = |\Phi_0\rangle + G_0(E)W|\Psi\rangle,
\]

(2)

where \( |\Phi_0\rangle \) is an electron eigenstate of an ideal left lead that is decoupled from the extended molecule, \( G_0(E) \) is the Green’s function for the decoupled system of the ideal leads and the extended molecule, \( W \) is the coupling between the extended molecule and leads, and \( |\Psi\rangle \) is the scattering eigenstate of the complete coupled system. In evaluating \( G_0(E) \) semiempirical extended Hückel theory13,14 was used to model the electronic structure of the extended molecule. Previous calculations based on extended Hückel theory have yielded elastic tunneling conductances in agreement with experiment for molecules thiol bonded to gold electrodes12,15,16 and have accounted for transport phenomena observed in molecular arrays on silicon10 as well as electroluminescence data17 current–voltage characteristics17 and STM images18 of molecules on complex substrates.

We calculated the zero bias tunneling conductances for gold-PDT-gold molecular wires from the Landauer formula

\[
g = g_0 \sum_{ij} |t_{ji}^{tel}(0)|^2 v_j/v_i \quad \text{with} \quad g_0 = 2e^2/h ,
\]

where \( g \) is the conductance step height as the bias voltage applied across the extended molecule.

We then calculated the vibrational modes, their frequencies, and IETS intensities as described above for many gold-PDT-gold extended molecules with various gold–sulfur bond geometries. Representative values of these theoretical calculations are shown in Fig. 2 for several extended molecules with gold clusters of various sizes together with the experimental IETS phonon mode histogram7 that extends from 39 to 52 meV.

We show the vibrational modes that we find in this energy range for model top and bridge site bonding geometries in Fig. 1. The calculated IETS spectra (phonon energies and IETS intensities) in the same energy range are shown in Fig. 2 for several extended molecules with gold clusters of various sizes together with the experimental IETS phonon mode histogram.7

The mode with the strongest calculated IETS intensities is shown in Fig. 2 is mode I shown in the top row of Fig. 1. In this mode the sulfur atoms have the strongest vibrational amplitudes and move in antiphase, approximately along the axis of the molecule. The other mode in this energy range is mode II shown in the lower row of Fig. 1. It is similar to mode I except that the sulfur atoms move in phase with each other.

![FIG. 1. Calculated vibrational modes in phonon energy range from 39 to 52 MeV for trans-PDT-bridging gold nanoclusters with sulfur atoms bonded to gold in top-site and bridge-site geometries. Red arrows show un-normalized atomic displacements. Mode I has the stronger IETS intensity (Ref. 20).](image)
As is seen in Fig. 2 the calculated IETS intensities for mode II are much weaker than those for mode I for both top and bridge site bonding.

The reason for this difference between the IETS intensities of modes I and II can be understood intuitively by considering the nature of the motion in relation to Eq. (1): Since in mode I the two sulfur atoms move in antiphase the gold–sulfur distances for both sulfur atoms either increase or decrease together as the extended molecule vibrates. These distances can be regarded as the widths of tunnel barriers between the molecule and the two gold electrodes. Thus, the motions of the two sulfur atoms act in concert to widen or narrow both tunnel barriers together and, therefore, to weaken or strengthen the electron transmission amplitude through the molecular wire. Thus, the magnitude of the difference between the elastic electron transmission amplitudes through the molecular wire in its equilibrium and vibrating geometries \( |t_{j1}^{\text{el}}(\{\text{Au}_{\text{top}}\}) - t_{j1}^{\text{el}}(\{0\})| \) in Eq. (1) is enhanced. By contrast in mode II when the gold–sulfur distance for one sulfur atom increases the gold–sulfur distance for the other sulfur atom decreases. Thus, the effects of the motions of the two sulfur atoms on the elastic transmission amplitude through the molecular wire tend to cancel. Thus \( |t_{j1}^{\text{el}}(\{\text{Au}_{\text{top}}\}) - t_{j1}^{\text{el}}(\{0\})| \) in Eq. (1) is smaller for mode II than mode I and, therefore, the IETS intensity \( \delta_{j1} \) for mode II is much smaller as is seen in Fig. 2.

Comparison of the calculated IETS spectra in Fig. 2 with the experimental phonon mode histogram indicates that vibrational mode I contributed most of the counts recorded in the histogram in the energy range shown. This is consistent with the fact that the calculated IETS intensities for mode I are much stronger than those for mode II and therefore mode I should be more readily detected in experimental IETS measurements.

The theoretical results for the dominant IETS mode I in Fig. 2 reveal that the prominent features of the histogram can be explained as arising from PDT molecules that bond to the gold electrodes in different ways: The main peak in the experimental histogram that is centered at \( \sim 46 \) meV matches our theoretical result for trans-PDT molecules that bond to both gold electrodes in the top site geometry. The weaker peak centered near 42 meV matches our predictions for molecules that bond to one gold electrode in the top site geometry and to the other electrode in the bridge site geometry. The shoulder of the experimental histogram at lower phonon energies between 39.5 and 41.5 meV corresponds to our results for molecules bonding to both electrodes in the bridge site geometry.

Notice that our theoretical results for phonon mode I of PDT molecules bonded to both electrodes in the top site geometry (the feature near 45.5 meV in the theoretical spectra in Fig. 2) are very well converged with respect to increasing gold cluster size: Both the calculated phonon energies and the IETS intensities are almost independent of the gold cluster size in the size range shown (10–13 gold atoms per cluster). The calculated phonon energy of this dominant mode matches the phonon energy of the main peak of the experimental phonon mode histogram in Fig. 2 very well. It is also well separated from the calculated phonon energies of the dominant mode I for the pure bridge and mixed bridge–top site bond geometries. As a check we calculated the vibrational mode energies and IETS intensities for a few examples of extended molecules using a different density functional and found similar results. Thus, our results identify unambiguously those specific realizations of the molecular wire that gave rise to the counts within the main peak of the experimental histogram reproduced in Fig. 2 as being those in which both sulfur atoms bonded to the gold electrodes in the top site geometry. The calculated mode I phonon energies in Fig. 2 for pure bridge site-bonded and mixed bridge-top site-bonded molecular wires show more variation with gold cluster size than do the calculated mode I phonon energies for molecules in the pure top site-bonded geometry. However, the ranges in which the calculated energies of the mode I phonons for pure bridge site-bonded and mixed bridge/top site-bonded molecular wires occur do not overlap. Also, the calculated phonon energies for these modes and bonding geometries do not show any systematic trend toward higher or lower values with increasing cluster size. Thus, it is plausible that the weaker peak centered near 42 meV in the experimental histogram is due to mixed bridge/top site-bonded molecular wires and the lower energy shoulder between 39.5 and 41.5 meV in the histogram is due to pure bridge site-bonded wires.

As the gold-PDT-gold junction was stretched in the experiment the energy of the prominent phonon mode in the IETS spectrum was observed to switch from \( \sim 42 \) to \( \sim 46 \) meV. It was conjectured that this switch may be due to a change in the contact configuration or between gauche and trans molecular geometries, but no evidence supporting either possibility was offered and the contact configurations involved were not identified. Here we point out that trans-PDT molecules switching from the mixed top–bridge site bonding (calculated phonon energy \( \sim 42 \) meV) to the pure top site bonding geometry (calculated phonon energy \( \sim 45.5 \) meV)
accounts for this observed transition. Our calculated distance between the gold clusters of the extended molecule is larger for pure top site bonding than for mixed top–bridge bonding. This is consistent with the transition from mixed top–bridge to pure top site bonding occurring as the molecular junction is stretched. For longer chain alkanedithiols, it has been conjectured\(^1\) that switching from mixed hollow site–top site bonding to top site bonding at both gold electrodes may occur. This conjecture does not account for the observed switch from the \(\sim 42\) meV mode to the \(\sim 46\) meV mode in the gold-PDT-gold junctions: As noted above, we find hollow-site bonding to be much more fragile (and thus less likely to be realized) than bridge site bonding. We also find the energy of the mode of the mixed hollow-top structure with the strongest IETS intensity to match neither the \(\sim 42\) meV nor the \(\sim 46\) meV phonon mode. The theoretical results presented above are for trans-PDT molecules. We have also studied many gold-PDT-gold structures with molecular gauche defects and find that such structures also do not account for the observed\(^7\) switching from the \(\sim 42\) meV phonon mode to the \(\sim 46\) meV phonon mode.

In conclusion: We have shown inelastic tunneling spectroscopy to be able to distinguish between different bonding geometries of the molecule and metal contacts in single-molecule molecular wires, an important and previously elusive goal in the field of single-molecule nanoelectronics. We have definitively identified particular realizations of gold-propanedithiolate-gold molecular wires in a recent experiment\(^7\) in which the molecule bonded to a single gold atom of each electrode. The success of our approach rests on the fact that \textit{ab initio} density functional theory calculations of vibrational modes and their frequencies are known to be accurate because in the Born–Oppenheimer approximation they are electronic \textit{ground state total energy} calculations.\(^1,5\) We rely on transport calculations only for the identification of the phonon mode in a particular frequency range that has the largest IETS intensity, and our identification of this mode is also supported by physical reasoning.

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\(^1\)For a review see G. Kirczenow, \textit{The Oxford Handbook of Nanoscience and Technology: Volume 1: Basic Aspects} (Oxford University Press, Oxford, UK, 2010), Chap. IV.
\(^8\)The \textsc{gaussian} 09 Revision: A.02 code was used with the B3PW91 hybrid functional and Lan12DZ basis. The functional PBE0(PBE1PBE) was used for comparison.
\(^14\)\textsc{yahemop} numerical package by G. A. Landrum and W. V. Glassy, Source-Forge, Fremont, California, 2001.