J. Phys. Chem. A **2004,** *108,* 5655−5661

Tunneling while Pulling: The Dependence of Tunneling Current on End-to-End Distance in a Flexible Molecule

Jianping Lin and David N. Beratan*

Departments of Chemistry and Biochemistry, Duke University, Durham, North Carolina 27708

Received: December 19, 2003; In Final Form: April 10, 2004

Most molecules access a broad range of conformations at room temperature. Since electron-tunneling interactions are exponentially sensitive to geometry changes, thermal fluctuations are expected to have a large influence on room-temperature tunneling currents and scanning tunneling microscope images. We explore the influence of conformational freedom on tunneling currents in a simple model for tunneling mediated by a single small molecule that bridges between a model tip and substrate. The tip and substrate are described as semi-infinite structures. The bridging molecule and the metals are all described with tight-binding Hamiltonians. The conformationally averaged tunneling matrix element, proportional to the tunneling currents, is computed from thermally accessible molecular conformations. We vary the sulfur-to-sulfur separation distance in $-S-(CH_2)_8-S-$ (*n*-octanedithiol) and, at each of these separations, compute the family of thermally accessible conformers. The two sulfur atoms are constrained to positions along a line perpendicular to the substrate surface. The conformationally averaged tunneling current computed for each fixed sulfur-to-sulfur distance is predicted to display an average distance dependence that is strikingly similar to the decay found in experiments performed on families of extended ("all trans") *n*-alkanes. That is, the tunneling current is predicted to decay exponentially with a decay parameter of $\sim$1.0 Å^{-1} based on the tip to substrate distance. This observation supports the notion that the most strongly coupled conformers in the ensemble dominate the STM tunneling current. This conclusion is also consistent with the analysis of protein electron-transfer systems, where thermal fluctuations are predicted to shorten coupling pathways and to minimize the influence on the rate of destructive interferences among multiple coupling pathways.

I. Introduction

Since its invention, the scanning tunneling microscope (STM) has become a key instrument in surface science, and it continues to provide exciting data regarding single-molecule properties, chemisorption, and physisorption.[1,2] Moreover, STM microscopy, conducting atomic force microscopy (CAFM), and related single molecule probes[3−8] provide a means for approaching the long-term goal of realizing molecular-scale electronic devices.

Many groups are probing single or few-molecule tunneling using STM and CAFM, especially, the dependence of tunneling current on molecular structure and conformation. Recently, Lindsay[6] studied the stochastic switching in wired molecules using STM, which may be caused by the mobility of molecules tethered to gold via a thiol linkage. Advances also included the observation of single molecular switching[9] and negative differential resistance.[4,5] Some of these effects may arise from molecular conformational changes. Other conformational-controlled molecular structures include amplifiers.[10] Several groups have identified STM signatures characteristic of semiflexible molecules such as porphyrin derivatives, 4,4′-dimethylbianthrone, C_{60}, methyl- and bromo-substituted alkanes and alkanols, etc.[11−14]

Molecular manipulations in STM experiments are generally divided into vertical (orthogonal to the substrate surface) and lateral (including pulling, pushing, and sliding) processes.[15] Several groups have employed lateral processes to manipulate single molecules on solid substrates with an STM tip.[11,16−18] In vertical extension experiments, Gaub[19] has explored the structural changes of single DNA molecules by stretching them with an AFM tip, while Cai has probed the conductivity of DNA in CAFM experiments.[20] CAFM studies promise to provide access to studies of tunneling current changes with molecular conformation.[21,22]

Many groups[23−29] are employing theoretical analysis to understand the mechanisms of electron transport through molecular structures and junctions. A variety of methods has been developed in the last 20 years to analyze and simulate tunneling currents and STM images.[30−38] These methods are relatively successful at predicting magnitudes of currents and qualitative features of STM images. Detailed comparisons are often difficult to make because the atomic details of the STM attachment geometry, molecular conformations, and tip structure are difficult to characterize. Relatively limited attention has been paid to details of how molecular conformation can influence tunneling currents. Conformational changes have been implicated in controlling a number of molecular switching phenomena observed in STM,[9,39] and conformational control of electron-transfer rates is well-known in the chemical literature.[40,41] Our goal is to characterize the influence of conformational freedom on the qualitative features of STM images, and to understand how constraining the end-to-end distance in a flexible molecule might influences the STM current that the molecule mediates.

Our analysis of STM currents follows the approach of Marcus and co-workers.[37] Their model includes a tight-binding description of the tip, molecule, and substrate. We use this strategy to

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* Address correspondence to this author. E-mail: david.beratan@duke.edu.

10.1021/jp0379502 CCC: $27.50

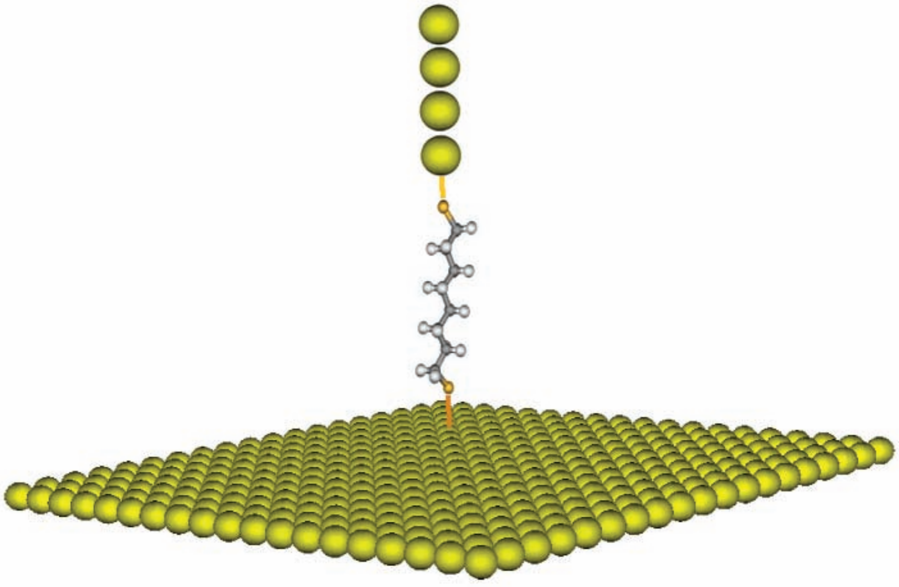

Figure 1. First layer of the gold (111) surface, the bridging molecule, and the model tip. The molecules interact with a 19 × 19 array of atoms. The molecule is tethered to the tip and substrate by Au−S bonds.

explore current variations among specific molecular conformations from which we compute the conformationally averaged currents for several fixed tip-to-substrate distances. Specifically, we apply this approach to analyze a model structure, octanedithiol ($-S-(CH_2)_8-S-$), linking the STM tip to the substrate.

II. Theoretical Model

A. Tip and Substrate. In the Marcus model,[37] the tip is described as a semi-infinite 1D chain of gold atoms and the substrate is modeled as a semi-infinite Au slab with the (111) surface exposed (each gold atom is represented with one 6s orbital[42]). The molecule is bound to the tip and surface through the terminal sulfur atoms, and we fixed the two sulfur atoms to the semi-infinite chain in a straight line that is perpendicular to the substrate (the sulfur atom that is closest to the substrate lies above a gold atom) as shown in Figure 1. We assume that the molecule interacts with the tip through the terminal gold atom of the tip and with substrate through the 19 × 19 atoms of the first layer. There is no assumption of nearest-neighbor interactions between the atoms of the bridge and these gold atoms of the first layer.

B. Tunneling Current for One Single Conformer. In the limit of small bias voltages and low temperature, the STM current is given by[37]

$$I = \frac{e^2 v}{|\gamma|}\int \mathrm{d}\mathbf{k}_\mathrm{s}\, |\langle \phi_\mathrm{t}|H|\phi_{\mathbf{k}_\mathrm{s}}\rangle|^2 \delta(E - E_\mathrm{F})$$
$$= \frac{e^2 v}{|\gamma|}\int \mathrm{d}\mathbf{k}_\mathrm{s}\, |H_{\mathrm{t},\mathbf{k}_\mathrm{s}}|^2 \delta(E - E_\mathrm{F}) \propto \frac{\rho_\mathrm{s}{}^0 \int \mathrm{d}\mathbf{k}_\mathbf{s}\, |H_{\mathrm{t},\mathbf{k}_\mathrm{s}}|^2 \delta(E - E_\mathrm{F})}{\int \mathrm{d}\mathbf{k}_\mathbf{s}\, \delta(E - E_\mathrm{F})} \quad (1)$$

where v is the bias voltage, γ is the coupling element between the nearest neighbor tip atoms and $\rho_\mathrm{s}{}^0$ denotes the gold substrate density of states at the Fermi energy, E_F, t and s denote tip and substrate, respectively. $\boldsymbol{k}_\mathrm{s}$ is the wave vector for the substrate states and the integral is over the Fermi surface of the substrate. ϕ_t and $\phi_{\mathbf{k}_\mathrm{s}}$ are the wave functions of the first tip atom and the substrate, respectively.

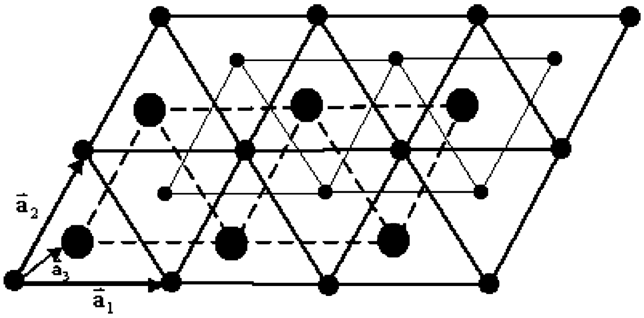

Figure 2. Geometry of the Au (111) surface. The large balls represent the first layer, the midsized balls represent the second layer, and the smallest balls layer represents the third layer.

The tight-binding wave functions for the semi-infinite Au with a (111) surface are (Figure 2 shows the geometry of the Au (111) surface) as follows:[43]

$$\phi_{\mathbf{k}_\mathrm{s}} = \sqrt{2} \sum_{l_1, l_2 = -\infty}^{\infty} \sum_{l_3 = 1}^{\infty} (|F|/F)^{l_3} \sin(2\pi k_3 l_3) \times \exp[i2\pi(k_1 l_1 + k_2 l_2)]\varphi_\mathrm{s}(\mathbf{r} - \mathbf{r}_l) \quad (2)$$

$$F = \alpha[\exp(i2\pi k_1) + \exp(i2\pi k_2) + 1] \quad (3)$$

where $\mathbf{r}_l = \sum_{i=1}^{3} l_i \mathbf{a}_i$, and $\mathbf{a}_i$ is a lattice vector and $\varphi_\mathrm{s}(\mathbf{r} - \mathbf{r}_l)$ is the wave function of a gold s-orbital at position $\mathbf{r}_l$. α is the coupling element between the nearest-neighbor gold atoms in the substrate.

The bridge-mediated coupling is

$$|H_{\mathrm{t},\mathbf{k}_\mathrm{s}}|^2 = |\langle \phi_t|H|\phi_{\mathbf{k}_\mathrm{s}}\rangle|^2 = 2 \sin^2(2\pi k_3)\Big[\Big[\sum_{l_1=1}^{19}\sum_{l_2=1}^{19} \cos 2\pi(k_1 l_1 + k_2 l_2)\langle \phi_t|H|\varphi_\mathrm{s}(\mathbf{r} - \mathbf{r}_l)\rangle\Big]^2 + \Big[\sum_{l_1=1}^{19}\sum_{l_2=1}^{19} \sin 2\pi(k_1 l_1 + k_2 l_2) \times \langle \phi_\mathrm{t}|H|\varphi_\mathrm{s}(\mathbf{r} - \mathbf{r}_l)\rangle\Big]^2\Big] \quad (4)$$

Using perturbation theory in the surface−molecule and tip−molecule interactions, the interactions between the tip and

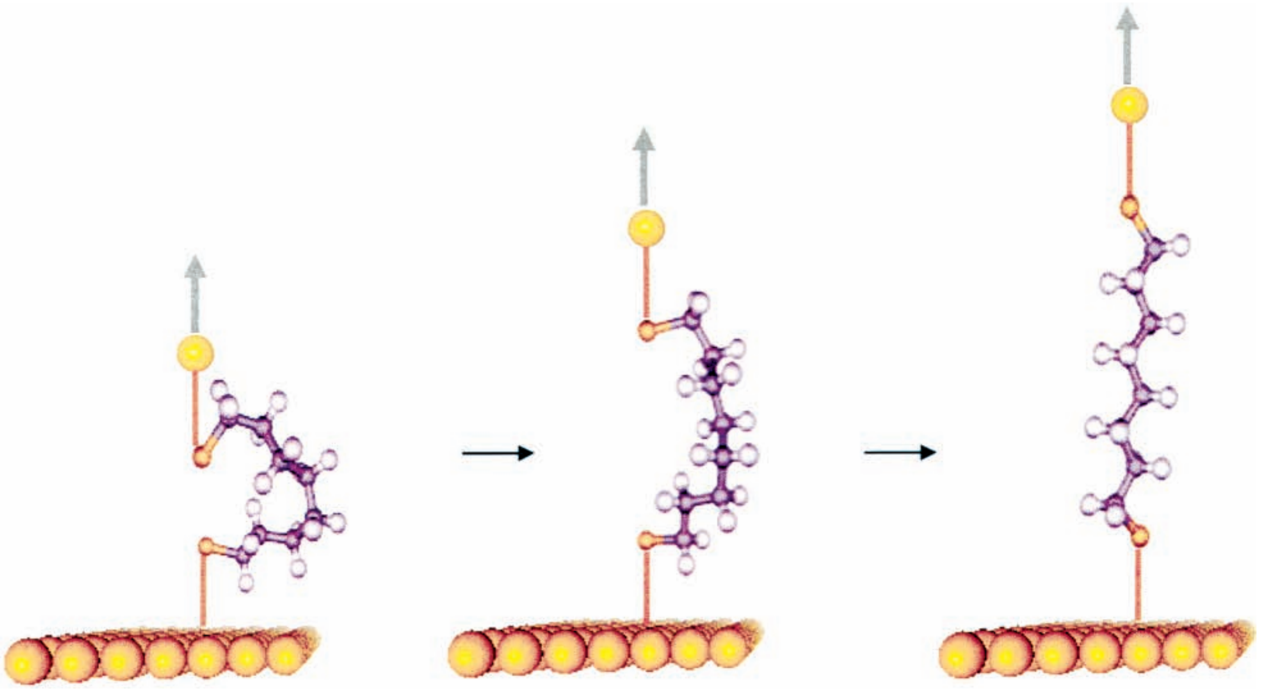

Figure 3. Typical molecular configurations for three molecular extension distances.

substrate mediated by the molecule is[44,45]

$$\langle \phi_t | H | \varphi_s(\mathbf{r} - \mathbf{r}_l) \rangle = \sum_i \sum_j (\mathbf{H} - E\mathbf{S})_{ti} (\mathbf{H} - E\mathbf{S})_{ij}^{-1} (\mathbf{H} - E\mathbf{S})_{js} \quad (5)$$

where i and j correspond to atomic orbitals of the molecule, t and s are the atomic orbitals of tip and substrate, respectively. **H** is the Hamiltonian matrix, **S** is the overlap matrix, and E is the tunneling energy.

We randomly selected 60 **k** points on the Fermi surface for the semi-infinite Au metal to compute the Fermi surface integral. We divided the Fermi surface into a mesh and chose 60 points from this surface (as in ref 37). Then

$$\frac{\int \mathrm{d}\mathbf{k}_\mathbf{s}\, |H_{\mathrm{t}\mathbf{k}_\mathrm{s}}|^2 \delta(E - E_\mathrm{F})}{\int \mathrm{d}\mathbf{k}_\mathbf{s}\, \delta(E - E_\mathrm{F})} \approx \sum_{a=1}^{60} |H_{\mathrm{t}\mathbf{k}_a}|^2/60 \quad (6)$$

We constructed the Hamiltonian and overlap matrices using the extended-Hückel approach.[46] The diagonal Hamiltonian elements H_{ii} of the molecule are set equal to the negative of atomic ionization potentials of the valence atomic orbitals i. The off-diagonal elements are, according to Hoffmann's prescription[46]

$$H_{ij} = 1.75 S_{ij} [(H_{ii} + H_{jj})/2]$$
$$S_{ij} = \langle \varphi_i | \varphi_j \rangle \quad (7)$$

where φ_i is the basis function of atomic orbital i.

C. Conformational Sampling and Averaging. We perform conformational analysis of the bridging molecule using the Macromodel program.[47] As a first simple approach, we assume that the gold tip and substrate constrain the end-to-end distance in the molecule without influencing the intramolecular potential, and nonbonded interactions between the molecule and tip/substrate are neglected. We use the MM2 force field with a 10 kJ/mol energy cutoff and a 3000 step comformational search in Macromodel.[47] Conformers with van der Waals overlap between the molecule and the surface are rejected.

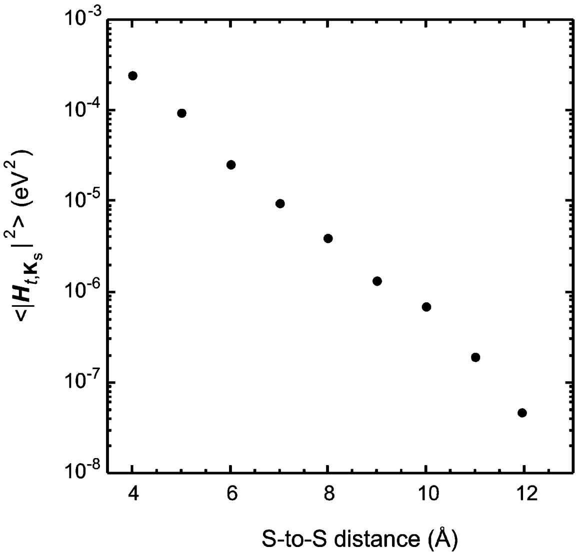

Figure 4. Computed dependence of the tunneling current on extension of an octanedithiol molecule, $\langle |H_{\mathrm{t},\mathbf{k}_\mathrm{s}}|^2 \rangle$, as a function of sulfur-to-sulfur distance.

For each fixed end-to-end distance, $\langle |H_{\mathrm{t}\mathbf{k}_\mathrm{s}}|^2 \rangle$, the conformationally averaged value of $\{\int \mathrm{d}\mathbf{k}_\mathbf{s}\, |H_{\mathrm{t},\mathbf{k}_\mathrm{s}}|^2 \delta(E - E_\mathrm{F})\}/\{\int \mathrm{d}\mathbf{k}_\mathbf{s}\, \delta(E - E_\mathrm{F})\}$ is computed using:

$$\langle |H_{\mathrm{t}\mathbf{k}_\mathrm{s}}|^2 \rangle = \left[\sum_i \exp(-E_i/RT) \left(\frac{\int \mathrm{d}\mathbf{k}_\mathbf{s}\, |H_{\mathrm{t},\mathbf{k}_\mathrm{s}}|^2 \delta(E - E_\mathrm{F})}{\int \mathrm{d}\mathbf{k}_\mathbf{s}\, \delta(E - E_\mathrm{F})} \right)_i \right] \times \left[\sum_j \exp(-E_j/RT) \right]^{-1} \quad (8)$$

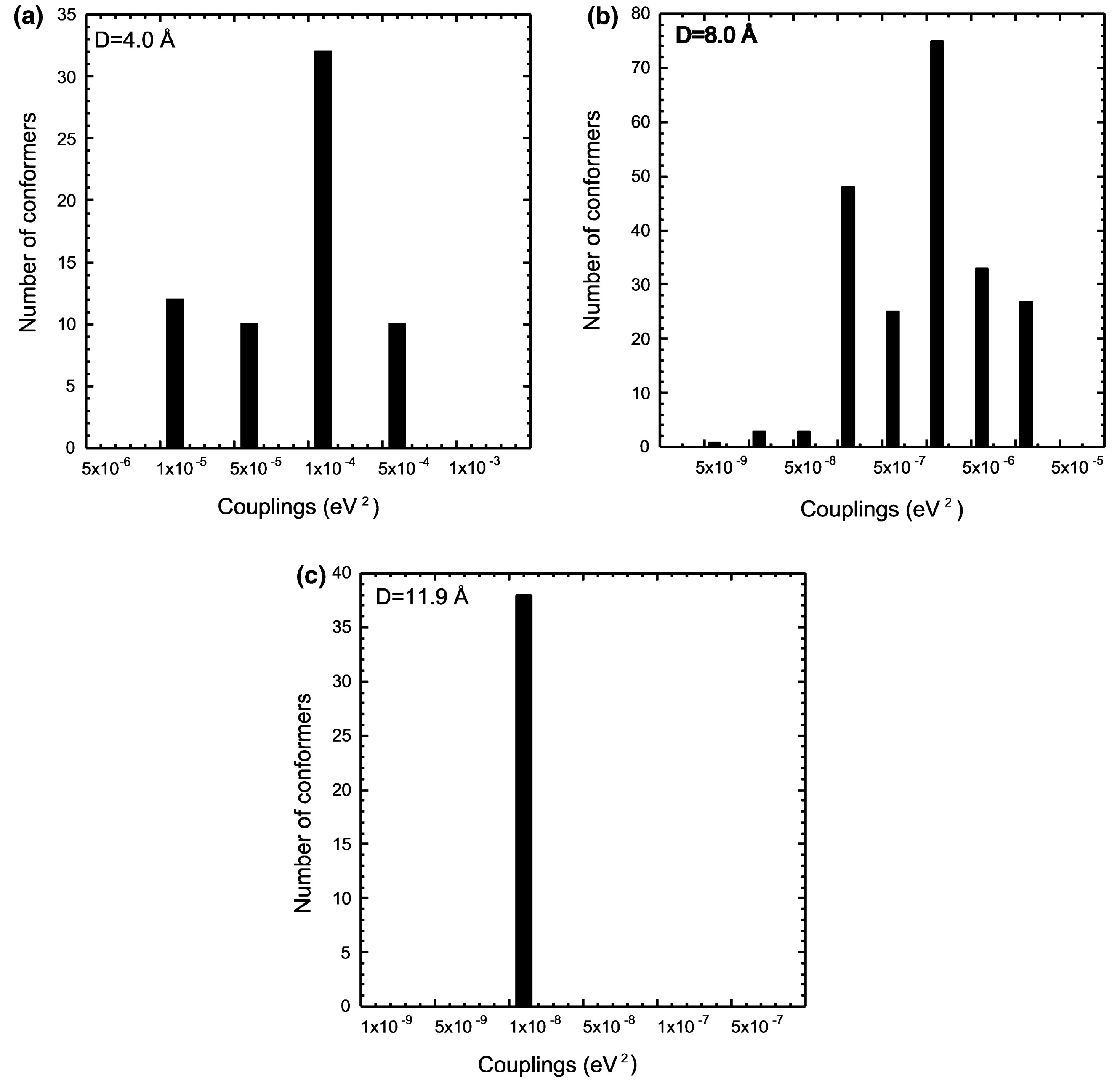

Figure 5. Histogram showing the distribution of couplings for three sulfur-to-sulfur distances. The number of conformers vs the **k**-space averaged coupling values ($\sum_{a=1}^{60}|H_{\mathrm{t},\mathbf{k}_a}|^2/60$) is shown for (a) 4.0, (b) 8.0, and (c) 12.9 Å S-to-S distances.

From eq 6,

$$\langle|H_{\mathrm{t}\mathbf{k}_s}|^2\rangle = \frac{\sum_i \sum_{a=1}^{60} |H_{\mathrm{t}\mathbf{k}_a}|_i^2 \exp(-E_i/RT)}{60\sum_i \exp(-E_i/RT)} \qquad (9)$$

Here, E_i is the molar energy of conformer i, R is the gas constant, and T is the absolute temperature.

D. The Nature of the Approximations. To equilibrate the tip Fermi energy (equal to the gold s-orbital site energy) with the Fermi energy of the substrate, we shift the site energies of the tip gold atoms to the Fermi energy of the substrate. The Fermi surface for the semi-infinite Au slab is approximated with the Fermi surface of bulk gold and the Fermi energy is −4.86 eV (calculated from the gold s-band using the tight-binding model). The allowed k_3 values for the semi-infinte slab are $0 < k_3 < {}^1/_2$.[37,43]

III. Results

We computed the tunneling current while extending the conformationally flexible octanedithiol molecule by varying the substrate-tip distance (see Figure 3). Collecting thermally accessible molecular conformations with the corresponding sulfur-to-sulfur distance, and integrating over the Fermi surface for each conformer, we varied the sulfur-to-sulfur distance from 4.0 to 11.9 Å (a fully extended octanedithiol). For each distance, we used the Macromodel program[47] to sample conformational space, and then calculated the $\langle|H_{\mathrm{t}\mathbf{k}_s}|^2\rangle$ values with eq 9. Figure 4 indicates that extending the octanedithiol molecule causes $\langle|H_{\mathrm{t}\mathbf{k}_s}|^2\rangle$ to decrease exponentially with distance, with a decay factor $\beta = 1.0$ Å^{-1}.

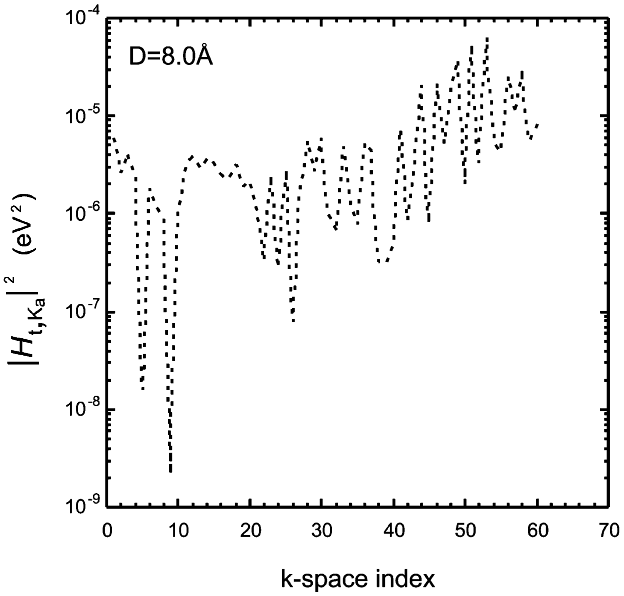

Figure 6. For a conformer with a sulfur-to-sulfur distance of 8.0 Å, the distribution of $|H_{t,\mathbf{k}_a}|^2$values over **k** space is shown.

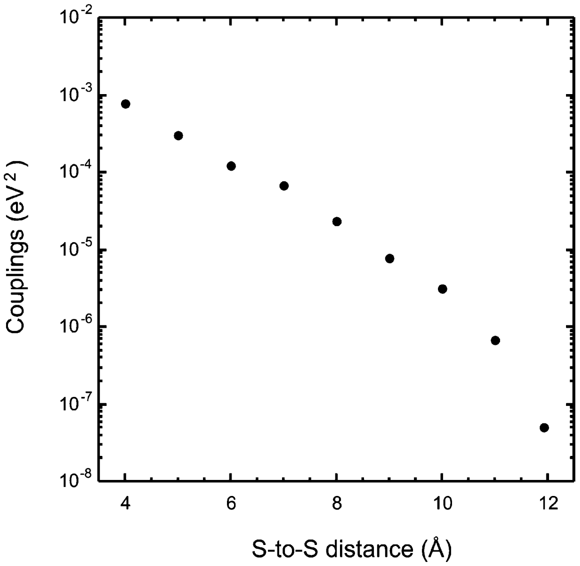

Figure 7. Strongest **k**-space average coupling values ($\sum_{a=1}^{60}|H_{t,\mathbf{k}_a}|^2/60$) for one molecular conformation at each end-to-end distance shown as a function of the sulfur-to-sulfur distance.

While our conformationally averaged results mirror STM and CAFM distance dependent currents as well as small molecular electron-transfer rate data,[48−59] the range of coupling values for each end-to-end distance is large. For the three sulfur−sulfur distances (4.0, 8.0, and 11.9 Å), Figure 5 shows the distribution of Fermi surface averaged couplings. Figure 5 shows that for a flexible octanedithiol molecule at a fixed sulfur−sulfur distance (4.0 or 8.0 Å), the $\sum_{a=1}^{60}|H_{t,\mathbf{k}_a}|^2/60$ values differ by as much as 4 orders of magnitude among conformers. For a fully extended octanedithiol molecule, the $\sum_{a=1}^{60}|H_{t,\mathbf{k}_a}|^2/60$ values do not change much among conformers. We also explored the dependence of coupling on the Fermi surface wave vector for an 8.00 Å S-to-S distance. The conformational averaged $|H_{t,\mathbf{k}_a}|^2$ values (Figure 6) vary by 5 orders of magnitude.

For each sulfur−sulfur distance, we selected the strongest **k**-space averaged coupling values from among the conformers and plotted these values vs distance in Figure 7. While extending the octanedithiol molecule, the full Fermi surface averaged coupling of the largest coupled conformer decreases with a decay factor of 0.9−1.0 Å^{-1}, suggesting that the overall conformationally averaged coupling is determined by the most strongly coupled members of the ensemble.

IV. Discussion

Figure 4 shows exponential decay with distance having a decay exponent $\beta = 1.0$ Å^{-1}. In the weak coupling limit, for tunneling through a periodic potential, the squared coupling ($|H_{DA}|^2$) decays approximately exponentially with distance,[48]

$$|H_{DA}|^2 \approx |H_{DA}^0|^2 e^{-\beta r} \qquad (10)$$

Values of β are observed to be about 1.0 Å^{-1} for electron tunneling through saturated hydrocarbon bridges. Experimentally, in bridge-mediated ET rate studies, Miller and co-workers[49] measured β to be slightly less than 1.0 Å^{-1}. Measurements from Chidsey,[50] Miller,[51] Paddon-Row,[52,53] and Finklea[54] support $\beta \sim 0.9$ Å^{-1} for interfacial or homogeneous phase electron transfer through saturated hydrocarbon spacers. In theoretical computations, Newton[55] found $\beta \sim 0.9$ Å^{-1} for extended saturated bridge, and from calculating the splitting for divinylalkanes, Jordan[56] found $\beta \sim 1.0$ Å^{-1}. Waldeck[57] studied solvent effects on electronic coupling for supermolecules (an anthracene donor and a nitroethylene acceptor mediated with a rigid bridge) and found that β varies from 0.64 to 0.97 Å^{-1} when the solvent is switched from CH_2Cl_2 to benzonitrile. Whitesides' thin films in metal−insulator−metal tunneling studies indicate $\beta = 0.87 \pm 0.1$ Å^{-1} for alkanethiols.[58] In electron transfer through Ferrocene-terminated alkanthiol monolayer on gold, Liu found a $\beta \sim 1.0$ Å^{-1}.[59] STM and CAFM studies indicate $\beta \sim 1.1-1.2$ Å^{-1} for alkane chains.[8,60] Recently, Reed and co-workers[61a] reported a zero-field β value of 0.79 ± 0.01 Å^{-1} for a self-assembled alkanethiol monolayer using a well-developed nanometer-scale device that excludes potential contamination effects from influencing the measurement. A recent review summarizes distance dependencies for tunneling through organic structures.[60b] The computational results found here are in qualitative agreement with this large body of experimental data.

Our systems are assumed to transport charge by a superexchange mechanism, so the averaged distance-dependent decay factors fall in a narrow range. DNA mediated electron transfer, in contrast, exhibits a wide range of distance dependencies, with a decay factor $\beta \sim 0.1-1.5$ Å^{-1},[62] because electron transfer in DNA can access tunneling or multistep hopping mechanisms.[63−68]

Figure 7 indicates that the strongest coupled conformers have conformationally averaged distance decay exponents that are nearly the same as for the ensemble average. This is consistent with a rule that "strong conformers win." Figure 5 shows that, at a fixed distance, the difference among couplings between conformers is quite large. This observation shows that the coupling is very sensitive to geometry. Recently, Stuchebrukhov and co-workers[69,70] and Yamato and co-workers[71] found a considerable variation of electronic coupling with geometry in Ru-modified azurin. Risser, Beratan, and co-workers[72] observed similar coupling fluctuations in oligopeptides. Balabin and Onuchic[40] demonstrated that tunneling interactions can be controlled by far-from-equilibrium protein conformations because of the exponential sensitivity to geometry.

Figure 6 indicates that integrating the coupling over the Fermi surface is necessary for making meaningful predictions. We used the approach of Marcus and co-workers[37] that averages over discrete points on the Fermi surface. More systematic averaging could be carried out using the tetrahedron method,[73,74] for example.

The methods and models used here are semiempirical, which has the advantage of being able to treat large systems with many conformations. Experimentally, the atomic structure of the STM tip is often unknown, so many approaches are possible.[75−82]

V. Summary and Conclusions

Our studies indicate that the tunneling current is expected to have a strong conformational dependence. In some experiments, conformational freedom is limited by steric crowding. However, in less hindered structures, conformational averaging is expected to be essential to reproduce the observed tunneling currents. The predicted tunneling currents in these saturated structures decrease approximately exponentially with distance as the structures are extended. The averaged decay is similar to that found in small molecule studies, despite the difference in the nature of the homogeneous and heterogeneous experiments and in the conformational sampling. This observation is consistent with a rule that “strong conformers win” (Figure 7).

Our method could be improved in several ways. For example, we neglected the molecule-tip and molecule-surface interactions when performing conformational sampling. This method is semiempirical, and the results provide a relatively simple interpretation of the STM tunneling currents. Ab initio and nonequilibrium methods would provide an improved description of the tunneling.[32,33,35,38] There is also uncertainty in the thiol attachment chemistry, and experimental characterization of this chemistry would provide further constraints on the calculations. However, the effects described here arise largely from alkane chains conformational flexibility; the influence of the tip and substrate attachment is largely a “prefactor effect” on the electron tunneling explored here.

Acknowledgment. We thank the National Institutes of Health (GM-48043) and Duke University for support of this research. This research is also supported by the W. M. Keck Center for Nanoscale Molecular Electronics and the NEDO Foundation.

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