Inelastic Effects on the Transport Properties of Alkanethiols

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ABSTRACT

Using first-principles approaches, we investigate local heating and the inelastic contribution to the current for various alkanethiols sandwiched between metal electrodes. In the absence of good heat dissipation into the bulk electrodes, we find that the local temperature of the alkanethiols is relatively insensitive to their length. This is due to the rates of heating and cooling processes scaling similarly with length. On the other hand, when considering heat dissipation into the bulk electrodes, the local temperature of alkanethiols decreases as their length increases. We also find that the inelastic scattering profile displays an odd−even effect with length which compares well with experimental results. This effect is due to the alternating direction of the CH_3 group motion with respect to current flow with increasing C atoms in the chain and is very sensitive to the structure of the carbon−sulfur−gold bond. Inelastic scattering profiles can therefore help illuminate the bonding configuration of molecules to metallic surfaces.

There is an ever-increasing interest in charge transport in organic molecules due to their potential application in electronic devices.[1−7] Recently, several laboratories have reported consistent data in the resistance of alkyl chains.[8−12] Some theoretical calculations support these results,[13] at least in the shape of the current−voltage (I−V) characteristics.[14,15] This seems to suggest that a reproducible contact can be created between the alkanethiols and the electrodes.[8,13,15−19] However, several current-induced mechanical effects such as forces on ions[20] and local heating[21−23] can generate substantial structural instabilities which can lead to atomic geometries quite different than those assumed theoretically.

In this paper, we focus on one current-induced mechanical effect, namely, inelastic scattering in alkanethiol molecular junctions. Our intent is (i) to explore the dependence of local heating on the length of the alkyl chains and gain insight into their stability under current flow and (ii) to determine the inelastic contribution to the current. We find that the local temperature of alkyl chains is smaller the longer the chain, provided that there is good thermal dissipation into the bulk electrodes. This is due to the insulating character of the alkanethiols and is in contrast to results for metallic quantum-point contacts.[20,21] We also find that the inelastic scattering profile displays an odd−even effect which is very sensitive to the structure of the carbon−sulfur−gold bond. This odd−even effect is in agreement with high-resolution electron energy loss spectroscopy (HREELS) experiments on the same systems.[24] This demonstrates that inelastic spectroscopy can be quite effective in determining the atomic-scale geometry of molecular junctions.[25]

We investigate these inelastic effects in the framework of static density-functional theory (DFT) in the local density approximation.[26] The calculations proceed as follows: first, the stationary scattering wave functions of ethanethiolate sandwiched between two bulk gold electrodes (represented with ideal metals, jellium model, $r_s \approx 3$) are calculated by solving the Lippmann−Schwinger equation self-consistently.[26] Due to their insulating character, the current in these systems decreases exponentially with length d as $I = I_0 \exp(-\beta d)$.[11,13,17,27] By exploiting the periodicity in $(CH_2)_2$ groups of the alkyl chains, we can then calculate the wave functions of the different molecules by a simple scaling argument. The vibrational mode energies and the transformation matrix which contains the character of the modes (longitudinal versus transverse with respect to current flow)[22] are evaluated using total-energy calculations.[28] Throughout the paper, the angle that the S−C bond makes with the surface normal has been fixed at 43 degrees, which was obtained by relaxing the structures at zero bias. This angle is in reasonable agreement with the one found in previous theoretical work.[29] Below we will show the sensitivity of the inelastic current to the variation of this angle. The electron−phonon coupling constant for each atom and mode of the chain is finally calculated as reported in ref 22. With

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these quantities we can then evaluate both the local temperature of the junction and the inelastic $I-V$ curve.

Local Heating. Let us first investigate the effect of heating due to electron−phonon interaction. This interaction allows for the exchange of energy between electrons and the lattice via absorption and emission of vibrational modes. Details of the theory of local heating in nanoscale structures can be found in refs 22 and 30. Here we just mention that there are two major inelastic channels that lead to a given local temperature in a nanojunction. One is due to inelastic processes that occur in the atomic region of the junction, i.e., involving the atoms of the alkanethiols and few atomic layers of the bulk electrodes. Electrons incident from the right or left electrode can absorb (cooling) or emit (heating) energy because of electron-vibration scattering with the ions of the junction. The other channel is due to dissipation of energy into the bulk electrodes via elastic phonon scattering. In quasi-ballistic systems, where the inelastic electron mean free path is large compared to the dimensions of the junction, elastic phonon scattering is the most efficient way of dissipating heat into the bulk electrodes.[22,30] Let us first focus on the inelastic scattering contribution assuming heat dissipation into the electrodes is negligible. This can be the result of, e.g., weak coupling of vibrational modes localized in the junction with the continuum of modes of the bulk electrodes.[22,21]

Denoting by $W_\nu^{L(R),1(2)}$ the power absorbed (emitted) by electrons incident from the left (right) via a vibrational mode ν, the total thermal power generated in the junction can be written as the sum over all vibrational modes of the above four scattering processes:[25]

$$P = \sum_{\nu \in \text{vib}} (W_\nu^{R,2} + W_\nu^{L,2} - W_\nu^{R,1} - W_\nu^{L,1}) \qquad (1)$$

This power can be expressed in terms of the electron−vibration coupling in the presence of current.[25] When the heating processes ($W_\nu^{R,2}$ and $W_\nu^{L,2}$) balance the cooling processes ($W_\nu^{R,1}$ and $W_\nu^{L,1}$), i.e., $P = 0$, a steady-state local temperature is established in the junction. This temperature is plotted in Figure 1a for various alkanethiols of different length, assuming zero background temperature. It is clear from the figure that the local temperature without heat dissipation depends weakly on the length of the molecule. This can be understood quite easily since the rate of energy transfer $W_\nu^{\alpha,k}$ scales similarly with length for all modes and processes (heating and cooling). In other words, even though the power *per mode* decreases exponentially with length by a factor $\exp(-\beta d)$ due to the corresponding exponential decrease of the current, the *total* power (eq 1) will be zero at approximately the same temperature, as the above exponential term factors out.

We now allow for the energy stored locally in the junction to dissipate away into the electrodes via the coupling between the normal modes of the molecule and the phonons of the electrodes. As in our previous work,[22] we estimate this thermal conductance by assuming the junction forms a weak mechanical link with a given stiffness K.[31] The thermal
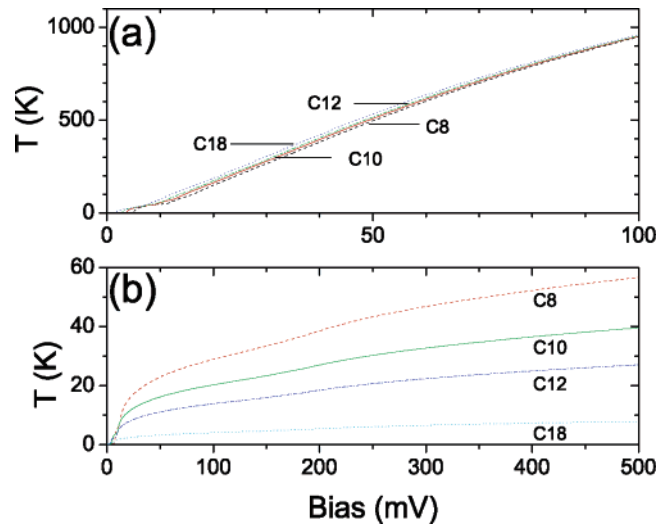
Figure 1. Local temperature as a function of bias for various lengths of alkanethiols. (a) No heat dissipation into the bulk electrodes is taken into account. (b) Heat dissipation into the bulk electrodes is taken into account.

current into the electrodes via elastic phonon scattering is thus

$$I_{\text{th}} = \frac{4\pi K^2}{\hbar} \int d\epsilon \epsilon N_L(\epsilon) N_R(\epsilon) [n_L(\epsilon) - n_R(\epsilon)] \qquad (2)$$

where $n_{L(R)}$ is the Bose−Einstein distribution function and $N_{L(R)}(\epsilon)$ is the spectral density of phonon states at the left (right) electrode surface. Since the stiffness K is proportional to d^{-1},[31] the thermal current I_{th} is proportional to d^{-2}. Therefore, while the local power in the junction (eq 1) that needs to be dissipated decreases exponentially with length, the thermal power into the electrodes that allows for this dissipation (eq 2) decreases only algebraically. This implies a lower temperature in the junction as a function of length (see Figure 1b). We note that this trend for alkanethiols is opposite to that found in atomic wires[20,21] and is due to their insulating character (conversely, the current in atomic wires is relatively independent of length[20]). This result combined with the fact that current-induced forces decrease with increasing length[20,32,33] suggest that longer alkanethiols are more stable against current flow. This is consistent with recent experimental results on similar systems.[9]

Inelastic Current. The coupling between electrons and molecular vibrations will cause small discontinuities in the conductance at biases corresponding to the energy of normal modes.[21,25,34] The position and magnitude of these discontinuities vary significantly from mode to mode and can be measured in experiments such as inelastic electron tunneling spectroscopy (IETS)[16,18] and HREELS.[19,24] The theory of inelastic scattering as we use it in this paper is reported in ref 25. We recall here that the relative strength of inelastic features is mainly determined by the character of the modes: those that have large longitudinal character with respect to current flow contribute most to the features in the inelastic conductance.[21,25,34]

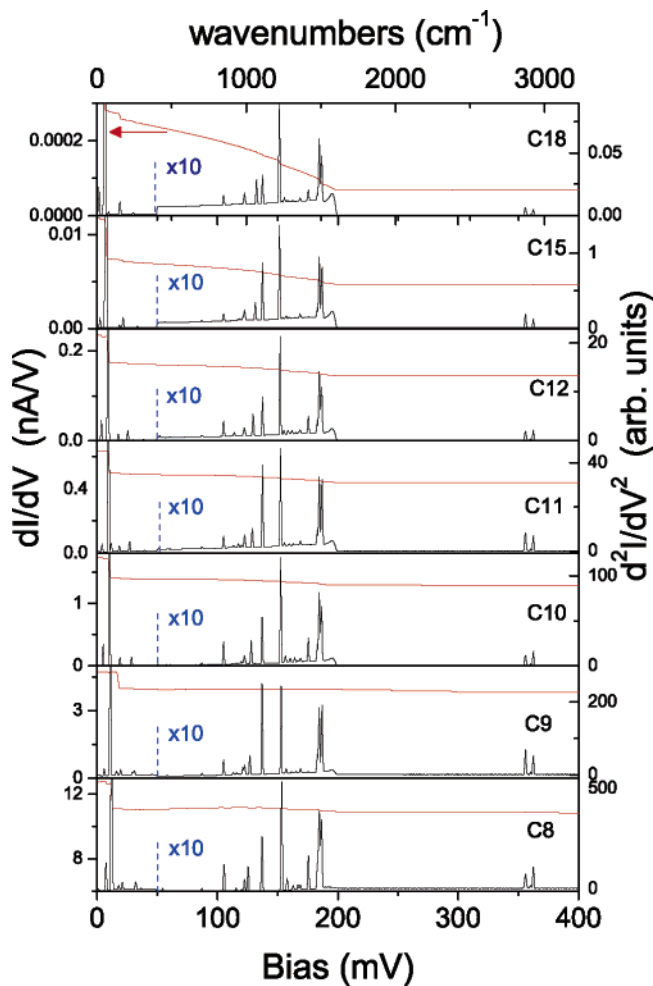In Figure 2 we plot the inelastic contribution to the conductance and its first derivative as a function of bias for

Figure 2. Differential conductance (left axis) and absolute value of d^2I/dV^2 (right axis) as a function of bias for various alkanethiols with different numbers of carbon atoms. Due to the large relative magnitude of the inelastic features of low-energy modes with respect to the high-energy modes, the curve d^2I/dV^2 has been multiplied by a factor of 10 for biases larger than 50 mV.

Figure 3. Differential conductance (left axis) and absolute value of d^2I/dV^2 (right axis) as a function of bias for undecanethiolate. The curve d^2I/dV^2 has been multiplied by a factor of 10 for biases larger than 50 mV.

Figure 4. Absolute value of d^2I/dV^2 as a function of bias for two different surface S$-$C angles of undecanethiolate. Top: the structure with an angle of 43 degrees. Bottom: the structure with an angle of 0 degrees. The change in angle transforms the mode at 176 mV (indicated by an asterisk) from quasi-transverse (top-left schematic) to quasi-longitudinal (bottom-left schematic) so that it appears as a new feature in the inelastic conductance.

various alkyl chains. A broadening of 1 meV, corresponding to elastic phonon scattering, has been introduced to make the curve d^2I/dV^2 finite. We show the modes that contribute the major peaks in Figure 3 for the case of undecanethiolate. The major vibrational modes in Figure 2 are in good agreement with the results of HREELS experiments on self-assembled monolayers.[19,24] The differences between the reported inelastic curves and the theoretical ones can be partly ascribed to modification of vibrational modes due to molecule$-$molecule interaction, an effect which we do not consider in this work. Most of the peaks at small bias ($V <$ 50 mV) are associated with stretching, bending, and twisting motions of the alkane backbone. The largest peak at low bias (also observed in IETS and HREELS experiments[16,24]) corresponds to a rigid motion of the whole molecule with respect to the electrodes. We also observe a weak odd$-$even effect in the spectrum of d^2I/dV^2 at wavenumbers 850, 1107, and 1420 cm^{-1}. This effect is due to the alternating direction of the CH$_3$ group motion with respect to current flow with increasing C atoms in the chain. It is most pronounced for
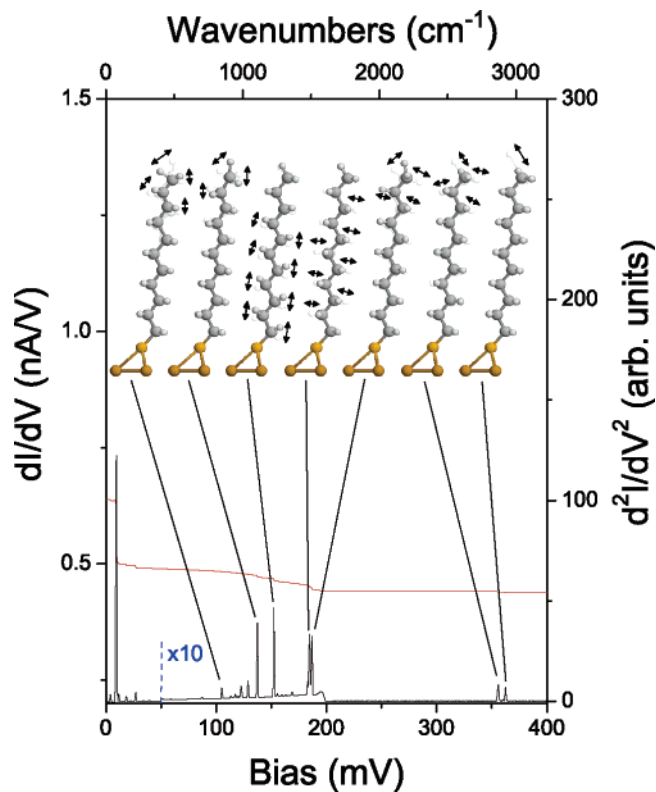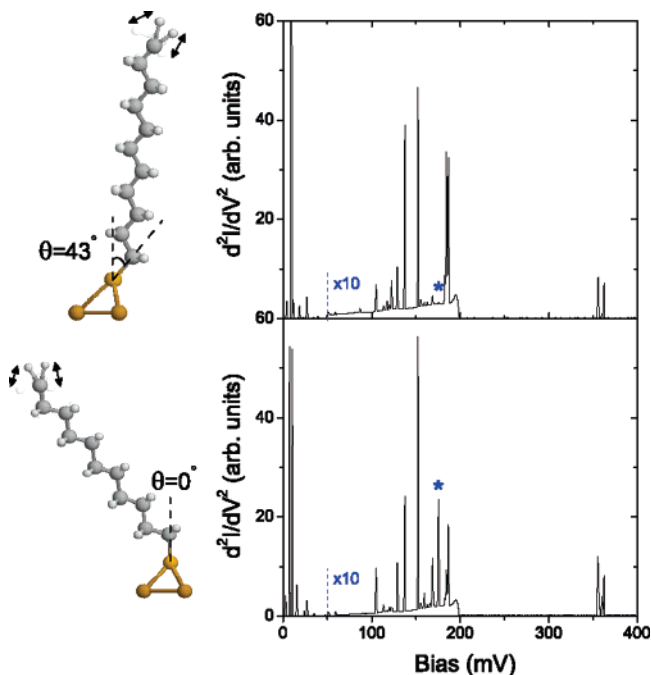
the 1420 cm^{-1} mode, which is in agreement with HREELS experiments.[24]

To conclude, we discuss how inelastic spectroscopy can probe the atomic-scale geometry of the alkanethiol—gold bond. In the above, we have considered a geometry where the S—C bond forms an angle of 43 degrees with the surface normal (see top-left schematic of Figure 4). However, recent calculations have found different energetically stable structures depending on the details of the computational methods employed.[29,35−38] The actual geometry will be determined by experimental conditions, including the way the contacts are formed. In Figure 4 we show that a change of the above angle from 43 degrees to, e.g., 0 degrees can change substantially the character of the modes in the structure. In this case, the change in angle transforms the quasi-transverse character of the mode at 1420 cm^{-1} to a quasi-longitudinal one (see Figure 4). This mode is the one responsible for the most pronounced odd—even effect we discussed above. Therefore, with a surface S—C bond angle of 0 degrees, this effect would be reversed as a function of the number of C atoms in the chain. Inelastic spectroscopy, combined with this type of detailed calculations, can therefore help illuminate the bonding configuration of molecules in metal—molecule—metal structures.

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(31) The stiffness is evaluated as $K = AY/d$, where $A \simeq 21.4$ (a.u.)^2 is the effective cross section and d is the effective length of the alkanethiol [see Patton, K. R.; Geller, M. R. *Phys. Rev. B* **2001**, *64*, 155320]. The Young's modulus, $Y \simeq 2.3 \times 10^{12}$ dyne/cm^2, is calculated with total energy calculations and is found to be almost independent of the alkyl chain length. The spectral densities are estimated using the longitudinal and transverse sound velocities for gold, $v_l = 3.2 \times 10^5$ cm/s and $v_t = 1.2 \times 10^5$ cm/s, respectively. Note that a change in the thermal current by an order of magnitude would change the local temperature by just a factor of 2.
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