Thermally Activated Conduction in Molecular Junctions

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Thermal effects on the conduction of molecular junctions have recently been the focus of substantial theoretical effort.[1] While conduction measurements of single molecules have been previously reported,[2] none have dealt with thermal effects. In this Communication, we report the first experimental demonstration of these thermal effects at the individual-molecule level.[3] Specifically, we show the effects of thermal activation on the conduction of a molecular junction composed of chemisorbed individual 1-nitro-2,5-di(phenylethynyl-4′-mercapto)benzene molecules (**1**) independently configured across a gold electrode gap with Au−S bonded contacts (see Figure 1).

Junctions were fabricated using published procedures.[2a−c] Wires defined by e-beam lithography and coated with a monolayer formed from **1**[4] were broken by electromigration at a temperature of 13 K by ramping a voltage across the wires until a sudden drop in their conductivity occurred as a result of their breaking. The resulting current at this point was governed by tunneling across the gap. All measurements were done in a temperature-controlled cryogenic chamber. The yield of devices showing molecular effects (see discussion below) was ∼10%.[5]

Molecule **1** is a previously studied conjugated π system "molecular wire" and was chosen as a representative molecule to study temperature effects on conduction. The structural properties of its self-assembled monolayer have been studied in depth.[4] Understanding charge transmission through this specific molecule should also help to elucidate the basis for its variable negative differential resistance (NDR) properties.[6]

$I-V$ measurements were taken at a temperature range of 13−296 K over a ±1 V bias range. At higher bias values, the junctions showed tendencies to become unstable under repeated cycling. A representative set of $I-V$ curves at different temperatures is shown in Figure 1. The magnitude of the measured currents is quite similar to those reported in previous studies of isolated single molecules with similar structure and which are bonded between gold contacts.[2e,h] In accordance with theoretical predictions,[1c−f] an Arrhenius plot for a typical junction (Figure 2) reveals a characteristic transition from temperature-independent behavior at low T, where conduction is dominated by coherent superexchange tunneling, to incoherent temperature-dependent hopping behavior at high T.[7] This result constitutes the first experimental observation of this phenomenon for individual molecules.

The transition from coherent to incoherent behavior is shifted to lower temperatures with increasing bias. There are two complementary reasons for this behavior: (i) This is a natural outcome of the correlation in Figure 2 which shows that ΔE, the activation energy for hopping, $\{\Delta E_{BARRIER} = -(1/k)[d(\ln I)/d(1/T)]\}$, decreases as a function of bias. As the hopping mechanism is proportional to a Boltzmann term of the form $\exp(-\Delta E/kT)$,[1c−f] it is initiated at a lower bath temperature as ΔE decreases. (ii) Due to inelastic effects,
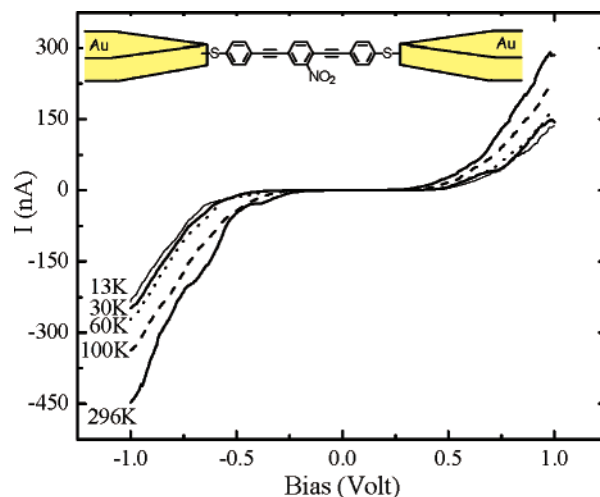

Figure 1. A set of $I-V$ curves measured on one of the junctions is shown here for several representative temperatures. The observed asymmetry is seen in all junctions with a bridging molecule (see ref 5). Because the molecule is not symmetrical, this suggests, as in ref 2e, that either a single molecule is bridging the gap between the two Au leads or possibly the electromigration gap opening event induces a small ensemble of a few similarly oriented molecules to bridge.
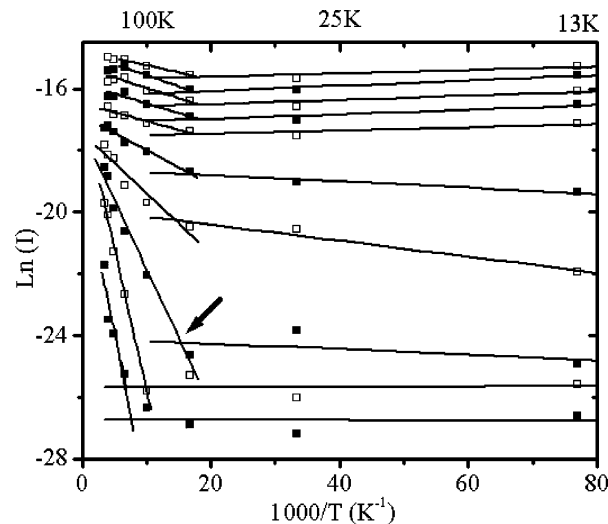

Figure 2. Arrhenius plots of Ln current (amperes) versus inverse T (K^{-1}) at different bias voltages showing a transition in conductance from T-independent tunneling behavior at low T to a thermally activated process at high T. The bias increment between curves is 0.1 V, and the bias of the lowest curve is 0.1 V. The transition temperatures between coherent and incoherent behavior are marked by the intersection between lines; see, for example, the arrow for 0.3 V.

part of the IV power applied on the junction dissipates as heat on the molecule(s).[1f] As a result, the temperature of the molecule(s) increases. With increasing bias, the vibrational temperature of the

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molecule(s) increases, and the transition to incoherent tunneling is induced at a lower bath temperature. Heat dissipation in the molecule then induces transition between the two conduction regimes.

For bias values ≥ 0.5 V, all of the activated processes have the same slope. Such behavior, which is T-dependent and V-independent, is characteristic of ohmic processes. This behavior can be described by $I \approx V[\exp(-c/T)]$, where c is a characteristic temperature of the system.[8] Analysis of our data yields $c = 55$ K, in good agreement with the transition temperature in Figure 2. On the basis of theoretical calculations for **1** and similar molecules,[9a-c] as well as of experimental observation,[9d] the measured value of ΔE (Figure 2) at zero bias, $\Delta E^0 = 0.13$ eV, does not correspond to the expected energy difference between the Fermi level and the HOMO or LUMO levels of the molecule. This suggests that the rate-limiting process in the hopping mechanism is not thermal population of electrons/holes from the electrode into the first hopping site, but rather the intramolecular hopping process (along the molecule).[1g] Three observations support this suggestion: (a) At $V > 2\Delta E°$ (i.e., at bias values where resonant tunneling would have been expected if ΔE was indeed half the HOMO−LUMO gap), ΔE reaches a constant limiting value greater than zero. (b) $\Delta E°$ corresponds very well with theoretical calculations of the barriers for rotations of the rings in this molecule.[9a-c] This suggests that electrons (or holes) hop between two adjacent rings when they are in a coplanar conformation. The hopping barrier is the energy needed to bring the rings into this conformation. (c) When the molecular levels are in resonance with the metal states, it can be shown[1g,10] that the conductance g of a molecule is related to the rate of electron transfer k_{et} through the molecule according to: $g \approx 5 \times 10^{-19} k_{et}/DOS$, where g is in Ω^{-1}, k_{et} is in s^{-1}, and DOS (density of states) is in eV^{-1}. On the basis of an electrochemically determined k_{et} for a similar molecule,[11] g is calculated to be 4×10^{-9} Ω^{-1}, in excellent agreement with g from this study, 5×10^{-9} Ω^{-1}. This also implies that no barrier exists to inject charge into the molecule and that at room temperature the dominant charge transport mechanism is hopping.

A possible explanation for the observed decrease in ΔE as a function of V is that hopping in this system is field assisted and that the barrier for hopping is decreased as a result of the electric field inside the molecule. Because hopping through the molecule occurs between neutral hopping sites, the observed effect of the external field may be a result of the external field acting on an internal dipole, which in this molecule is likely associated with the NO$_2$ group. A theoretical model of such mechanism in molecules is not yet available and depends critically on the distribution of potential across molecules, which is a subject of active debate.[12]

Finally, we note that all junctions that showed molecular behavior were eventually cycled up to ± 5 V and did not show NDR behavior. This result suggests that the ability of the core structure of molecule **1** to exhibit NDR behavior depends critically on the specific contact configuration and/or matrix effects for ensemble configurations, for example, organized monolayers, where vibrations and rotations can be hindered or frustrated.

This work shows that inelastic processes and accompanying heat dissipation in molecular conductance can play key roles in controlling charge transport in molecular junctions. Of particular importance is the correlation of low-temperature conduction with the various molecular vibration modes that cause heat dissipation via electron−phonon scattering. These effects should be manifested in the inelastic electron tunneling spectra at low bias, and such studies are currently in progress in our laboratory.

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