# Inelastic Tunneling Spectroscopy and Single-Electron Tunneling in an Adjustable Microscopic Tunnel Junction

Stephen Gregory
*Bellcore, Red Bank, New Jersey 07701*
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A remarkably stable microscopic tunnel junction can be made with two crossed wires separated by a monolayer of adsorbed molecules. Inelastic tunneling peaks of hydrocarbons are clearly resolved. A wide Coulomb blockade of single-electron tunneling is observed, indicating that stray capacitance does not influence the microscopic junction.

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The advent of the scanning tunneling microscope (STM) has focused attention on the physics of tunneling in junctions which can be classified as microscopic. For purposes of the present discussion, the essential feature identifying a junction as microscopic is that tunneling takes place between atomic-scale or near-atomic-scale asperities on the electrodes. Although STM's are capable of imaging surfaces on the atomic scale, a property which graphically emphasizes the microscopic nature of the tunnel junction, mechanical drift of STM's even at cryogenic temperatures makes tunneling spectroscopy extremely difficult.

Here I describe, and present the first results from, a new tunneling spectrometer which has a tunneling area of atomic dimensions. It involves crossed electrodes of very fine wire. By precisely controlling the spacing of the wires a "self-assembling" tunnel junction (SATJ) can be created in which a molecular film adsorbed on the wires serves both as the tunnel barrier and as the source of long-term mechanical stability. As a result, inelastic tunneling spectroscopy (IETS) of adsorbed molecules is now possible without the need of an additional (usually oxide) barrier. The observation of a Coulomb blockade of single-electron tunneling is evidence that the junction is truly microscopic.

Although it is possible to take $I$-$V$ curves rapidly with an STM before the tip drifts (current-imaging tunneling spectroscopy),[1] resolution is very limited. In order to perform true IETS one must have the stability to take the second derivative of current. Traditionally, IETS has been possible for molecular species incorporated into the oxide barriers of large-area ($\sim 1$ mm$^2$) crossed-metal-film junctions. These, of course, possess inherent mechanical stability but are clearly macroscopic and the interaction of the molecules under study with the oxide is problematic. An attempt to develop an oxide-free tunnel junction which could be used for IETS was the "squeezable" junction of Moreland *et al.*[2] but, as mentioned by Hansma,[3] this apparatus was unable to maintain the stability necessary for a study of molecular vibrations.

Figure 1(a) shows the geometry of a SATJ. Two gold wires of 17 $\mu$m diameter and about 2 cm long are bowed slightly and glued to contacts with colloidal graphite. The contacts are mounted on a micromanipulator stage in such a way that the wires are crossed. The gap between them is coarsely adjusted before cooling the apparatus. Fine adjustment of the gap is accomplished by placing the wires in a magnetic field which is perpendicular to one of them. Passing a small ($\approx 10$ $\mu$A) dc current through this wire deflects it toward the other wire. Although the present apparatus uses a field of 2.6 T generated by a superconducting solenoid, permanent magnet fields of less than 0.1 T are quite satisfactory. (Note that no dependence of tunneling spectra on field has been detected.)

The tunnel junction is formed as follows. A monolayer or so of gas (argon in the present work) is adsorbed

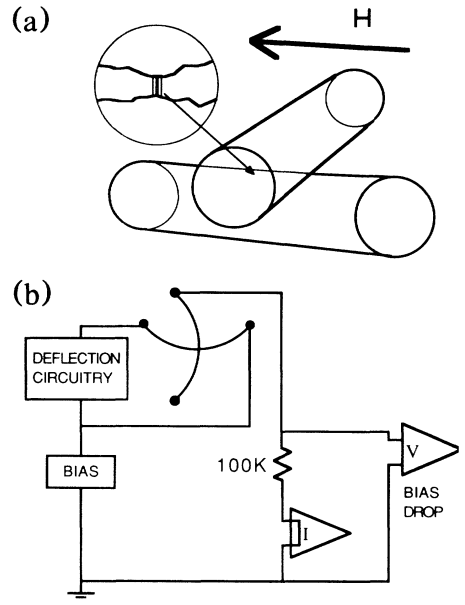


FIG. 1. (a) Physical arrangement of crossed wires and (b) schematic circuit used for deflecting wires and performing tunneling spectroscopy. The "bias drop" amplifier reading is used to correct for voltage dropped across the load resistor and current amplifier.

on the wires at an elevated (e.g., 120 K) temperature and then the sample cell is cooled to liquid-helium temperature. Next, a bias voltage is applied as shown in Fig. 1(b) and the deflecting current is increased while the tunneling current is monitored. A discontinuous onset of the tunnel current is observed as the wires come together and then stick. Further increase in the deflection current causes a rapid, but quite adjustable, increase in tunnel current. The exceedingly fine control over the tunnel resistance is a result of the extreme flexibility of the wires and the fact that they effectively constitute a double-spring reduction arrangement. Several features contribute to the long-term stability of the SATJ: First, external vibrations are greatly attenuated in the long, slender gold wires. Second, the surface forces in the junction are able to maintain the registry of the surface relief necessary to ensure that the tunneling geometry is fixed, with the barrier film in a sense acting as a glue. While the junction geometry appears quite stable, one often observes random "switching" between two or occasionally three well-defined conductance states of the junction, this behavior being more prevalent at higher currents, where it constitutes telegraph noise.

The conductance spectrum, $\partial I/\partial V$ vs $V$, and the IETS spectrum, $\partial^2 I/\partial V^2$ vs $V$, of the SATJ are obtained by applying a small ac modulation and measuring the fundamental and second-harmonic responses of the tunnel current. Figure 2 shows a typical IETS spectrum from an SATJ formed with a mixture of argon and carbon monoxide as the tunnel barrier using 10-mV peak-to-peak modulation. 10 mV is typically used for full-range spectral sweeps because the linewidths of the IETS features are typically 20 mV and hence are not limited by modulation at this level or less, as shown in the inset of Fig. 2. However, 3-mV modulation is used in signal-averaged sweeps of features of interest. The IETS spectrum clearly shows several identifiable features. The 359-mV (2900 $cm^{-1}$) and 173-mV (1400 $cm^{-1}$) features are respectively consistent with C-H stretching and bending excitations of hydrocarbons "contaminating" the junction. The bending structure actually comprises several peaks, two of which are sometimes resolved by the SATJ, and hence has a ramplike shape. The C-H features, as would be expected for a microscopic junction containing only a very few molecules, are not always seen and, in fact, can be eliminated by Ohmically heating the wires to clean them. Interestingly, carbon monoxide displays only a very weak and broad feature around the expected C-O stretch voltage of 230 mV and is only noticeable in the spectrum of Fig. 2 as a slight "filling in" of the region between the C-H features.

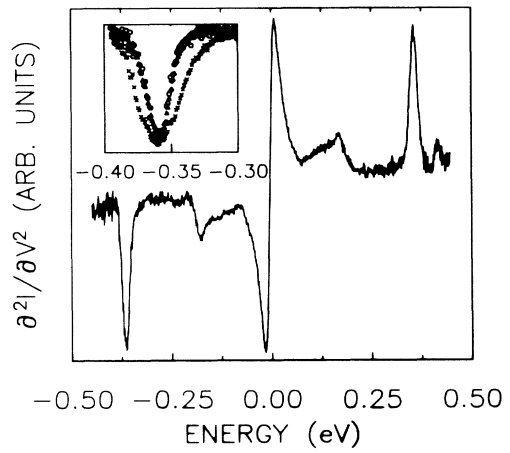


FIG. 2. IETS spectrum of hydrocarbons in a SATJ taken at 4.3 K in a single pass with 10-mV modulation. Inset: 359-mV feature taken with 6- (circles), 10- (triangles), and 20-mV (crosses) modulation, each averaged over five passes.

While the tunnel currents are intrinsically small, the SATJ has more sensitivity in IETS than would an oxide-barrier junction of the same size. The increase in conductivity at the C-H stretch peak, $\Delta\sigma/\sigma$, is about 10%. Binnig, Garcia, and Rohrer[4] and Persson and Demuth[5] estimate $\Delta\sigma/\sigma \approx (2\text{-}4)\%$ for tunneling from a metal tip through adsorbed molecules and vacuum, this value being several times larger than that for oxide-barrier IETS because of the absence of screening by the dielectric constant of the oxide. It is clear that tunneling through single or small groups of molecules is a unique physical situation and, as pointed out by Persson and Demuth,[5] resonance and impact scattering may dominate dipole scattering, leading to a considerable further enhancement of $\Delta\sigma/\sigma$. This issue has been addressed in the "conventional" IETS situation by Kirtley and Soven[6] who showed that the intensities of inelastic tunneling processes are enhanced when a short-range interaction between the tunneling electron and a molecular dipole is considered.

In addition to the C-H features, there is a very prominent structure between $-42$ and $+42$ mV which can be identified with the Coulomb blockade. (An alternative explanation in terms of gross phonon structure is ruled out by the fact that this should display a $V^2$ dependence in the IETS spectrum at small bias, which it clearly does not.) As pointed out by Averin and Likharev[7] a distinguishing feature of the Coulomb blockade is that in the zero-temperature limit the $I$-$V$ curve should be parabolic for small bias and therefore the conductance should be linear in $V$. Specifically,

$$\frac{\partial I}{\partial V} = \frac{4C_J}{\pi e R_J} V, \tag{1}$$

where $e$ is the electronic charge, $C_J$ is the junction capacitance, and $R_J$ is the junction tunneling resistance. The conductance spectrum of Fig. 3 clearly shows a blockade feature reducing the conductance at zero bias by about 10%. This is less than that observed by van Bentum *et al.*[8] using a point-contact technique, indicat-

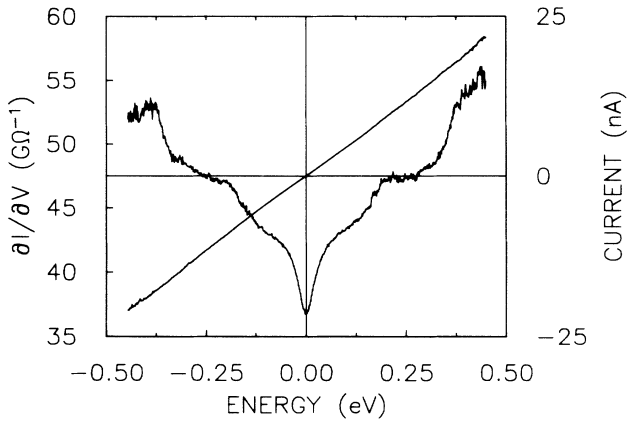


FIG. 3. Current, $I$, and conductance, $\partial I/\partial V$, vs bias voltage for the junction of Fig. 2.

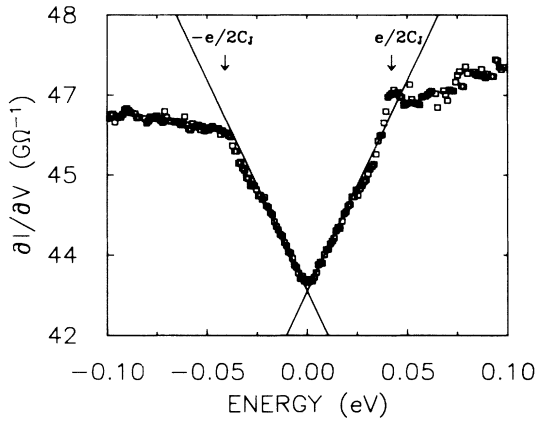


FIG. 4. Conductance, $\partial I/\partial V$, vs bias voltage using 3-mV modulation in the region of the Coulomb blockade. Arrows indicating $\pm e/2C_J$ mark the intersection of the straight lines with parabola fits to the unblockaded conductance. The deviation from linearity within the blockade region is probably due to phonon structure.

ing the existence of a larger parallel tunneling conductance in the present experiment. It is, however, comparable with the 6% dip measured by Delsing *et al.*[9] for a lithographically fabricated junction with 2 orders of magnitude larger effective capacitance than the SATJ. As can be seen in Fig. 4, a conductance spectrum taken with 3-mV modulation and a 3 times slower bias sweep rate, the small-bias region is indeed linear. I determine $e/2C_J$ from $\partial I/\partial V$ vs $V$ rather than from $I$ vs $V$ because there is a considerable linear, Ohmic contribution to the total tunnel current and this prevents determination of the Coulomb-blockade offset by simply extrapolating the asymptotic $I$-$V$ curve to the voltage axis. However, all linear contributions result in a constant conductance in $\partial I/\partial V$ vs $V$ and the value of $e/2C_J$ is obtained by extrapolating the linear conductance to a shallow parabola fitted to the conductance data for each polarity. (The parabola is a consequence of the finiteness of the tunnel barrier height.) Using Eq. (1) and the value for $e/2C_J$ determined from the data of Fig. 4, a value of $R_J = 192$ MΩ is obtained. This is about 10% of the value 22 MΩ obtained from the large-bias slope of the $I$-$V$ curve and confirms that only about 10% of the tunneling current is actually subject to the Coulomb blockade.

I now consider $C_J$. In contrast to Ref. 8, the SATJ displays no measurable change of blockade width for junction resistances from 0.5 to 110 MΩ. Specifically, the constant value of $e/C_J$ is $84 \pm 6$ mV. This implies that $C_J$ is $2.0 \times 10^{-18}$ F and is independent of the tunnel barrier width. This may be explained as follows: Let

$$C_J = C_M + C_S , \tag{2}$$

where $C_M$ is the capacitance of the truly microscopic region and $C_S$ is an effective stray shunt capacitance. This formulation is also used in Ref. 8, in which the large observed value of the blockade voltage was explained by proposing that the stray capacitance from regions beyond a certain distance of the microscopic tunneling region cannot affect the tunneling process. (The physical origin of this "cutoff" distance will be addressed below.) It seems likely that, in the present SATJ, $C_S \gg C_M$. Thus, changing the microscopic barrier spacing does not appreciably change $C_J$. In fact, a distinct $C_M$ term is probably inappropriate and one could simply say that all capacitance within the cutoff distance contributes to a total $C_J$ which affects the tunneling behavior taking place at the asperity.

van Bentum *et al.*[8] pointed out that most of the stray capacitance in their apparatus must be unable to affect the Coulomb blockade in order to explain the $C_J$ value of order $10^{-18}$ F implied by their measurements. They suggested that the redistribution of charge accompanying a tunneling event occurs over a length $\tau c \approx 0.15$ μm where $\tau \approx 5 \times 10^{-16}$ s is the time for an electron to traverse the tunneling barrier traveling at the Fermi velocity and $c$ is the speed of light. This seems quite plausible as the value of $\tau$ is similar to that suggested from other perspectives, for instance that of Büttiker and Landauer[10] who considered tunneling through a time-modulated barrier. Here, I suggest another possible origin of the capacitance cutoff. Tunneling is a coherent process in which the electron may be thought of as "probing" the barrier during its traversal time. During this probing the electron passes from one electrode into the other and unless inelastically scattered can return unscathed and try again without violating the Heisenberg uncertainty principle. This is a weak-localization picture, with successive attempts identified with repeated scattering of the electron over time-reversed paths. In this scheme, the region within the electrode in which the tunneling electron may dwell is of the order of the electron phase-breaking length in size. The redistribution of charge in the coherent process is cut off by this length. In the gold wires this should be the inelastic-scattering

length, a reasonable value for which at 4.2 K might be of order 100 nm. If this argument is valid, then it should be possible to decrease $C_J$ yet further by increasing the electron phase-breaking rate. So far, attempting to detect an increase in $C_J$ for gold wires as temperature is increased is inconclusive. However, use of wire materials doped with magnetic impurities to increase the phase-breaking rate should be possible.

The data presented here already demonstrate the promise of the SATJ. However, considerable improvements can be envisioned, leading to better spectral resolution; bridge and resonant techniques in particular may be useful. Junctions constructed with superconducting wires would have interesting possibilities in regard both to superconductor properties and also to the fact that the singularities in the density of states of superconductors are often used to enhance IETS resolution. The use of refractory materials such as platinum or graphite would allow the wires to be very effectively cleaned of adsorbed material by Ohmic heating. Last, using wires of smaller radius or, more likely, wires with greater surface irregularity, one should be able to further decrease $C_J$ leading to larger blockade voltage and also to a decrease in the parallel conductance. With these improvements, the SATJ should open up avenues of study of both single-electron tunneling and electrical conduction at the single-molecule level.

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