

Supplemental Information for:
Effects of Hydration on Molecular Junction Transport
Long, D. *et al.* Nature Materials (2006).

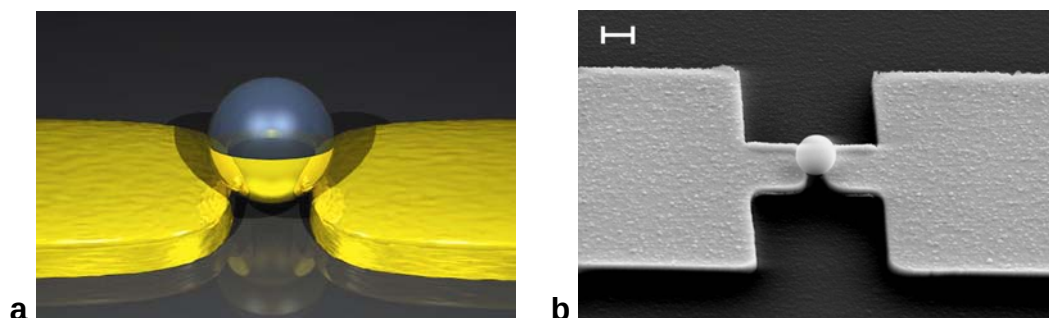


Figure 1 Images depicting magnetic-assembled microsphere molecular junctions. **a**, Illustration and **b**, scanning electron micrograph (SEM) depicting device architecture. A magnetic field generated inside the 0.5 μm gap directs the selective entrapment of metallized silica colloid (1.5 μm diameter) to close the electrical circuit. Molecular tunnel junctions are formed when molecules are trapped between the sphere and the SAM-functionalized source/drain electrodes. Surrounding surface is thermally deposited SiO_2 . Scale bar = 1 μm .

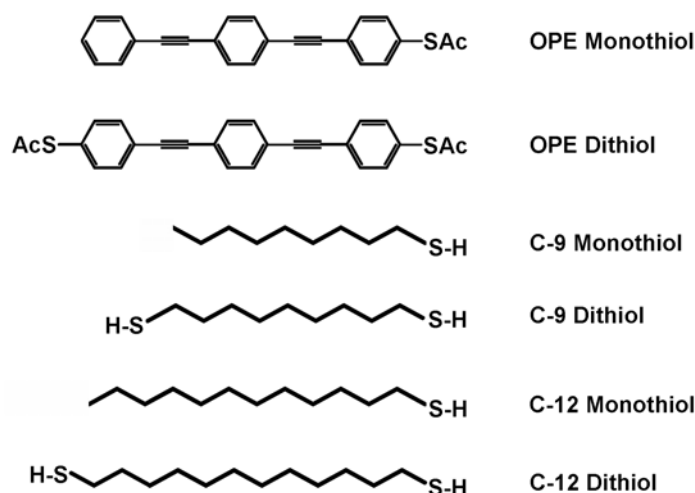


Figure 2 Structure of molecules used for environmental dependence study. The above molecules were chosen since they do not incorporate additional chemical functionality (NO_2 , NH_2 , bipyridyl, etc.) which could react with atmospheric constituents and interfere with an analysis of interactions at the gold-thiol contacts. As a result, our final molecular junctions contained primarily hydrophobic non-reactive molecules (having low affinity for polar water) which incorporated electronegative sulfur contacts. The difference in polarizability between the terminal sulfur groups and the hydrophobic molecules restricted dipole interactions to predominately the electrode-molecule interface where charge on the thiolate could attract and bind polar water molecules and permit a conclusive study of hydration at the gold-sulfur contacts. Also, the use of unsubstituted alkanethiol and OPE molecules was advantageous since IET spectra have been obtained on these “standard” molecular systems which we could then compare directly to our results^{26, 29, 30}.

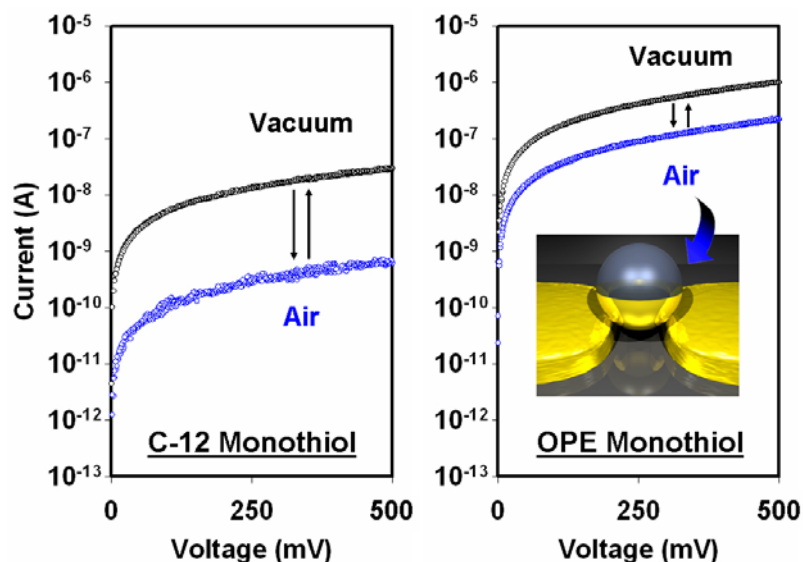


Figure 3 Decrease in molecular conductance as a result of atmospheric exposure.

C-12 and OPE microsphere junctions under vacuum (black) and after exposure to ambient conditions (blue). Typically, a 1-2 order of magnitude decrease in current is observed on exposure to air. Application of vacuum returns devices to their high conducting state suggesting interaction with the atmosphere is reversible and non-covalent. Alkanethiols consistently show greater reactivity compared to OPE-based devices (in both rate and magnitude of measured effect) and attributed to greater electron donor ability of the sulfur atom due to the bound alkyl moiety. Measured decrease in current in monothiol OPE is seen to be approximately one half that of the dithiol when exposed to water vapor (article Fig. 1d). The consistent 2:1 ratios found when comparing results between the dithiol and monothiol systems supports the conclusion that the primary interaction taking place is occurring at the Au-S contacts.

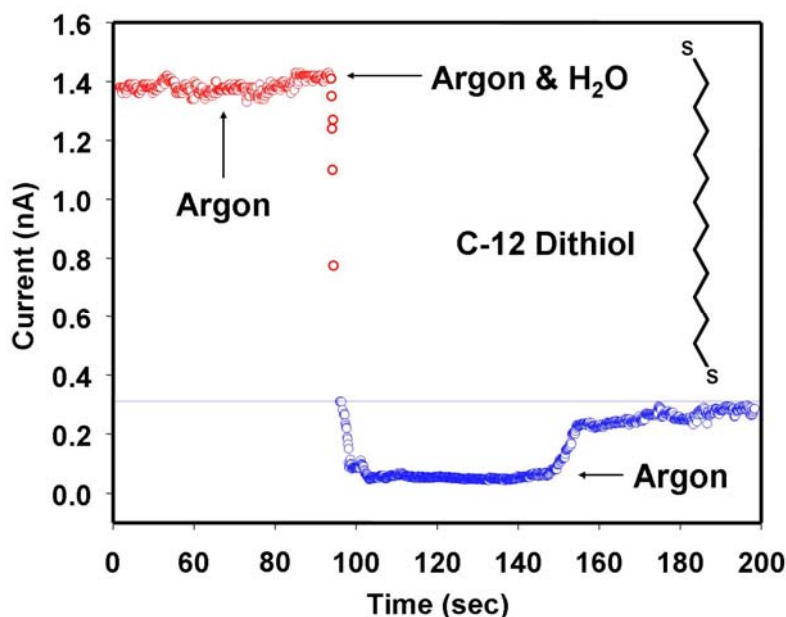


Figure 4 Effects of hydration on microsphere junction $I(V)$ characteristics. Current as a function of time for a C-12 dithiol microsphere junction during exposure to water vapor (saturated in argon gas) at 23°C / 760 torr. Data points acquired every 100 milliseconds while applying a 100 mV bias. The inability of the device to recover after the gas stream is switched back to pure argon (similar to OPE, article Fig. 1b) suggests water is retained within the device (horizontal blue line/0.3 nA) by strong non-covalent interactions preventing full recovery of conductance. Application of vacuum however, removes this bound water, increasing conductance (Supp. Fig. 5). Junctions incorporating alkanethiols were found to react with water vapor on average four times faster than OPE and consistently displayed a greater decrease in conductance. The higher reactivity found in alkyl junctions is consistent with stronger interactions between polar water molecules and the negatively charged sulfur atom of the thiolate and caused by increased basicity (electron donor ability) of the sulfur atom due to the alkyl vs. the aromatic moieties. Aryl systems such as OPE delocalize charge across their ring systems, reducing charge on the sulfur.

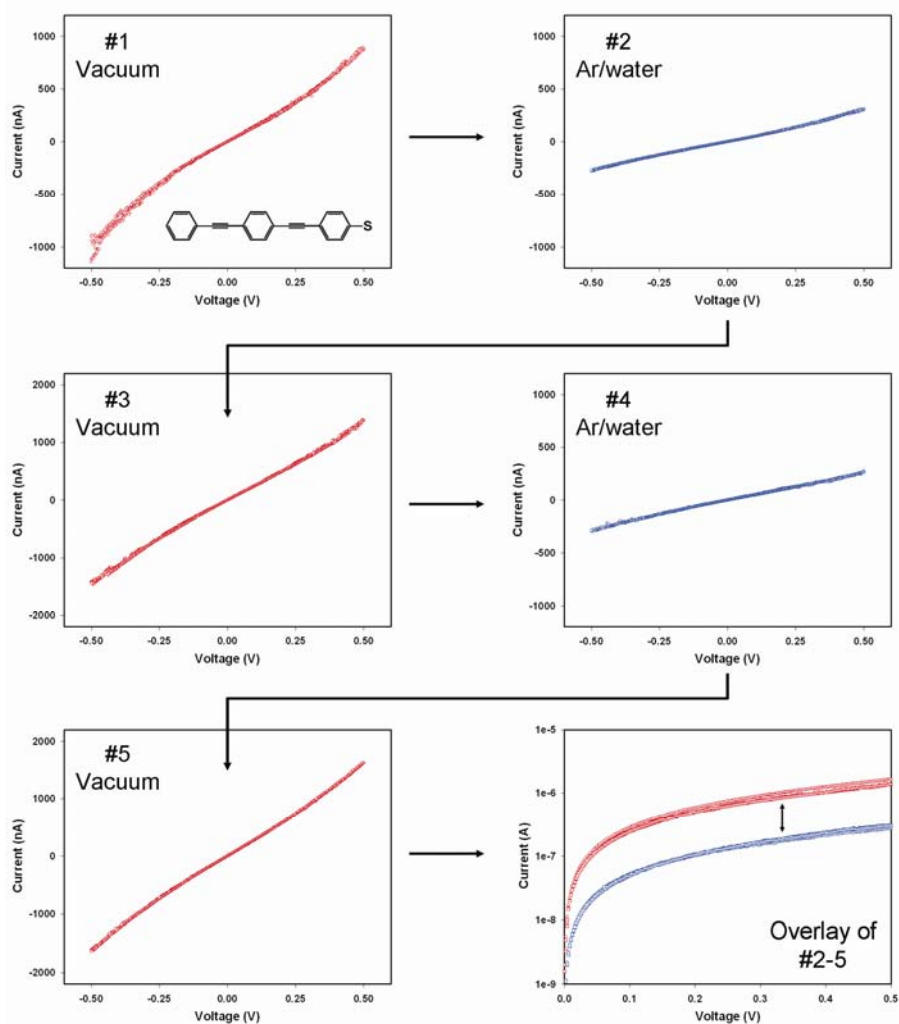


Figure 5 Cycling between vacuum and hydrated environments OPE monothiol microsphere junction repeatedly cycled between high vacuum (10^{-6} torr) and hydrated environments (argon/water). Although some irreversible annealing is observed from vacuum #1 to #3, the device displays excellent repeatability in switching between high and low conductivity states depending on the chemical environment $I(V)$ was acquired in. Junctions were not stressed beyond 500 mV and do not show instability at these voltages. Last plot shows overlay of $I(V)$ traces #2-5 on a logarithmic scale. Observation of discrete conductance levels is suggestive of hydration at specific sites within the junction (sulfur atoms) rather than indiscriminate adsorption of water into the bulk of the monolayer.

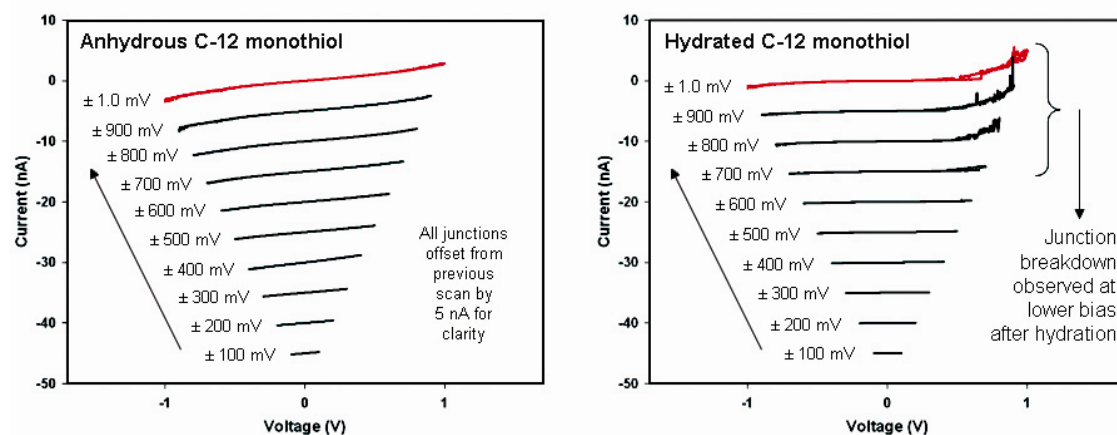


Figure 6 Stability of molecular conduction under inert and hydrated environments. Plots show sequential $I(V)$ scans beginning at ± 100 mV and ending at ± 1.0 V with measurements taken every 100 mV. Topmost curves shown in red correspond to current (y) axis. Each black trace is offset from the one above by 5 nA to allow visualization of all scans simultaneously. Anhydrous C-12 monothiol SAM (on left) remains electrically stable to increasing $I(V)$ scans up to and exceeding 1.0 V, but after hydration (right) the same device shows early breakdown of the junction beginning at approximately 700 mV. Instability in hydrated devices is attributed to the loss of strong gold-sulfur coupling to the electrode surface which allows increased molecular mobility within the monolayer and disordered packing in the SAM. Instability of the junction was observed in the positive bias only.

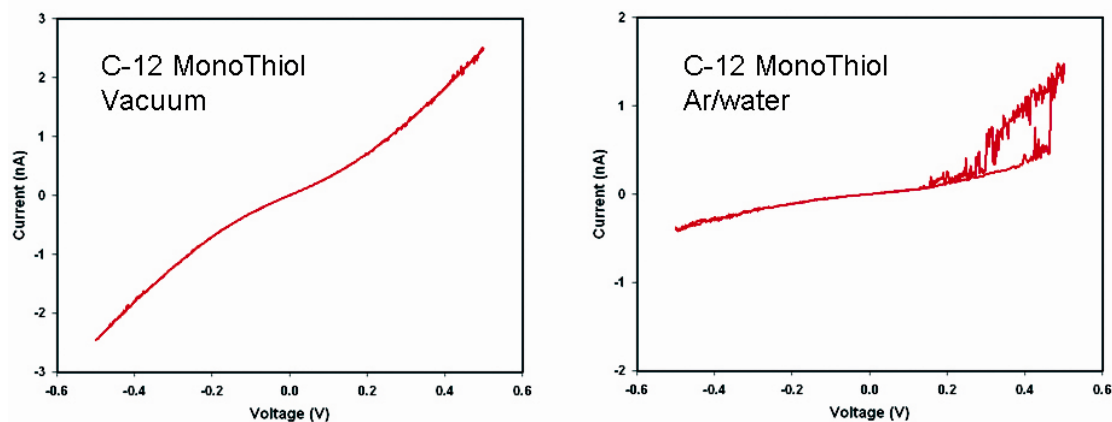


Figure 7 Stability of molecular conduction under inert and hydrated environments. C-12 monothiol after two vacuum, argon/water cycles. Repeated cycling between inert and hydrated environments leads to increasing instability in junction and attributed to irreversible disorder introduced in the SAM due to loss of gold-sulfur coupling^{18,22}. Here after two cycles, initial sign of junction breakdown has decreased to approximately 200 mV. Asymmetry found in breakdown may be due to hydration of the gold-thiol contact anchoring the alkyl monothiol to the gold electrode on one side of the junction only.

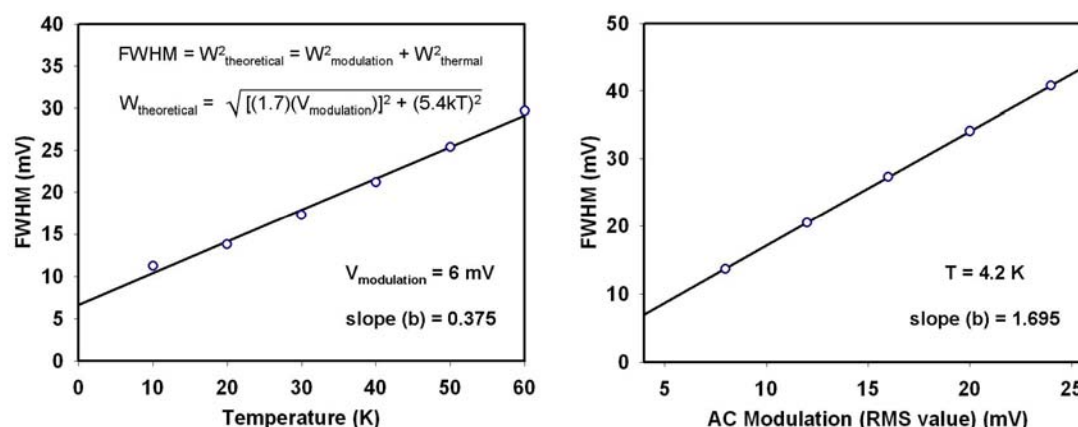


Figure 8 Calculated FWHM values for temperature and AC modulation dependence. Plots assume finite temperature and voltage modulation effects based on $W_{\text{theoretical}}^2 = W_{\text{modulation}}^2 + W_{\text{thermal}}^2$ as described in references 10 and 33. The modulation broadening is an instrumental effect because there is a limit to the AC modulation which can be applied and yet still acquire viable IETS, while the thermal broadening is an effect caused by mixing of the electron energy distributions in the metal electrodes. Calculated thermal broadening (left) assumes a fixed 6 mV modulation voltage while the calculated modulation broadening (right) assumes a constant temperature of 4.2 K. Theoretical values were calculated for temperature and modulation voltages identical to the settings used to acquire IETS experimental data. Linear regression was used to determine the slope of the lines in order to compare to experimentally determined values (article Figure 2).

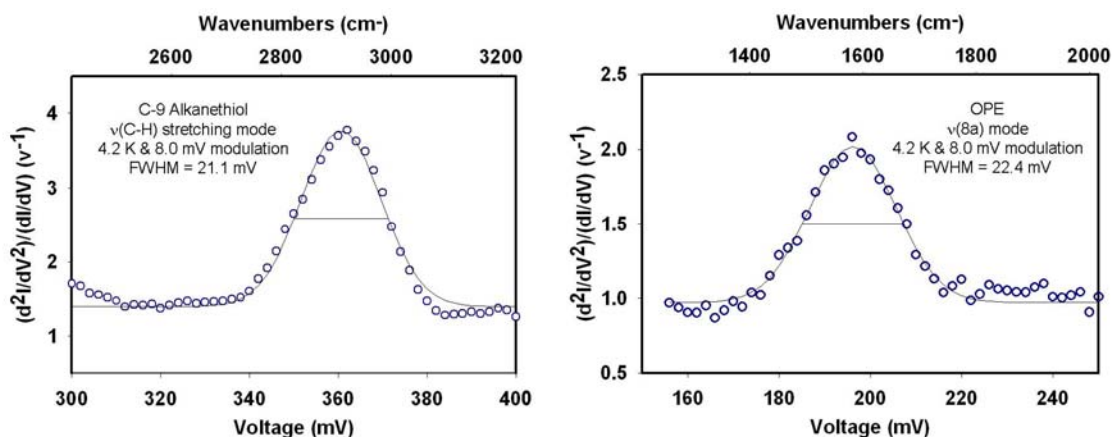


Figure 9 Experimental linewidth (FWHM) for C-9 alkanethiol and OPE microsphere junctions. Both IET spectra were acquired at 4.2 K using a modulation voltage of 8 mV. A C-9 $\nu(\text{C-H})$ stretching mode is shown at left and a OPE $\nu(8a)$ vibrational mode at right. Spectra (shown as open circles) are plotted from experimental data as the average of the forward and reverse traces using identical voltage scales (100 mV in width) so plots can be directly compared. Data has been fit with a Gaussian distribution function (black curve) to determine FWHM values for each peak. Using these instrumental conditions, the microsphere test-bed yields linewidths of approximately 21.1 to 22.4 mV, placing this technique close in resolution to the crossed-wire test-bed but slightly broader than the nanopore system^{26,33}.

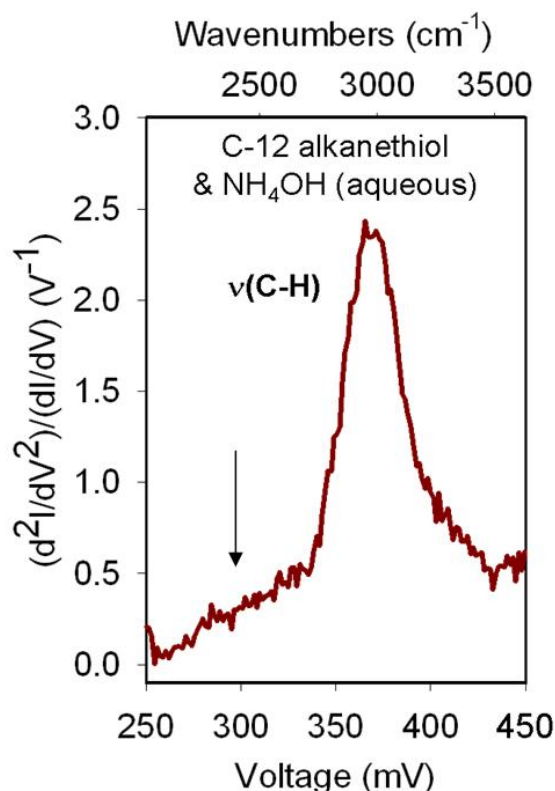


Figure 10 IETS control experiment using deprotecting agent with C-12 alkanethiol.

IETS from 250 – 450 mV of a C-12 SAM deposited in the presence of 2 μL of 30% ammonium hydroxide in H_2O followed by exposure to high vacuum conditions (10^{-6} torr / 2 days). A prominent C-H stretching vibration is visible at 362 mV. The lack of S-H stretching vibrations around 300 mV (marked with arrow) suggests the use of the aqueous-based deprotecting agent during SAM deposition is not responsible for observed peaks in IETS attributed to S-H modes and is instead the result of hydration immediately prior to IETS analysis. Cooling to cryogenic temperatures coupled with simultaneous pumping to high vacuum, traps bound water molecules in place within the SAM and allows IETS analysis of junctions under partially hydrated conditions. Exposure of the above device to high vacuum for two days after treatment with the aqueous base removes all traces of bound water remaining from the deprotecting agent.

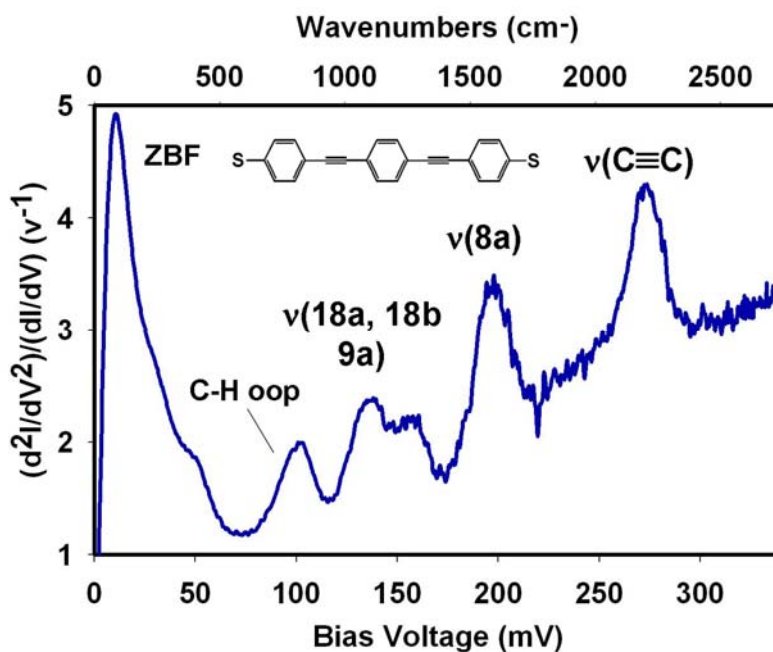


Figure 11 IETS analysis of anhydrous OPE microsphere junction. Spectrum is plotted from experimental data without the use of smoothing techniques and shown as the average of the forward and reverse traces. Absence of peaks associated with free thiol suggests the molecule has assembled on the surface as the thiolate and does not incorporate a bound proton. Peak marked as C-H out-of-plane bending (oop) matches location of a predicted mode associated with electron injection from the electrode to the σ -orbital of the OPE sulfur atom and indicative of strong gold-sulfur coupling predicted in anhydrous devices³⁹. Vibrational modes are in excellent agreement with previous experimental results and theoretical calculations for this molecule, suggesting valid IET spectra are generated using this method^{26,29,30}.

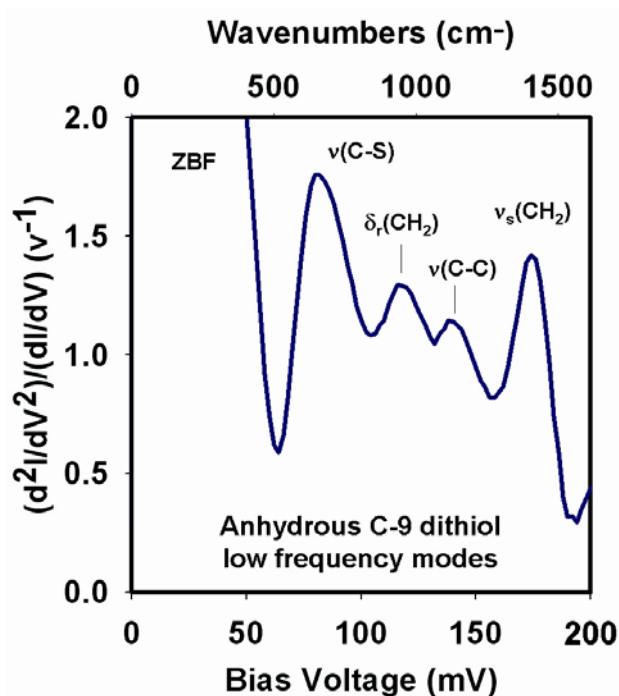


Figure 12 IETS analysis of anhydrous C-9 dithiol microsphere junction. Spectrum is plotted from experimental data without the use of smoothing techniques and shown as the average of the forward and reverse traces. Vibrational modes are in excellent agreement with previous experimental results and theoretical calculations for this molecule, suggesting valid IETS are generated using this method^{26,29,30}. C-H stretching vibration (362 mV, 2929 cm⁻¹) is shown in article Fig. 3 and supplemental Fig. 10.