Inelastic Electron Tunneling Spectroscopy on Decanethiol at Elevated Temperatures

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ABSTRACT

Inelastic electron tunneling spectroscopy (IETS) measurements using scanning tunneling microscopy (STM) on a decanethiol self-assembled monolayer on Au(111) are presented. The results presented are obtained in the temperature range 77−300 K, which is a much higher temperature than what is commonly used for STM-IETS measurements. Two peaks at ±34 meV (probably Au−S or S−C stretch mode) and ±156 meV (C−C stretch mode or a CH_2 mode) are resolved.

Self-assembled monolayers of alkanethiols have been studied extensively during the past decade.[1−4] The alkanethiol molecules have been observed to form stable, well ordered monolayers on Au(111) surfaces, a property which makes them attractive for different applications.

Starting from the mid 1960s, inelastic electron tunneling spectroscopy (IETS) has provided an interesting technique for studying organic molecules buried within a junction.[5] With the invention of the scanning tunneling microscope (STM), new ways opened up; inelastic electron tunneling spectroscopy could be combined with the scanning tunneling microscopy, and now even vibrational spectroscopy measurements on single molecules adsorbed on a surface are being performed. The pioneering work in this field was done by the group of Ho.[6,7] With the STM-IETS technique, chemical fingerprinting of molecules adsorbed on a surface is possible.[8]

We here report STM-IETS measurements on a decanethiol, $CH_3(CH_2)_9SH$, shortly denoted C10SH, self-assembled monolayer on Au(111) performed at 77 and 300 K. For the measurements, a commercially available scanning tunneling microscope (LT-STM Omicron GmbH) and a lock-in amplifier were used. With a similar setup, vibrational spectra as well as vibrational mapping were obtained for individual *trans*-2-butene molecules on a Pd(110) surface at 4.8 K.[8]

In contrast to the major part of the reported STM-IETS results, which are performed at temperatures in the 4−10 K range, we can see clearly distinguishable peaks already at 77 K, which can be assigned to vibrational features of the molecules of the self-assembled monolayer. To the best of our knowledge this is also the first report on STM-IETS measurements on an alkanethiol monolayer. IETS measurements on an octanedithiol self-assembled monolayer at various temperatures using a special device where the monolayer is sandwiched between two gold electrodes has been reported recently.[9] In these measurements, features that could be assigned to different vibrational modes of the molecules were observed. At 80 K two different peaks could be resolved, while at 4.2 K several peaks were resolved and could be assigned to the vibrational modes of the molecules. However, for these measurements no results for negative bias voltage were reported, hence lacking one essential feature of IETS spectra. Our measurements show corresponding peaks at both bias voltages.

We have used electrochemically etched W tips. For the low-temperature measurements the system was cooled with liquid nitrogen to reach a temperature of 77 K. The pressure in the UHV system was $< 3 \times 10^{-11}$ Torr during all measurements. The sample consists of a C10SH monolayer self-assembled from solution on annealed Au(111). The sample was prepared outside vacuum and then introduced into the vacuum system.

Before starting a spectroscopic measurement, topographic imaging of the sample was always performed. Two typical

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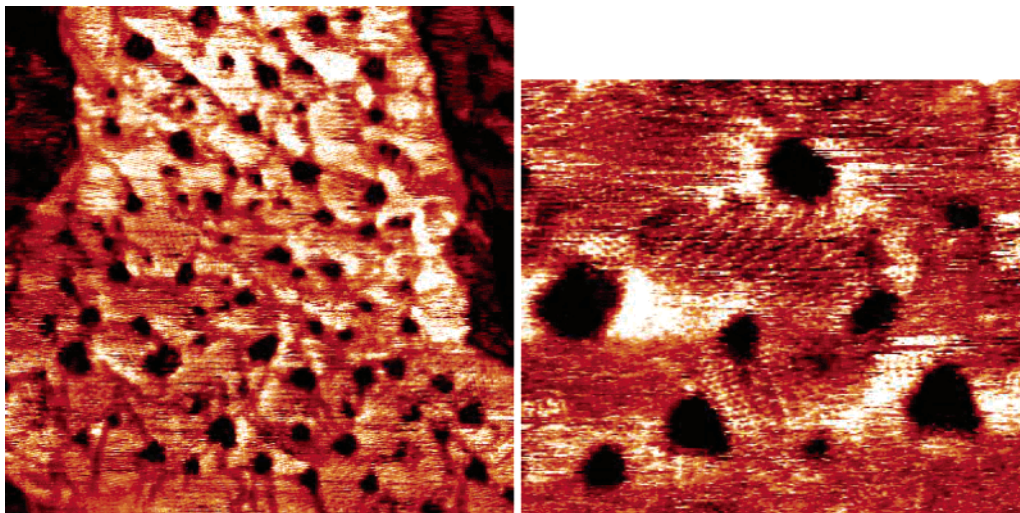
Figure 1. (a) 100×100 nm topographic image of the C10SH SAM. Sample bias voltage +325 mV, tunneling current 20 pA. (b) 35.6×30.5 nm. Sample bias voltage +325 mV, tunneling current 25 pA. Both images were recorded at room temperature.

topographic images, showing the vacancy islands and different domains typical for an alkanethiol SAM,[1−3] are shown in Figure 1. These images were recorded at tunneling currents in the range from 10 to 30 pA, to avoid deterioration of the monolayers.

After the topography of the monolayer was checked, the STM was put into the point mode for the spectroscopic measurements. In this mode the scanning is turned off, hence the STM tip is kept fixed at one point. Still, there will be some lateral drift, but this should not give rise to a problem, since we have a full monolayer of identical molecules and the position of the tip is chosen so that it is not close to any vacancy island or other defect, and the lateral drift is quite low at 77 K, approximately a few Å per hour. The set point tunneling current is 28 pA at a sample bias voltage of +250 mV. After the feedback loop has been turned off, the bias voltage is swept from +264 mV to −244 mV, while recording the resulting current at steps of 4.2 mV. The acquisition time at each voltage level being 160 ms, a voltage sweep takes approximately 20 s. After each voltage sweep the feedback loop is turned on again and the tip height is readjusted, before the next voltage sweep. A modulation voltage of 20 mV rms with a frequency of 797 Hz was added to the bias voltage by means of a lock-in amplifier. The integration time of the lock-in amplifier was chosen to 100 ms. By detecting the second-harmonic component of the modulated signal a measure of the second derivative of the tunneling current, d^2I/dV^2, can be obtained. From STM images recorded after the IETS measurements, no damage in the monolayer could be observed.

All the spectroscopic data were recorded overnight, to reduce influence of noise, and the average was taken over some thousand curves. At room temperature the peaks are broadened so much that effectively no vibrational features can be distinguished. This is just what one would expect, as will be explained later in this letter. In the spectrum shown in Figure 2, some broad features at 144 meV and −154 meV and some shoulders in between can be faintly seen. A similar measurement on a bare Au(111) substrate reveals no features,
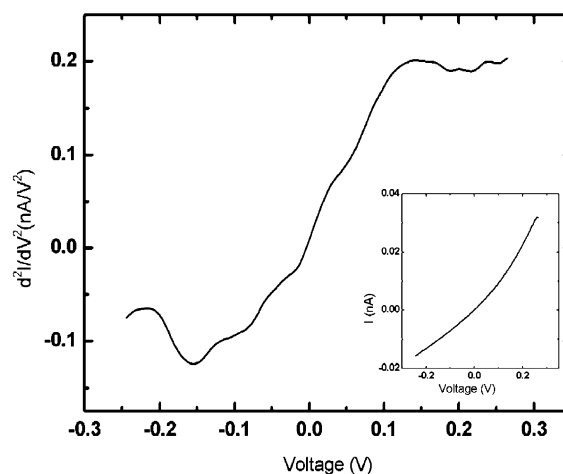
Figure 2. Inelastic electron tunneling spectrum of the C10SH SAM recorded at room temperature. Average over 2400 curves. (Inset) *I/V* curve recorded simultaneously as the IET spectrum.

which indicates that the results presented here originate purely from the molecular monolayer.

For the measurements performed at 77 K, the data were stored in four different subsets, each containing 625 curves. There is very good agreement between the data in these four different subsets. In the spectrum shown in Figure 3, which is an average of all 2500 curves, two main features can be seen. These are wide peaks occurring at 33 mV and 153 mV, respectively. Corresponding negative peaks are located at −35 mV and −159 mV, respectively. Interestingly, the peak positions show mirror symmetry with respect to zero voltage. Hence, they fulfill an important criterion for assignment of features in IETS spectra to vibrational features.[7] The deviation from mirror symmetry can be explained by the fact that the tunnel junction is not symmetric.[10] The measurement configuration is STM tip−vacuum gap−SAM−Au substrate, hence, the tunneling barrier is asymmetric and the interaction path of the electron will depend on if the electron tunnels from the tip to the substrate or in the other direction.
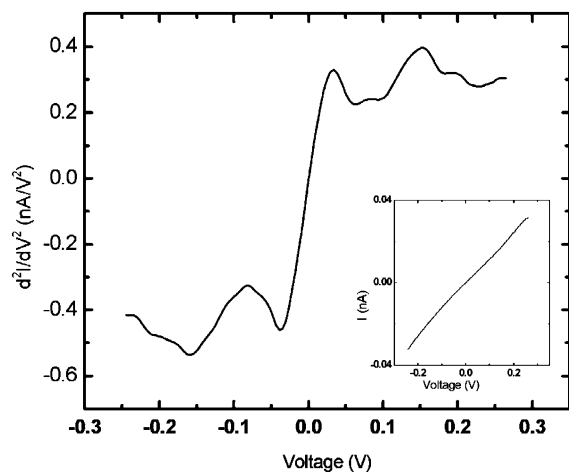
Figure 3. Inelastic electron tunneling spectrum of the C10SH−SAM at 77 K. The solid line represents the measured curve, the dotted curve is the result of mirroring this curve. (Inset) *I/V* curve recorded simultaneously as the IET spectrum. Both curves are averages over 2500 curves.

The peak at 33 mV might be related to the Au−S stretch (29 meV), the S−C stretch, SCC and CCC deformations (38 meV). The 153 mV peak probably originates from the CH_2 twist (155 meV) with influences from the C−C stretch (131 meV), the CH_2 wag mode (163), and possibly the CH_3 s-deform, as far as that can be observed in these measurements.[11] A shoulder appears at the end of the 153 (−159) mV peak, at 200 (−210) mV.

The width of the peaks is influenced by thermal broadening, modulation voltage, and intrinsic peak width according to

$$W = \sqrt{\left(5.4\frac{kT}{e}\right)^2 + (1.7V_{mod})^2 + W_I^2}$$

where k is the Boltzmann constant, T the temperature, V_{mod} the modulation voltage (rms value), and W_I is the intrinsic width of the peak. Assuming a negligible intrinsic peak width, this gives a peak broadening of approximately 49 meV at 77 K using a modulation voltage of 20 mV rms. At this modulation voltage, the second term will dominate; hence it might be useful to lower the voltage. Also, this large peak broadening means that peaks originating from different vibrational modes will overlap, if their energy separation is less than about 49 meV, and in the IET spectrum the resulting peaks cannot be resolved. This was seen in Figure 3b, as discussed above.

At room temperature, the thermal broadening will be dominant and the modulation voltage will have a minor influence of the peak broadening. At a modulation voltage of 20 mV rms, the peak width will be approximately 140 meV, assuming a negligible intrinsic peak width, and hence the peaks will not be resolved. This was also confirmed by the measurement performed at room temperature, showing that this technique is not applicable at that temperature.

Applying a nonlinear curve fit (based on the amplitude version of the Gaussian peak function) procedure to the data obtained at 77 K, the experimental full widths at half-maximum (fwhm) values are determined. For the modulation voltage of 20 mV, these are 54 mV for the peak at 33 mV and 109 mV for the peak at 153 mV. From these, the intrinsic peak widths are estimated to 22 meV for the peak at 33 mV and 97 meV for the peak at 153 mV, using the formula above. This also indicates that the peaks observed are superposed from two or more vibrational modes, as intrinsic peak widths calculated from IETS results usually are some few meV[6,9] for a molecular vibration mode. Taking these estimated intrinsic width values into account, we would expect a peak width of 45 mV for the 33 mV peak and 105 mV for the 153 mV peak using a modulation voltage of 10 mV at 77 K. Neglecting the intrinsic peak widths would give a broadening of 20 mV. An explanation for this is that the peaks observed at 77 K are superposed from peaks related to different vibrational modes, since the vibrational modes are much closer in energy than the 49 meV broadening caused by the contribution from thermal energy and modulation voltage.[11] Hence, this gives an error when calculating the intrinsic peak widths from the data obtained at this temperature. This all indicates that lower temperatures are necessary in order to resolve the vibrational peaks.

In conclusion, we have reported the first STM-IETS spectra on decanethiol SAMs recorded at 77 K. Already at this relatively high-temperature, features related to molecular vibrational modes could be distinguished. However, the peak broadening is too large to assign these features to specific molecular vibrations. To resolve the peaks from different vibrational modes lower temperatures are necessary.

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