Theoretical Interpretation of Intrinsic Line widths Observed in Inelastic Electron Tunneling Scattering Experiments

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We report ab initio calculations of the frequency spectrum of an alkanedithiol molecule to explain an intrinsic line width found in an electron scattering tunneling spectroscopy experiment. It is found that the so-called intrinsic line width found in the experiment is because the fine structure nature of the vibrational spectrum. As nanoscale dimensions are approached, the fine structure of the vibrational spectrum becomes an important factor for the characterization of molecular electronics systems.

Introduction

Molecular electronics offers the possibility to complement standard microelectronics to reach minimum feature size of atomistic dimensions.[1−3] Using devices with size in the range of 1 nm would allow us to implement a large density of logic and memory functions in areas where only one single switch or transistor can be allowed using standard microelectronic techniques; thus this possibility is being investigated by several groups[4,5] with the use of chemical deposition, self-assembling, and a few other techniques, which allow making layers of only one molecule thick. Most of the present work is oriented to the challenge of measuring systems where the characteristics of single molecules can be determined. These experiments of current−voltage characteristics are important design inputs for the implementation of molecular circuits. However, when measurements are performed, it is difficult to characterize or to make sure that the actual molecule of interest is being approached because the device embodiment has the molecules embedded between juxtaposed metallic electrodes that are spaced by only ∼2 nm. One of the techniques that allows us to determine whether the molecule is being measured is the inelastic electron tunneling spectroscopy (IETS) technique via the second derivative of the current through the molecule with respect to the bias voltage. The importance of measuring the second derivative is that it shows the vibrational spectrum of the molecules under the contacts and can be compared to precisely determined theoretical and experimental results. For the sake of numerical precision, the second derivative is not obtained by differentiation of the current but through an alternate method whereby a small sinusoidal signal (ac) is added to the bias signal (dc) and the second derivative of the current is obtained by tuning to the second harmonic of the ac signal using a lock-in amplifier.[6,7] Although, IETS does not guarantee a particular geometric arrangement of the molecule, it ensures us that the molecule is there if it can be associated with a known spectrum, either theoretical or experimental. Approaches in molecular electronics need to include theoretical and experimental analyses; otherwise, it is impossible to determine correct characteristics and mechanisms. On one hand, it is almost impossible to characterize the precise structure of the systems being measured; and on the other hand, it is similarly difficult to construct the correct Hamiltonian representing the experiment. However, combined studies complement information from both ends, providing a good picture of the physics and chemistry involved in molecular electronics and consistency of results from both is so far the only means of verification.

Recently Wang et al.[8] (referred to as the experiment) measured the spectrum of a self-assembled monolayer of an octanedithiolate, $-S-(CH_2)_8-S-$, bonded to gold electrodes using the IETS technique. They found peaks corresponding to the vibrational modes perpendicular to the junction interface of AuS at 33 mV and CC at 133 mV, and wagging mode of CH_2 at 158 mV. These authors examined the peak broadening of the stretching mode ν(C−C) at 133 meV as a function of the temperature and modulation voltage. They found an intrinsic line width of 3.78 ± 0.98 meV (30.2 ± 7.8 cm^{-1}) for this line that is not accounted for by the thermal broadening or by the ac modulation. The goal of this communication is to establish the origin of this “solid rock” intrinsic line widths.[8] Thus other effects that may produce these line widths, like temperature and ac modulation, are already considered in the experiment and are not responsible for the line widths. Certainly, there are other factors that can contribute to the line widths, including electron−hole pair excitation of the metal surfaces, and electron−phonon coupling within the molecular junction, but we are focusing on the intrinsic line width observed in the experiment, a line width that extrapolates to 0 K and to 0 ac. The effects of other factors external to the molecule cannot be considered as part of the intrinsic molecular line width.

Theoretical Approach

We performed ab initio density functional theory calculations of second derivates of the energies with respect to the coordinates of the isolated molecule, $HS-(CH_2)_8-SH$, at the B3PW91/6-311G** level of theory to determine the molecule vibrational spectrum using the program Gaussian-2003.[9] This level of theory is considered suitable for practical purposes for the study of molecules containing hydrogen, first, and second row atoms.[10] We have also performed calculations including gold atoms (using the LANL2DZ effective core potential and basis set) at the two ends of the molecule, and the vibrational spectrum of the C−C stretching modes is practically the same within the tolerance of the methods. It is a common practice to

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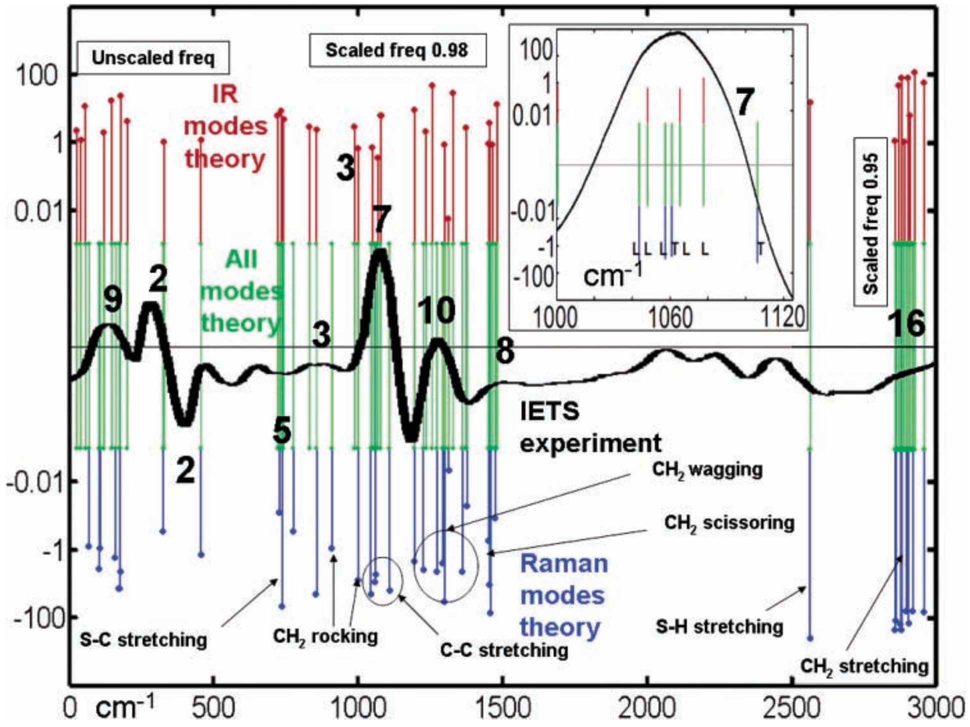

Figure 1. Theoretical spectrum of HS−(CH$_2$)$_8$−SH (colored vertical lines) and experimental IETS (black curve).[8] All modes are indicated with the equal size green lines. IR active modes are indicated with red lines and their intensity is shown in a logarithmic scale starting at the top of the green lines. The Raman active modes are indicated by the blue lines, and their intensity is shown with a logarithmic scale starting at the bottom of the green lines. The numbers on top of most of the peaks indicate the number of vibrational lines in the small region covering the width of each experimental peak. We can distinguish three well-defined regions for the theoretical spectrum. The spectrum in the neighborhood of 1000 cm^{-1}, the focus of the present work, has been scaled by a factor of 0.98 to consider corrections due to the use of the harmonic approximation. The inset shows an expanded view of the region 1000−1120 cm^{-1} covering the experimental C−C stretching peak. Longitudinal modes (L) inside the peak are within a region of 34 cm^{-1} and are the reason of the intrinsic line width observed experimentally.

use theoretical ab initio calculations of the vibrational spectra of single molecules to characterize vibrational modes in experimental data. Although, any ab initio calculation is sensitive to the level of theory used, it is known from our past experience that frequencies are overestimated by ~5% due to the use of the harmonic approximation in the determination of frequencies in the theoretical methods. In the worst case scenario, the prediction of the width is still acceptable although the exact location of the vibrational modes may not be precise; however, such locations may not be precise with any available method because the exact evaluation of energy separations would require tolerances within small fractions of kcal/mol. Notice also that the applied bias voltage used in the experiment is too small to be able to take the molecule to an excited electronic state or to a charge state, which might yield sharp changes in the vibrational spectrum. Therefore, all these considerations justify our selection of the theoretical model as sufficient to determine the signature of the C−C stretching vibrational modes.

Results and Discussion

Figure 1 shows the entire spectrum (vertical lines) of HS−(CH$_2$)$_8$−SH as well as the IETS experimental results. The existence of an intrinsic line width can be clearly induced from this figure. It is due to the lack of high resolution that would be needed to resolve between specific lines of a vibrational type. The peak at ~1000 cm^{-1}, which is observed as a single peak experimentally is actually located in the region of the spectrum where at least seven vibrational normal modes are distributed, as can be seen in the inset of Figure 1. In this inset the longitudinal and transversal modes have been characterized. This finer detail shows, as expected, that the actual peak corresponds to seven possible linear combinations of the seven C−C bond stretching (or internal modes) available in HS−(CH$_2$)$_8$−SH. A further analysis indicates that these internal modes also combine with several CH$_2$ internal modes yielding longitudinal and transversal modes in the neighborhood of the observed experimental peak. Because IETS affects primarily longitudinal modes along the electron-transfer direction, we calculate the width spanned by the five longitudinal normal modes shown in the inset of Figure 1. This width is 34 cm^{-1} or ~4.2 meV, which is in excellent agreement with the experimentally calculated intrinsic line width. Notice that this theoretical width is simply obtained from the range covered by the zero line width lines corresponding to the five longitudinal (L) C−C vibrations, which are shown in the inset of Figure 1. For completeness the transversal modes (T) in the same range are also shown in the inset.

The calculated frequencies correspond to the harmonic approximation; thus we scale the frequencies in the neighborhood of 1000 cm^{-1} by a factor of 0.98 and the frequencies in the neighborhood of 3000 cm^{-1} by a factor of 0.95. These factors were obtained by comparing the theoretical frequencies with infrared (IR) experiments.[11] The frequencies in the lower region of the spectrum are left unscaled, as indicated in Figure 1. The figure shows all vibrational modes in green using same size lines, the infrared (IR) intensities are shown in red, and the Raman intensities are in blue. IR and Raman intensities are plotted in logarithmic scales that start from the ends of the green lines (Raman intensities are shown as negative). Several other details that are not the focus of the present work can be obtained from Figure 1. Starting from the upper part of spectrum, the 16 normal stretching modes corresponding to the 16 C−H bonds of $HS-(CH_2)_8-SH$ are packed together but do not seem to strongly affect the electron transfer through the molecule, as no visible experimental peak is observed. Several of the other CH_2 group modes (rocking, wagging, scissoring) distribute below and above the energy of the CC stretching modes. Actually, several normal modes in this region are a mixture of CC and CH_2 internal modes, yielding longitudinal and transversal normal modes inside the observed peak assigned to the CC stretching. Therefore, the peak frequencies assigned to the C−C stretching include peaks that are not longitudinal or pure C−C stretching.

Conclusion

As can be observed from Figure 1, the fine structure of the vibrational frequencies plays an important role in the characterization of the molecules approached by the contacts and it should be considered for precise analysis of IETS or any other molecular vibrational related data. We conclude from this analysis that the intrinsic width observed in the experiment is due to the width spanned by the fine structure of the longitudinal C−C vibrational modes in the alkanedithiol molecule.

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