# Resonant Vibrations, Peak Broadening, and Noise in Single Molecule Contacts: The Nature of the First Conductance Peak

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We carry out experiments on single-molecule junctions at low temperatures, using the mechanically controlled break junction technique. Analyzing the results obtained with various molecules, the nature of the first peak in the differential conductance spectra is elucidated. We observe an electronic transition with a vibronic fine structure, if the first peak occurs at small voltages. This regime can accurately be described by the resonant tunneling model. At higher voltages, additional smearing is observed and no fine structure can be resolved. A detailed analysis of the noise signal indicates that the onset of current is associated with strong fluctuations as a precursor of current flow. The data indicate that a complex fluctuation-driven transport mechanism takes over in this regime.

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We consider charge transport across single conjugated molecules. The fundamental picture to understand the current-voltage characteristics is the resonant tunneling model [1,2]. At low bias, no charge transport occurs due to the absence of a resonant level and Coulomb blockade. In the lowest order, current starts to flow at a certain threshold, at which the electrons are energetically allowed to occupy an orbital in the molecule. The consequence is a steplike increase of the current $I(V)$, or correspondingly a peak in the differential conductance $dI/dV(V)$. In the framework of a purely electronic transition, it is well known that the peak width of the differential conductance is determined by the temperature $T$ and the coupling constant $\Gamma$ which in turn determines the current level. We have measured more than ten molecular species and none of them showed correspondingly narrow peaks at the onset of conductance, even at low temperatures (significantly smaller than 10 mV, in contrast to the observed 100–300 mV). Hence there is a qualitative mismatch between the purely electronic resonant tunneling model and experimental data: the peaks appear by far too broad.

This issue is partially resolved when vibrations are considered [3]. Their impact on $IV$ characteristics is expected to be inelastic side peaks to the electronic peaks. Such signatures have been resolved in rather few experiments, where the first peak is explicitly tuned towards low bias voltages ($< 100$ mV) by an external gate [4–6]. However, it is not obvious how many and which vibrational modes are excited and show up as additional transport channels in the differential conductance. Theory shows that a single vibronic mode can trigger a variety of excitations [7]. We have also observed resistance noise which we attributed to atomic-scale reconfigurations in the junction area [8]. In this manuscript we discuss limitations of the resonant tunneling model (including vibrations) and show that this is only suitable for the description of the first peak, when this peak occurs at small voltages. Otherwise the resonant tunneling picture is insufficient and bias-induced fluctuations have to be taken into account as soon as current flows.

We use the mechanically controlled break junction (MCBJ) technique at low temperatures. The method is described elsewhere [9,10]. The features discussed here have been found to be general for several ($> 10$) organic compounds and we are not aware of counterexamples. All molecules have a delocalized $\pi$-electron system and a length of about 2 nm, some of them containing at least one metal ion center. As a representative example, the molecule $Fe^{2+}$-bis(pyrazolyl)pyridine (Fe compound) [11] is used for the measurements presented in Figs. 1, 3, and 4 and an oligo(phenylene vinylene) (OPV-3) molecule in Fig. 5.

We first turn our attention to the low-voltage regime. Typically the first conductance peak occurs at some hundred millivolts. However, this value varies substantially from junction to junction as a consequence of the uncontrolled local environment [9]. In few junctions, the onset of current occurs at a few tens of millivolts. We present a detailed analysis of such a junction which shows that in this regime the resonant tunneling model describes the first peak very accurately.

A measurement of current and voltage in Fig. 1, taken with a resolution of 0.5 mV per step reveals a substructure in the general peak form. Several peaks appear on a background of a rather large peak structure.

We analyze the equidistant fine structure and find that the peak separation at negative and positive bias voltages has a ratio of $8.3/5.2 = 1.6$. Correspondingly, the onset of current has the same ratio of $|-43.2/28.0| = 1.6$. This can readily be explained by a molecular electronic level

 

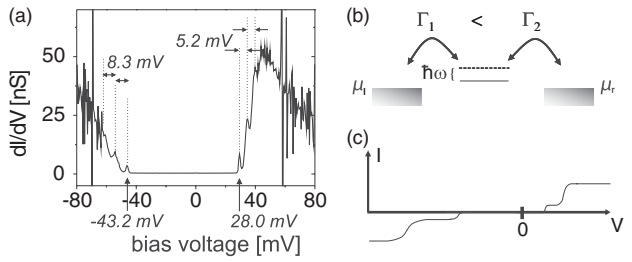


FIG. 1. (a) $dI/dV$ measurement at the first electronic peak for a small blockade region. Several single excitations can be recognized, for positive voltages the distance is $\approx 5.2$ mV, for negative $\approx 8.3$ mV. The onset of current shows the same asymmetry, taking place at $-43.2$ mV and at $+28.0$ mV. (b) Schematic representation of two leads with chemical potentials $\mu_l$ and $\mu_r$ coupled asymmetrically ($\Gamma_1 < \Gamma_2$) to a molecular level, which is accompanied by a vibrational state $\hbar\omega$. (c) Resulting current-voltage characteristic. The onset of current and peak distance is lower for positive voltages, when the left electrode is weaklier coupled (in case of LUMO transport).

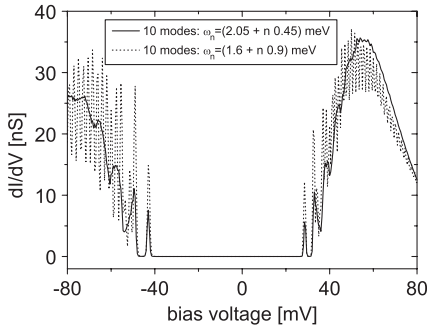


FIG. 2. $dI/dV$ characteristics obtained from a nonequilibrium Green's function calculation for a resonant level model [7,13,14]. The model comprises an electronic state 39 meV above the Fermi energy and ten vibrational modes with frequencies $\omega_n$ that are coupled to this state with a uniform coupling strength such that the reorganization energy amounts to 22 meV for both plots. In the calculation, the vibrational modes are assumed to be in their thermal equilibrium state determined by the junction's temperature $T = 1$ K. The level-width functions $\Gamma_1 = 9$ $\mu$eV and $\Gamma_2 = 13$ $\mu$eV have been chosen to model the current and voltage drop retrieved from Fig. 1(a).

that is accompanied by vibronic levels at intervals of $\hbar\omega$ and coupled asymmetrically to the electrodes, as illustrated in Fig. 1(b). This asymmetry creates asymmetric voltage drops at the two molecule-metal interfaces. So in one voltage direction the molecular levels will be in resonance at smaller absolute voltages, and also the peak separation will be larger if the stronger coupled electrode moves along the levels. This leads to a current-voltage characteristic as plotted in Fig. 1(c). The onset of current and the peak separation at both polarities fulfill the same relation as the coupling to the electrodes, if the voltage drop is assumed to satisfy the same ratio. A vibrational excitation energy of $E_{\mathrm{vib}} \approx 3.2$ meV can be extracted. Similar structures have been observed for a variety of molecular junctions [12].

To understand the observed peak shape we simulate transport in the junction with a generic resonant tunneling model, assuming electronic-vibrational coupling to a multitude of vibrational modes. Figure 2 shows results of nonequilibrium Green's function model calculations [7,13,14], which reproduce the experimental data in Fig. 1(a) rather well. The underlying model includes a single electronic state on the molecular bridge, located 39 meV above the Fermi energy, which is coupled uniformly to ten harmonic vibrational modes (with a corresponding reorganization energy of 22 meV for both plots). The frequencies of the vibrational modes are chosen as $\omega_n = 2.05 + n0.45$ meV and $\omega_n = 1.6 + n0.9$ meV for the solid and the dotted line, respectively, ($n \in \{1 \ldots 10\}$) to mimic the distribution of low-frequency vibrational modes in larger molecules. This simple set of parameters is not a result of *ab initio* calculations, but a realistic model. For example, DFT calculations (BP86/def-TVZP) for the free molecule considered above (Fe compound) show that there are 13 modes with frequencies in the range from 0.8 to 10 meV.

In agreement with the experimental data, the model calculations result in a broad peak in the conductance. It is emphasized that the width of this peak is not related to molecule-lead coupling ($\Gamma_{1/2} \approx 0.01$ meV) or thermal broadening ($k_B T \approx 0.1$ meV) but is a result of the coupling to the distribution of vibrational modes and is approximately determined by the overall reorganization energy of 22 meV. A more detailed analysis of the conductance reveals a complex substructure, the details of which depend on the specifics of the model [13]. The first narrow peak appears once the chemical potential in one of the leads allows the population of the resonant level. At larger bias voltages the single conductance peaks overlap with each other and form a broad peak. The small gap between the first narrow peak and the following broadened structures is determined by the frequency $\omega_1$. It is noted that vibrational relaxation processes, e.g., due to coupling to phonons in the gold contacts, as well as anharmonic effects, which are neglected in the present calculation, will result in a further broadening of the peak structures.

We conclude that the calculations within the resonant tunneling model can explain the observed peak structure and the broadening, at least in the low bias regime. The following experiments, however, indicate a more complex physics. With the MCBJ technique, we are able to increase the electrodes' distance of stable junctions. Over the years we have learned that this goes always along with an enlargement of the blockade regime, up to a point of a sudden change of the current level. Microscopically we assign the first effect to a pullout of the atomic gold tips, resulting in a reduction of the self-capacitance of the molecular junction. This bears the opportunity of changing the position of the first peak towards higher voltages without significant changes of the junction geometry. As the molecule's length is fixed the onset of current thus occurs at higher electric fields.

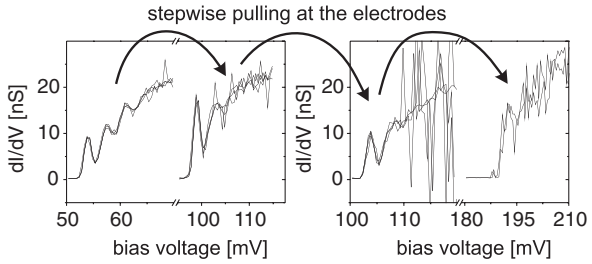


FIG. 3. $dI/dV$ measurements at the onset of current for a small blockade region (left curve) and after pulling at the electrodes in three subsequent steps. With increasing onset voltage the vibrational features smear out step by step.

Figure 3 displays data obtained during pulling the junction apart, without a sudden change. In the first measurement three distinct excitations can be resolved, the second shows only two of them, in the third only the first appears clearly while the fourth does not reveal a clear substructure anymore [15]. The data suggest that the successively enhanced electric fields cause an additional smearing of the peak's fine structure. Indeed we never observe a vibrational fine structure of the first peak, if the peak position is $\gtrsim 300$ mV (among more than ten molecules, we have found only one exception: in [16] we investigated a stringlike polyyne molecule, and longitudinal stringlike excitations were resolved as a distinct peak sequence). We propose that the electric field drives fluctuations providing additional broadening. As a result, the vibronic fine structure is obscured at higher fields.

At this point, a detailed analysis of the first peak with respect to fluctuations is desirable. We show in Fig. 4 a relatively sharp onset of current in the high-bias regime ($\approx -700$ mV). An apparently stable current-voltage characteristic is observed at a measurement speed of the voltage sweep of 75 mV/s (inset). Repeating the measurement at a slower speed of 15 mV/s in this case (not always) leads to high current fluctuations. We conclude that there are instabilities of the $IV$ characteristics, which due to their slow time scales are associated to structural reconfigurations. They are precursors of bistable hysteretic behavior as in Ref. [17].

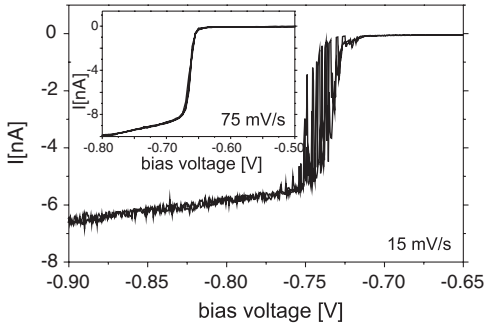


FIG. 4. $IV$ measurements that show high fluctuations at the onset of current when lowering the scanning speed from 75 mV/s (inset) by a factor of 5.

In order to obtain a deeper understanding of the time scales of these fluctuations noise measurements are carried out parallel to the $IV$ characteristics at a similar molecular contact. Figure 5(a) shows the spectral noise density $S_{II}$ as a function of voltage for three chosen frequencies as well as the differential conductance (red curve) at the first peak with an FWHM of $\approx 150$ mV. The current noise is low in the blockade region, and increases by 4 orders of magnitude close to the maximum of the conductance peak. It then decreases again by 2 orders of magnitude after the first peak. We think that this is a key finding for the understanding of the first peak, not anticipated by the resonant tunneling model. A closer look reveals that the maximum of noise is actually at lower bias than the maximum of the conductance peak, in particular, at lower frequencies. In other words, the fluctuations are maximum when the current starts to flow. This reminds a model proposed by Koch *et al.* [18]. The authors considered a model with strong electron-vibration coupling and obtained very large shot noise. The basic idea is that in the transport model tunneling is energetically allowed when the first electronic level is reached, but suppressed due to a weak wave function overlap (Franck-Condon blockade). When reaching a bias which also allows us to excite a vibration, the molecule starts to vibrate as a consequence of a first tunneling event, and under realistic assumptions a stronger overlap will allow more electrons to tunnel through the junction. In their model, avalanchelike amplification of the current occurs and leads to giant shot noise signals at

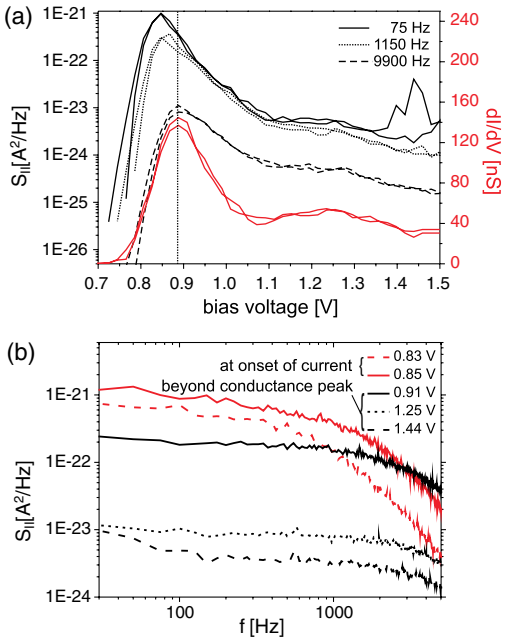


FIG. 5 (color online). (a) Spectral noise density $S_{II}$ at three different frequencies and $dI/dV$ curve (red or gray) at the first conductance peak. At the onset of current the noise is enhanced by several orders of magnitude. (b) Noise spectra at the onset of current (red or gray) and beyond the conductance peak (black) show different frequency dependence ($f^{-2}$ vs $f^{-1}$) above 1 kHz.

the onset of current flow. We now transfer the essential ideas to our experiments in the high-bias regime. The experimental situation is more complex than this theoretical model and, in addition, is not limited to shot noise but includes configurational noise. We consider the case that the onset of current triggers configurational fluctuations. One may suspect that there exist field-sensitive bistabilities, which need a certain field strength to be active. The onset of current and eventually of first vibrational excitations may be the trigger of further field-induced structural reconfigurations, which appear as low-frequency noise or instabilities. Alternatively, a deformation of the molecule might act on the threshold value itself, providing a situation similar to a polaron instability [3,19,20]. As it is known, the average charge on the molecule changes when the current sets in. This may induce a structural change, or may create structural bistabilities, also on slow time scales. Common to these illustrative considerations is the observed phenomenon that the onset of current triggers reconfigurations, accompanied by large fluctuations. When further increasing the bias the system undergoes a strongly fluctuating regime, with first a maximum in the noise signal and subsequently a maximum in $dI/dV$. Beyond the two maxima, the current reaches a higher level (similar to the resonant tunneling model), whereas the noise is reduced. The noise measurements reveal that the physics of the first peak is much more complicated than its similarity to the resonant tunneling model suggests.

Further information can be extracted from the frequency dependence of the current noise density [Fig. 5(b)]. The presented curves at five different voltages split into two pairs, the red (or gray) curves at the onset of current, and the black ones for bias voltages beyond the maximum of the differential conductance. The first pair approximately follows a decay $\propto f^{-2}$, whereas the rest resembles more to a $f^{-1}$ dependence. While the higher exponent is ascribed to a single fluctuator by a simple Lorentz oscillator model [21], the latter can be explained by the superposition of several oscillators with uniformly distributed time constants [22,23].

Hence, there are two different origins of noise identified. On the one hand the first electronic transition is accompanied by one dominating bistability of the molecular contact configuration. This was surprising to us and may point to an intrinsic effect, for example, the polaron model, rather than to fluctuations in the gold leads. Beyond the peak, many fluctuators are active. Hence, the first current plateau should be understood as a dynamic interplay of charge flow, vibrations and dynamical reconfigurations of the molecule. This picture goes well beyond the resonant tunneling model.

Altogether, from many experiments with more than ten conjugated molecules and from detailed calculations, we receive the following picture of charge transport through single molecules: the purely electronic transmission is accompanied by distinct vibrational resonant conduction channels. At low voltage, the broadened peak shape is fully consistent with the resonant tunneling model. More complex physics happens at higher electric field. The transition from the blockade regime to the conducting regime shows configurational fluctuations, with a noise maximum before the maximum of the differential conductance. At these higher bias thresholds, vibrational excitations, structural dynamics, and fluctuations at the onset of current may not be described independently but are interrelated in a complex manner. Hence the similarity of the $IV$ characteristics to the resonant tunneling model may be rather fortuitous at higher bias.

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