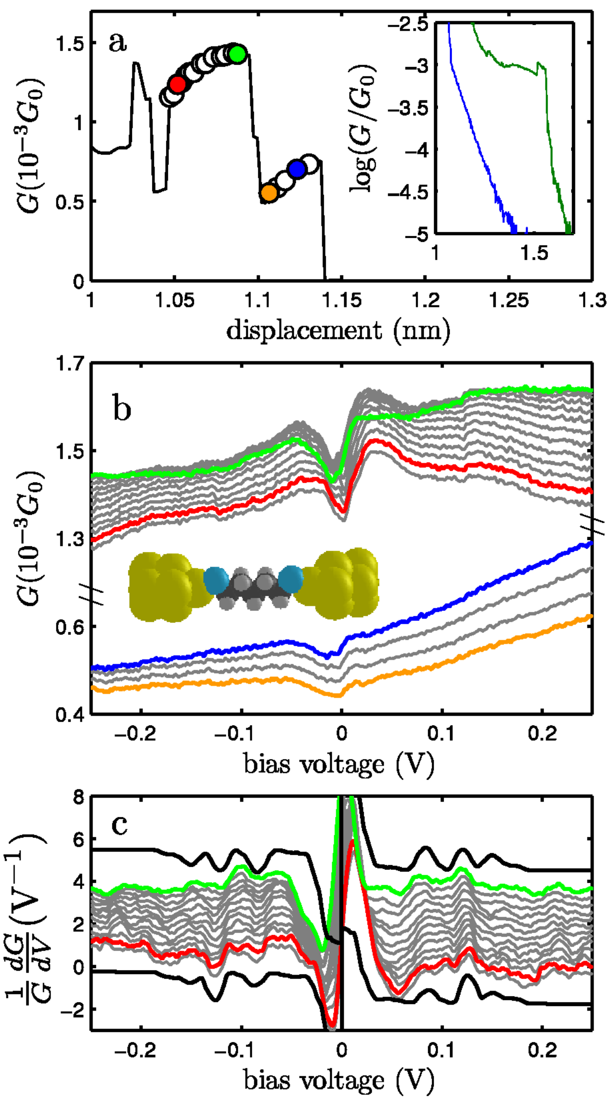

FIG. 1: (Color online) (a) Selected conductance trace corresponding to the formation of a stable molecular junction. Note the jump in conductance at a displacement of about 1.1 nm, caused by the strain relaxation in the junction. (Inset) Low-voltage conductance traces during electrode separation after breaking a gold contact for a clean metal junction (blue trace) and for a junction in which a molecule is present (green trace). (b) Differential conductance vs voltage acquired at the positions indicated by the circles in panel (a). (c) Derivative of the differential conductance (normalized by the conductance), $G^{-1}d^2I/dV^2$, of the curves in panel (b). For clarity, the experimental curves have been shifted upwards as the molecular junction is stretched. The black thick curves are calculated spectra for two different electrode separations that differ by 0.1 nm (top curve corresponds to a more stretched configuration than bottom curve).

single molecule suspended between substrate and tip in a stable configuration [14]. Consistently with the deposition conditions, the initial distribution of molecules on the substrate is quite homogeneous. However, repeated junction formation on the same spot resulted in a depletion of molecules. When one of these low conductance plateaus is detected, tip retraction is stopped, and the current I, and differential conductance, dI/dV, are measured as a function of the applied bias voltage V. The differential conductance is measured using a lockin technique with an ac voltage modulation of $V_{\mathrm{rms}} = 5$ mV. The measurement is repeated in small incremental steps of tip retraction, leading to the acquisition of data such as those summarized in Fig. 1. The continuous parts of the conductance trace indicate regions where the junction deforms elastically, while the sudden jumps in the conductance result from the relaxation of the accumulated stress in the junction. Most likely these relaxations are due to atomic rearrangements at the electrodes in the immediate proximity of the junction, as demonstrated in atomic wires of gold [15].

The differential conductance curves, as those shown in Fig. 1(b), show a continuous evolution within a conductance plateau, while sudden changes in the overall shape of the curves are observed at the conductance jumps. As in the case of atomic contacts [16, 17], the large-scale features of the differential conductance curves do not reflect the properties of the junction itself but are a consequence of elastic scattering of the electrons in the vicinity of the junction and vary markedly from junction to junction. Often the differential conductance curves show a dip at low voltages. These so-called zero-bias anomalies are poorly understood and typical of low temperature junctions. We will not give them further consideration in this work.

Careful inspection of the differential conductance curves in Fig. 1(b) shows small conductance jumps of the order of one percent at certain voltages, the most prominent of which occurs at ± 120 mV. These sudden changes in conductance are known signatures of inelastic scattering in the junction [12]. At low temperatures the vibrational motion of the molecule, which are almost completely frozen, can only be excited by the passing electrons provided the applied bias exceeds the quantum of a given vibration. In the low-transmission, off-resonance case this onset of inelastic scattering leads to enhanced conductance [18, 19], and hence to peaks (dips) in d^2I/dV^2 at positive (negative) bias polarity. Fig. 1(c) shows the IETS spectra, calculated by taking the numerical derivative of the measured differential conductance curves in Fig. 1(b). Indeed, we observe antisymmetric features expected for the inelastic scattering processes.

We have studied 33 different stable molecular junctions characterized by a well-defined conductance plateau at low conductance, obtaining a total of 540 IETS spectra from the measured differential conductance curves. The probability density function (PDF) of the low-bias conductance, plotted in Fig. 2(a), shows that most of the mechanically stable junctions have a conductance of approximately $10^{-3}G_0$. This value is consistent with the conductance peak in the PDF observed at room temperature in solution shown in Fig. 2(b), and supports the idea that transport through these molecular junctions