The ability to measure the conductance of a single molecule not only promises a better understanding of electron transfer in molecules, but also is a necessary step towards the goal of building a functional device using single molecules. Rapid progress has been made in recent years, but such measurements are still a difficult task. In order to reliably measure single molecule conductance, one must provide a reproducible and efficient electronic coupling between the molecule and the probing electrodes. Due to the apparent difficulty of forming microscopically identical molecule-electrode contacts, a statistical analysis over a large number of electrode/molecule/electrode junctions is necessary for a complete picture. One must also find a signature to identify that the measured conductance is due to not only the sample molecules but also a single sample molecule.

We have developed a method to determine the conductance of single molecules covalently bonded to gold electrodes by repeatedly forming a large number of molecular junctions. We create each molecular junction by separating two Au electrodes from contact in a solution containing the sample molecules. During the separation, we simultaneously measure the conductance and the force between the two electrodes. The conductance decreases in discrete steps, corresponding to the breakdown of individual molecules covalently bonded to the electrodes. Each discrete drop in the conductance is accompanied by a discrete drop in the force, which allows us to determine the bonding strength of the molecule to the electrodes. We have also determined the effective spring constant of a single molecule and the dependence of the conductance on the applied force. Using the method, we have studied both electron transport and mechanical properties of a number of different molecules, ranging from simple alkanedithiols to oligopeptides, covalently bonded to two Au electrodes via S-Au bonds.

Our method has the following distinctive features: First, pronounced peaks in the conductance histogram constructed from thousands of individual measurements can be used to identify with the conductance of a single molecule. Second, since each molecular junction is formed by mechanically separating two electrodes, only the molecules bonded to the electrodes contribute to the measured conductance. In fact, the mechanical force provides direct information on the bonding nature of the molecules to the gold electrodes. Third, statistical analysis reduces mistaking signals from impurities for those from the sample. Finally, our method works in aqueous solution, which opens the door to the study of biological molecules under physiological conditions.

Acknowledgement  We thank Stuart Lindsay, Larry Nagahara, Devens Gust, Thomas Moore, Anna Moore and Otto Sankey for their contributions, and DOE(DE-FG03-01ER45943) and NSF(CHE-0243423) for financial support.
Fig. 1. Schematic illustration of a molecule covalently bonded to two Au electrodes under mechanical stretching, during which both the conductance and the force are measured.

Fig. 2 (a) Simultaneously recorded conductance and force curves of 1,8-octanediolthiol during stretching. The discrete changes in the conductance and the force are due to the breakdown of individual molecules, which are used to count the number of molecules bridged to two Au electrodes. (b) shows that two molecules can break simultaneously at the last stage, resulting twice as much change in the conductance and the force. (c-d) show the conductance and the force histograms, revealing conductance quantum $2.5 \times 10^{-4} G_0$ and force quantum $1.5$ nN, corresponding to the conductance of a single 1,8-octanediolthiol covalently attached to two Au electrodes, and the force required to break a Au-Au bond at the molecule-Au contacts.