

Electronic Transparency of a Single C₆₀ Molecule

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We report the first study of electrical contact with an individual molecule (C₆₀). Using a scanning tunneling microscope tip, the electrical current I flowing as a function of tip displacement s towards the molecule is investigated [$I(s)$ characteristics]. The tunneling current increases approximately exponentially with tip displacement in the tunnel regime, but this behavior changes significantly as contact is established. From the $I(s)$ data and calculations for C₆₀ we determine an apparent electrical resistance of 54.80 M Ω for the junction at "tip contact." In the Landauer formalism, this value is a measurement of the electronic transparency 2.35×10^{-4} of the molecule under the tip.

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The scanning tunneling microscope (STM) is an exceptional tool to image surfaces with atomic resolution [1], to manipulate atoms on an individual basis [2], to perform spectroscopy on single atoms [3], and to study the electrical and mechanical properties of metal contacts on the atomic scale [4,5]. In this Letter we discuss its use for measuring the apparent electrical resistance of a single molecule. The electrical conductance (resistance) of a metal-vacuum-metal junction is given by the slope of the I - V characteristics at low applied voltage where a linear relationship is observed ($|V_t| < 100$ mV) [6]. If we introduce a molecule into such a junction, it will change the slope of the I - V characteristic, which nevertheless remains linear at low values of V_t with respect to the energy gap between the highest occupied molecular orbitals (HOMO) and the lowest unoccupied molecular orbitals (LUMO) of the adsorbed molecule. As we approach the two electrodes in this low-voltage regime, a point will be reached where the current flowing through the molecule is maximized while maintaining a minimum in its mechanical deformation. Here one can define the electrical contact point of the two electrodes with the molecule. In the low-voltage regime, such a junction has a characteristic electrical resistance, which we have measured using a STM.

The STM tip is carefully positioned above a C₆₀ molecule by repeatedly imaging to ascertain the tip's lateral position in the tunneling mode with a vacuum gap, before it is then moved forward to contact. Electrical contact occurs at a distance s between tip apex and surface, whereby deformation of chemical transformations of C₆₀ are not induced. As the tip approaches the top of an adsorbed molecule, our calculations indicate that a first deviation from the linear $\log I(s)$ current-distance variation occurs at mechanical contact, i.e., at a distance where the van der Waals (vdW) and the repulsive forces are balanced at the tip-surface junction. At yet closer proximity, a second change in the slope of $\log I(s)$ takes place owing to compression of the adsorbate by the tip. This modifies

the electronic structure of the adsorbate. Electrical contact occurs after mechanical contact, at the beginning of molecular-orbital mixing between adsorbate and tip apex, but before the transformation of the electronic structure of C₆₀ induced at smaller s by the compression. Such mixing does not exist at vdW distances.

We studied $I(s)$ curves for C₆₀ adsorbed on Au(110). C₆₀ was chosen for the following reasons. Theoretically and experimentally, we find that moderate compression does not force it to escape the tip by a lateral motion nor change its overall conformation, as do, for example, adsorbed thiol-alkane molecules which adopt a natural tilt angle with respect to the surface normal [7]. In a cluster, adjacent C₆₀ molecules mechanically stabilize the position of C₆₀ for $I(s)$ measurements. However, owing to lateral vdW intermolecular interactions, they do not modify each other's electronic structure. Experiments have also shown that bulk solid C₆₀ can be elastically compressed before the collapse of the C₆₀ due to sp^2 to sp^3 rehybridization of the carbon orbitals [8]. A final appealing feature is that the C₆₀ HOMO-LUMO gap is not too wide in its adsorbed state on Au (~ 1 eV) [9], leading to a reasonable current intensity at the low bias voltage.

The experiment was performed using a STM operating at 300 K in ultrahigh vacuum (UHV) [10]. The Au(110)-(1 \times 2) surface was prepared in UHV [10], and the C₆₀ molecules sublimed from an Ohmically heated oven to a coverage of 0.1 monolayer. We used a W tip prepared *in situ* by sputtering, annealing, and field emission at a tunnel voltage of $V_t = 0.7$ V and current of $I_t = 0.2$ nA. Individual C₆₀ molecules clustered in small islands in Fig. 1(a) are clearly resolved. They nucleate at [001] kink sites; the structure within each island is shown in detail in Fig. 1(b). It is also possible to resolve the missing atomic row structure of the (1 \times 2) Au reconstruction running along the surface in [110] separated by 8.14 Å with a corrugation amplitude of ~ 1 Å interspersed by Au atomic steps. The tip was positioned "atop" a C₆₀ [indicated in

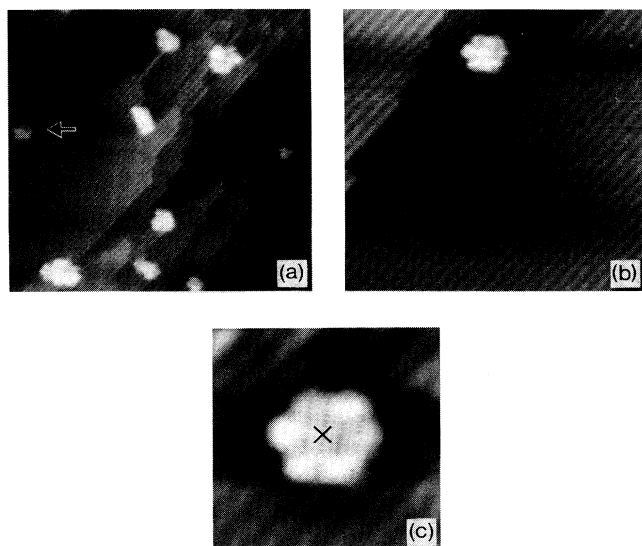


FIG. 1. STM gray scale topographic images of C_{60} molecular clusters deposited at 300 K on Au(110)-(1 \times 2). The atomic rows of Au are separated by 8.14 Å with a corrugation amplitude of ~ 1 Å. (a) Overview scan of the clusters which nucleate at kink sites in [001]. (b) Detailed topograph of a cluster selected for $I(s)$ measurements. $I(s)$ curves were kept for situations where topographic details imaged before and after the measurement are similar. The selected cluster is indicated by an arrow in (a), and the $I(s)$ measurement position by an "X" in (c).

Fig. 1(c)] of a selected island, and the $I(s)$ characteristics were recorded as follows. First, the STM regulation loop was frozen at a distance defined by the imaging conditions. The tip was then mechanically positioned in the surface normal direction by introducing an additional retraction offset, and then by a defined ramp distance towards the surface during which the current was recorded at 128 points using a special current-voltage converter [11] at a freely chosen bias voltage. For comparison with theory we selected a 50 mV bias voltage $I(s)$ and ramped the tip forward by various distances (in the range of 10–20 Å). We confirmed that, to within ± 200 mV, I - V characteristics recorded at fixed s are linear for a series of tip altitudes. This was achieved by superimposing a series of offsets Δs and recording individual I - V characteristics over a range of resistances varying from $R \approx 5$ M Ω to $R \approx 5000$ M Ω . All the I - V characteristics remain linear within the HOMO-LUMO gap, which drops to ~ 0.9 eV for the lower resistance. This linearity permits us to define the tunneling resistance by $I(s)$ measurements at constant $V_t = 50$ mV. The contact resistance will later be defined within this tunneling transport regime as opposed to the ballistic regime.

Figure 2 shows a representative $I(s)$ curve averaged over some 20 measurements. All the $I(s)$ curves display a linear $\log(I)$ variation as the tip is ramped forward, fol-

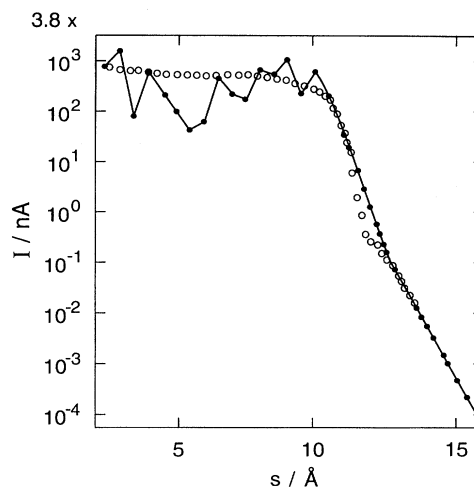


FIG. 2. Variation of the tunneling current intensity $I(s)$ through a C_{60} molecule as a function of the tip apex to surface distance s . The open circles indicate the experimental values; the solid line indicates the calculated values with a full deformation of the C_{60} upon the tip approach. In both cases, the bias voltage of 50 mV is chosen.

lowed by a large positive deviation at smaller gap values which is reversible. Unlike the case of a metal-tip contact, which generally results in irreversible characteristics associated with adhesion [4], contact with a C_{60} molecule appears more similar to that of graphite, which also exhibits reversible behavior at low tunnel voltages. The data shown in Fig. 2 were calibrated by calculating the theoretical $I(s)$ curve using our elastic scattering quantum chemistry technique configured for STM (STM-ESQC) [12]. The full atomic structure and valence orbitals of the tip, the C_{60} molecule, and the Au(110) substrate were considered in these calculations. The tip was made of Au bulk terminated by a Au(110) face upon which the three-layer pyramidal W tip had been deposited. The substrate was a Au(110) face [12]. The C_{60} deformation was included in STM-ESQC using the MM2 routine with a standard sp^2 carbon parametrization [13], and the C_{60} conformation was optimized for each s . Then we calculated I through the molecule for each conformation. The experimental and calculated $I(s)$ curves display an encouraging similarity, as shown in Fig. 2. The calculated deviations in the $I(s)$ curves from a linear $\log(I)$ variation is directly related to the closure of the C_{60} HOMO-LUMO gap upon compression of C_{60} . The deformation of C_{60} by the W tip apex is presented in Fig. 3, as optimized during the STM-ESQC calculations. Upon compression, many degenerate C_{60} electronic levels split, and some of them move toward the electrode Fermi level: The deformation of the C_{60} skeleton produces an increase of the electronic interactions between nonconsecutive cycles in C_{60} . Without compression (i.e., for large s) C_{60} adds approximately 6 orders of magnitude of current compared

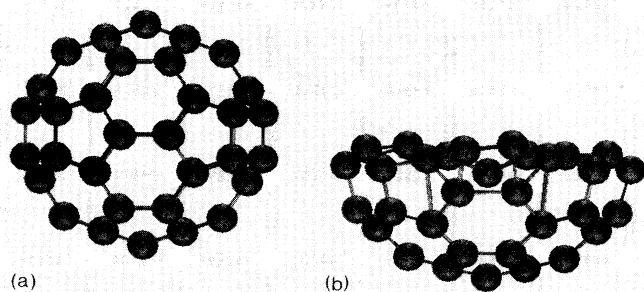


FIG. 3. Optimized structure of the C_{60} molecule in the tunneling junction for a tip apex to surface distance of (a) $s = 14 \text{ \AA}$ and (b) $s = 7.35 \text{ \AA}$. The W tip apex was considered rigid during the approach.

with the same s without C_{60} in the junction. Deformation of the molecule at small s contributes an additional 2 orders of magnitude to the current. The latter observation clearly indicates why certain adsorbates, which exist as insulators in the bulk, can be imaged using STM: A transformation of the adsorbate electronic structure is induced by the tip compression. This compression increases intramolecular electronic coupling, shifting some electronic levels toward the electrode Fermi level. Nevertheless, a resonance between an adsorbate energy level and the electrode Fermi level is not required to produce a detectable tunneling current even at low voltage, as demonstrated experimentally [2] and theoretically [14,15]. Consequently, moderate compression opens new tunneling channels through an adsorbate which makes STM imaging of this adsorbate possible, similar to the proposal by Lindsay *et al.* [16].

In Fig. 4, we present the resistance-distance $R(s)$ curve of the junction together with the calculated C_{60} optimized energy $E(C_{60})$ in the tip-surface junction. As s decreases from 16 to $\sim 13 \text{ \AA}$, a small deformation of the C_{60} cage occurs due to vdW tip attraction and manifests itself as a small deviation from the linearity of $\log R(s)$. Up to this distance the junction is still in a tunneling regime. Mechanical contact is established at $s = 13.2 \text{ \AA}$, corresponding to zero force of the C_{60} in the junction ($d[E(C_{60})]/ds = 0$). At this point the C_{60} is slightly attracted by the tip. At $s = 12.3 \text{ \AA}$, the vdW expansion is compensated by the tip compression, and C_{60} recovers approximately its original shape. By $s < 12.0 \text{ \AA}$, the cage undergoes compression, and $R(s)$ decreases rapidly towards the quantum resistance limit of $R_0 = h/2e^2$. At this limit the molecule is almost totally transparent to the tunneling electrons, and consequently R_0 is the Sharvin resistance of a one-atom point contact. This trend is in contrast to previous $I(s)$ experiments on metallic junctions, from which discontinuities and instabilities are observed in the $I(s)$ characteristics due to spontaneous adhesion [17]. At small s we find that C_{60} prevents such a collapse of the tunneling junction.

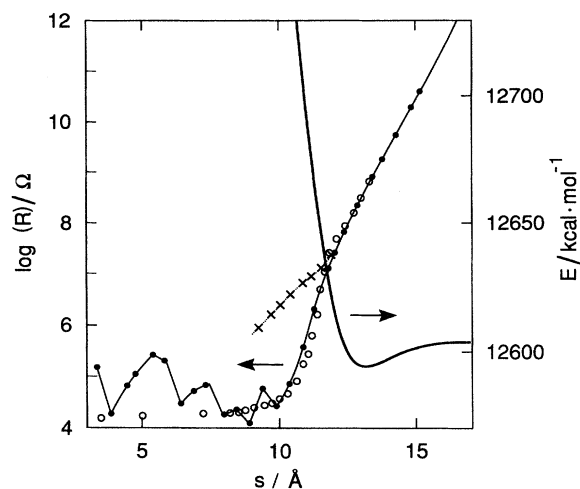


FIG. 4. Variation of the tip apex- C_{60} -gold surface tunneling junction resistance $R(s)$ as a function of the tip apex to surface distance s (experimental, open circles; calculated, solid dots) compared with the optimized $E(C_{60})$ energy in the junction (heavy solid line). The junction resistance calculated with a rigid, nondeformed C_{60} is shown for reference (dotted line with \times symbols).

Differences between the calculated and experimental $I(s)$ curves exist at small s (see Fig. 2). This is due in part to the fact that the theoretical $I(s)$ was calculated at 0 K. In this case and at low voltage, each peak at $s < 9 \text{ \AA}$ in Fig. 2 corresponds to the splitting of some of the HOMO states, which, as they increase in energy by the deformation, pass one by one through $\pm 50 \text{ mV}$ of the Fermi level. This leads to resonances at the Fermi level at 0 K. These resonances are smeared out by thermal broadening at 300 K. Consequently, the experimental curve displays only their average behavior. An additional consideration in this regime of strong deformation may be that the experimentally defined excursion or calibration of the tip may be slightly less than the calibration factor determined in the tunneling regime [18].

Returning to the electrical contact altitude at $s = 12.3 \text{ \AA}$, we find experimentally that the resistance of the total junction with C_{60} is $54.807 \pm 13 \text{ M}\Omega$. We shall now discuss to what extent, if any, is this resistance the intrinsic electrical resistance of an individual C_{60} molecule? At low bias voltage, the tunneling current through C_{60} is dependent on the symmetry and spatial extension of its molecular orbits [12]. In this sense, the resistance contains an intrinsic characteristic of the molecule. Nevertheless, the current flows because the C_{60} molecular orbitals are broadened and shifted by their electronic coupling with the tip and surface. In addition, the R_0 limit reached upon compression is an indication that inelastic scattering is a rare event in C_{60} for the low current intensity measured.

Therefore, what we actually track in this study is the elastic resistance of a nanoscopic metal cavity containing

a C_{60} molecule with its electronic structure dressed by the interaction. To evaluate the apparent resistance of a C_{60} molecule, R_0 is subtracted using the Büttiker-Landauer formula [19] $V = R_0(1 + r/t)I$. In this formula, t is the nanoelectronic transmission coefficient (the transmittance) at the Fermi level of an electronic Bloch wave passing elastically from one electrode of the junction to the other via a single C_{60} . The term r is the corresponding reflection coefficient (the reflectance). This gives the apparent elastic resistance of a single C_{60} molecule to be $54.794 \pm 13 \text{ M}\Omega$. As the electron transfer process through C_{60} is assumed to be elastic in a first approximation, it is more appropriate to speak of the transparenance t/r (at the Fermi level) instead of the resistance of a single C_{60} to characterize its ability to let a tunneling current flow. The C_{60} electronic transparenance is 2.53×10^{-4} . Our observation of a pressure dependence of the electronic transparenance of an individual C_{60} is a step toward a realistic characterization of the electrical properties of a single molecule in a nanoscopic environment, and this study indicates key differences in the physics of C_{60} confined in such a situation compared to bulk solid C_{60} [8].

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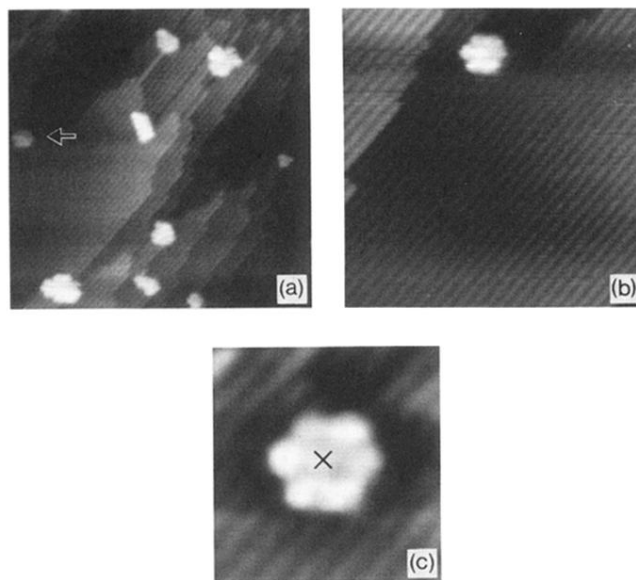


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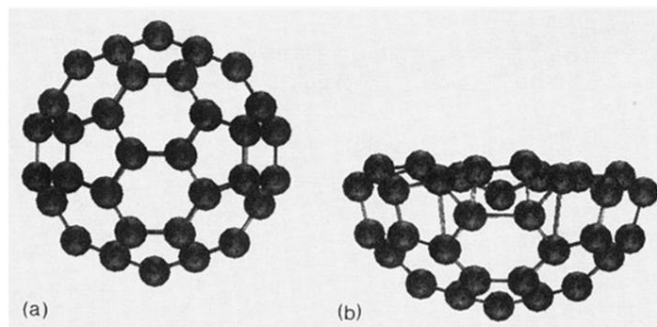


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