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RESONANT TUNNELING THROUGH DISCRETE ELECTRONIC LEVELS OF A C₆₀ MOLECULE IN THE PRESENCE OF CHARGING EFFECTS

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We have conducted tunneling spectroscopy studies for isolated C₆₀ molecules in the double barrier tunnel junction configuration. The tunneling current-voltage ($I-V$) and dI/dV vs. V spectra of these molecules exhibit rich structures resulting from both resonant tunneling through the discrete levels and single electron charging effects. In particular, we observe degeneracy lifting within the molecular orbitals, probably due to the Jahn-Teller effect and local electric fields. Theoretical fits, performed using the "orthodox" model for single-electron tunneling modified to account for the discrete level spectrum of C₆₀, agree well with our data.

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Tunneling spectroscopy is one of the primary tools for exploration of the properties of nanometer-scale structures. For example, studies of quantum dots have illustrated that single-electron tunneling (SET) effects [1], in particular the Coulomb blockade (CB) and the Coulomb staircase, and resonant tunneling through quantized electron levels regulate transport through nanostructures. These effects form the basis for development of nanoscale electronic devices, such as single electron (and single molecule) transistors [1, 2]. So far, related studies were conducted mainly for *metallic* nanoparticles in the double barrier tunnel junction (DBTJ) configuration, where the particle is coupled via two tunnel junctions to two macroscopic electrodes [1, 3-5]. Recently, the interplay between quantum-size effects (e.g., resonant tunneling) and SET effects has been observed also in carbon based nanotubes [2, 6]. However, all the experiments above were performed at sub-Kelvin temperatures and in the regime where the level separation, ΔE_L , is much smaller than the charging energy, E_C .

In a previous publication [7] we presented scanning tunneling microscopy (STM) measurements on isolated C₆₀ molecules in a DBTJ configuration (Fig. 1a). Our data clearly manifested both SET and quantum size effects. The extremely small size of the molecule (≈ 8 Å in diameter), resulting in large E_C and ΔE_L , enables observation of both effects even at room temperature. Moreover, two regimes

could be simultaneously studied, one where ΔE_L is larger than E_C (due to large molecular orbital spacing), and the other where $\Delta E_L < E_C$. The second case results from splitting of degenerate molecular orbitals due to charging, strong local fields and the Jahn–Teller (JT) effect. Surprisingly, we have found [7] that despite its small size, one can attribute a “classical” (geometrical) capacitance to the C_{60} molecule, and describe the observed SET effects in terms of that, using the “orthodox” model [1]. In this short report we focus on resonant tunneling into the discrete molecular levels and on the effect of the junction geometry, namely, the capacitance ratio between the two junctions, C_1/C_2 , on the tunneling I – V curves.

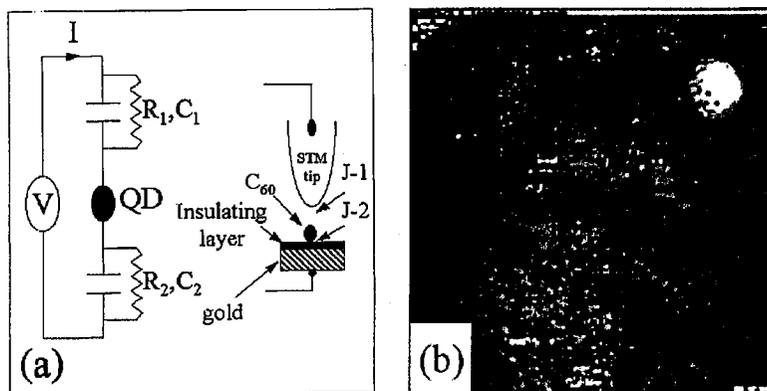


Fig. 1. (a) Schematic and equivalent circuit of the experimental setup: a C_{60} molecule (QD) coupled via two tunnel junctions to the STM tip and gold substrate. (b) A topographic image of side 60 Å showing a single C_{60} molecule adsorbed on a gold film covered by an insulating layer. The quality of the background is degraded due to the insulating layer.

C_{60} molecules were thermally evaporated onto a gold substrate covered by a thin insulating layer, either amorphous carbon and hydrocarbons [7] or polymethyl-methacrylate (PMMA). (Qualitatively, the results did not depend on the nature of the insulating layer.) The evaporation parameters were adjusted to obtain submonolayer coverage, and more importantly, isolated molecules, as can be seen in the cryogenic STM image presented in Fig. 1b. In this way we have realized a DBTJ configuration in which a C_{60} molecule is coupled via two tunnel junctions to the gold substrate and the tip of the STM (Fig. 1a). For each molecule we took I – V curves with different settings of the STM bias voltage, V_S , and tunneling current, I_S (before disconnecting the feedback circuit) and thus for various tip– C_{60} separations. In this way we could change the capacitance C_1 associated with the tip– C_{60} junction (J-1 in Fig. 1a) and consequently the “fractional charge” Q_0 on the dot and thus the width of the CB [1, 8]*. Indeed, the I – V

* $Q_0 = (C_1\Delta\Phi_1 - C_2\Delta\Phi_2)/e$, where the C_i is the capacitance and $\Delta\Phi_i$ is the contact potential across junction $i = 1, 2$.

curves presented in Ref. [7] exhibit periodic oscillations of the width of the CB (even at 300 K) due periodic variations of $Q_0(\text{mod. } e)$, consistent with the “orthodox” theory and an effective “classical” capacitance of the molecule. These latter data were *all* measured with a setting where $C_1 < C_2$; even a *small* change in C_1 is sufficient to vary Q_0 significantly [8] (see the note below). Below we discuss the effect of *large* changes in the ratio C_1/C_2 on the $I-V$ characteristics and the way they manifest the discrete molecular level spectrum of C_{60} .

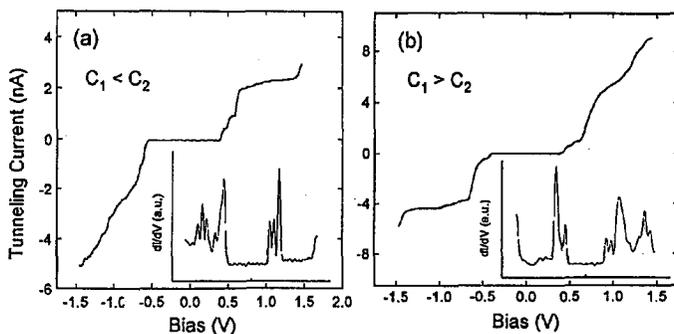


Fig. 2. Tunneling $I-V$ curves obtained on one molecule, for two different settings: $I_S = 1.8$ nA, $V_S = 0.75$ V and $I_S = 6$ nA, $V_S = 0.75$ V, for (a) and (b) respectively. In (a) $C_1 < C_2$ and in (b) $C_1 > C_2$. Insets: the corresponding dI/dV vs. V traces.

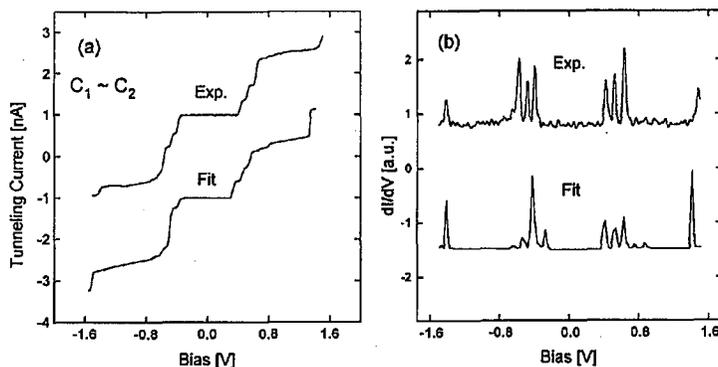


Fig. 3. Tunneling $I-V$ and dI/dV curves [(a) and (b) — upper curves], and corresponding theoretical fits [(a) and (b) — lower curves] for C_{60} in a symmetric DBTJ ($C_1 \approx C_2$).

In Figs. 2 and 3 we plot $I-V$ and dI/dV vs. V curves acquired at 4.2 K with different DBTJ configuration, where $C_1 < C_2$, $C_1 > C_2$ and $C_1 \sim C_2$ for Figs. 2a, b, and 3, respectively. (Electrons flow from tip to sample for positive bias.) It is evident that *all* these $I-V$ curves contain additional steps, beyond those related to SET effects, which reflect the discrete electronic structure of the

C_{60} molecule. This structure is exhibited in a more pronounced way in the derivative traces, where each peak corresponds to resonant tunneling through a discrete level. The effect of the capacitance ratio on the shape of these traces (e.g., on the symmetry) can also be clearly seen. We wish to point that ohmic (structureless) curves were obtained everywhere, except over the molecules. This confirms that the rich structures in our data are indeed exclusively related to C_{60} .

The theoretical curves in Fig. 3 were calculated using the "orthodox" model for SET modified to account for the discrete level spectrum of C_{60} . Details of the calculation, and fits obtained for other experimental curves measured for DBTJ having different capacitance ratios will be presented elsewhere [9]. Here we shall only note that the fits provide information on both the junction parameters (capacitance, resistance and Q_0) and the electronic molecular level spectrum, and that we are able to fit *all* our data, in particular the positions of the peaks in the derivative curves, using a *single* set of levels which corresponds to the calculated [10] spectrum of C_{60} . In the voltage range applied in our experiment the spectrum consists of a fivefold degenerate h_{1u} , highest occupied molecular orbital (HOMO), threefold degenerate t_{1u} , lowest unoccupied molecular orbital (LUMO), and threefold degenerate LUMO+1 (t_{1g}). These degeneracies are lifted in our experiment by several means that break the icosahedral symmetry of unperturbed C_{60} . Among these are: (1) The electric field between the tip and the substrate. (2) The JT effect, which is prominent in the ionized and excited states of the molecule, its possible states in the intermediate stage of tunneling through the DBTJ. Accordingly, we have fitted all our curves using three groups of levels, related to the HOMO, LUMO and the LUMO+1 orbitals: five (split) HOMO levels in the range -0.8 to -0.6 eV, three LUMO levels in the range 0 to 0.15 eV and the LUMO+1 onset at ≈ 0.6 eV. We note here that the HOMO-LUMO level spacing which we observe, ≈ 0.7 eV, is smaller than the level spacing in the free neutral molecule. It should be pointed out, however, that we are actually measuring the gap between the LUMO(C_{60}^-) and the HOMO(C_{60}^+), since the threshold for tunneling in our DBTJ is determined by the energy of the final, *ionized state*, of the molecule. The typical level splitting that we obtain, ≈ 0.05 eV, is somewhat smaller than the prediction [10] for the JT effect (≈ 0.1 eV).

We shall now discuss the effect of the junction capacitances on the shapes of the $I-V$ curves. The $I-V$ and derivative curves in Fig. 2a were measured with STM settings of $I_S = 1.8$ nA and $V_S = 0.75$ V, and our fits yield $C_1 \approx 0.07$ aF and $C_2 \approx 0.15$ aF, thus $E_C \approx 0.35$ eV. Since $C_1 < C_2$, tunneling through the DBTJ is an onset at junction 1, for the level configuration at hand, where electrons tunnel into the LUMO for positive sample-bias polarity, and off the HOMO for negative bias. (The group at negative bias may also have a small contribution from electrons tunneling onto the LUMO from junction 2.) This is a major source for the pronounced asymmetry observed in the curves. Indeed, all the curves obtained when $C_1 < C_2$ (e.g., by further increasing the tip-molecule separation) exhibit a group of up to three peaks at the onset of current at positive bias and five major peaks at negative bias. Support for the interpretation above serves the fact that in the opposite case, when $C_1 > C_2$, we obtained $I-V$ curves which are nearly an inversion (with respect to $V = 0$) of those in Fig. 2a. This is exhibited by the curves

in Fig. 2b, obtained after reducing the tip-molecule distance (by increasing I_S to 6 nA) to achieve $C_1 > C_2$. Indeed, here the LUMO levels (not completely resolved) appear at negative bias and the HOMO at positive bias. One should also keep in mind that, as a consequence of the voltage division between the junctions, the real zero bias gaps and molecular level spacings are smaller than those apparent in the $I-V$ curves.

The characteristics plotted in Fig. 3 are by far more symmetric than those in Fig. 2. Best fits to these curves (lower lines), were achieved for $C_1 \approx C_2 \approx 0.15$ aF. In this case tunneling is the onset in junction 1 for positive bias and junction 2 for negative bias, through the LUMO levels that are closer to the Fermi energy. Indeed, the dI/dV traces (Fig. 3b) contain groups of three peaks nearly symmetrically positioned around zero bias. At larger voltages the symmetry of the traces should be lost, as the HOMO and the LUMO+1 orbitals will start to contribute. Note that one can observe in all the curves presented an onset of a large step at the highest applied bias voltage (≈ 1.5 V). This may be due to the onset of a second Coulomb staircase step and/or to tunneling through the LUMO+1, as discussed in Ref. [10].

In summary, we have probed the *discrete* tunneling spectra of isolated C_{60} fullerenes, including splitting within the HOMO and LUMO levels. The spectra manifest the interplay between charging and quantum size effects *simultaneously in two regimes*: $\Delta E_L > E_C$ and $\Delta E_L < E_C$. Theoretical curves, calculated using the "orthodox" model for SET modified to account for the discrete level spectrum of C_{60} , agree well with our data.

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