Single electron tunneling and level spectroscopy of isolated C\textsubscript{60} molecules

Danny Porath and Oded Millo\textsuperscript{a}  
Racah Institute of Physics, The Hebrew University, Jerusalem 91904, Israel  
(Received 30 September 1996; accepted for publication 19 November 1996)

The interplay between single electron tunneling effects and the discrete molecular levels of C\textsubscript{60} molecules is studied using scanning tunneling microscopy. Isolated C\textsubscript{60} molecules were deposited onto a gold substrate, covered by a thin insulating layer. The tunneling current–voltage characteristics of isolated molecules, both at room temperature and at 4.2 K, exhibit rich structures, resulting from the interplay between charging effects and the electronic spectrum. In particular, we observe degeneracy lifting within the C\textsubscript{60} molecular orbitals, probably due to the Jahn–Teller effect and local electric fields. © 1997 American Institute of Physics. [S0021-8979(97)01305-4]

INTRODUCTION

Significant effort was devoted recently to studies of the interplay between single electron tunneling (SET) effects and quantum size effects in isolated nanoparticles, referred to as "quantum dots" (QD).\textsuperscript{1–5} Such an interplay can be experimentally observed most clearly when the charging energy of the dot by a single electron, \(E_c\), is comparable to the electronic level separation \(\Delta E_1\), and both energy scales are larger than \(k_B T\). Both effects are relevant to the development of nanoscale electronic devices, such as single electron transistors, and have been studied for various mesoscopic tunnel junction configurations. One example is the double barrier tunnel junction (DBTJ) geometry, where a QD is coupled via two tunnel junctions to two macroscopic electrodes.\textsuperscript{1–5} In this system, SET effects, such as the Coulomb blockade (CB) and the Coulomb staircase, can be observed in the current–voltage (\(I–V\)) characteristics. The former manifests itself by a suppression of the current around zero bias voltage, while the latter exhibits a sequence of steps in the \(I–V\) curve.\textsuperscript{6} C\textsubscript{60} molecules and ions were studied intensively over the last decade and are considered to have promising future applications, including for optoelectronic and photovoltaic devices.\textsuperscript{7} A special effort is directed to electronic molecular level spectroscopy of C\textsubscript{60}, and, in particular, to effects that result in shifting and splitting of the electronic levels of excited and ionized molecules, such as the Jahn–Teller (JT) distortion.\textsuperscript{7,8}

Our present work combines the two experimental efforts discussed above, namely, we exploit C\textsubscript{60} molecules as QDs in mesoscopic tunnel junctions. An isolated C\textsubscript{60} molecule may serve as an ideal model system for studies of the interplay between charging effects and discrete electronic levels, due to its size, much smaller than the nanoparticles investigated so far, and to its rich electronic spectrum. In particular, one can observe the effect of charging on the C\textsubscript{60} molecular level spectrum, e.g., due to breaking of the icosahedral symmetry. Moreover, this system enables a simultaneous study of the interplay in two regimes, one where the level spacing \(\Delta E_1\) is larger than \(E_c\), and the other where \(\Delta E_1 < E_c\). Previous works, done on metallic nanoparticles, have treated the case where \(\Delta E_1 < E_c\).\textsuperscript{1–4}

EXPERIMENT

We have thermally evaporated gold films on glass and then annealed the samples, so that large and smooth surfaces were obtained.\textsuperscript{9} C\textsubscript{60} powder (Aldrich Chemical Co.) was first dissolved in toluene and then transferred to a tungsten boat in a thermal evaporator used only for C\textsubscript{60}. The solution was let to dry and the molecules were evaporated onto the gold substrate. We were able to control the evaporation parameters to routinely obtain submonolayer coverage, and more importantly, isolated molecules, as can be seen in our scanning tunneling microscope (STM) images (Fig. 1). In this way, we have realized a DBTJ configuration in which a C\textsubscript{60} molecule is coupled via two tunnel junctions to the gold substrate and the tip of a STM [Fig. 2(a)]. (The origin of the C\textsubscript{60}–gold tunnel barrier will be explained below.) The C\textsubscript{60} molecules were studied spectroscopically by taking tunneling \(I–V\) characteristics, both at room temperature and at 4.2 K. The \(I–V\) traces exhibit rich structures, and manifest the interplay between charging effects and the discrete molecular levels of the C\textsubscript{60} molecule. In addition, they resolve the splitting of degenerate molecular levels of the unperturbed molecule due to symmetry breaking that may be caused by charging, external fields, or the JT effect.

The measurement procedure was to first acquire a topographic image and then move the tip above an isolated C\textsubscript{60} molecule for the tunneling spectroscopy measurements. For each molecule we have taken \(I–V\) curves for different settings of the STM bias voltage, \(V_s\), and tunneling current, \(I_t\), and, thus, for various tip–C\textsubscript{60} separations. In this way, we could change the capacitance \(C_1\) associated with the tip–C\textsubscript{60} junction [Fig. 2(a)] and, consequently, the "fractional charge" \(Q_0\) on the dot and, thus, the width of the CB.\textsuperscript{6,10} Each curve was acquired while momentarily disconnecting the feedback circuit, and therefore, with constant tip–C\textsubscript{60} tunnel junction parameters. The \(I–V\) measurements were frequently interrupted in order to acquire topographic images and ensure that the tip and the molecule did not drift apart.

RESULTS AND DISCUSSION

As will be shown below, the tunneling \(I–V\) curves taken on the isolated fullerenes conform (in most cases) to a DBTJ
configuration, in particular, they exhibit the Coulomb blockade and staircase. One barrier is obviously the tip–C$_{60}$ tunnel junction. The existence of a tunnel barrier between the C$_{60}$ molecule and the gold substrate is evident from the fact that in order to observe clearly SET effects, the tunneling resistance of each junction should exceed the quantum resistance, $\hbar/e^2 \approx 26 \text{k}\Omega$. We note here that SET effects were observed only on the fullerenes, whereas Ohmic traces were obtained everywhere else. The barrier probably originates from a layer of amorphous carbon and hydrocarbons adsorbed on the gold surface that was generated due to overheating the boat during evaporation. This interpretation is supported by Raman measurements of a thick layer of C$_{60}$ that was evaporated using the procedure and conditions described above. The spectrum contains additional lines, as compared to bulk C$_{60}$, typical to amorphous carbon and hydrocarbons. The exact nature of the barrier is, however, not essential to the interpretation of our spectroscopic results, only its existence. Moreover, the Ohmic traces obtained away from the C$_{60}$ molecules indicate that the structures of the curves obtained on the molecules are not due to contaminants. Finally, we wish to note that since the C$_{60}$–substrate tunnel barrier was not prepared in a controlled manner, we have also found molecules that did not exhibit SET effects. The $I$–$V$ characteristics obtained in these cases resembled those reported for C$_{60}$ deposited onto clean metallic substrates.$^{11}$

In Fig. 1 we present four topographic images showing a C$_{60}$ monolayer [Fig. 1(a)], a group of molecules [Figs. 1(b) and 1(c)], and a single C$_{60}$ molecule [Fig. 1(d)], deposited on the gold substrate. The molecules are all 8–9 Å in diameter and are typical to many such images. The quality of the background is degraded in comparison to images of the gold films taken before the C$_{60}$ evaporation,$^9$ probably due to the carbon/hydrocarbon layer. In images of about a monolayer coverage we observe the close packed formation expected for solid C$_{60}$ [Fig. 1(a)].

We shall now focus on the spectroscopic results, namely the $I$–$V$ and $dI/dV$ characteristics. In Fig. 2(a) we present a scheme of the DBTJ realization of our experiment, as described above, and its equivalent circuit. In Figs. 2(b) and 2(c) we plot sets of $I$–$V$ characteristics (shifted for clarity) taken for single molecules at 4.2 and 300 K, respectively.
molecular spectrum that cannot be eliminated even at room temperature. However, from the amplitude of the CB gap oscillations around zero bias, we estimate the charging energy, $E_c = 0.4$ eV for Fig. 2(b). Close values ($\pm 0.1$ eV) are obtained for all other cases that showed SET effects. We can also estimate the ratio $C_1/C_2$ between the capacitances of the tip–C$_{60}$ and C$_{60}$–substrate junctions, respectively, and thus, the voltage–drop division, in the following way: The charging energy is given by $E_c = e^2/(2(C_1 + C_2))$, thus in our case, $C_1 + C_2 \approx 2 \times 10^{-19}$ F. An isolated metallic sphere having the radius of a C$_{60}$ molecule, $\sim 4$ Å, has a considerably smaller self-capacitance, $\sim 0.45 \times 10^{-19}$ F. We expect a comparable value for an isolated C$_{60}$ molecule due to the nearly hollow-spherical distribution of its electronic charge. Thus, in our experimental configuration the C$_{60}$ molecule is only weakly decoupled from its environment, at least in one junction. We have also found experimentally that $E_c$ depended only very weakly on the tip–C$_{60}$ separation (over a wide range of total tunneling resistances, 0.1–5 GΩ), so we conclude that $C_2 > C_1$. Furthermore, in previous measurements on isolated metallic nanoparticles, we have found that for the same range of tunneling resistances (for both junctions), the junction capacitances were comparable to the self-capacitance of the grains.

We, therefore, assume that, here too, $C_1$ is of the order of the expected self-capacitance, and thus, $C_1/C_2 \approx C_1/(C_1 + C_2) \approx 2/9$, meaning that, due to capacitance division, 7/9 of the total applied voltage drops on junction 1. This latter result has important implications for the spectroscopic measurements: Tunneling through the DBTJ is onset at junction 1 (for the level configuration at hand), where electrons tunnel into the lowest unoccupied molecular orbital (LUMO) for positive bias polarity, and off the highest occupied molecular orbital (HOMO) for negative bias. This is a major source for the pronounced asymmetry observed in our curves. It means also that small changes in the carbon layer thickness should not affect considerably our spectroscopic results, as long as the junction resistance is large enough ($>h/e^2$). One should also note that as a consequence of the voltage division, the real zero bias gaps and molecular level spacings are 7/9 of those measured in the $I$–$V$ curves.

We note here that the molecular orbital configuration is not isotropic and depends on the spatial location within the molecule. Since the tunneling path through the molecule may change from one tip position to another, the $I$–$V$ characteristics are sensitive to the exact lateral tip position over the molecule. Additional variations among $I$–$V$ traces may result from the various molecular orientations with respect to the substrate.

A more detailed analysis of our data is obtained from the $dI/dV$ traces. These traces enable us to resolve the molecular level structure of negatively and positively ionized C$_{60}$, the possible states of the molecule in the intermediate stage of tunneling through the DBTJ. The molecular level spectrum of the unperturbed, neutral molecule is well understood. The spherical $L=5$ levels are split into three groups: fivefold degenerate $h_{1u}$ (HOMO) levels, and threefold degenerate $t_{1u}$ (LUMO) and $t_{2u}$ (LUMO + 2) levels. The LUMO + 1 level (threelfold degenerate) originates from the $L=6$ lev-

FIG. 3. Tunneling spectroscopic $dI/dV$ traces at 4.2 K [(a), (b), and right inset] and at 300 K (c). The traces were acquired with different STM settings. A $I$–$V$ curve corresponding to trace (a) is shown in the left inset.
els. These degeneracies can be lifted by several means that break the icosahedral symmetry. Among these are (1) the electric fields due to the tip and to the carbons below the molecule, and (2) the JT effect that is prominent in the ionized and excited states of the molecule. Our data (Fig. 3) indeed reflect this structure, including full splitting of degenerate levels in some cases, and partial splitting in others. The magnitude of the splitting (~0.1–0.2 eV) is in good agreement with predictions for the JT effect. It should be noted that tunneling spectroscopy is not limited by selection rules as is optical spectroscopy.

In Fig. 3 we present an I–V trace (left inset) and four dI/dV curves taken at 4.2 K [Fig. 3(a), Fig. 3(b), and right inset] and at 300 K [Fig. 3(c)]. In curve (a), which corresponds to the I–V trace, one can observe a full splitting of the five HOMO levels and the three LUMO levels. In the right inset we observe a doubly split LUMO and another group of three levels, about 0.5 V to the right of the LUMO group. This group can be associated either with the fully split LUMO+1 levels or with a replica of the LUMO group at the onset of the second step of the CB, i.e., the LUMO (C_{60}^{-2}) levels. It can, of course, be a combination of the two. Preliminary theoretical fits to our data indeed show that both channels may contribute to this group of spectral lines. The HOMO and LUMO levels are shown in Fig. 3(b), with only partially lifted degeneracy. The HOMO levels are split into three peaks and the LUMO levels are split only into two peaks. The onset of the LUMO+1 or the LUMO (C_{60}^{-2}) levels can also be seen, about 0.5 eV to the right of the LUMO. Note, that tunneling spectra showing SET and quantum-size effects were obtained also at room temperature, as can be seen in Figs. 2(c) and 3(c).

The level splittings observed in all of the traces are in good agreement with predictions for the JT effect. The degree of splitting and the peak amplitudes depend also on the orientation of the molecule with respect to the substrate, the tip position, and the local fields, as discussed above. The spectroscopic gap between the HOMO and the LUMO is a combination of the CB and the energy-level separation. The minimal gap, ~0.5 eV, that we obtain reflects the net HOMO–LUMO spacing, which is much smaller than the level spacing in the free molecule. It should be pointed out, however, that we are actually measuring the gap between the LUMO (C_{60}^{-}) and the HOMO (C_{60}^{+}). Note that the threshold for tunneling in our DBTJ is determined by the energy of the final ionized state of the molecule.

SUMMARY

In summary, the C_{60} molecule serves as an ideal QD in mesoscopic tunnel junctions, due to its small size and spatial symmetry. We have investigated, using scanning tunneling microscopy and spectroscopy, the interplay between SET effects and quantum-size effects for an isolated C_{60} molecule in a DBTJ configuration. The degenerate HOMO, LUMO, and possibly the LUMO+1 levels of the unperturbed molecule were split and fully resolved spectroscopically. The degree of splitting is consistent with the JT effect, although other mechanisms yielding this degeneracy lifting are also possible. These effects were observed both at 4.2 K as well as at room temperature.

ACKNOWLEDGMENTS

The authors thank I. Balberg for providing and discussing the Raman spectroscopy data. This work was supported by the Israel Academy of Sciences, Grant No. 032-7625.