A transistor with an active region consisting of a single small molecule is the ultimate limit of the miniaturization of three-terminal electronic devices. Such single-molecule transistors (SMTs) have been demonstrated using molecules of C$_{60}$, C$_{140}$, cobalt coordination complexes, and divanadium complexes. These SMTs function as single-electron transistors, with conduction dominated by Coulomb blockade effects. Because of the small size of the molecules, charging energies and single-particle level spacings in these devices are of the same order (∼1 eV), and are much larger than those in semiconductor or metal single-electron devices.

Devices incorporating the latter two molecules exhibit signatures of the Kondo effect in their conduction properties. In a single-electron device with a localized unpaired spin, it is possible to observe Kondo physics, the growth of a correlated many-body state comprising an unpaired spin on the surface is cleaned by UV ozone for 5 minutes and O$_2$ plasma for 1 minute. Then 80 μL of C$_{60}$ toluene solution (1 mg C$_{60}$ / 1 mL toluene) are spin cast (spin speed ∼ 900 RPM) onto the array of junctions. Scanning tunneling microscopy (STM) images of C$_{60}$ deposited in this manner on an evaporated Ti/Au film show approximately monolayer coverage of the metal by the adsorbed molecules. An indium contact to the p+ silicon substrate, which serves as our back gate, is then made. The C$_{60}$-decorated junctions are place in a variable temperature vacuum probe station (Desert Cryogenics) for the electromigration procedure and subsequent electrical characterization. The probe station is evacuated by turbo-molecular pump (base pressure of probe station at 300 K is 5 × 10$^{-5}$ mB) and cryopumped by a carbon felt sorption pump thermally anchored to the incoming cryogen line.

In this letter, we report measurements on SMTs incorporating individual C$_{60}$ molecules coupled to gold source and drain electrodes. We describe the fabrication procedure in detail, including the statistics of the conduction properties of the resulting devices and the protocols used to infer the successful formation of a SMT. We confirm the presence of C$_{60}$ vibrational resonances in devices in the Coulomb blockade regime. In several devices we report observations consistent with Kondo physics. The Kondo temperatures inferred from the transport data typically exceed 50 K, significantly higher than previously reported values in single-electron devices. The data also suggest that signatures of inelastic vibrational processes can persist well into the Kondo regime, evidence of coupling between a vibrational excitation and the coherent many-body state.

The fabrication process is based on the electromigration technique employed in previous SMT investigations. E-beam lithography (EBL) and lift-off processing are used to define 15-60 metal constrictions connected to contact pads on degenerately doped p+ silicon substrates topped by 200 nm of thermal SiO$_2$. An example of such a constriction is shown in Fig. 1(a). The metal, 1 nm of Ti (0.1 nm/s) and 15 nm of Au (0.2 nm/s), is deposited in an e-beam evaporator with base pressure of 10$^{-7}$ mB. After liftoff the surface is cleaned by UV ozone for 5 minutes and O$_2$ plasma for 1 minute. Then 80 μL of C$_{60}$ in toluene solution (1 mg C$_{60}$/1 mL toluene) are spin cast (spin speed ∼ 900 RPM) onto the array of junctions. Scanning tunneling microscopy (STM) images of C$_{60}$ deposited in this manner on an evaporated Ti/Au film show approximately monolayer coverage of the metal by the adsorbed molecules. An indium contact to the p+ silicon substrate, which serves as our back gate, is then made. The C$_{60}$-decorated junctions are place in a variable temperature vacuum probe station (Desert Cryogenics) for the electromigration procedure and subsequent electrical characterization. The probe station is evacuated by turbo-molecular pump (base pressure of probe station at 300 K is 5 × 10$^{-5}$ mB) and cryopumped by a carbon felt sorption pump thermally anchored to the incoming cryogen line.

A two-step variation of the electromigration technique is employed to separate the constrictions into distinct source and drain electrodes. Using an HP
4145B semiconductor parameter analyzer, at 300 K the voltage across each junction is ramped from 0 to 400 mV while monitoring the resulting current. When electromigration-induced junction breaking begins, indicated by decreased junction conductance, the maximum voltage across the junction is reduced in steps of 40 mV until the junction resistance is increased to 400-1000 Ω. Once each junction is “partially broken,” the sample is cooled to liquid helium temperatures. At 4.2 K the electromigration process is continued, with the maximum voltage ramps across the junction increased in steps of 200 mV as the junction conductance decreases. This process is halted when the resistance of the resulting electrodes is > 100 kΩ. This two-step electromigration technique allows us to make relatively high conductance electrodes consistently, which we infer corresponds to a very small interelectrode gap. Accurate scanning electron microscopy (SEM) assessment of the interelectrode gap is difficult because the newly exposed metal surfaces reconstruct when the electrodes are warmed back to room temperature. From SEM images of these resulting electrodes (Fig. 1b), we can see that the separation is less than 2 nm, the resolution of the SEM. Since the diameter of a C60 molecule is only 0.7 nm, closely spaced electrodes are essential for C60 SMTs.

Due to the stochastic nature of the electromigration process, every electrode pair differs at the atomic scale. Even if the closest interelectrode separation is the right size, the presence of a C60 molecule at that location is probabilistic, and depends strongly on the initial surface coverage of C60. If a molecule is present, its couplings to the source, drain, and gate electrodes are determined by the microscopic arrangement of the junction region, which is different in every device. We know of no atomic-scale imaging technique at present that is capable of directly assessing in-situ the presence of an individual molecule between source and drain electrodes and the morphology of the gold electrodes adjacent to the molecule. Furthermore, the local charge environment of the SMT is unknown a priori due to the existence of surface trap states at the oxide surface. However, by analyzing many samples statistically we can estimate the percentage of the starting junctions that will become SMT given our fabrication procedure.

From a sample size of 1094 electrode pairs created using the above electromigration procedure, including control samples (no molecules; different solvent exposures; different cleaning procedures), 70% show measurable source-drain currents after electromigration at 4.2 K. We have examined 475 junctions decorated with C60 and electromigrated as described above. There are four classes of conductance characteristics in the resulting electrode pairs. (1) No detectable source-drain current at $|V_{SD}| = 0.1$ V (34%). The simplest explanation of these devices is that the breaking procedure resulted in significantly too large a source-drain separation to permit conduction. (2) Linear or slightly superlinear $I_D - V_{SD}$ curves, consistent with simple tunneling behavior with thermionic or field emission contributions at high bias (40%). The most likely explanation for these devices is that no molecule is present near the region of the source-drain gap that dominates conduction. (3) Nontrivial $I_D - V_{SD}$ curves with steps and abrupt changes in slope, but no detectable dependence on gate voltage, $V_G$ (15.3%). These devices likely have a molecule or metal nanoparticle at the critical region of the interelectrode gap, but local geometry screens the object from the effects of the gate potential. (4) Nontrivial $I_D - V_{SD}$ curves that may be tuned significantly by varying $V_G$ (10.7%). Conduction in these devices may be examined as a function of $V_G$, $V_{SD}$, and $T$, and compared with expectations for Coulomb blockade dominated single-molecule transistors. Occasionally some electrode pairs that initially have linear or nongateable $I_D - V_{SD}$ characteristics can change to exhibit interesting conductance features upon thermal cycling to 300 K and back to 4.2 K. Presumably this is results from a combination of molecular rearrangement and metal reconstruction at 300 K.

In a single-molecule transistor in the Coulomb blockade regime, the energetic cost of adding (removing) an electron to (from) the molecule, given by the Coulomb charging energy of the molecule and the energy difference between molecular levels, is sufficiently large, and the coupling between molecules and leads is sufficiently poor, that at most gate voltages the average charge on the molecule is fixed. The result of this charge quantization is a conductance gap, a region of $V_{SD}$ near zero bias where the conductance is suppressed. The energetic alignment of the molecular orbitals with respect to the Fermi levels of the source and drain electrodes is determined by: the work function of the metal; the electron affinity of the molecule; the presence of any nearby charged defects or traps; and the capacitive coupling to the gate electrode. Because of this gate coupling, the size of the conductance gap varies linearly and reversibly with $V_G$, since a more positive value of gate voltage makes it energetically favorable to add an electron to the molecule. At biases larger than the conductance gap, conduction is permitted because the source-drain potential difference is sufficient to overcome the electron addition (subtrac-
tion) energy. At certain values of gate voltage (charge degeneracy points), it becomes energetically degenerate for the charge of the molecule to change by one electron. The result is that the conductance gap vanishes at zero bias, and as \( V_G \) is increased through such a charge degeneracy point, the average number of electrons on the molecule is increased by one. Because of the extremely small size of the molecule, the Coulomb charging energy of the molecule and the single-particle level spacing are both large (\( > > 100 \text{ meV} \)).

Previous investigations of single-molecule transistors\(^1\) and other molecular devices\(^1\) have reported additional resonances in the differential conductance at finite bias, corresponding to excitations of molecular vibrational modes during the transport process. For \( C_{60} \) devices\(^1\), excitations of both the molecule-surface binding oscillation (\( \sim 5 \text{ meV} \)) and a mode intrinsic to the \( C_{60} \) molecule (\( \sim 35 \text{ meV} \)) have been reported (\( \sim 35 \text{ meV} \)). To characterize the electronic conduction in a SMT at a fixed temperature, it is useful to plot the differential conductance, \( \partial I_D / \partial V_{SD} \), as a function of \( V_{SD} \) and \( V_G \). The data shown here were acquired by measuring \( I_D \) as a function of \( V_{SD} \) for each value of \( V_G \) using the HP 4145B semiconductor parameter analyzer. The differential conductance is obtained by numerically differentiation of this data, using Savitzky-Golay smoothing to help reduce the noise in the resulting curves at the cost of \( V_{SD} \) resolution. For a given temperature the resulting differential conductance is plotted as a function of \( V_{SD} \) and \( V_G \) in a conductance contour map, where the color of the map represents different levels of conductance.

It is clear that not all gateable devices are \( C_{60} \) SMTs because about 5% of control samples (with no molecules) show some gateability. Approximately half the gateable control samples have clear Coulomb blockade style transport features, and the significant majority of these are consistent (charging energy \( \sim 30 \text{ meV} \); many accessible charge states) with metal islands left behind following electromigration. The existence of these metal islands has been confirmed by SEM imaging. However, in two control devices on one substrate we observed Coulomb blockade features with charging energies as large as 400 meV, though no apparent vibrational excited levels. It is conceivable that some unintended adsorbed molecules contaminated this particular set of devices during the preparation process.

We have developed criteria for deciding if a particular device with nontrivial and gateable conductance is a SMT. The existence of Coulomb blockade is necessary but not sufficient. The charging energy of the Coulomb blockade feature must be relatively large, \( > > 100 \text{ meV} \) (This is a challenging experimental requirement, because device stability can be poor at such large biases.). The number of accessible charge states should be reasonable, in light of solution-based electrochemical redox information about the molecule. Finally, the existence of one or more vibrational resonances characteristic of the molecule (\( e.g. \) 35 meV for \( C_{60} \) in the conductance map is the most indicative evidence that the device is a SMT. The conductance maps of two devices meeting these criteria are shown in Fig. 2. Note that the existence of surface trap states with charges that vary in time leads to instability in some devices. The random changes of the local charge environment near the tips of the electrodes contribute to some of the difficulties we have in observing the 35 meV vibrational state. In some of devices there appear to be multiple Coulomb blockade features overlapping each other, possibly due to the presence of multiple molecules between the electrodes.
Kondo effect in single-electron devices, where the Kondo resonance can only exist when the active region of the device has an odd number of electrons.

When describing Kondo phenomena in single-electron devices, the width of the localized state, $\Gamma$, is defined as the sum of the level widths due to the couplings, $\Gamma_S, \Gamma_D$ of the localized state to the source and drain, respectively. The energy difference between the localized state (tunable by gate voltage) and the Fermi level of the leads is $-\epsilon$. When $0 < \epsilon/\Gamma < 1$, the system is said to be in the “mixed-valence” regime, while $\epsilon/\Gamma >> 1$ corresponds to the Kondo regime. In this limit, the Kondo temperature is given by $T_K = 0.5(\Gamma U)^{1/2}\exp(-\pi\epsilon/\Gamma)$.

Note that $T_K$ depends exponentially on $\Gamma$, and in a single-molecule transistor $\Gamma$ depends exponentially on the relative position of the molecule with respect to the leads. This steep dependence has made it extremely challenging to examine this physics over a large temperature range, due to temporal instability of the molecule-metal configuration. For example, in one device of the type shown in Fig. 3, while acquiring conductance data the device switched irreversibly from exhibiting a Kondo-like zero bias peak, as shown, to standard Coulomb blockade of the type shown in Fig. 2, without a change in the charge degeneracy point. Within the Kondo picture, this change corresponds to the molecule-lead coupling changing to lower $T_K$ below $T$. We have been able to acquire data over a limited temperature range for two devices exhibiting the Kondo-like resonance.

To analyze the zero bias resonance data in the context of Kondo physics, we follow previous SMT Kondo investigations\[3,4\]. The Kondo temperature may be inferred in two different ways. First, assuming spin-1/2, at fixed gate voltage the zero bias conductance $G$ may be monitored as a function of temperature, and fit with the formula $G(T) = G_0/(1 + 2^{1/2}T^2/\gamma^2)^s$, where $G_0$ is a constant and $s \approx 0.22$ in the Kondo regime\[10\]. In both devices mentioned above, $G(T)$ is nearly constant, decreasing only slightly from 4.2 K up to $\sim 30$ K. This is consistent with large Kondo temperatures, $T_K > 100$ K, though the data do not put an upper bound on $T_K$.

Further analysis is possible making use of the conductance maps. Consider the device shown in Fig. 4. The slopes of the Coulomb blockade gap edges approximately give $\alpha$, the conversion factor between gate voltage and the source-drain bias energy scale. For this sample, $\alpha \approx 2$ meV/V$_G$, not surprising given the 200 nm thickness of the gate oxide. As $T \rightarrow 0$, the width of the zero bias Coulomb blockade conductance peak as a function of gate voltage saturates to $\Gamma \approx 32$ meV. Using $\alpha$, and knowing that $\epsilon = 0$ at the charge degeneracy point, we can find $\epsilon(V_G)$. In a Kondo device the full-width at half maximum of the zero bias conductance peak is expected to be $\sim k_B T_K/\epsilon$. Fig. 4 shows this FWHM as a function of $\epsilon/T$ for that particular device. As with $G(T)$, this data is, within the noise, nearly temperature independent below 20 K, and an average of several low temperatures is plotted. This FWHM increase as
temperature Kondo resonance in C$_{60}$ adsorbed on a noble metal electrodes would explain the surprisingly narrow local density of states observed in scanning tunneling microscopy experiments with C$_{60}$ tips.[21]

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