

Tuning the Kondo Effect with a Mechanically Controllable Break Junction

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We study electron transport through C_{60} molecules in the Kondo regime using a mechanically controllable break junction. By varying the electrode spacing, we are able to change both the width and the height of the Kondo resonance, indicating modification of the Kondo temperature and the relative strength of coupling to the two electrodes. The linear conductance as a function of T/T_K agrees with the scaling function expected for the spin-1/2 Kondo problem. We are also able to tune finite-bias Kondo features which appear at the energy of the first C_{60} intracage vibrational mode.

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The Kondo effect is a many-body phenomenon that can arise from the coupling between a localized spin and a sea of conduction electrons. At low temperature, a spin-singlet state may be formed from a localized spin-1/2 electron and the delocalized Fermi sea, leading to a correlated state reflected in transport as a zero-bias conductance anomaly [1]. This feature has been observed in devices containing lithographically defined quantum dots [2], carbon nanotubes [3], and single molecules [4–7]. Other more exotic Kondo effects involving higher spin states [8,9], nonequilibrium effects [10–12], and orbital degeneracies [13] have also been observed.

While the Kondo effect has been intensely studied, previous experiments on nanotubes and molecules have lacked control over the molecule-electrode coupling. In this Letter, we address the influence of coupling on transport in the Kondo regime by tuning the Kondo effect in C_{60} molecules with a mechanically controllable break junction (MCBJ) [14]. By varying the electrode spacing, we show that both the Kondo temperature T_K and the magnitude of the zero-bias conductance signal associated with the Kondo resonance are modified. These changes allow a determination of how the motion modifies the relative coupling of the molecule to the two electrodes. The normalized linear conductance exhibits scaling behavior as expected within the theory of the Anderson model. The same devices can also exhibit finite-bias inelastic Kondo features at an energy that corresponds to the lowest-energy intracage vibrational mode of C_{60} . Changes in electrode spacing can tune the energy and amplitude of these signals, in ways that present a challenge to existing theory.

Our devices consist initially of continuous gold lines (32 nm thick, 500 nm long, and with a minimum width of 50 nm) suspended 40 nm above a 200 μm thick Si wafer [15] [Fig. 1(a)]. To incorporate C_{60} molecules, we clean unbroken wires in an oxygen plasma (1 min at 30 mtorr, 0.25 W/cm²) to remove any organic contaminants. We then deposit 25 μL of a 100 μM solution of C_{60} in toluene, wait 1 min and blow dry. We cool the samples to 1.6 K. The range of motion permitted by bending the Si

substrate is generally too small to break the Au wires by mechanical motion alone, so we use electromigration to create a molecular-scale break in the wires before beginning studies as a function of mechanical motion [16]. We minimize the series resistance in our circuit during the electromigration process (the total series resistance is $\approx 6 \Omega$) and ramp a voltage stepwise until the resistance of a Au wire begins to change with time at constant V . This occurs consistently for $V \approx 650$ mV. We then hold V fixed until the wire breaks. After electromigration, we find that one or a few molecules can sometimes ($\approx 20\%$ of 194 devices studied) be found bridging the gap between electrodes, as inferred from the existence of a Coulomb blockade characteristic in the I - V curve rather than a linear characteristic typical of bare junctions [4,6]. In approximately 3/4 of devices exhibiting Coulomb blockade, dI/dV displayed a peak at $V = 0$, which is a signature of the Kondo effect. We performed control experiments with more than 200 bare Au junctions as well as 76 junctions treated with toluene but without C_{60} , and found a zero-bias feature in $<2\%$ of these devices: 3 bare Au junctions and 1 device exposed to toluene.

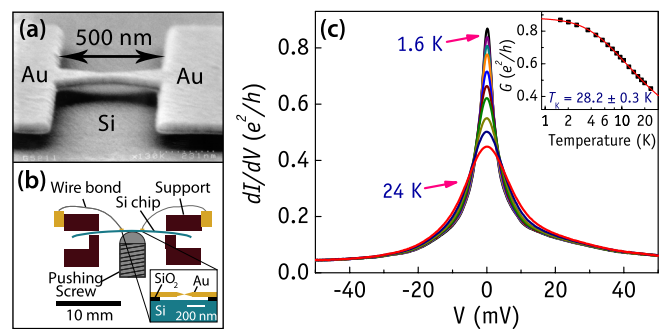


FIG. 1 (color online). (a) Scanning electron micrograph of a Au bridge suspended 40 nm above a Si substrate. (b) Schematic of the MCBJ apparatus. (c) dI/dV traces of device A at various temperatures. Inset: A fit of the linear conductance to the NRG interpolation function [Eq. (1)] yields a Kondo temperature of 28.2 ± 0.3 K.

We choose to study C_{60} molecules because they are sufficiently durable to survive high temperatures present during electromigration [17] and because previous work on single-molecule C_{60} devices has observed the Kondo effect [6,7]. Photoemission studies of C_{60} in contact with Au have shown that the molecule tends to gain an electron from the Au due to the molecule's high electronegativity [18,19], so that in our work C_{60} is likely to often possess an unpaired spin in equilibrium, providing conditions needed for the Kondo effect.

We can control the size of the interelectrode gap in our devices by using a stepper motor attached to a pushing screw to bend the silicon substrate at cryogenic temperatures [Fig. 1(b)]. To calibrate the changes in electrode spacing d , we measure the conductance of bare Au junctions as a function of motor turns and fit to the tunneling conductance expression $G \propto \exp(-2d\sqrt{2m_e\phi}/\hbar)$, where $\phi = 5.1$ eV is the work function of Au. The mean calibration over 14 bare junctions is 6.1 ± 0.4 pm per motor turn; we apply this value to determine electrode displacements in identically prepared devices containing C_{60} .

Figure 1(c) shows differential conductance curves of a C_{60} device (device A) at several temperatures. We observe a prominent zero-bias peak that is suppressed with increasing temperature, in accordance with predictions for the Kondo effect. Shown in the inset of Fig. 1(c), we fit the linear response conductance as a function of temperature to an interpolation expression [20] that is a good fit to the numerical renormalization group (NRG) result [21] for conductance in the Kondo regime with the addition of a constant background conductance [22],

$$G(T) = G_0 \left[1 + \frac{T^2}{T_K^2} (2^{1/s} - 1) \right]^{-s} + G_{el} \quad (1)$$

using $s = 0.22$, and leaving T_K , G_0 , and G_{el} as free parameters. Our data are well described by this expression, and we extract $T_K = 28.2 \pm 0.3$ K. The value for the Kondo temperature also agrees with that obtained by setting the full-width at half maximum (FWHM) of the base temperature zero-bias peak (5.14 ± 0.06 mV) to $2k_B T_K/e$ [3], yielding $T_K \approx 30$ K.

Figure 2 displays the evolution of the zero-bias peak as we vary the electrode spacing for device A [Fig. 2(a)] and for device B [Fig. 2(b)]. For each electrode spacing, we can determine the Kondo temperature from the FWHM of the zero-bias resonance, and we can also deduce the relative coupling Γ_M/Γ_L of the molecule to the more- and less-strongly coupled electrode based on the magnitude of the linear conductance near $T = 0$ [1]:

$$G = \frac{2e^2}{h} \frac{4\Gamma_M\Gamma_L}{(\Gamma_M + \Gamma_L)^2} f(T/T_K) + G_{el} \quad (2)$$

To describe the dependence on T , we adopt Eq. (1) and use $f(T/T_K) = [1 + T^2/T_K^2(2^{1/s} - 1)]^{-s}$ with $s = 0.22$. The value of the background conductance is determined from fits of the dI/dV as a function of V to a Lorentzian plus a

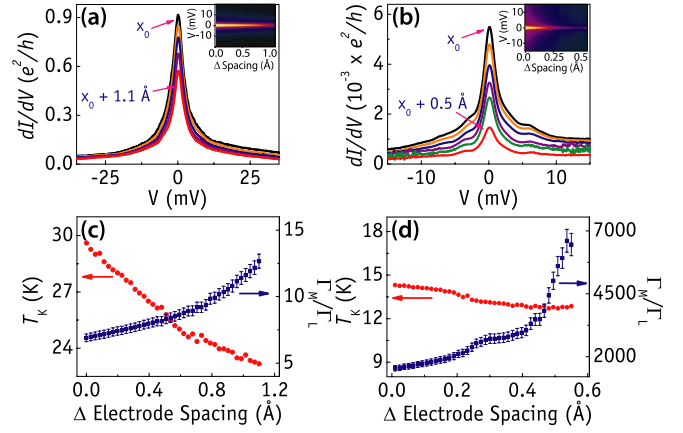


FIG. 2 (color online). dI/dV traces of (a) device A and (b) device B at various electrode spacings for $T = 1.6$ K. Insets of (a),(b): dI/dV (in color scale) as a function of bias voltage and electrode spacing at $T = 1.6$ K. (c),(d) The Kondo temperature and the relative coupling Γ_M/Γ_L as a function of electrode spacing for devices A and B at $T = 1.6$ K. The uncertainty in the determination of the Kondo temperatures is smaller than ± 0.4 K.

constant. The low value of the peak conductance of device B indicates that the molecule is coupled quite asymmetrically to its electrodes. In Figs. 2(c) and 2(d), we plot the evolution of the Kondo temperature and relative coupling as a function of electrode spacing for devices A and B.

We find that as the electrode spacing is varied, Γ_M/Γ_L increases by $\approx 330\%$ for a displacement of 0.55 Å in the asymmetrically coupled device B, while the increase is just $\approx 80\%$ over a larger displacement of 1.1 Å in the more-symmetrically coupled device A. This suggests that as the electrodes are pulled apart, the molecule in device B remains well coupled to one of the leads so that the motion affects primarily Γ_L , whereas in device A, Γ_M and Γ_L are both modified, although not exactly equally. The background conductance G_{el} is always $\leq 0.045e^2/h$ in device A and $\leq 6.4 \times 10^{-4}e^2/h$ in device B, and decreases by approximately a factor of 10 with 1.1 Å motion in device A, and by approximately a factor of 3 over 0.55 Å motion in device B.

In the more-symmetric device A, the Kondo temperature can be tuned from ≈ 30 to ≈ 23 K as the interelectrode spacing is increased, whereas in asymmetric device B, the Kondo temperature remains within a narrow range of 13–14 K. We can analyze these changes using the Haldane expression for the Kondo temperature in the limit of large charging energy U [23],

$$T_K = \frac{\sqrt{\Gamma U}}{2} e^{\pi\epsilon_0(\epsilon_0+U)/\Gamma U} \sim e^{\pi\epsilon_0/\Gamma}, \quad (3)$$

where $\Gamma = \Gamma_M + \Gamma_L$ and ϵ_0 is the energy relative to the Fermi level of the localized state that produces the Kondo effect. We can expect both Γ and ϵ_0 to vary as a function of electrode spacing: Γ because the coupling of the molecule

to at least one of the electrodes must decrease as the electrodes are moved apart, and ϵ_0 because break junctions generally exhibit large built-in electric fields even when $V = 0$, so that motion of the electrodes produces a gating effect on energy levels in the molecule [15]. If Γ_M and Γ_L are significantly asymmetric, then varying the electrode spacing will likely have little effect on the overall Γ , as only the weaker coupling may change significantly. This regime applies to device *B*, where the coupling ratio always exceeds 1500. The observation of only a small change in T_K as a function of electrode displacement for device *B* is consistent with this picture. For device *A*, we cannot distinguish the relative contributions of changes in Γ and ϵ_0 to the tuning of T_K , based on our data. In principle, a gate electrode that can independently adjust ϵ_0 could help to disentangle the effects of adjusting electrode spacing. However, we find that the gate coupling for our device geometry is too weak to adjust ϵ_0 measurably for devices in the Kondo regime.

In Fig. 3(a), we show the temperature dependence of linear conductance for device *C* at several different electrode spacings. In this device, the Kondo temperature could be tuned over a significant range, from 60.3 ± 2.4 K (top curve) to 38.1 ± 1.2 K (bottom curve). In the Kondo regime, the conductance normalized to its zero-temperature value is expected to be dependent solely on T/T_K and thus to exhibit universal scaling behavior. In Fig. 3(b), we show that $G(T/T_K)/G_0$ does indeed exhibit a reasonable collapse onto a function that is in close agreement with the universal function predicted by NRG calculations [21].

The evolution of transport properties as a function of electrode spacing is not always as smooth as we measured for devices *A*, *B*, and *C*. In other devices, the conductance could exhibit sudden changes, and zero-bias conductance resonances could fluctuate in and out of existence. We ascribe these abrupt changes to motion of the C_{60} molecule within the junction region.

In addition to a zero-bias peak in dI/dV , in 5 out of 23 devices with Kondo temperatures greater than 20 K we

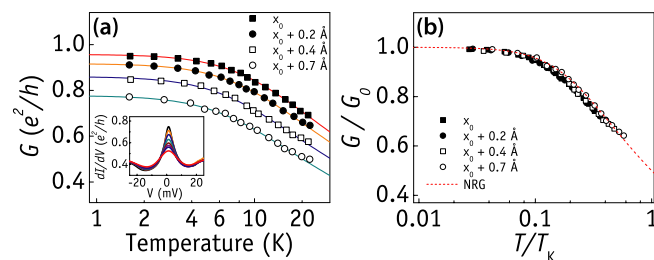


FIG. 3 (color online). (a) Linear conductance of device *C* as a function of temperature, fit to the NRG interpolation expression [Eq. (1)]. The extracted Kondo temperatures are (from the top trace to the bottom): 60.3 ± 2.4 , 55.5 ± 0.9 , 45.6 ± 1.9 , 38.1 ± 1.2 K. Inset: dI/dV traces at $x_0 + 0.7$ Å. (b) The normalized conductance, $G(T/T_K)/G_0$, is a universal function of T/T_K . Scale conductance data are compared with the NRG calculation (dotted line).

have also observed peaks in dI/dV at symmetric values of V near ± 33 mV (specifically, at 29.6, 32.8, 33.5, 36.9, and 37.2 mV in the five devices); see Fig. 4(a). We did not observe any other similar features for $|V| < 60$ mV. The energy of 33 meV is known to correspond to the lowest intracage vibrational mode of isolated C_{60} , in which the molecule oscillates between a sphere and a prolate ellipsoid shape [Fig. 4(a), inset] [24]. Previous investigations have shown that molecular vibrations can enhance dI/dV at energies corresponding to vibrational quanta [25–27]. For devices in the Kondo regime, coupling to a vibrational mode has been predicted to result in an inelastic Kondo effect, which is manifested as sidebands in dI/dV at $V \neq 0$ [28]. Finite-bias features in the Kondo regime have been observed in single-molecule transistors coupled to a vibrational mode [4,6,29], in quantum dots coupled to an applied microwave field [30], and in quantum dots due to Kondo screening of excited states [11,12,31].

Figures 4(b) and 4(c) show d^2I/dV^2 for devices *D* and *E* as a function of bias voltage and electrode spacing. Consistent with what we found for devices *A* and *B*, as the electrodes are pulled apart the magnitude of the zero-bias peak decreases more strongly in the less-symmetrically coupled (lower conductance) device *E* than in the more-symmetrically coupled device *D*. The strength of the sidebands is also different in the two devices; the satellite peaks are significantly more prominent in the more-symmetrically coupled device *D* compared to the less-symmetrically coupled device *E*, as predicted in Ref. [28]. As the electrode spacing, and hence the coupling asymmetry, is in-

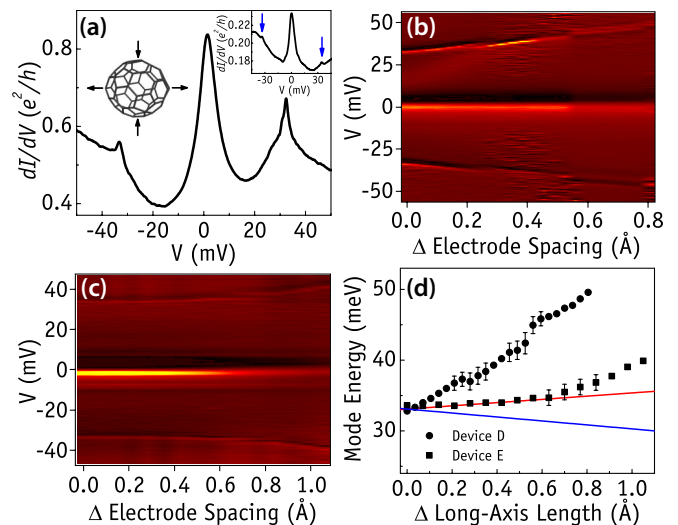


FIG. 4 (color online). (a) dI/dV for device *D* at $T = 1.6$ K showing satellite peaks near ± 33 mV. Left inset: Schematic of the $H_g(1)$ intracage vibrational mode. Right inset: dI/dV for device *E* at $T = 1.6$ K. (b),(c) d^2I/dV^2 as a function of bias voltage and electrode spacing for devices *D* and *E* at $T = 1.6$ K. (d) Stretching dependence of mode energies from devices *D* and *E*. Lines: short-axis (negative slope) and long-axis (positive slope) vibrational energies calculated using the PM3 semiempirical method.

creased, the amplitude of the nonequilibrium peaks decreases in device *D*, but the small peaks of device *E* do not seem to be strongly modified. In both devices, the positions of the inelastic features increase in $|V|$ as the electrodes are pulled apart, suggesting that the mechanical motion increases the energy of the active vibrational mode.

The changes in vibrational frequency as a function of mechanical motion are larger than what we anticipated based on molecular modeling. We performed calculations in GAUSSIAN 03 using the PM3 semiempirical Hamiltonian, which has been accurate in predicting the vibrational frequencies of fullerenes [32]. The geometries and harmonic frequencies were calculated under C_{2h} symmetry using the native structure and by setting distance constraints on two atoms at opposite ends of the neutrally charged C_{60} cage to define the long axis from the native length of 7.092 to 7.792 Å. The calculations indicate that the fivefold degenerate $H_g(1)$ mode at 33 meV is broken upon distortion into a set of two nearly degenerate “short-axis” modes (involving motion perpendicular to the direction of stretching) which decrease in energy as the molecule is stretched and three “long-axis” modes which increase in energy [Fig. 4(d)]. Only increases in energy are observed experimentally; we speculate that the long-axis modes may couple more strongly to electron transport. If we assume that the increase in molecular diameter is equal to the increase in the electrode spacing, so as to determine an upper limit for the estimated frequency shift, then we find that the measured shift for device *E* is comparable to the calculated frequencies of the long-axis modes, with the main deviations coming at large molecular diameter. However, the peak positions in the more-symmetrically coupled device *D* shift more strongly than predicted, by roughly a factor of 10. This discrepancy suggests that more rigorous theoretical work may be needed to understand electron-vibration coupling in single-molecule systems, when including coupling to the electrodes and the Kondo effect.

In summary, we have demonstrated how the Kondo effect is modified by tuning the spacing between electrodes in mechanically controllable break junction devices containing C_{60} molecules. We measure changes in both the Kondo temperature and zero-bias conductance that are in good accord with theoretical expectations and that allow us to characterize how the mechanical motion changes the relative coupling of the molecule to the electrodes. We have also observed and tuned finite-bias Kondo features which appear at energies corresponding to an intracage vibrational mode of C_{60} . We find that the vibrational energy can change more strongly as a function of stretching than predicted by a simple semiempirical Hamiltonian, thereby presenting a challenge for more accurate theory.

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