We study electron transport through C₆₀ 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 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 C₆₀ intracage vibrational mode.

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during electromigration \cite{17} and because previous work on single-molecule C_{60} devices has observed the Kondo effect \cite{6} \cite{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 \cite{18} \cite{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 inter-electrode 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, we measure the conductance of bare Au junctions as a function of motor turns and fit to the tunneling conductance expression 

\[ G \propto \exp(-2d\sqrt{2m_ee\phi/h}) \]

where \( \phi = 5.1 \text{ eV} \) is the work function of Au. The mean calibration over 14 bare junctions is \( 6.1 \pm 0.4 \) 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 figure 1(c), we fit the linear response conductance as a function of increasing temperature, in accordance with predictions \cite{6} \cite{7}.

The value of the background conductance is determined as a function of motor turns and fit to the tunneling conductance expression \cite{3}, yielding \( T_K \approx 28 \pm 2 \text{ K} \) and \( G_0 \) as free parameters. Our data are well described by this expression, and we extract \( T_K = 28.2 \pm 0.3 \text{ K} \). 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 \pm 0.06 mV) to 2\( k_B T_K/e \) as free parameters, yielding \( T_K \approx 30 \text{ K} \).

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 \( \Gamma_M/\Gamma_L \) of the molecule to the more- and less-strongly-coupled electrode based on the magnitude of the linear conductance near \( T = 0 \) \cite{1}.

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

To describe the dependence on \( T \), we adopt Eq. \cite{1} and use 

\[ f(T/T_K) = \left[ 1 + T^2/T_K^2(2^{1/s} - 1) \right]^{-s} \]

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 constant. The low value of the peak conductance of Device B indicates that the molecule is coupled quite asymmetrically to its electrodes. In figures 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, \( \Gamma_M/\Gamma_L \) 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 \( \Gamma_L \), whereas in Device A, \( \Gamma_M \) and \( \Gamma_L \) are both modified, although not exactly equally. The background conductance \( G_{el} \) is always \( \leq 0.045 e^2/h \) 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 \( \approx 30 \text{ K} \) to \( \approx 23 \text{ K} \) as the inter-electrode 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 \( U \) \cite{23},

\[ T_K = \frac{\sqrt{U}}{2} e^{\pi\varepsilon_0/(e\varepsilon_0 + U)/U} \sim e^{\pi\varepsilon_0/G} \]

where \( \Gamma = \Gamma_M + \Gamma_L \) and \( \varepsilon_0 \) is the energy relative to the Fermi level of the localized state that produces the Kondo effect. We can expect both \( \Gamma \) and \( \varepsilon_0 \) to vary as a function of electrode spacing; \( \Gamma \) because the coupling of the molecule to at least one of the electrodes must de-
increase as the electrodes are moved apart and $\varepsilon_0$ 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 [13]. If $\Gamma_M$ and $\Gamma_L$ are significantly asymmetric, then varying the electrode spacing will likely have little effect on the overall $\Gamma$, 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 $\Gamma$ and $\varepsilon_0$ to the tuning of $T_K$, based on our data. In principle, a gate electrode that can independently adjust $\varepsilon_0$ 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 $\varepsilon_0$ measurably for devices in the Kondo regime.

In figure 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 $60.3 \pm 2.4$ K (top curve) to $38.1 \pm 1.2$ 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 figure 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 have also observed peaks in $dI/dV$ at symmetric values of $V$ near $\pm 33$ mV (specifically, at 29.6, 32.8, 33.5, 36.9, and 37.2 mV in the five devices); see figure 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, 26, 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 [11, 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 increased, the amplitude of the non-equilibrium 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 Å to 7.792 Å. The calculations indicate that the five-fold 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 specu-
late 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 C₆₀ molecules. We measure changes in both the Kondo temperature and zero-bias conductance 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 C₆₀. 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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