sets. Analyses of multiexponential decays with three or more components and with decay rates differing by less than a factor of 2 may fail. However, accessible diffusion coefficients range over 4 orders of magnitude, and usually only one or two diffusing components are encountered at a given chemical shift. DOSY is especially good for complex mixtures having a large range of particle sizes, e.g., proteins with cofactors and microemulsion systems. For polydisperse systems, DISCRETE can be replaced by CONTIN, as is common in dynamic light scattering applications, to obtain the distribution of diffusion rates and, through the Stokes–Einstein relation, particle sizes.[16] Also, accuracy and consistency can be improved by incorporating programs that can simultaneously transform data for a range of chemical shifts. DOSY is expected to be widely accessible to chemists because of currently available gradient accessories for NMR systems, inexpensive computer workstations, and freely distributed software. We note in closing that DOSY is a special case of "relaxation resolved spectroscopy", a point that will be explored elsewhere for other nuclear spin relaxation processes.

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Synthesis of Pure $^{13}C_{60}$ and Determination of the Isotope Effect for Fullerene Superconductors

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Herein we report the synthesis of 99% $^{13}C_{60}$ and the measurement of the isotope effect on the superconducting transition temperature (T_c) in potassium-doped materials. To our knowledge, this work represents the first preparation of isotopically pure material and has thus enabled an unambiguous analysis of the isotope shift. Our results demonstrate that T_c is depressed significantly in $K_3{}^{13}C_{60}$ versus $K_3{}^{12}C_{60}$. The depression of T_c for the ^{13}C material indicates that superconductivity arises from phonon-mediated pairing and is not purely electronic in origin.[1,2] The value of the isotope exponent, $\alpha = 0.3$ ($T_c \propto M^{-\alpha}$), is smaller than the theoretical prediction of $\alpha = 0.5$ for a simple phonon mechanism[3] and therefore also suggests that other interactions play a role in determining superconductivity in these cluster-based solids.

Several methods have been used to prepare C_{60} enriched with ^{13}C. One technique involves packing hollow carbon-12 rods with ^{13}C powder and then resistively vaporizing the rods to produce a distribution of $^{13}C/^{12}C$ fullerenes.[4] More recently, Ramirez et al. prepared carbon rods from a mixture of carbon-13 powder and [^{13}C]glucose, but found significant ^{12}C incorporated into the C_{60} product.[5] Pure $^{13}C_{60}$ and not a distribution of $^{13}C/^{12}C$ is needed, however, to determine unambiguously the isotope effect on T_c and other physical properties.

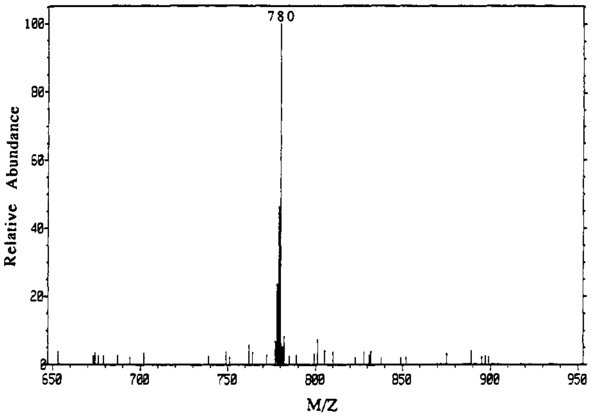

Figure 1. Field desorption (FD) mass spectrum of a purified $^{13}C_{60}$ sample (M^+, 780) recorded using a JEOL AX505H spectrometer. Experimental conditions were as follows: 30 mA FD emitter current; 3 keV ion energy; 9 keV extraction energy. Similar spectra were recorded using fast atom bombardment.

Table I. Experimental and Calculated Infrared Absorption Bands for $^{12}C_{60}$ and $^{13}C_{60}$

	frequency (cm^{-1})			
$^{12}C_{60}$ (exptl)	1429	1183	576	527
$^{13}C_{60}$ (calcd^a)	1373	1137	553	506
$^{13}C_{60}$ (exptl)	1375	1138	554	506

^{a}Calculated from the $^{12}C_{60}$ experimental data using $\nu(^{13}C_{60}) = \nu(^{12}C_{60})[M(^{12}C)/M(^{13}C)]^{1/2}$. IR spectra were recorded on C_{60} thin films using a Nicolet-5PC FT-IR.

To obtain $^{13}C_{60}$ we prepare isotopically pure carbon-13 rods using a straightforward method that can be carried out with standard equipment. First, ^{13}C powder (99% ^{13}C, Aldrich) was placed in a 0.125-in. i.d. quartz tube between two tantalum rods, and then this assembly was evacuated to ca. 10^{-2} Torr. A constant pressure of 2000 lbs/in^2 was applied using a laboratory press while current pulses (10 A, 2–3 s) were passed through the sample to drive out air and water. The carbon rods were then formed by sequentially increasing the applied current while the powder was under compression. We found that a sequence of 10-, 50-, and 100-A currents, each applied for 10 s, resulted in the formation of high-quality rods. The rods fabricated in this way were 10–15 mm long and similar in density to commercial ^{12}C rods. The ^{13}C rods were resistively vaporized,[6,7] and pure $^{13}C_{60}$ was isolated from the resulting carbon soot by chromatography, as discussed previously.[8,9]

Figure 1 shows the field desorption mass spectrum of purified $^{13}C_{60}$. The M^+ signal is at *m/z* 780. The ions at *m/z* 779 and 778 are isotope peaks resulting from the presence of 1% ^{12}C in the starting material. Since essentially no signal is observed above the background level from *m/z* 700–777, we can conclude that our material is not contaminated with $^{12}C_{60}$. Furthermore, no signal was detected at *m/z* 910 (mass $^{13}C_{70}$ = 910) in spectra recorded on purified $^{13}C_{60}$ samples. ^{13}C NMR spectra (Brucker AM-500) obtained in C_6D_6 showed the single peak at 143.2 ppm expected for $^{13}C_{60}$;[4] no resonances were detected for $^{13}C_{70}$. In

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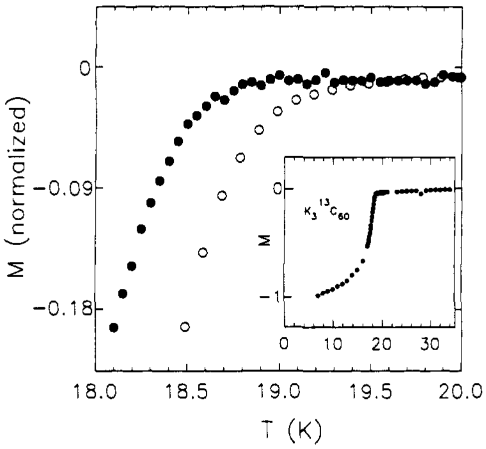

Figure 2. High-resolution temperature-dependent magnetization measurements obtained on $K_3{}^{13}C_{60}$ (●) and $K_3{}^{12}C_{60}$ (○) samples highlighting the depression in T_c for the isotopically substituted material. The samples were initially cooled in zero field to 5 K, and then the curves were recorded on warming in a field of 20 Oe. The curves were normalized to the value of the magnetization at 5 K. The inset shows a full magnetization curve for a $K_3{}^{13}C_{60}$ sample.

addition, we characterized the infrared active modes of $^{13}C_{60}$ and found that the four modes exhibited a classical isotope shift (Table I). These analytical data demonstrate that we prepared isotopically pure $^{13}C_{60}$ and that the purified samples were free from $^{13}C_{70}$ contaminant.

To elucidate the isotope effect on superconductivity, we have studied potassium-doped $^{13}C_{60}$. $K_3{}^{13}C_{60}$ and $K_3{}^{12}C_{60}$ samples were synthesized by heating stoichiometric amounts of solvent-free $^{13}C_{60}$ and $^{12}C_{60}$ with K metal (3:1, K:C_{60}) in sealed quartz tubes (10^{-3} Torr); typically, 1–2 mg of C_{60} was used.[9] The temperature was ramped from 200 to 400 °C over a 1-week period during the reaction.[10,11] $K_3{}^{13}C_{60}$ and $K_3{}^{12}C_{60}$ samples were prepared simultaneously in the same furnace to minimize differences due to the preparative conditions.

Typical temperature-dependent shielding magnetization data obtained from $K_3{}^{13}C_{60}$ and $K_3{}^{12}C_{60}$ samples using a SQUID-based magnetometer (MPMS2, Quantum Design, San Diego, CA) are shown in Figure 2. The full shielding curve for $K_3{}^{13}C_{60}$ (Figure 2, inset) exhibits a sharp transition with an onset at 18.8 K; sharp transition onsets are also observed for the $K_3{}^{12}C_{60}$ samples. The rounding in the low-temperature data is expected since the grain size of these polycrystalline materials is similar to the magnetic penetration depth; similar broadening is observed in the $K_3{}^{12}C_{60}$ results obtained in this study and reported elsewhere.[5,10] Since the transition onsets are sharp in both the $K_3{}^{13}C_{60}$ and $K_3{}^{12}C_{60}$ curves, we assign T_c as the onset temperature of diamagnetic shielding.[12] The key experimental result of this study shown in Figure 2 is the depression of T_c from 19.2 K for $K_3{}^{12}C_{60}$ to 18.8 K for isotopically pure $K_3{}^{13}C_{60}$. Our analytical data indicate it is unlikely that the decrease in T_c for $K_3{}^{13}C_{60}$ is due to impurities, and thus we attribute the shift in T_c to a true mass effect. Taking into account the uncertainty in all of our data, we find that $\Delta T_c = 0.45 \pm 0.1$ K. Since these data are obtained on isotopically pure compounds, they represent unambiguously the $^{13}C/^{12}C$ isotope effect on T_c.

It is important to compare the observed depression of T_c for isotopically pure $K_3{}^{13}C_{60}$ material with different models of superconductivity. Conventional Bardeen–Cooper–Schrieffer (BCS) theory predicts an isotope effect of $T_c \propto M^{-\alpha}$, where M is the ionic mass and $\alpha = 0.5$.[3] Using the value of ΔT_c determined above we find that $\alpha = 0.3 \pm 0.06$. This experimentally determined value of α places important constraints on the mechanism of superconductivity. First, the observation of the isotope effect strongly suggests that pairing mechanisms involving only electronic interactions are unlikely for these new materials.[1] Secondly, while it is apparent that phonons are important, the value of α indicates that the standard BCS model must be modified to account for superconductivity in the fullerenes. Since a similar value of α is deduced from studies of incompletely ^{13}C-substituted Rb_3C_{60} ($\alpha = 0.37$),[5] we believe that this conclusion is robust. It is known from studies of conventional superconductors that strong coupling can reduce the value of α from the BCS limit of 0.5.[13,14] Interestingly, our recent tunneling measurements on K_3C_{60} and Rb_3C_{60}[15] and theoretical calculations[16] have indicated that these may be strong coupling superconductors.

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New Approaches to the Generation of Phosphinidenes

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The chemistry of phosphinidenes (phosphanediyls, RP) is much less developed than that of carbenes, nitrenes, and silylenes. Evidence for the intermediacy of phosphinidenes has been adduced from metal-promoted dehalogenation of dihalophosphines, cyclopolyphosphine thermolysis, diphosphene photolysis, and various cycloreversion reactions.[1] However, in many of these cases, it is possible to devise alternative trapping mechanisms that do not involve a phosphinidene.[1c] It occurred to us that, as in the case of nitrenes,[2] for example, phosphinidenes might be generated more efficiently by elimination of thermodynamically stable molecules such as N_2 and CO from suitable precursors.

Polyazides of phosphorus(V) are well known;[3] however, $P(N_3)_3$ is reported to be very unstable[4] and, in fact, isolable phosphorus(III) azides are confined to mono(azides) of the general type

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