Production of $\text{C}_{59}\text{N}:\text{C}_{60}$ Solid Solution

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Abstract. We describe a simple way to produce large quantities of solid solutions of monomer $\text{C}_{59}\text{N}$ in pure $\text{C}_{60}$ using an electric gas discharge tube. Typical concentrations are $10^{-3}$ to $10^{-4}$ $\text{C}_{59}\text{N}$ with respect to $\text{C}_{60}$. The $^{14}\text{N}$ and several $^{13}\text{C}$ hyperfine constants were measured by ESR. These are a sensitive test for electronic structure calculations of the monomer. As the temperature is raised towards the $sc$ to $fcc$ structural transition at 261 K, the ESR spectrum motionally narrows and the activation energy for reorientation is measured. The rotational dynamics of the $\text{C}_{59}\text{N}$ monomer between 130 and 600 K parallels that of $\text{C}_{60}$ in the bulk thus interactions between $\text{C}_{59}\text{N}$ and $\text{C}_{60}$ are surprisingly weak.

INTRODUCTION

Azafullerene, $\text{C}_{59}\text{N}$, is one of the most interesting chemical modifications of the fullerene $\text{C}_{60}$ as it carries magnetic and electric dipole moments and is only slightly deformed$^1$. The solid is formed of $(\text{C}_{59}\text{N})_2$ dimers and is non-magnetic$^2$. Dimerization has been a major obstacle to the study of monomeric $\text{C}_{59}\text{N}$ and although several calculations of the electronic and molecular structure of $\text{C}_{59}\text{N}$ were published$^3$ the extent of delocalization of the charge over the cage could not be measured as the monomer was not available in sufficient amounts.

Here we describe a simple way to produce solid solutions of $\text{C}_{59}\text{N}$ in $\text{C}_{60}$ $(\text{C}_{59}\text{N}:\text{C}_{60})$ in an electric gas discharge tube. We find that monomeric $\text{C}_{59}\text{N}$ is stable in this solid solution and its rotational dynamics parallels that of $\text{C}_{60}$ in the bulk. The production of $\text{C}_{59}\text{N}:\text{C}_{60}$ in large quantities allowed us to measure the various $^{14}\text{N}$ and $^{13}\text{C}$ hyperfine constants that are a sensitive test of electronic structure calculations. A more detailed account of this work is published in Ref. 4.

PRODUCTION OF $\text{C}_{59}\text{N}$ IN A $\text{N}_2$ GAS DISCHARGE TUBE

We produced $\text{C}_{59}\text{N}$ in a $\text{N}_2$ gas discharge tube originally designed for the production of endohedral N@$\text{C}_{60}$ following the method of Pietzak et al.$^5$. The set-up is shown in Fig. 1. Typical experimental conditions were: 1 mbar $\text{N}_2$ pressure, 1 mA
discharge current, 10 cm electrode distance. The tube is heated to about 550 °C at one electrode (usually the anode) while the other electrode is water-cooled and is at ambient temperature. C$_{60}$ powder placed between the electrodes at the bottom of the tube is sublimed and deposited onto the wall of the quartz tube and the cooled electrode. As the electric discharge is turned on, N ions in the plasma react with C$_{60}$ to form N@C$_{60}$ and C$_{59}$N simultaneously. Endohedral N@C$_{60}$ is collected from the water-cooled electrode. C$_{59}$N/C$_{60}$ is collected from the heated surface of the quartz tube. The highest concentration of C$_{59}$N in C$_{60}$ of about 100 ppm (determined from the ESR intensity) was found in narrow stripes on the quartz tube at the hottest regions where deposition still occurred i.e. where the temperature is roughly 400 °C. The yield of C$_{59}$N:C$_{60}$ (with concentration of 100 ppm) is about 5% of the starting C$_{60}$ material. After deposition, the discharge tube was opened to air before sealing the samples in quartz tubes under helium. The material is stable in He atmosphere. In air, C$_{59}$N decays at ambient temperatures in about a week. X-ray diffraction showed that the deposited powder mainly consists of crystalline C$_{60}$. The ESR spectrum shows a low concentration of unknown free radicals formed during the production. We have not attempted to purify the material.

![Diagram of N$_2$ gas electric discharge tube]

FIGURE 1. C$_{59}$N:C$_{60}$ production in a N$_2$ gas electric discharge tube.

**ESR SPECTRUM AND ROTATIONAL DYNAMICS**

Electron spin resonance (ESR) was performed at 9 GHz (X-band), 75 and 225 GHz. We identified the material as a solid solution of C$_{59}$N in C$_{60}$ from the similarity of the ESR spectrum to that of monomers produced by photo- or thermolysis. At 300 K
(Fig. 2) the three $^{14}$N (I=1) hyperfine lines characteristic of rapidly tumbling free radicals are observed with $g_N = 2.0014(2)$ and an isotropic hyperfine coupling constant, $A_{\text{iso}} = 0.363(1)$ mT.

The ESR spectrum is temperature independent between 257 and 290 K. As shown in Fig. 2, the spectrum consists of narrow $^{14}$N hyperfine and a series of well resolved $^{13}$C lines. In this temperature range the C$_{60}$N molecules are rapidly reorienting in all three directions together with the C$_{60}$ molecules of the matrix. The reorientation is fast on the time scale of the ESR measurement and all anisotropic interactions are averaged to zero. The motional narrowing of the ESR spectrum of the rapidly reorienting C$_{60}$N molecule remains effective even at high ESR frequencies where relaxation due to g-factor anisotropy is more important. At 290 K and 225 GHz the linewidth was less than the instrumental resolution of 0.05 mT.

**FIGURE 2.** Motionaly narrowed ESR spectrum of tumbling C$_{60}$N substituted in C$_{60}$ at 290 K and 9 GHz. Wings are 10 times magnified. The $^{14}$N and $^{13}$C hyperfine lines of various sites are indicated. Other lines are unassigned $^{13}$C lines and an unidentified free radical line, denoted by "X".

Isotropic Fermi contact couplings were calculated by the density functional *ab initio* method, B3LYP with 6-31G* basis set on a PM3 optimized molecular geometry of C$_{60}$N. The calculations were carried out using the Gaussian 98 software. The electronic structures of the monomer and the dimer forms of C$_{60}$N were determined previously by Andreoni et al. applying a similar method. The agreement between calculated and measured hyperfine constants is not particularly good. However, the calculation shows, in agreement with the experiment, that the extra spin density is not localized to the first C neighbors of N.

Pure C$_{60}$ has a first order phase transition at 261 K from a low temperature simple cubic (sc) to the high temperature face centered cubic (fcc) structure. At low temperatures the molecular orientations are arranged preferentially in two standard configurations with respect to each other and there is a merohedral disorder of regions with differing configurations. As the temperature is raised, molecules fluctuate more and more rapidly between the possible orientations with large angle jumps. The
fluctuations shorten the spin lattice relaxation time, T₁, and above about 200 K motionally narrow the anisotropic ESR spectrum. The width of the spectral components is proportional to the spin-spin relaxation rate 1/T₂. The activation energy of monomeric C₅₉N in C₆₀ measured from T₁ and 1/T₂ is about ΔEC₅₉N / kₐ = 2300 K. This value is remarkably close to ΔEC₆₀ = 2980 K, the activation energy of the correlation time of the rotation of C₆₀ molecules measured in pure C₆₀. The close agreement between ΔEC₅₉N and ΔEC₆₀ indicates that the reorientation dynamics of C₅₉N follows that of the bulk. This would not be so if interactions between C₅₉N and C₆₀ were strong.

SUMMARY

In summary, C₅₉N is a stable substituent molecule in C₆₀ crystals at all temperatures below the formation of the solid solution at 400°C. Hyperfine interactions of the free radical with ¹⁴N and ¹³C show a partial delocalization of the extra electron over the cage. Interactions with neighboring C₆₀ molecules is small and thus rotational dynamics are similar.

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