

Electron Delocalization and Dimerization in Solid C₅₉N Doped C₆₀ Fullerene

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Electron spin resonance and *ab initio* electronic structure calculations show an intricate relation between molecular rotation and chemical bonding in the dilute solid solution. The unpaired electron of C₅₉N is delocalized over several C₆₀ molecules above 700 K, while at lower temperatures it remains localized within short range. The data suggest that below 350 K rigid C₅₉N-C₆₀ heterodimers are formed in thermodynamic equilibrium with dissociated rotating molecules. The structural fluctuations between heterodimers and dissociated molecules are accompanied by simultaneous electron spin transfer between C₆₀ and C₅₉N molecules. The calculation confirms that in the C₅₉N-C₆₀ heterodimer the spin density resides mostly on the C₆₀ moiety, while it is almost entirely on C₅₉N in the dissociated case.

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Pure C₆₀ fullerene is an insulating solid with an energy gap of about 1.5 eV [1] between the valence and conduction bands. It is natural to expect that suitably doped fullerenes may be semiconductors. However, introducing donors or acceptors in a controllable way into C₆₀ is very difficult. Highly conducting alkali fulleride compounds and polymers are well known, but these are “line compounds” with well defined, fixed stoichiometry. Andreoni *et al.* [2] suggested as early as 1992 that the modified fullerene molecules, C₅₉N and C₅₉B, are electron and hole donors, respectively, and in their pure solid forms could be metallic or even superconducting. Unfortunately, C₅₉B has not been synthesized in significant quantities [3] and pure C₅₉N is an insulating crystal of covalent (C₅₉N)₂ dimers [4,5].

The production of dilute solid solutions of monomeric C₅₉N in C₆₀ (C₅₉N : C₆₀) in macroscopic quantities [6] opens a new possibility. A filled electron state 1.5 eV above the last filled shell is the main difference between C₅₉N and C₆₀ and the distortion of the cage by the substitution of a nitrogen atom for carbon is small. The molecular energy scheme suggests that electrons may transfer from C₅₉N to the surrounding C₆₀ molecules, but so far only neutral C₅₉N was observed [6] in C₅₉N : C₆₀. In this Letter, we consider the interplay between chemical binding, rotation, and ionization of C₅₉N and C₆₀ molecules. We argue that the ground state is a C₅₉N-C₆₀ heterodimer. Below 350 K there are fluctuations between spatially fixed heterodimers and dissociated, rotating C₅₉N. The structural fluctuations are accompanied by spin fluctuations between C₆₀ and C₅₉N. The unpaired electrons are bound to C₅₉N between 350 and 700 K, and are delocalized over several C₆₀ molecules above 700 K.

Most C₅₉N : C₆₀ samples were produced by subliming pure C₆₀ in a N₂ gas electric discharge tube [6]. Some samples were made by dissolving pure (C₅₉N)₂ and C₆₀ in toluene and then subliming the extracted mixture under vacuum. No difference was noted between the ESR spectra of samples made by the two methods. C₅₉N concentrations determined from ESR spectral intensities range up to 2000 ppm. C₅₉N is an extremely stable molecule that withstands temperatures of at least 1000 °C for a few minutes. Samples were purified by sublimation in dynamic vacuum at 560 °C and then sealed into quartz tubes under He atmosphere. C₅₉N : C₆₀ is air sensitive at ambient temperatures but monomeric C₅₉N is regenerated at high temperatures under vacuum. ESR spectra were recorded at 9, 36, 150, and 225 GHz frequencies.

Ab initio calculations of the molecular structure were performed using the Cambridge CASTEP plane-wave density functional theory code [7,8]. All calculations were done in a 12 × 12 × 22 Å orthorhombic unit cell using the Perdew–Burke–Ernzerhof gradient corrected functional [9] with a 240 eV energy cutoff and Vanderbilt ultrasoft pseudopotentials. The Brillouin zone was sampled at the Γ point. The ¹⁴N hyperfine constant was calculated using the projector augmented wave (PAW) method as in Refs. [10,11] using the DFT++ package [12].

Below 350 K, two ESR active species appear in C₅₉N : C₆₀ [Fig. 1(a)]. Both species are embedded in the C₆₀ matrix since their ESR spectra change abruptly at the $T_c = 261$ K phase transition of solid C₆₀. We assign one component of the ESR spectrum to C₅₉N-C₆₀ heterodimers formed from C₅₉N and one of its 12 C₆₀ neighbors. The other component arises from C₅₉N free radicals and was investigated in detail in an earlier work [6].

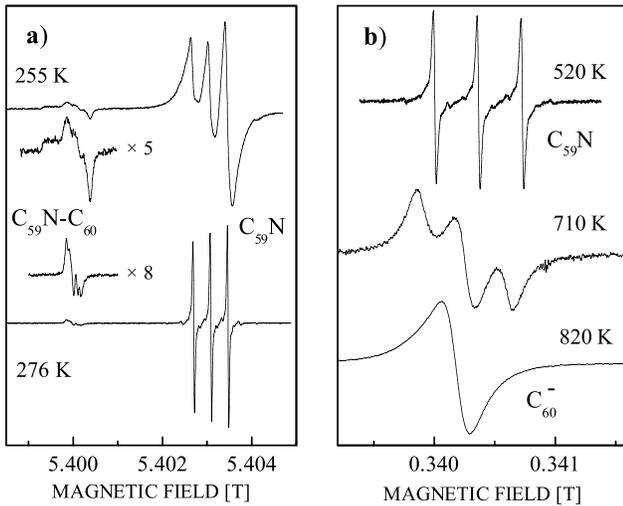


FIG. 1. ESR spectra in dilute $C_{59}N:C_{60}$ solid solution. (a) Spectra at 150 GHz near the $T_c = 261$ K phase transition of solid C_{60} . The two ESR lines are assigned to nonrotating $C_{59}N-C_{60}$ heterodimers and neutral, rotating $C_{59}N$. We propose that structural fluctuations lead to a simultaneous observation of the two species. The $C_{59}N-C_{60}$ signals are also shown magnified. (b) 9.4 GHz ESR spectra at high temperatures. Above 600 K the $C_{59}N$ ESR is gradually replaced by the ESR of C_{60}^- anions. This is attributed to delocalization of electrons over many C_{60} sites.

Between 120 and 600 K the molecular dynamics of $C_{59}N$ measured by ESR resembles the dynamics of neutral C_{60} in pure solid C_{60} measured by NMR [13]. At T_c , the sc phase with a well defined order of C_{60} molecular orientations changes to the fcc phase where molecules rotate quasi-independently. The activation energies of rotational correlation times of C_{60} and $C_{59}N$ molecules are similar both above and below T_c . Below 200 K, the large g factor and hyperfine anisotropies of $C_{59}N$ result in a broad ESR line with a complicated structure in the powder samples. Between 220 and 261 K, the frequency of $C_{59}N$ rotations between energetically similar positions becomes faster than the frequency spread of the anisotropy, and the ESR spectrum gradually narrows. Above T_c , the $C_{59}N$ molecules rotate nearly freely and the ESR spectrum consists of extremely narrow lines of a ^{14}N triplet and a series of weak satellites from ^{13}C doublets.

We find a dramatic change in the ESR spectrum between 600 and 820 K [Fig. 1(b)]. The ^{14}N triplet with an isotropic g factor of 2.00137 transforms gradually into a single line shifted to lower fields at $g = 2.0024$. We are not simply dealing with a lifetime broadening of the hyperfine components. Rather, a new line emerges and the $C_{59}N$ spectrum disappears. The same reversible transformation was found in various samples. We explain these observations as a delocalization of electrons, first over a cluster of $C_{59}N$ and 12 first neighbor C_{60} molecules and then at higher temperatures to larger distances. The reason for the somewhat higher g factor of C_{60}^- at high temperatures in a C_{60}

matrix with respect to values of about 2.000 measured in frozen solutions [14] is unclear. The decrease of free energy associated with this delocalization overcomes the Coulomb attraction of the $C_{59}N^+$ ion left behind.

We now turn to the assignment of the second ESR active species as $C_{59}N-C_{60}$ heterodimers that form below 340 K. The highest resolution (3 ppm) spectra indicate more than one very similar species. At a somewhat poorer resolution of 6 ppm a single (average) species describes well the spectra with g factors of 2.00232, 2.00245, 2.00265 just below T_c and 2.00240, 2.00247, 2.00251 above T_c . At 261 K the extra line changes abruptly [Fig. 1(a)]; the g factor anisotropy narrows but does not disappear. This g factor anisotropy is due to a molecular distortion; the g factor of an undistorted C_{60}^- ion would be isotropic. Thus the second species does not rotate freely since in that case the g factor distribution would be motionally narrowed.

We suggest that this complex ESR spectrum reflects a thermal distribution of two molecular structures: a ground state $C_{59}N-C_{60}$ heterodimer with a covalent bond between the component molecules and a higher energy state of dissociated neutral molecules. The heterodimer appears as a distorted C_{60} molecule in the ESR spectrum as the unpaired electron spin resides mostly on the C_{60} moiety while in the dissociated state the spin is on the $C_{59}N$ molecule. This spin transfer is plausible since the covalent bond takes one electron from the $C_{59}N$ and the other from the C_{60} moiety. There is a structural change of the heterodimer at the 261 K phase transition.

In the following, we discuss observations supporting the assignment. The extra line is intrinsic to $C_{59}N:C_{60}$ since its intensity relative to the $C_{59}N$ line is sample independent. We measured—mostly at temperatures above T_c —a large number of samples of various purity and made by different methods. The samples had a wide range of $C_{59}N$ radical concentrations between less than 100 ppm and 2000 ppm. Yet, for all samples, $R(T)$, the concentration ratio of the species of the extra line to monomeric $C_{59}N$ is the same at any given temperature, T . [$R(T)$ is measured by the relative ESR spectral intensities of the two species.] Degrading the sample in air reduces both the ESR active $C_{59}N$ concentration and the intensity of the extra line, leaving $R(T)$ unchanged. $R(T)$ is well explained if the unpaired electron spin hops with a low frequency between two states: in one it is localized to $C_{59}N$ and in the other mainly to a neighboring C_{60} . Since the observed C_{60} -like radical has a static distortion, it is natural to assign it to C_{60} covalently bound to the neighboring $C_{59}N$ molecule. The sample independent intensity ratio rules out the earlier assumption [6] that the extra line is from impurities.

$R(T)$, the concentration ratio of $C_{59}N-C_{60}$ to $C_{59}N$ is determined by a dynamic thermal equilibrium between the two states. Above T_c , $R(T)$ decreases rapidly with increasing temperature and is independent of the ESR resonance frequency (Fig. 2); the heterodimer line is no more de-

tected above 360 K. There is no hysteresis in $R(T)$ when the temperature is cycled between 270 and 350 K. The decrease of the ESR line intensity reflects a decrease of the heterodimer concentration and not an excessive line broadening which could result in an apparent intensity loss. Only above 315 K is the transverse spin relaxation time short enough to broaden the 9 GHz line measurably.

Dimerization (and polymerization) of both charged and neutral C_{60} molecules are well known in compounds [15]; KC_{60} is a well studied example. Depolymerization is an endothermic phase transition where the binding energy of the intermolecular covalent bond is overcome by the rotational entropy gain. We suggest that a similar phenomenon is observed in $C_{59}N : C_{60}$. However, instead of a phase transition, in the small clusters of $C_{59}N$ and neighboring C_{60} molecules fluctuate between the heterodimer and the dissociated state in a broad temperature range. The dissociation of rigid $C_{59}N-C_{60}$ heterodimers into rotating neutral $C_{59}N$ and C_{60} molecules increases the entropy and thus decreases $R(T)$ at high T . Denoting the binding energy and entropy differences between the dissociated and heterodimer states by ΔE_b and ΔS respectively, and neglecting their T dependence, the concentration ratio is $R(T) = \exp(\Delta E_b/k_B T - \Delta S/k_B)$. The experimental values are: $\Delta E_{b>}/k_B = 2400 \pm 600$ K, $\Delta S_{>}/k_B = 11 \pm 2$ and $\Delta E_{b<}/k_B = 600 \pm 100$ K, $\Delta S_{<}/k_B = 5.3 \pm 0.4$ where the subscript “>” (“<”) denotes above (below) the transition.

The entropy jump at the phase transition, $\Delta S_{>} - \Delta S_{<} \approx 6k_B$, is roughly twice the measured entropy change in C_{60} fullerene, $\Delta S_{C_{60}} = 2-3k_B$ [16,17]. $\Delta S_{>} - \Delta S_{<}$ arises mainly from the change in the dissociated state since the entropy of the heterodimer is small. The entropy change of $C_{59}N$ is similar to that of C_{60} since activation

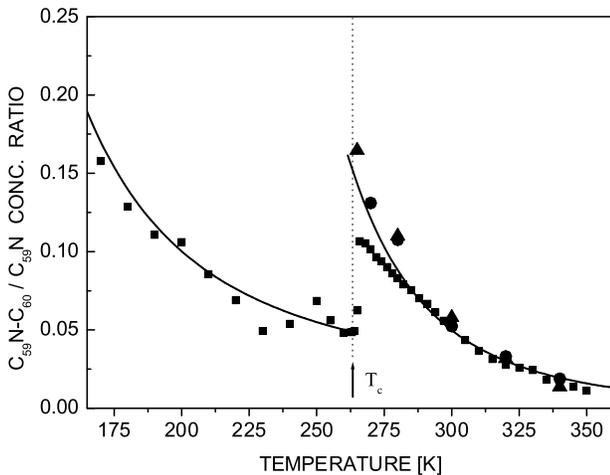


FIG. 2. Temperature dependence of the ESR intensity ratio, $R(T)$, of the species attributed to $C_{59}N-C_{60}$ heterodimers and $C_{59}N$ at 9 (squares), 75 (dots), and 225 (triangles) GHz. $R(T)$ is approximately proportional to the heterodimer concentration. Solid lines: calculated curves; see text.

energies of the molecular rotation are similar both above and below T_c . The large value $\Delta S_{>}/k_B = 11$ for the dissociated $C_{59}N$ and C_{60} molecules is in qualitative agreement with a simple model of solid C_{60} [18] which assumes that above the phase transition the rotational entropy is $\ln 90 = 4.5$ per molecule.

Figure 3 summarizes the energy scheme with approximate entropies when the particular levels are occupied. The large entropy differences allow the observation of the various configurations at moderate temperatures. Above $T_i = 700$ K electrons become delocalized over the cluster of 12 first neighbor C_{60} molecules and $C_{59}N$. As a rough estimate, the corresponding entropy gain is $\Delta S_i = \ln 13$ and the approximate energy difference $E_i - E_{>} = T_i * \Delta S_i = 1800$ K. Finally, the electrostatic energy of the electron to escape from the first neighbor is $E_{free} - E_i = e^2/(\epsilon a_0)$ (with $\epsilon = 4.4$ [19] and the first neighbor distance $a_0 = 1$ nm).

The *ab initio* calculation of the electronic structure with all atomic positions relaxed shows a $C_{59}N-C_{60}$ heterodimer with a $d_0 = 0.164$ nm long C-C covalent bond between the C1 first neighbor to the nitrogen atom of $C_{59}N$ (in the notation of [6]) and a C atom of C_{60} [Fig. 4(a)]. It has a mirror plane that includes the N atom and the C atoms of the intermolecular covalent bond. Twisting the C_{60} and $C_{59}N$ molecules around the bond confirms that the minimum energy configuration is the *trans* conformation with a mirror plane, shown in Fig. 4(a). This type of bonding is expected since C1 is the most reactive atom, as it has the largest spin density in the isolated $C_{59}N$ molecule. Figure 4(a) also shows the extra spin density, $\rho(z)$, along the molecular bond direction z , integrated over (x, y) planes perpendicular to z . Remarkably, $\rho(z)$ is almost entirely on the C_{60} moiety and is not at all spherically distributed. These characteristics are in agreement with the

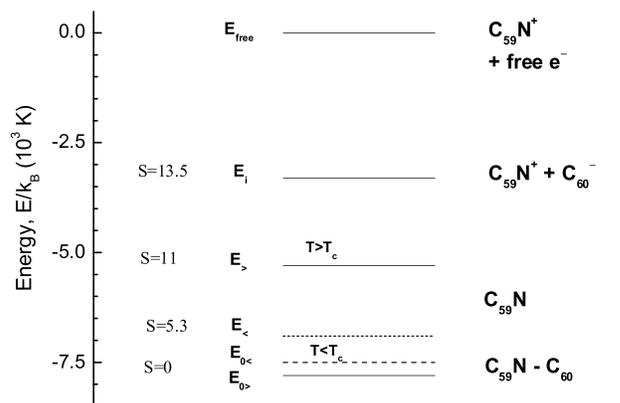


FIG. 3. Proposed energy level diagram of $C_{59}N : C_{60}$. $E_{0>}(E_{0<})$: heterodimer $T > T_c$, ($T < T_c$); $E_{>}(E_{<})$: dissociated neutral $C_{59}N$ free radical $T > T_c$, ($T < T_c$); E_i : pair of $C_{59}N+$ and first neighbor C_{60}^- ions (electron delocalized to a cluster of $C_{59}N$ and 12 C_{60} molecules); E_{free} : electron delocalized over large distances.

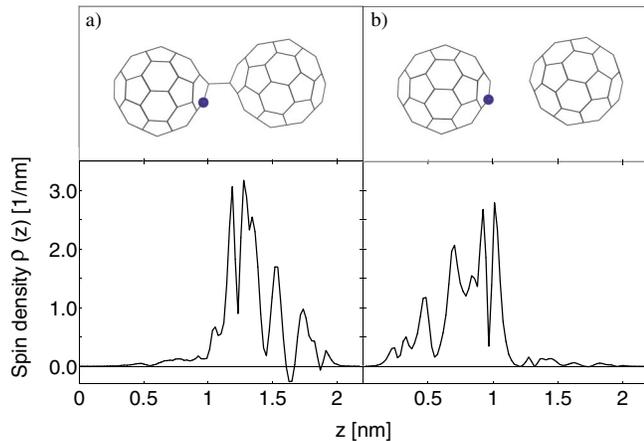


FIG. 4 (color online). *Ab initio* calculation of molecular structures and the spin densities, $\rho(z)$, along the molecular axis z integrated in the plane perpendicular to z . (a) The ground state heterodimer and (b) the dissociated pair with a fixed intermolecular C-C separation $d = 0.30$ nm. Note the almost complete transfer of an electron spin from C₆₀ to C₅₉N with the dissociation of the heterodimer.

ESR assignment of a distorted C₆₀-like molecule. We calculated a very small ¹⁴N hyperfine constant of $A = 0.016$ mT from the 10% spin density remaining on the C₅₉N molecule. We observed, however, no hyperfine splitting with a precision of 0.01 mT above and 0.05 mT below T_c , showing again that the spin transfer to the C₆₀ moiety is nearly complete.

We calculated the way the heterodimer is torn apart by fixing larger and larger nearest intermolecular C-C distances, d , while relaxing all other atomic positions. Figure 4(b) shows the structure of the dissociated molecule for $d = 0.30$ nm; this is about the nearest neighbor distance in solid C₆₀. In contrast to the heterodimer, in the dissociated case most of the spin density resides on the C₅₉N molecule. The energy difference between the heterodimer and the dissociated pair of C₅₉N and C₆₀ molecules is small. We find a barrier between the heterodimer and the dissociated pair with an energy maximum of 0.5 eV at $d = 0.21$ nm.

Thus, the calculation is in qualitative agreement with the picture derived from the experiment. At finite temperatures the configuration fluctuates between the covalently bonded heterodimer and dissociated molecules since these configurations have similar energies and the barrier between them is small. Dissociation of the heterodimer is accompanied by transfer of an electron spin. In the experiments at intermediate temperatures we detect simultaneously the distorted C₆₀ moiety of the heterodimer and the neutral

C₅₉N of the dissociated pair. The spin lifetime of the heterodimer is limited by the lifetime of the heterodimer itself. From the increase of the spin-spin relaxation time measured at 9 GHz we estimate a slow fluctuation frequency of the order of 10^7 Hz at 350 K. The extra electron is localized to C₅₉N from 350 K to about 700 K and only above this high temperature is C₅₉N:C₆₀ a doped semiconductor.

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