

Electron delocalization and dimerization in solid C₅₉N doped C₆₀ fullerene

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Abstract. Electron spin resonance and ab initio electronic structure calculations show an intricate relation between molecular rotation and chemical bonding in the dilute solid solution C₅₉N:C₆₀. 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.

Keywords: electron spin resonance, fullerene, molecular semiconductor, density functional theory

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INTRODUCTION

Pure C₆₀ fullerene is an insulating solid with an energy gap of about 1.5 eV between the valence and conduction bands[1, 2, 3, 4, 5, 6]. 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.

In the dilute solid solution of C₅₉N in C₆₀ the C₅₉N molecules substitute for C₆₀. There are two possible low energy configurations of the system. In one case, the C₅₉N molecule remains isolated, in the other case a covalent bond forms with one of the neighbouring C₆₀ molecules. First principles calculations show two distinct energy minima with a barrier between them. In the ESR experiments, we observe below 350 K a temperature dependent dynamic fluctuation between these two states. The ground state is the covalently bound heterodimer, in which the rotation of the molecules is not possible or is limited to rotations around the covalent bond joining the C₆₀ and C₅₉N molecules. At higher temperatures, the free energy associated to the large rotational

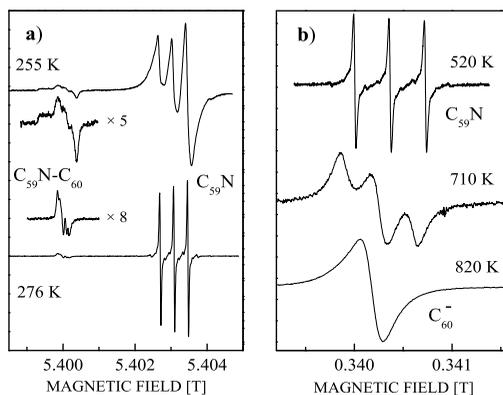


FIGURE 1. ESR spectra in dilute $C_{59}N:C_{60}$ solid solution. a) Spectra at 150 GHz near the $T_c = 261$ K phase transition of solid C_{60} . The two ESR lines are assigned to non-rotating $C_{59}N-C_{60}$ heterodimers and neutral, rotating $C_{59}N$. We propose that structural fluctuations lead to 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.

entropy overcomes the binding energy of the heterodimer. Between 350 K and 600 K all $C_{59}N$ molecules are in the unbound state. Above 600 K, the configurational entropy of the unpaired electron overcomes the coulomb attraction, and the electron is observed to delocalize in the crystal[7].

RESULTS AND DISCUSSION

Figure 1 shows the ESR spectra in the various states of $C_{59}N$ in the C_{60} matrix. Below 350 K, two ESR active species appear in $C_{59}N:C_{60}$ (Figure 1a). Both species are embedded in the C_{60} matrix since their ESR spectra change abruptly at the $T_c = 261$ K phase transition of solid C_{60} . We assign one component of the ESR spectrum to $C_{59}N-C_{60}$ heterodimers formed from $C_{59}N$ and one of its 12 C_{60} neighbors. The other component arises from $C_{59}N$ free radicals and was investigated in detail in an earlier work[6].

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[8]. 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 (Figure 1b). The ^{14}N triplet with an isotropic g factor of 2.00137 transforms gradually into a single line shifted to lower fields at $g = 2.0024$ and the $C_{59}N$ spectrum disappears. 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 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. At 261 K the extra line changes abruptly (Figure 1a), 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.

The following observations support this 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, in a wide range of $C_{59}N$ concentrations. Yet, for all samples, the concentration ratio of the species of the extra line to monomeric $C_{59}N$ is the same at any given temperature. This 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 *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} (Figure 2a). 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 Figure 2a. 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 2a 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 ESR assignment of a distorted C_{60} like molecule. We calculated a very small ^{14}N hyperfine constant of $A = 0.016$ mT from the 10% spin density remaining on the $C_{59}N$ 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 C_{60} moiety is nearly complete.

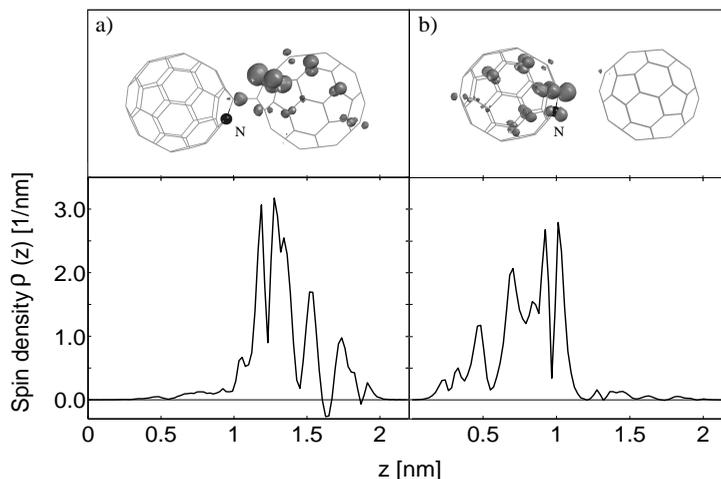


FIGURE 2. *Ab initio* calculation of molecular structures and the spin densities, $\rho(z)$, along the molecular axis z integrated in the plane perpendicular to z . a) the ground state heterodimer and b) the dissociated pair with a fixed intermolecular C–C separation $d = 0.30$ nm. Note the almost complete transfer of an electron spin from C_{60} to $C_{59}N$ with the dissociation of the heterodimer.

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. The total energy of the molecule as a function of d is shown on Figure 3 and Figure 2b shows the structure of the dissociated molecule for $d = 0.30$ nm, which is about the nearest neighbor distance in solid C_{60} . Note that the lack of an energy minimum in the curve for the dissociated species reflects the fact the density functional theory does not include attractive dispersion forces. In contrast to the heterodimer, in the dissociated case most of the spin density resides on the $C_{59}N$ molecule. The energy difference between the heterodimer and the dissociated pair of $C_{59}N$ and C_{60} 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. The energy difference between the dimer molecule and the dissociated species (both indicated by arrows on Figure 3) is 0.18 eV, which is in excellent agreement with the experimental binding energy of dimer (2400 K corresponds to about 0.2 eV.)

CONCLUSION

Thus, the calculation is in quantitative 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 tem-

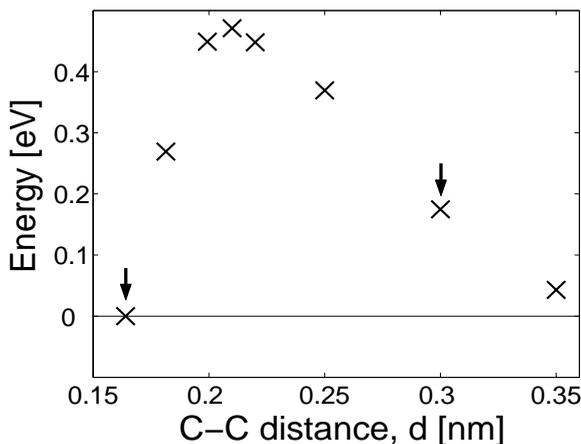


FIGURE 3. *Ab initio* calculation of the dissociation curve of $C_{59}N-C_{60}$, showing the total energy as a function of the length of the C-C bond being broken. Black arrows indicate the bond lengths corresponding to the bound heterodimer and the equilibrium intermolecular distance in the solid.

peratures we detect simultaneously the distorted C_{60} moiety of the heterodimer and the neutral $C_{59}N$ of the dissociated pair. The extra electron is localized to $C_{59}N$ from 350 K to about 700 K and only above this high temperature is $C_{59}N:C_{60}$ a doped semiconductor.

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