Observation of Atomlike Nitrogen in Nitrogen-Implanted Solid C_{60}

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A new paramagnetic defect in solid C_{60} was produced by nitrogen implantation in solid C_{60}. The hyperfine splitting and the isotope effect unambiguously show that the paramagnetic center contains one nitrogen nucleus. The hyperfine interaction is isotropic, its value is comparable to that of the free nitrogen atom, and the spin of the electron system is $S = 3/2$, as in atomic nitrogen. The complex responsible for this center is soluble in toluene and CS_2 and is stable. We suggest that the complex consists of nitrogen inside C_{60}. [S0031-9007(96)00806-X]

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The encapsulation of atoms or molecules into the hollow fullerenes is an intriguing idea since the beginning of the fullerene research [1]. Usually these endohedral complexes are prepared by adding the appropriate materials during the formation of the fullerenes [2,3]. Alternative methods are the application of high temperatures and high pressures for the encapsulation of rare gas atoms into C_{60} [4], atomic collisions in beams [5], or ion implantation. A successful experiment of this latter kind is the implantation of positive muons (μ^+) into C_{60} and C_{70} and the formation of endohedral muonium ($\mu^+ e^-$) [6–8]. Stimulated by these investigations we tried nitrogen implantation into C_{60}.

Nitrogen implantation produces a paramagnetic center with hyperfine interaction properties very close to that of atomic nitrogen. This paramagnetic complex is soluble in organic solvents, is stable at room temperature, and withstands (at least for short times) exposure to air. These properties strongly suggest that endohedral nitrogen in C_{60} has been produced.

This complex has not been reported in the literature before. In experiments especially designed to look for the interaction of nitrogen with fullerenes, e.g., during fullerene formation, no such structures were observed or discussed [9,10]. In a recent electron paramagnetic resonance (EPR) study [11] on untreated fullerenes, a weak doublet with a splitting of 1.12 mT was reported. We presume that these two lines are the outer components of the triplet found here but in [11] these lines were assigned to a fullerene dimer.

C_{60} was bombarded with nitrogen ions from a conventional plasma discharge ion source which is otherwise used as a spatter gun for surface cleaning. In the present case the sputter gun was approximately 10 cm from our target and we applied an extraction voltage of 800 V, yielding ions with energies of several 100 eV. The bombardment was carried out in a vacuum of 10^{-5} mbar.

After this preparation, the bombarded C_{60} material was scratched from the substrate in air and dissolved in toluene. In order to increase the solubility, the solution was treated in an ultrasound bath; subsequently it was filtered. Approximately 20% of the starting bombarded material remained in the filter (probably C_{60} fragments). The filtered solution was then dried at room temperature in an N_2 stream, filled into quartz ampules and sealed under argon for the EPR and electron nuclear double resonance (ENDOR) measurements.

The EPR measurements in the X band ($\nu \approx 9.4$ GHz) and Q band ($\nu \approx 35$ GHz) were performed with commercial EPR spectrometers and EPR-ENDOR experiments were made with a custom-built EPR-ENDOR spectrometer. The measurements were carried out between liquid He temperature and room temperature.

Figure 1 shows an EPR spectrum (Q band) of an ion bombarded C_{60} sample prepared in the way described above. A dominant triplet (assigned to ^{14}N with nuclear spin $I = 1$) and a weak but clearly visible doublet (assigned to ^{15}N with $I = 1/2$) are seen. The position of the middle line of the triplet corresponds to a g factor of $g = 2.0030(\pm 2)$. The intensity ratio of the ^{14}N and ^{15}N lines (170:1) is consistent with the ratio expected from the natural abundance of the two N isotopes (abundance of ^{15}N:0.37%). The ratio of the splitting, assumed to be of hyperfine nature (this is confirmed by the ENDOR measurements; see below), corresponds exactly to that expected from the g_n values of the isotopes. The lines are fairly sharp indicating that the powder averaging does not broaden the lines appreciably.

Figure 2 shows variants of this experiment. Figure 2(a) shows the EPR spectrum of a C_{60} sample treated in the same was as the others except for the ion bombardment. Clearly, the hyperfine split paramagnetic center of Fig. 1 is absent and only a weak unsplit signal at $g \approx 2$ is seen. Figure 2(b) shows the EPR spectrum of C_{60} bombarded with 99.9% enriched ^{15}N ions. Now the doublet from

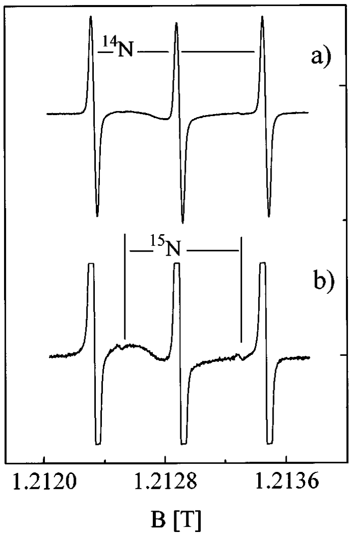

FIG. 1. Q band EPR spectra of ion bombarded C_{60} measured at room temperature. The lower trace (b) is measured with higher sensitivity than the upper trace (a). The triplet splitting is due to the hyperfine interaction with ^{14}N nucleus ($I = 1$), and the weak doublet to the hypterfine interaction with ^{15}N nucleus ($I = 1/2$).

^{15}N is dominant and the triplet from ^{14}N is absent. In Figure 2(c) the triplet due to ^{14}N is shown for comparison.

The derivative peak-to-peak linewidth ΔB_{pp} of the three ^{14}N lines is 0.016 mT in the X band at RT, and 0.028 mT in the Q band. The increase of the linewidth with the EPR frequency implies that the width of the EPR lines is not determined by unresolved hyperfine interactions. The linewidth is apparently determined by a distribution of electronic g factors. Upon cooling to 4 K the nonsaturated linewidth in the X band increases to $\Delta B_{pp} = 0.022$ mT. We conclude from the measurements that the defect undergoes a thermally activated motional averaging starting already at approximately 70 K. Using CS_2 as a solvent, which dissolves fullerenes in higher concentrations than toluene, we succeeded to observe the signal also in solution inspite of the low concentration of the defect centers. Since the signal was weak and therefore noisy, the linewidth could not be determined accurately. However, the linewidth seems to be comparable to that in the solid sample.

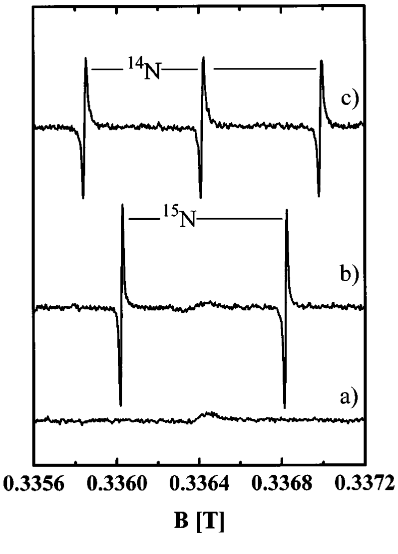

FIG. 2. X band EPR spectra of (a) a C_{60} sample without ion bombardment but otherwise treated the same way as the others. (b) A C_{60} sample bombarded with 99.9% enriched ^{15}N. (c) Same but bombarded with N in natural isotope abundance (mainly ^{14}N). Spectrum (a) was taken at 7 K, (b) and (c) at 300 K. All measurements were done with a microwave power of 20 μW.

ENDOR powder spectra from measurements in the X band at 7 K are shown in Fig. 3. We observe the Larmor freuqency of ^{13}C at 3.57 MHz ($B = 333.16$ mT) and that of ^{1}H at 14.18 MHz as well as four other lines at 6.8, 8.9, 22.6, and 24.6 MHz (see Table I). Figure 3(a) was measured on the high field line of the triplet and Fig. 3(b) on the low field line. The ENDOR frequencies are given to first order by

$$\nu = \left| \frac{1}{h} g_n \mu_n B_0 \pm A m_S \right|, \tag{1}$$

where the first term is the nuclear Zeeman energy and A is the hyperfine coupling constant [12]. The fine structure and quadrupole terms are omitted. The ENDOR spectrum can be explained assuming one nucleus with $I = 1$ (for ^{14}N) and an electron spin of $3/2$. The two low frequency liens are due to $m_S = \pm 1/2$. The difference is twice the Larmor frequency of ^{14}N ($\nu_K = g_n \mu_n B_0 / h$) and the two high frequency lines belong to $m_S = \pm 3/2$ again separated by twice the Larmor frequency of ^{14}N. The average value of the two low frequency lines is $\frac{1}{2} A$ and the average of the two high frequency lines is $\frac{3}{2} A$. The existence of the upper doublet is a clear indication that the electron spin is $S = 3/2$ [since $g = 2.0030(2)$, there is practically

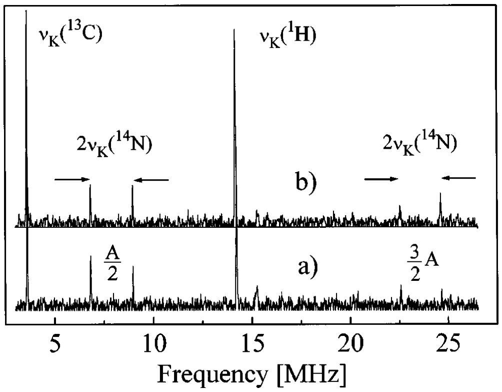

FIG. 3. X band ENDOR spectra of an ^{14}N irradiated sample measured on (a) the high field line (334.30 mT) and (b) the low field line (333.16 mT).

TABLE I. Comparison of the ENDOR experimental line positions shown in Fig. 3 with the calculated line positions. The hyperfine constant used for the calculations was 15.730 MHz. The widths of the ENDOR lines are ≈25 kHz.

Frequency (MHz)	$B_0 = 333.16$ mT		$B_0 = 334.30$ mT	
	Experiment	Calculation	Experiment	Calculation
ν_1	6.791	6.786	6.805	6.799
ν_2	8.931	8.929	8.950	8.942
ν_3	22.527	22.526	22.566	22.566
ν_4	24.619	24.617	24.658	24.656

no orbital contribution to the paramagnetism of the center [12]].

A quantitative comparison between theory and experiment is given in Table I. In the calculation of the line positions, the adjustable parameter is the hyperfine interaction of one of the isotopes. The calculations were made with $A(^{14}\mathrm{N}) = 15.730$ MHz (best fit value). There is a small difference in frequency of the ENDOR lines measured on the high field EPR line compared to those measured on the low field line. This difference is due to the fact that on the low field EPR line only the $m_I = 0 \leftrightarrow m_I = 1$ NMR transition can be excited, on the high field line only the $M_I = -1 \leftrightarrow m_I = 0$ NMR transition. The resulting ENDOR frequencies can be calculated precisely by a full diagonalization of the spin Hamiltonian. The calculated frequencies are in excellent agreement with the observed ENDOR transitions (see Table I).

ENDOR spectra of the fullerene sample that had been bombarded with ^{15}N enriched nitrogen [Fig. 2(b)] show besides the two Larmor frequencies of ^{13}C and ^{1}H also four additional ENDOR lines. They are again divided into groups of two with the average frequency at $\frac{1}{2}A$ and $\frac{3}{2}A$. Because of the larger nuclear moment of ^{15}N compared to ^{14}N the splitting of the pairs of ENDOR lines is larger. The isotropic hyperfine interactions scale with the different nuclear moments of the two isotopes. We measure an isotropic hyperfine interaction of $A(^{15}\mathrm{N}) = 22.021$ MHz. This value, divided by the hyperfine interaction of ^{14}N, gives a ratio of $1.400(\pm 2)$ which is in excellent agreement with the ratio of the nuclear moments of 1.4027 [12].

The narrow width of the ENDOR lines, unusual for a powder spectrum, indicates that the hyperfine interaction is purely isotropic. Thus the ENDOR measurements not only confirm the presence of one nitrogen nucleus in the defect, but they also were able to determine the electronic spin of that defect to be $S = 3/2$. The measurements also show that there are protons and ^{13}C nuclei coupled to the defect. However, the hyperfine coupling is too weak to be observed or purely anisotropic and averages out. It is remarkable that the ^{13}C line is so intense considering that the abundance of ^{13}C is only 1%. This is an indication that many carbons are coupled weakly. The protons are probably from the solvent.

A mass spectroscopy identification of the complex is difficult since the concentration of the paramagnetic centers is only in the order of 10^{-7} per C_{60} molecule. Our mass spectroscopy measurements on similar samples show that impurity lines in the relevant mass region are much stronger than the ones expected from these centers. At this low concentration level (10^{-7}) also UV and IR spectroscopy suffer from background problems originating directly from C_{60} or from impurities in particular from the solvent remainders. The EPR and ENDOR methods have the advantage that the main component of the sample, i.e., C_{60}, and most of the impurities are diamagnetic and therefore do not give a signal allowing a very sensitive detection of the paramagnetic centers.

The paramagnetic center reported here resembles in many aspects free atomic nitrogen [13,14] which has an $S = 3/2$ ground state, an isotropic hyperfine interaction, and shows no fine structure. But other than atomic nitrogen, the present center is stable and most importantly it is soluble in organic solvents. These features and their significance for the identification of the defect will be discussed in the following.

(i) The experimental finding that the electron spin is $S = 3/2$ indicates that three unpaired electrons are present in the paramagnetic center. This is very unusual and unexpected for nitrogen in a bonded configuration where usually only $S = 1/2$ occurs (e.g., in NO and NO_2). Nitrogen as a paramagnetic shallow donor in semiconductors is also expected to have $S = 1/2$ [15,16]. Thus the present configuration should not resemble such a state. However, in the atomic configuration of nitrogen, Hund's rule predicts $S = 3/2$ for the three electrons in the p shell in the ground state.

(ii) The observed isotropy of the hyperfine interaction is expected for atomic nitrogen which has $L = 0$ in the ground state. For strongly bonded configurations we would expect contrary to our experimental findings some anisotropy in the hyperfine interaction.

(iii) The value of the isotropic hyperfine interaction constant $[A(^{14}\mathrm{N}) = 15.73 \text{ MHz}]$ is approximately 50% larger than that of atomic nitrogen [14]. However, in the case of nitrogen the ground state hyperfine interaction is very small (for nonrelativistic L-S coupling it is expected to be zero) whereas the low-lying excited states have much larger hyperfine interactions [13]. Thus the slight admixture of excited states due to an interaction with the surrounding C_{60} shell can explain the increase of the hyperfine constant.

(iv) The stability of the complex in air during transfers and in solutions is not in accord with the usual behavior of radicals but it is understandable if nitrogen is encapsulated inside an inert C_{60} cage.

These findings strongly suggest that the paramagnetic center consists of nitrogen inside C_{60}. The atomlike electronic configuration ($S = 3/2$ and isotropy) is naturally explained is this model. The stability of the center is a consequence of the protective shielding by the inert C_{60} shell. On the other hand, the assumption of any bounded configuration which we could think of is in conflict with the experimental findings. The $S = 3/2$ result cannot be reconciled with a strong binding which would be required in order that the defect on the outside of C_{60} survives in solution. Similarly, the isotropy of the hyperfine interaction is not understandable for an outside bonded system. The assumption that rotational motion would average out the anisotropy even at 4 K seems little plausible considering the steric hindrance expected for such a system.

On the basis of these results and arguments we propose that the observed center corresponds to endohedral nitrogen in C_{60}.

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