Alignment of the endohedral fullerenes N@C$_{60}$ and N@C$_{70}$ in a liquid-crystal matrix

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Endohedral fullerenes N@C$_{60}$ and N@C$_{70}$ were dissolved in a liquid crystal and investigated by electron paramagnetic resonance. Sharp, liquid solution like spectra are observed. However, contrary to the usual solution spectra, the lines are split, indicating that the electron shell of the enclosed nitrogen atom is deformed and that an alignment with respect to the magnetic-field axis is achieved. The present results are of practical interest for controlling the interaction of endohedral fullerenes in a quantum computer.

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As was shown previously [1–5], molecules formed by nitrogen encapsulation in C$_{60}$ or C$_{70}$ have exceptional properties in the sense that open shell and therefore highly reactive atoms are stabilized in the fullerenes without any binding or charge exchange with the cage. The encased atoms are almost freely suspended in the middle of the cage and keep their atomic ground-state configuration (three electrons in the $2p$ shell coupled to $^4S_{3/2}$). The excellent shielding from the outside of the enclosed atoms gives rise to extremely sharp electron paramagnetic resonance (EPR) lines and, most important for applications, to long electron-spin life times [6]. The systems studied in this work are N@C$_{60}$ and N@C$_{70}$, i.e., atomic nitrogen encapsulated in the highly symmetric fullerene C$_{60}$ or in the slightly cigar shaped fullerene C$_{70}$.

Nonspherical molecules can be geometrically aligned by embedding them in liquid crystals that have a preferred orientation axis in an external field. Such an alignment of molecules can be extremely useful because elements of second-rank tensor interactions like dipolar coupling, nuclear quadruple interaction, or fine-structure interaction can be determined with liquid solutionlike spectral resolution [7,8].

We are in particular interested in aligning endohedral fullerenes in connection with the construction of a quantum computer where endohedral fullerenes are envisaged to serve as quantum bit carriers [9,10]. The magnetic dipolar interaction will serve as mediator between the enclosed paramagnetic atoms to provide the necessary entanglement of the paramagnetic states. It is obvious that a control of the interaction angle is necessary if a welldefined and changeable interaction is to be established. The embedding of the endohedral fullerenes in a liquid-crystal matrix provides an ideal solution of this requirement. We found evidence that even the almost spherical C$_{60}$ fullerene can be aligned in a liquid crystal.

The endohedral fullerenes are produced by ion implantation [11]. The as-prepared material is highly diluted (concentration ca. 10^{-4}) but can be enriched by high performance liquid chromatography [2]. In the present experiment, as-prepared or slightly enriched (up to a factor of ten) material was used. The fullerenes were dissolved at room temperature in the liquid-crystal 4-methoxybenzylidene-4'-*n*-butylaniline

(MBBA) [12] in an ultrasonic bath. A surplus of fullerenes was added in order to obtain a saturated mixture that was then decanted after the surplus fullerenes had sedimented at the bottom. In the nematic phase (between 293 K and 321 K for MBBA), the solute molecules are directionally ordered due to the alignment of the elongated liquid-crystal molecules in the external magnetic field (0.33 T).

The EPR measurements were performed with the Bruker ELEXSYS E 580 spectrometer at 9.5 GHz (X band) in continuous-wave mode. Due to the weakness of the signals in some cases, the EPR modulation amplitude was set such that an optimum signal to noise ratio was reached. This lead to a slight overmodulation of the EPR lines which was accounted for by fitting with Voigt line shapes.

N@C$_{60}$ and N@C$_{70}$ in solution show a three line spectrum in EPR due to the hyperfine interaction of the electrons with the nuclear spin $I=1$ of ^{14}N (top of Fig. 1). Since the electron spin of nitrogen is $S=3/2$, each of these hyperfine lines consists by itself again of three lines that are degenerate for a spherically symmetric electron distribution or in case of
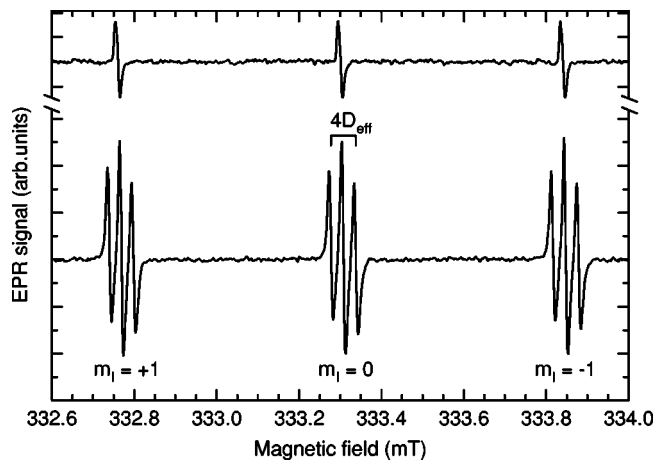

FIG. 1. EPR spectrum of N@C$_{70}$ in toluene solution (upper graph) and N@C$_{70}$ in MBBA liquid crystal (lower graph) at 299 K. The magnetic quantum number m_I of the nuclear spin $I=1$ and the splitting of the outer lines by $4D_{eff}$ (see text) for the $m_I=0$ hyperfine line are indicated.

temporal averaging as in solutions (the second-order hyperfine splitting in the X band is 27 kHz and can be neglected in most cases [13]). However, for nonspherical atoms the degeneracy is lifted and the three lines become visible (see lower part of Fig. 1). This is due to the fine-structure term

$$H_{FS} = S\mathbf{D}S \qquad (1)$$

arising from the spin-spin interaction of the three unpaired electrons of nitrogen. Here S is the electron spin of nitrogen and $\mathbf{D}$ is a traceless second-rank tensor. For an axially symmetric interaction this tensor can be characterized by a single parameter D, being defined by $D = 3/2 D_{zz}$, in which the unique axis is denoted by z. In a high external field (Zeeman interaction large compared to the hyperfine splitting), the fine-structure splitting $\Delta \nu$ (separation between two successive peaks in each hyperfine multiplet) in the EPR spectrum can be represented as

$$\Delta \nu = 2 D_{eff} = 2 D O_{33} \qquad (2)$$

with

$$O_{33} = \frac{1}{2} (3 \overline{\cos^2 \vartheta} - 1), \qquad (3)$$

where D_{eff} is an abbreviation defined by Eq. (2) and O_{33} the order parameter of the uniaxial solute molecule in the liquid crystal, ϑ describing the average angle between the unique axis of the solute and the external magnetic field. In cases where the fine-structure splitting is due to an induced deformation (see below) a clear separation into an intrinsic D and an orientation dependent O_{33} is not always possible, therefore mainly the product D_{eff} is used in the following discussion.

The fine-structure interaction splits each hyperfine line into three lines, one at the original position and one shifted to lower and one to higher fields. Figure 1 shows this additional line splitting for N@C_{70} in MBBA. The value of D_{eff}, deduced from the $m_I = 0$ hyperfine line where the splitting is not affected by the second-order hyperfine interaction, is $D_{eff} = 0.418(3)$ MHz [14]. The width of the center line at 299 K is 170(10) kHz, the outer lines being slightly broader by 20%. The line intensities exhibit the expected ratio of 3:4:3 for the outer, center, outer line, respectively.

Figure 2 shows the temperature dependence of D_{eff} for N@C_{70} in MBBA. It can be seen that the measurements performed at room temperature are close to the maximum value observed in the supercooled nematic (solid) phase. The transition to the isotropic phase is marked by the disappearance of the splitting. It occurs in the temperature range where the phase transition of pure MBBA is known to take place [12]. The N@C_{70} concentration of about 0.1 mM is very low and probably does not alter the phase transition.

Because size and sign of the order parameter O_{33} are not known, only an upper limit $|D| < 0.418(3)$ MHz can be deduced. An anisotropic electron distribution in N@C_{70} can be expected due to the elongated shape of the fullerene. In a recent ENDOR study [15], anisotropic hyperfine and quad-
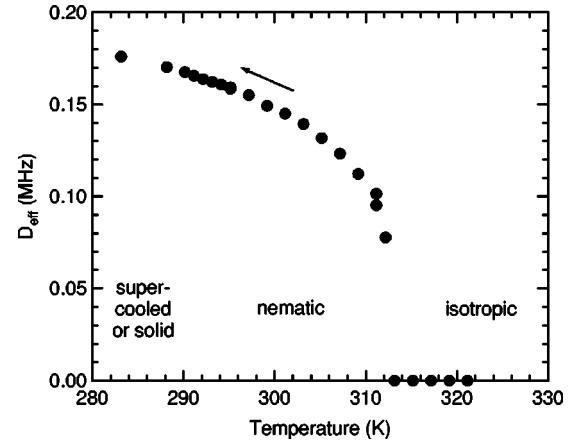

FIG. 2. Temperature dependence of the effective fine-structure interaction D_{eff} for N@C_{70} in MBBA liquid crystal. The data were taken in the cooling direction where a supercooled intermediate region occurs at temperatures below about 290 K. In a measurement with increasing temperatures, the line splitting below 290 K could not be determined since the lines were too broad.

rupole interactions were measured for N@C_{70} in a solid C_{70} matrix. It is expected that there is also a fine-structure interaction in these cases but its value has not been determined yet. Thus a direct comparison with the present case is not possible.

C_{60}, other than C_{70} with its elongated shape, has no natural axis for alignment in a liquid crystal. However, as Fig. 3 shows, there is also a splitting of the EPR line, and thus an alignment for N@C_{60}. The line splitting at 296 K gives $D_{eff} = 0.090(5)$ MHz, more than a factor of four smaller than the corresponding value for N@C_{70}. The widths of the lines (corrected for the modulation broadening) are 120(10)
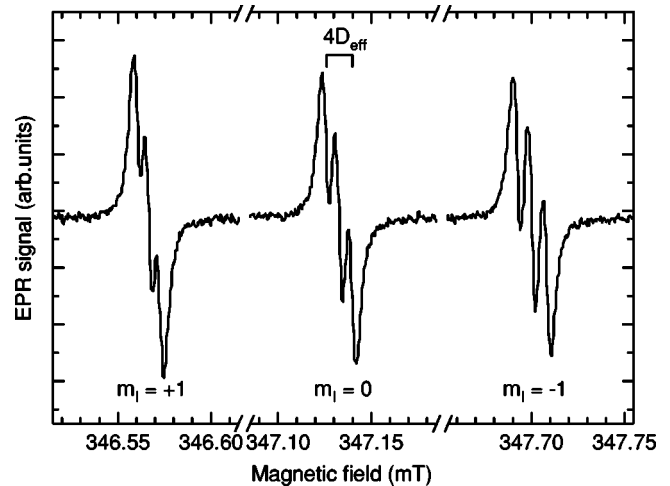

FIG. 3. EPR spectrum of N@C_{60} in MBBA liquid crystal at 296 K. Note that the field axis is interrupted between the lines in order to emphasize the splitting. The magnetic quantum number m_I of the nuclear spin $I = 1$ and the splitting of the outer lines by $4D_{eff}$ (see text) for the $m_I = 0$ hyperfine line are indicated. The splitting is slightly different for the different m_I multiplets due to a second-order hyperfine splitting.

kHz with no noticeable difference between the outer lines and the center line.

The observed splitting shows that the spin-density distribution of the enclosed nitrogen atom in C_{60} slightly deviates from spherical. The explanation is that the contact of C_{60} with the aligned liquid-crystal molecules induces a slight deformation of the electron shell of C_{60}, which in turn affects the electron-density distribution of the enclosed nitrogen.

Similar effects have been observed in crystalline C_{60} where neighboring C_{60} molecules impose a potential sufficient for ordering at low temperatures. X-ray diffraction measurements [16,17] revealed a nonuniform charge-density distribution of C_{60} even at room temperature where the molecules rotate rapidly. This observation implies that the deviation of the charge cloud from uniformity remains fixed in space even if the constituent parts of the fullerene rotate freely. A similar situation is supposed to exist in the presently studied liquid-crystal system. Here, we have direct spectroscopic evidence for this deformation at room temperature.

Most other experiments in this context were performed in the low temperature, simple cubic phase of crystalline C_{60}. Raman measurements show a splitting of lines due to crystal-field effects [18,19]. The experiment closest to the present one is the EPR measurement on diluted $N@C_{60}$ in polycrystalline C_{60} below the phase-transition temperature of 260 K [4]. There, a well resolved powder pattern originating from the fine-structure interaction with $D = 0.52$ MHz is observed. This value is approximately five times larger than $D_{eff} = D O_{33}$ in the present case. Considering that the order parameter O_{33} may be considerably smaller than one, the intrinsic D value, which represents the induced deformation of $N@C_{60}$, may well be of similar magnitude in the two cases.

It is noteworthy that the widths of EPR transitions in the liquid crystal are significantly larger than those observed in solvents like CS_2 or toluene [15,20]. As was shown previously, the dominant source of spin relaxation of $N@C_{60}$ is modulation of the fine-structure interaction by collision-induced cage deformation [3]. The size of this effect is dominated by the variance of these fluctuations, which in turn depend on the mass of the solvent molecules. The larger width of the outer components of the resolved line triplet supports this hypothesis.

Effects originating from unresolved hyperfine couplings could also contribute to the line width. Taking the natural abundance of 1.11% of the ^{13}C isotope, 49% of C_{60} and 54% of C_{70} have one or more ^{13}C nuclei on the cage. The couplings with nuclear moments are estimated to be in the order of 400 kHz for both cages, using values determined by an analysis of powder ENDOR spectra of $N@C_{60}$ [4]. Because of rapid rotation about the unique molecular axis, only values projected on this axis are time invariant and have to be considered. The product of these values with the order parameter O_{33} finally leads to an effective hyperfine coupling in the nematic phase. Because of a homogeneous line width of 55 kHz, we were not able to resolve these predicted subcomponents.

TABLE I. Fine-structure parameter $D_{eff} = O_{33}D$ and average widths of the lines (see text) from the present experiments for $N@C_{60}$ and $N@C_{70}$ in comparison with the axial parts of the fine structure for solid $N@C_{60}$ [4], the monoadduct $N@C_{61}(COOC_2H_5)_2$ [5], and the half filled dimer $N@C_{60}$-C_{60} [21].

	D_{eff} or D (MHz)	Width (MHz)
$N@C_{60}$ in MBBA	0.090(5)	0.120(10)
$N@C_{70}$ in MBBA	0.418(3)	0.170(10)[a]
$N@C_{60}$ in solid, $T < 260$ K	0.52	
$N@C_{61}(COOC_2H_5)_2$	6.02	
$N@C_{60}$-C_{60}	13.44	

[a]The value of the middle line (see text) is given. The outer lines are 20% broader.

We have shown that $N@C_{60}$ and $N@C_{70}$ can be oriented by embedding them into liquid crystals. In case of C_{70} the alignment of the molecule is a natural consequence of its elongated shape. For C_{60}, the nearby liquid-crystal molecules must induce the observed anisotropy. The values of the effective fine-structure parameters (see Table I) give a measure for the anisotropy of the electron-spin-density distribution around the nitrogen center. As expected, the intrinsic effect from the elongated shape of the C_{70} cage is larger than that induced externally for C_{60}. Both values, however, are of the same order of magnitude as those observed for $N@C_{60}$ in polycrystalline C_{60} [4], in which weak (van der Waals) forces from the neighboring C_{60} molecules induce the deformation. On the other hand, the observed fine-structure interactions are much smaller than those found for externally modified fullerenes, as the monoadduct $N@C_{61}(COOC_2H_5)_2$ [5] and the dimer $N@C_{60}$-C_{60} [21] (see Table I).

An interesting spectroscopic side effect of embedding $N@C_{60}$ and $N@C_{70}$ in the liquid-crystal matrix is that the degeneracy of the transitions is lifted and therefore their properties, e.g., individual spin lattice and spin dephasing relaxation rates, can be studied separately. This allows a more detailed investigation of the relaxation mechanism.

The alignment of the endohedral fullerenes in a liquid-crystal matrix is of great importance in connection with quantum computing. There, one can construct by chemical means a chain of endohedral fullerenes, e.g., dimers [21] or polymers, and embed them in a liquid crystal. Since the magnetic interaction between the fullerenes is dipolar, the arrangement in a chain and the orientation with respect to the external field ensures that the interaction is unique and even changeable if the angle between the chain axis and the external field is varied. Since the fullerenes are diluted in the liquid crystal, the interchain interaction is negligible as required for independent small qubit assemblies.

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