Carbon Nanotubes Investigated by $N@C_{60}$ and $N@C_{70}$ Spin Probes

B. Corzilius*, A. Gembus*, K.-P. Dinse*, F. Simon#, and H. Kuzmany#

**) Chem. Dept., Darmstadt University of Technology, Petersenstr. 20, D-64287 Darmstadt, Germany*
#) Institut für Materialphysik, Universität Wien, Strudlhofgasse 4, A-1090 Wien, Austria

Abstract. Nitrogen atoms encapsulated in C_{60} can be used to detect small deviations from spherical symmetry via deformation-induced non-vanishing Zero-Field-Splitting (ZFS). In this context, experiments were performed by using these electronic quartet spin probes to investigate single wall carbon nanotubes. Time-fluctuating ZFS interaction would be indicative for rotational and/or translational degrees of freedom. Using pulsed EPR techniques, spin relaxation rates of $N@C_{60}$ and also of $N@C_{70}$ molecules with inherent static ZFS were measured. The analysis of their temperature dependence gave information about the dynamics of $N@C_{60}$ and $N@C_{70}$ molecules confined to the inside of the tubes.

INTRODUCTION

In contrast to the large group of metallo-endofullerenes (MEF) which can be classified as internal salts with strong Coulomb interactions, group 15-derived endofullerenes like $N@C_{60}$ and $N@C_{70}$ can be classified as atoms, which are freely suspended in a “chemical trap”, thus forming a compound that is localized in space with negligible interaction with its confinement [1]. For this reason, these compounds are ideal sensors because spin or charge transfer is practically absent, and the localized paramagnetic atom in its quartet spin ground state probes the electric multipole moments at the site of the encased atom. In particular, deviations from spherical symmetry, as expected for $N@C_{60}$ embedded in single wall carbon nanotubes (SWCNT), could in principle be detected. Furthermore, thermally activated processes encountered by the incorporated spin probe, like reorientation within the multidimensional potential surface, should lead to temperature dependent spin relaxation processes.

EXPERIMENTAL

Peapods generated by inserting $N@C_{60}$ or $N@C_{70}$ in SWCNT were prepared using an optimized purification and insertion protocol as described in the contribution of Corzilius *et al*. in this proceedings [2]. Samples of $N@C_{60}$ and $N@C_{70}$ of various spin concentration were prepared as described elsewhere [3]. EPR spectra were measured using either a continuous wave (c. w.) EPR spectrometer (Bruker ESP 300E) or a pulse spectrometer (Bruker ElexSys 680), both equipped with Helium cryostats.

CP786, *Electronic Properties of Novel Nanostructures,* edited by H. Kuzmany, J. Fink, M. Mehring, and S. Roth

RESULTS AND DISCUSSION

N@C$_{60}$ based peapods

The most striking result noted in the first study of N@C$_{60}$-based peapods by Simon *et al.* [4], was the observation that incorporation into nanotubes increased the EPR line width by more than an order of magnitude. This contrasts with the previous observation of record setting narrow lines of N@C$_{60}$ of less than 10 μT even in condensed matrices, which was taken as proof for the preserved near spherical symmetry at the site of the nitrogen atom. This observation was rationalized by assuming a "stiff" atomic cage, also allowing only negligible spin exchange. As seen in Fig. 1a, information about line width details were difficult to obtain in the first studies because of strong background signals, probably originating from defects in the SWCNT [4, 5]. Using the optimized preparation protocol [2], the early findings could be verified (Fig. 1b). For this comparison, N@C$_{60}$/C$_{60}$ samples of equal relative concentration (500 ppm) were used for peapod preparation.

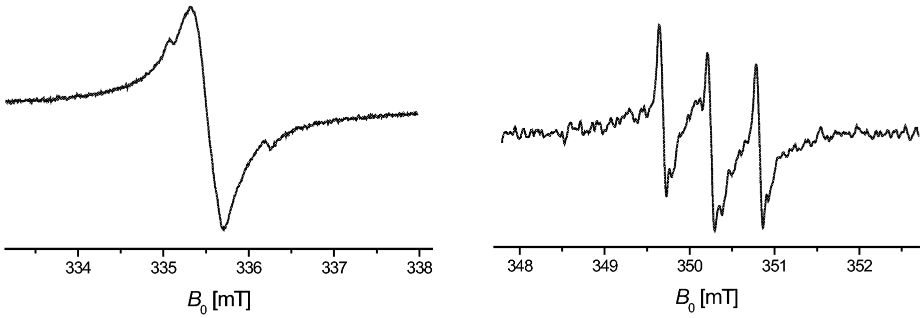

Fig. 1: Room temperature c. w. EPR spectra of N@C$_{60}$ peapods prepared as described previously (left) and using the improved protocol (right).

The interfering broad unstructured signal, which originates from empty SWCNT after preparation for insertion, can be suppressed by more than one order of magnitude, thus enabling spectral analysis of the nitrogen line triplet. In order to distinguish homogeneous and inhomogeneous line broadening, 2-pulse echo-induced EPR spectra were recorded. As shown in Fig. 2, N@C$_{60}$ as well as the broad line contribute to the echo-detected signal, i. e., both components are inhomogeneously broadened. Spectral decomposition is facilitated when measuring at 95 GHz, because first, the small g value difference of both signals leads to a more pronounced down field shift of the background signal, and, second, the width of the background signal scales nearly linearly with the field, thus increasing the relative N@C$_{60}$ signal intensity. This is in contrast to line width scaling behavior of N@C$_{60}$, for which only a factor of 3 increase in line width is observed.

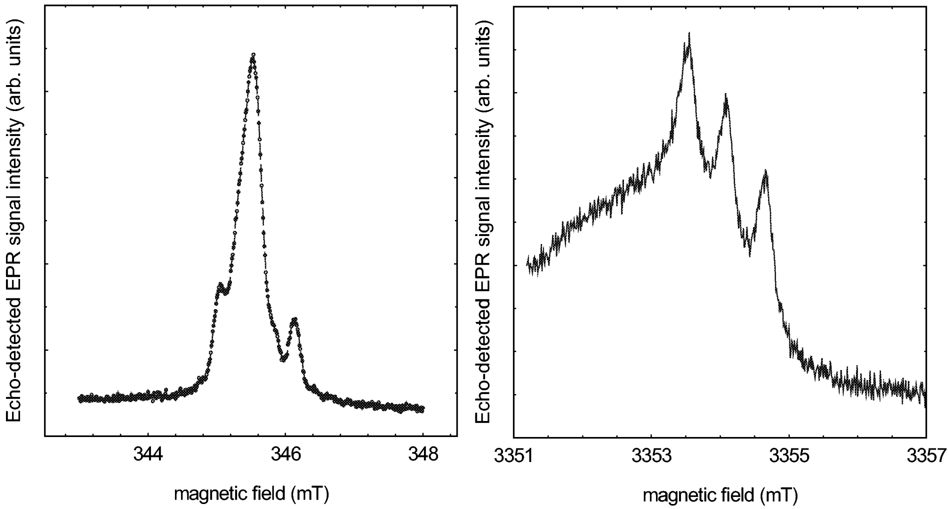

Fig. 2: Echo-induced EPR spectra of N@C_{60} peapods measured at 9.4 GHz (left) and 94 GHz (right) microwave frequencies.

For an identification of the dominant spin interaction, the temperature dependence of T_1 and T_2 relaxation times were studied. Using standard 2- and 3-pulse echo

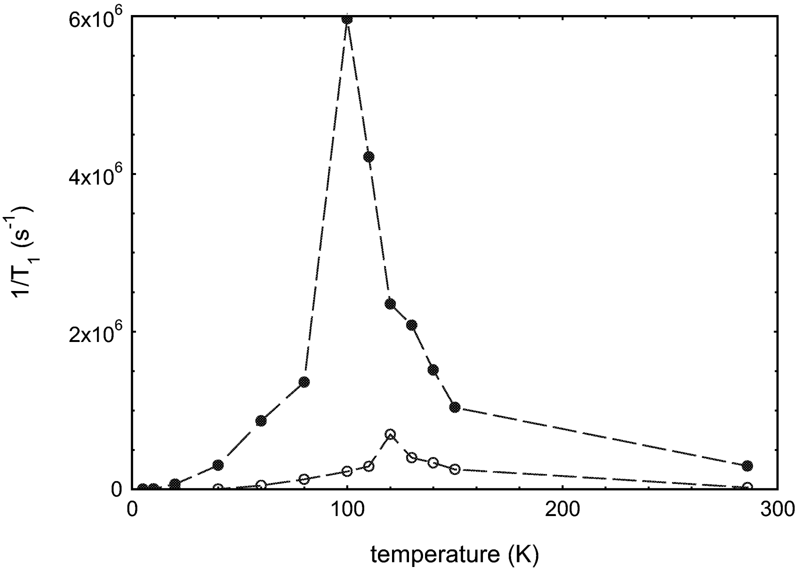

Fig. 3: Spin-lattice relaxation rates of N@C_{60}@SWCNT as function of temperature. Data are derived by fitting the echo signal intensity as function of T measured with a π-T-$\pi/2$-τ-π sequence. Both components of the bi-exponential fitting function are shown.

sequences for the determination of T_2 and T_1, respectively, the observed time dependence could be fitted by bi-exponential functions each. As shown in Fig. 3, the spin lattice relaxation rate T_1^{-1} shows a distinct rate maximum around 100 K. A spin-lattice relaxation rate maximum can be expected if the correlation time τ_c of the dynamic process is equal to the energy difference $\hbar\omega$ between electron spin levels, i. e., the condition $\omega\tau_c = 1$ is met. Assuming that spin relaxation is driven by a temperature-activated process, the temperature dependence of τ_c can be modeled as

$$\tau_c = \tau_0 \exp(E_a / k_B T) \tag{1}$$

with activation energy E_a and a fictitious high temperature lower bound τ_0 for the correlation time. The resulting T_1 rate is given by

$$T_1^{-1} \propto \frac{\exp(E_a / k_B T)}{1 + \omega^2 \tau_0^2 \exp(2E_a / k_B T)} \tag{2}$$

Using this simple model, the experimental data set can be described with E_a and τ_0 as fit parameters. The result is depicted in Fig. 4.

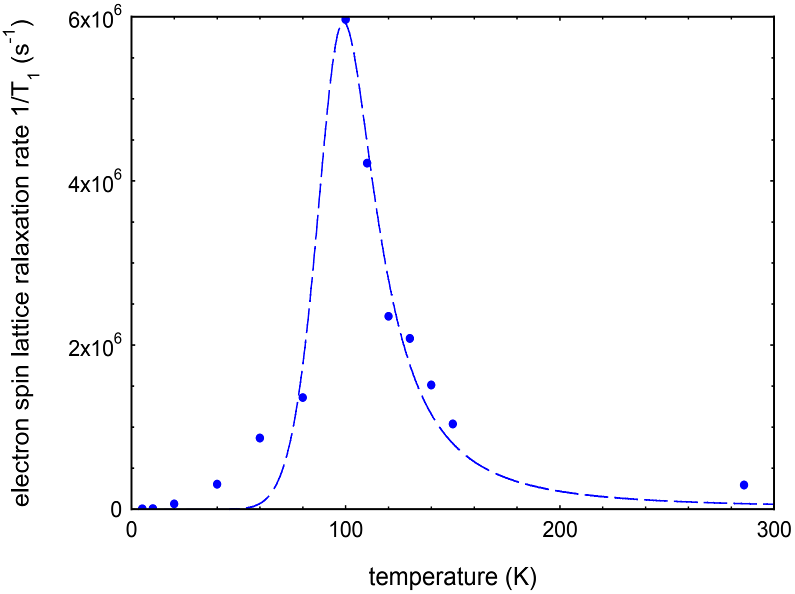

Fig. 4: Fit of the “fast” component of T_1^{-1} shown in Fig.3 using E_a = 67 meV and τ_0 = 6.3 fs.

According to Eq. (2), the width of the relaxation peak is only determined by E_a, whereas the peak position is also dependent on τ_0. The value of E_a can be related to the binding potential of C_{60} to the inner wall of the SWCNT of a few eV. To find an activation energy of a few percent of the total binding energy is not unexpected, considering the various possible binding sites. What is more surprising is that the dispersion of tube diameters is not mapped into a corresponding variation of activation energies.

For verification of the observed effect the relaxation rates of N@C_{70}@SWCNT were also determined. Here we found that two close lying rate maxima at 80 K and 110 K were observed. We tentatively correlate these maxima with different potential minima originating from C_{70} cages being stabilized parallel or perpendicular to the long axis of the SWCNT.

A further test for the validity of the presented relaxation model can be performed by increasing the Larmor frequency for instance by a factor of 10. Here from Eq.(2) it is predicted that first, the rate maximum is slightly shifted to higher temperatures, and second, the peak maximum is significantly depressed. This predicted reduction results from the decrease in spectral density because of a wider frequency spread of the total relaxation power. First experiments performed on the N@C_{70}@SWCNT sample were in qualitative agreement with this prediction.

ACKNOWLEDGMENTS

Financial support by the Deutsche Forschungsgemeinschaft under various grants, the MEIF-CT-2003-501099 EU project and the Austrian Science Funds FWF 14893 are gratefully acknowledged.

REFERENCES

1. Akasaka, T. and Nagase, S. , Eds., *Endofullerenes, A New Family of Carbon Clusters*, Kluwer Academic Publishers, Dordrecht, (2002)
2. Corzilius, B., Gembus, A., Weiden, N., Dinse, K.-P., Simon, F., and Kuzmany, H. in: *Molecular Nanostructures*, Eds.: H. Kuzmany, J. Fink, M. Mehring, S. Roth; AIP Conference Proceedings, N. Y. (2005)
3. Jakes, P., Dinse, K.-P., Meyer, C., Harneit, W., and Weidinger, A., *Phys. Chem. Chem. Phys.* **5,** 4080-4083 (2003).
4. Simon, F., Kuzmany, H., Rauf, H., Pichler, T., Bernardi, J., Peterlik, H., Korecz, L., Fülöp, F., and Jánossy, A., *Chem. Phys. Lett.* **383**, 362-367 (2004)
5. Gembus, A., Simon, F., Jánossy, A., Kuzmany, H., and Dinse, K.-P. in *Electronic Properties of Synthetic Nanostructures*, Eds.: H. Kuzmany, J. Fink, M. Mehring, S. Roth; AIP Conference Proceedings 723, N. Y. (2004), p. 259-263.