6 Conclusions and Perspectives

6.1 Conclusions

The properties of nitrogen and phosphorous encapsulated in the Buckminster–fullerene C_{60} have been investigated in view of an application as qubits in a quantum computer. Experiments have been done gathering information about the hyperfine coupling, the relaxation properties and the zero–field splitting of the group V endohedral fullerenes. Conclusions concerning the operation of a quantum computer built with these molecules have been drawn from this information.

The main focus was on P@C_{60}, as very little has been known about this material so far. Since the configuration of the outer electron shells is the same, P@C_{60} is expected to have similar properties as N@C_{60}. However, the larger van der Waals radius of phosphorous, the lower ionisation potential, and the positive electron affinity tend to increase the interaction of the encapsulated atom with the fullerene shell. Therefore, a lot of properties of the group V endohedral fullerenes show up more distinctly in P@C_{60}.

For the first time, the enrichment of P@C_{60} with HPLC has been shown. The retention time between the empty and the endohedral fullerene is more than twice as large as for N@C_{60}, indicating that P@C_{60} has a higher polarisability. Therefore, P@C_{60} is easier to enrich than N@C_{60}.

The hyperfine coupling of P@C_{60} is much larger than for N@C_{60}. Its temperature dependence is due to vibrations of the atom inside the C_{60} molecule. These vibrations could be described with a harmonic oscillator of energy $h\nu_0$ = 15 meV. This is a confirmation of the centre position of the phosphorous atom in the fullerene molecule.

The oscillatory motion of the endohedral atom is the main source of spin–lattice relaxation T_1 at temperatures T > 35 K. The vibrations of the endohedral atom lead to fluctuations of the hyperfine and fine structure coupling. As both interactions are stronger for P@C_{60} than for N@C_{60}, T_1 is shorter for P@C_{60} in this temperature regime.

Dipolar coupling of the endohedral electron spins to ^{13}C nuclear spins on neighbouring molecules and other endohedral spins takes over the relaxation process at temperatures T < 35 K. They are modulated by acoustic phonon modes of the C_{60} crystal. Therefore, the relaxation time and its temperature dependence are similar for P@C_{60} and N@C_{60} in this temperature regime. At low temperature, T_1 reaches seconds.

The spin–spin relaxation T_2 of P@C_{60} is quasi temperature independent. In contrast to ^{14}N@C_{60}, T_2 is affected by the spin–lattice relaxation at T > 35 K for P@C_{60} due to the shorter T_1 time. T_2 increases with decreasing spin concentration. Relaxation times T_2 up

to 28 µs have been measured for a sample with the spin concentration of 10^{-6} (ratio of filled to empty fullerene molecules). The "infinite dilution" limit was not reached in these experiments and spin–"flipflops" due to dipolar interactions were dominating the transverse relaxation. The maximum T_2, one can hope to reach for powder samples of endohedral fullerenes, is 1/2 T_1, which is about one second.

For the first time, transient nutation has been used to investigate spectroscopic properties of endohedral fullerenes. No evidence for anisotropic components of the hyperfine coupling could be found for P@C_{60}. From the dependence of the nutation frequency as a function of the applied magnetic field B_1, a zero–field splitting of $D/g_e\mu_B$ ~ 240 µT has been estimated at room temperature and $D/g_e\mu_B$ > 400 µT at T = 10 K. This is an interesting result, as no direct measurement of the zero–field splitting at room temperature has been possible so far, due to strong relaxation broadening of the (±3/2, ±1/2) transitions.

Different nutation frequencies for the (1/2, -1/2) transition and the (±3/2, ±1/2) transitions have been observed at T = 10 K. The ratio of the nutation frequencies is 2/v3, as expected from theory.

Nutation experiments do not only resolve spectroscopic properties of the material but are also important for quantum computing itself, since the nutation of a spin corresponds to one–qubit operations. It has been demonstrated that, without any refocusing, about 100 one–qubit operations can be done with N@C_{60} and still 60 for P@C_{60} at room temperature.

The time needed for a two–qubit gate depends on the coupling strength of the qubits. In the case of the endohedral fullerenes the dipolar interaction is supposed to mediate the qubit coupling. The maximum coupling of two endohedral spins with touching fullerenes is J/h = 52 MHz corresponding to a gate operation time of T_{gate} = 10 ns, which is of the same order as the one–qubit operations.

Unfortunately, such a strong dipolar interaction also leads to strong spin–spin relaxation and line broadening in a disordered ensemble. However, if the dipolar interaction is made uniform over the entire ensemble, this broadening can be avoided. The simplest model system for the demonstration of the control would be a dimer of endohedral fullerenes. Here, the distance between coupled spins is the same for each molecule. In order to achieve identical coupling it suffices to orient these dimers with respect to the external magnetic field B_0.

The orientation of molecules can be achieved using a liquid crystal matrix. This has been shown first for the monomers N@C_{60} and N@C_{70}. The orientation of these molecules is reflected in the splitting of the three ESR transitions due to the finestructure coupling. With this zero–field splitting, an order parameter O_{33} = 0.18 of the monomers in the liquid crystal matrix could be deduced.

In the next step this experiment has been repeated with "half–filled" $N@C_{60}–C_{60}$ dimers, which were produced especially for this purpose. However, in this case the order parameter was only $O_{33} = 0.013$.

Summarising the results, three important conclusions can be drawn for quantum computing with endohedral fullerenes:

(1) The relaxation properties of group–V endohedral fullerenes are mainly molecular. As long as the dipolar coupling is controlled, neither the spin–lattice relaxation nor the spin–spin relaxation will increase with increasing spin concentration. This means that additional qubits do not cause additional dephasing.

Thus, the experiments indicate that a quantum computer built from endohedral fullerenes is scalable with regard to the relaxation properties.

(2) 60 to 100 one–qubit operations can be performed without refocusing to eliminate the inhomogeneities. The same number of two–qubit operations should be achieved, if the coupling between the qubits is well defined. Using refocusing techniques, up to 2000 operations will be feasible as can be estimated from the maximum $T_2 = 28$ µs measured up to now. T_2 is expected to be much longer in the “high dilution” limit. A factor of 10 would be enough for quantum computing with error correction.

The experiments show that a sufficient number of quantum operations can be done for a proof of concept, once the dipolar coupling is controlled.

(3) The zero–field splitting observed in solid state $P@C_{60}$ and in $N@C_{60}$ in a liquid crystal matrix allows the selective excitation of the three ESR transitions. In principle it is possible to implement two qubits in one S = 3/2 spin.

6.2 Perspectives

As an extension to the single qubit operations measured by transient nutation spectroscopy, which used only the electron spin of the endohedral atom, one can now investigate two–qubit operations on fullerenes. This can be done in three different ways:

First, one can now try to make use of the S = 3/2 character of the spin system and try to implement the Grover Algorithm in a monomer aligned in a liquid crystal. A similar experiment has been done with a nuclear spin I = 3/2 with quadrupolar coupling [1]. However, this requires three different ESR frequencies and pulse shaping.

A second method to implement two–qubit operations in endohedral monomers would be to use all spin degrees of freedom, the electron as well as the nuclear, of the endohedral atom. Such an experiment will be feasible with a combined ENDOR (electron–nuclear double resonance) and ELDOR (electron–electron double resonance) set–up.

Third, in order to show the dipolar coupling concept the next obvious experiment is to use the "doubly–filled" dimer $(N@C_{60})_2$. The preparation of this material is now within experimental reach. However, a high degree of orientation is needed to control the

dipolar coupling. With the liquid crystals tested in this work, this goal could not be reached. Thus, a liquid crystal with a better order parameter for fullerene dimers has to be found.

Alternative ways should be investigated to align fullerene quantum registers and thus to control the dipolar coupling:

It is possible to synthesise fullerene molecules that show a liquid crystal behaviour themselves [2,3]. If endohedral fullerenes were stable during these types of chemical reactions, the orientation is expected to be very good.

A solid state approach, alignment of fullerenes in nano–pores, e.g. in PET foils [4] or aluminium oxide [5], would allow low temperature experiments. In this case, the dipolar coupling can be turned off by enforcing the magic angle, and it is possible to measure T_2 in the "high dilution" limit.

Last but not least, single–spin read out is necessary for the solid state implementation of a spin quantum computer. The problem of single spin measurements has attracted world–wide attention in the last years and experimental progress was made using STM–ESR (Scanning Tunneling Microscope ESR) [6,7] or MRFM (Magnetic Resonance Force Microscope) techniques [8], and optical read–out [9]. The application of these methods to $N@C_{60}$ and $P@C_{60}$ is the topic of a current European research project [10].