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MICROWAVE INDUCED OPTICAL NUCLEAR POLARIZATION

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ABSTRACT

The paramagnetic impurities used for dynamic nuclear polarization (DNP) are the main cause of nuclear spin-lattice relaxation and hence the origin of the finite life time of the nuclear polarization in frozen targets. We have shown that this problem can be overcome by using photoexcited triplet states for DNP.

1. Introduction.

As is well known dynamic nuclear polarization (DNP) is performed in solids doped with a small amount of paramagnetic centres. The electron spins of these centres are polarized by cooling the sample in a strong magnetic field. Then DNP is obtained by transfering this electron spin polarization to the nuclear spins by means of a strong microwave field.

A disturbing problem associated with DNP is due to the fact, that in isolating solids doped with paramagnetic centres the nuclear relaxation is completely due to these very centres. This means that nuclear polarization is destroyed by the same centres that are necessary for its creation by DNP. This problem is especially troublesome in the case of frozen spin targets, where one has to cool the sample by means of strong ^{3}He-^{4}He-dilution refrigerators in order to lengthen the nuclear relaxation time to an acceptable value.

A solution to this problem is the use of paramagnetic centres that can be hired when needed for DNP and subsequently fired when the nuclei are polarized. Such centres occur in molecular crystals: the molecules are diamagnetic in the ground state, but can be photoexcited into a paramagnetic triplet state. At present two groups are known to work on DNP using these optically excited triplet states. In Heidelberg one is able to obtain proton polarizations of about 30% [1,2]. In our group in Leiden we have reached a proton polarization of 42%. The present paper is intended to explain this method, which is called Microwave Induced Optical Nuclear Polarization (MIONP) [2].

2. The excited triplet state in molecular crystals.

Basic for the understanding of MIONP are the lowest excited states of a molecule in a molecular crystal as shown in Fig. 1. The molecule can be excited by means of ultraviolet light from a mercury arc into the lowest excited singlet state. Although most of the molecules decay back to the ground state via fluorescence, some molecules relax via so-called inter system crossing (ISC) into the lowest triplet state. This state lives in the order of milliseconds to seconds before the molecule decays via phosphorescence to the original singlet ground state.

The triplet state is a non-Kramers state with an electron spin S=1. Normally there is a zero field splitting of the order of a few GHz. Furthermore a magnetic field will cause a Zeeman splitting with a g-value, which is very close to 2. Of course this triplet spin is subjected to electron spin-

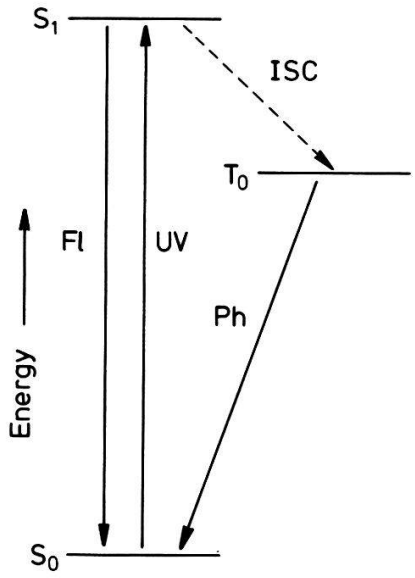

Fig. 1 The level scheme of a molecule in a molecular crystal.

lattice relaxation. However the life time of the triplet state is finite as well. Therefore one can discern two different cases. In the first case the electron spin-lattice relaxation time is much shorter than the life time of the triplet states. As a result the spin states will be populated according to the Boltzman distribution corresponding with the lattice temperature and the applied magnetic field. In the opposite case when the life time of the triplet spins is much shorter than the electron spin-lattice relaxation time, the lattice can be neglected. Then the population of the electron spin levels is determined by the optical transition probabilities governing the creation and annihilation of the triplet spins.

3. DNP with photoexcited triplet spins.

The Heidelberg group has concentrated on the case that the electron spin-lattice relaxation time is long compared to the life time of the triplet states. They use samples where directly after an exciting light pulse the electron spin polarization is very close to 100%. Subsequently this polarization is transfered to the nuclear spins by means of a microwave pulse [1]. The advantage of their method is, that the high electron spin polarization is obtained at very modest magnetic fields and temperatures. Using GHz microwave irradiation at liquid ^{4}He-temperatures they are able to reach about 30% proton polarization [2]. However, each triplet spin can be used only once to polarize a nucleus, because afterwards it has lost its own polarization. Hence the polarization process is very slow.

Our group in Leiden works on the opposite case where the electron spin-lattice relaxation time is short compared to the life time of the triplet state. Our experiments are performed on crystals of fluorene doped with phenanthrene (Fig. 2). Using a mercury arc the phenanthrene guest molecules are excited into the triplet state. The life time of this triplet state is

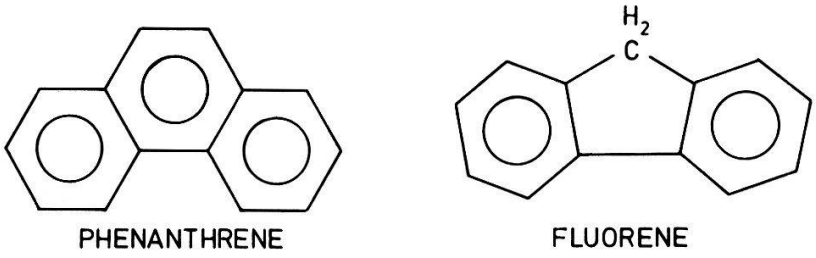

Fig. 2 The molecular structures of phenanthrene and fluorene.

about 10 s. while the electron spin-lattice relaxation time is only 10 ms. at 1.4 K and 2.7 T. Hence the spin states are populated according to the Boltzman distribution corresponding with the lattice temperature. DNP can now be achieved as in the classical case by means of a microwave field transfering the electron spin polarization to the nuclear spins. As in the classical case we need low temperatures and high magnetic fields to polarize the electron spins sufficiently in order to obtain subsequently a high nuclear spin polarization. The advantage of our case compared to that of the Heidelberg group is that each triplet spin can be used many times to polarize a nucleus, so the process is significantly faster.

For our experiments a special DNP-apparatus was built, operating at 1.4 K and 75 GHz, and featuring optical access to the sample. With this apparatus proton spin polarizations of 42% were achieved [3]. Figure 3 shows the growth of the nuclear polarization as a function of time. A detailed investigation of the nuclear polarization process showed that it is due to the solid effect [4].

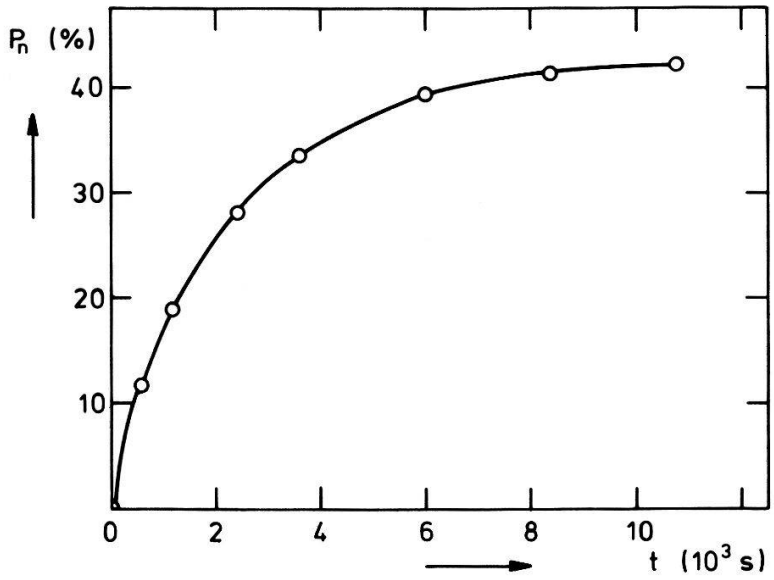

Fig. 3 The growth of the proton spin polarization during an experiment of MIONP.

4. Conclusion.

It has been shown that it is possible to obtain high nuclear spin polarizations in molecular crystals using photoexcited triplet states as paramagnetic centres. The results of MIONP-experiments in fluorene doped with phenanthrene at 1.4 K and 75 GHz yield a polarization which can easily compete with that obtained with the classical type of DNP. We expect that polarizations of 80% and higher are within reach if the experiments are extended to higher magnetic fields or to lower temperatures. Then, the procedure of MIONP might prove to be an interesting alternative to produce a frozen target.

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References

[1] M. Deimling, H. Brunner, K.P. Dinse, K.H. Hausser, J.P. Colpa, J. Magn. Reson. 39 (1980) 185.
[2] K.H. Hausser, private communication.
[3] H.W. van Kesteren, W.Th. Wenckebach, J. Schmidt, Production of high long-lasting dynamic proton polarization by way of photoexcited triplet states. Phys. Rev. Lett. 55 (1985) 1642.
[4] H.W. van Kesteren, W.Th. Wenckebach, J. Schmidt, The mechanism of microwave induced optical nuclear polarization in the system fluorene doped with phenanthrene. A qualitative analysis. Chem. Phys. Lett. 121 (1985) 440.

See also secretary's report, session(D), B. van den Brandt.