

Nuclear spin orientation via pulsed EPR and optically cooled triplet electron spins

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Abstract - In this paper we discuss a method to achieve high nuclear polarizations at room temperature using optically "cooled" triplet spins and pulsed EPR techniques. We present the results of experiments performed on a single crystal of naphthalene doped with pentacene guest molecules. By using pulsed laser excitation we populate the pentacene molecules almost exclusively in one sublevel of the lowest, metastable triplet state. Then by applying pulsed microwave fields we create an efficient transfer of polarization, via the Hartmann-Hahn condition for cross-relaxation, between the electron spins and the proton spins. Further we ensure that all electron spins in the inhomogeneously broadened EPR line participate in the transfer process. The result of our experiments shows that an unusually high proton spin polarization can be achieved and that the transfer occurs in a time determined by the dipolar interaction between the electron spins of the pentacene guests and the proton spins on the surrounding naphthalene molecules.

INTRODUCTION

One of the best known techniques to enhance the sensitivity of NMR is to increase the nuclear spin polarization by means of Dynamic Nuclear Polarization (DNP) [1]. In this method one usually introduces ground state paramagnetic centers into the sample and the larger electron spin polarization of these centers is transferred to the nuclear spins under microwave irradiation. Unfortunately, the ultimate enhancement of the nuclear polarization and hence of the NMR sensitivity is limited to the ratio of the gyromagnetic ratio of the electron spin and nuclear spin. Thus for proton spins the theoretical limit is about 660 and in practice rarely an enhancement of more than 300 is reached. To obtain high nuclear polarizations one therefore usually resorts to very low temperatures and strong magnetic fields.

An interesting development in DNP is the use of photo-excited triplet state molecules instead of ground state paramagnetic centers [2,3]. The attraction of these continuous wave, Microwave Induced Optical Nuclear Polarization (MIONP), experiments is that one can dispose of the paramagnetic states after the DNP process by simply shutting off the exciting light. In this way an important contribution to the relaxation of the nuclear polarization is suppressed. In the experiments by van Kesteren et al [2], where a final nuclear polarization was reported of 42 %, long-lived triplet states were used in thermal equilibrium with the lattice at 1.2 K. Here, however the MIONP technique suffers from the same limitations as in normal DNP. In a similar experiment, also performed at liquid helium temperatures, Brunner et al [3] used short-lived triplet states exhibiting a high non-equilibrium spin polarization resulting from a relatively slow spin-lattice relaxation rate. They showed that one can surpass the theoretical limit of 660 but the rate of polarization was prohibitively slow.

The solution to these problems is the use of pulsed EPR techniques in combination with pulsed lasers. The pulsed laser serves to create a strong electron spin polarization of the photo-excited triplet state molecules by taking advantage of the spin

selectivity in the optical pumping process. This polarization is subsequently transferred to the protons of the host crystal by applying strong pulsed microwave fields resonant with one of the EPR transitions of the triplet state. The purpose of the microwave field is to create a situation similar to the Hartmann-Hahn condition for cross-relaxation between rare and abundant spins in NMR experiments [4]. In our case the resonance frequency of the electron spins in their rotating frame is made equal to the resonance frequency of the nuclear spins in the laboratory frame and the exchange of spin polarization can take place very rapidly via the dipolar interactions that couple the two systems.

In this paper we shall discuss these experiments. First we present the results of an investigation of the cross-polarization dynamics between the triplet spin and the proton spins in a naphthalene crystal doped with pentacene using the method of Nuclear Orientation Via Electron Spin Locking (NOVEL) [3,5,6]. Then we show that by sweeping the magnetic field through the resonance condition in the presence of a strong pulsed microwave field an unusual large enhancement of the proton spins by a factor of 10^4 can be achieved at room temperature [7]. This method, which we have called the "Integrated Solid Effect" (ISE), promises to become an attractive technique for the enhancement of nuclear polarization.

EXPERIMENTAL

The DNP studies are performed on a single crystal of naphthalene containing about 0.01 mol % pentacene. The structure of the naphthalene crystal is monoclinic, of space group $P2_1/1$, with two molecules in the unit cell. The pentacene molecule replaces two translationally equivalent naphthalene molecules along the c-axis [8]. The experiments are performed with the magnetic field oriented along the long molecular axis, which makes an angle of 10° with the c-axis. In this orientation both sites become magnetically equivalent [9]. This orientation is established via a study of the angular dependence of the EPR lines of the triplet state. The EPR spectrum is obtained via Electron Spin Echo (ESE) detection and sweeping the magnetic field.

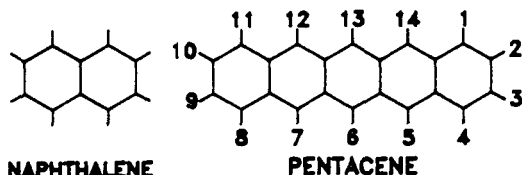


Figure 1. The guest molecule pentacene and the host molecule naphthalene.

The pentacene guest molecules are excited into their lowest triplet state with a nitrogen laser with a repetition rate of 50 Hz and an average power of about 70 mW. The microwave pulses needed for the ESE, NOVEL, and ISE experiments are provided by a pulsed EPR spectrometer operating at 9.15 GHz. A triple loop-gap resonator is used designed by Brunner *et al.* [10]. Two sets of coils situated right next to the sample serve to supply the fast magnetic field sweeps for the ISE experiments. After polarizing the nuclei the laser and the microwaves are shut off and the crystal is transferred to an NMR coil located outside the resonator to improve the NMR sensitivity. The nuclear polarization is obtained from NMR signals observed at a frequency of 26 MHz and a magnetic field of 0.61 Tesla using a simple Q-meter.

NUCLEAR ORIENTATION VIA ELECTRON SPIN LOCKING AND THE INTEGRATED SOLID EFFECT

Before discussing the experimental results we shall briefly describe the principles of NOVEL and ISE. In the two experiments a microwave field of amplitude B_1 and frequency ω is applied resonant with one of the EPR transitions. Then the effect on a spin packet in the inhomogeneously broadened line can best be described in a frame of reference rotating at frequency ω about the z-axis. In the NOVEL experiment a composite microwave pulse is applied consisting of a $\pi/2$ -pulse followed by a pulse of variable duration and with its phase shifted by an angle $\phi = \pi/2$ with respect to the $\pi/2$ -pulse. The microwave frequency is assumed to be equal to ω_s , the resonance frequency of our spin packet. As can be seen from Fig.2 the full electron spin polarization P_G is then locked to the microwave B_1 field of this pulse. When the amplitude B_1 of the locking pulse is adjusted such that $\sqrt{2}\gamma_s B_1 = \gamma_I B_0$ we fulfill the Hartmann-Hahn condition. In other words we have made the effective Zeeman splitting of

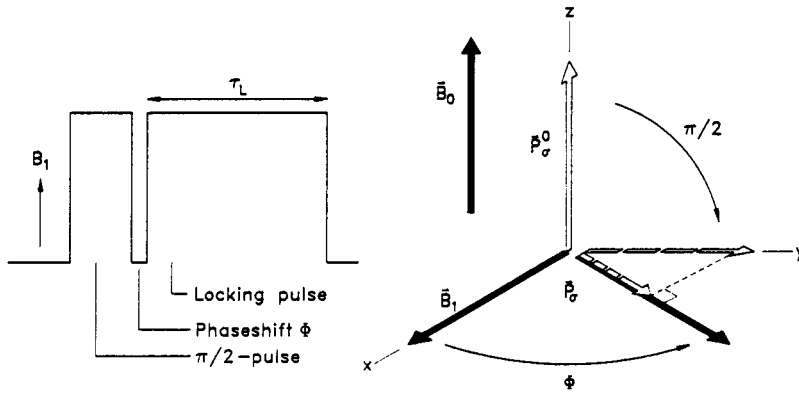


Figure 2. The composite microwave pulse in the NOVEL experiment and its effect on the electron spin polarization in the frame rotating with frequency ω about the externally applied magnetic field B_0 .

the electron spins in their rotating frame equal to the resonance frequency of the nuclear spins which experience the external magnetic field B_0 in the laboratory frame. As a result the electron spin polarization can flow to the nuclear spins under the influence of the dipolar interaction between the two spin systems.

We again consider the electron spin packet in the rotating frame but we assume that it is off-resonance by an amount $(\omega_s - \omega)$. As shown in Fig.3 it then experiences a reduced effective field

$$\omega_{eff} = \omega_R \bar{e}_x + (\omega_s - \omega) \bar{e}_z \tag{1}$$

which is canted by an angle α with respect to the original static magnetic field B_0 .

In the ISE experiment we perform an adiabatic passage through the complete EPR line. This is achieved by using a fast magnetic field sweep accompanied by a high power microwave irradiation at a fixed frequency. The resulting time-evolution of the effective frequency ω_{eff} is indicated in Fig.3.(a) If the passage is adiabatic, the electron polarization vector P_σ follows i.e. it stays parallel to ω_{eff} during the passage. We see from Fig.3. (b) that the condition for resonant transfer to the nuclear spins

$$\omega_{eff} = \gamma_I B_0 = \omega_I \tag{2}$$

is fulfilled twice and that both times the full amount of electron spin polarization is available for the transfer to the nuclei. Moreover all electron spin packets in the inhomogeneously broadened EPR line are involved in the same way.

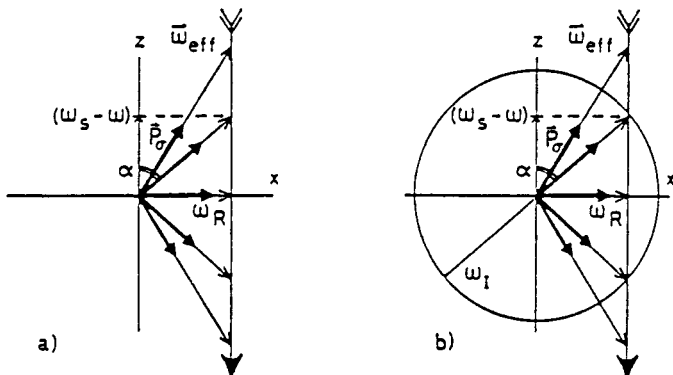


Figure 3. (a) The evolution of the effective frequency experienced by a spin packet at frequency ω_s during a sweep as performed in ISE. (b) The same scheme but now including a circle with radius ω_1 .

RESULTS AND DISCUSSION

The preparatory steps for the two cross-polarization experiment are the following. First a laser flash is given that excites the pentacene molecule into the vibrational manifold of the first excited singlet state. Subsequently it undergoes intersystem crossing to the lowest metastable triplet state. In this process the zero-field sublevel T_L , corresponding with the long molecular axis, is preferentially populated [11]. With an external magnetic field B_0 applied parallel to this axis we have the favourable situation that the sublevel $m_S = 0$ is equal to T_L and moreover that only two $\Delta m = \pm 1$ transitions are observable [9], occurring at 0.30 T and 0.35 T with our microwave frequency of 9.15 GHz. After the laser flash the effective electron spin polarization P_0^e pertaining to the high field transition, is no less than 73 % corresponding with a spin temperature of 0.23 K. Since the electron spin-lattice relaxation time is slow compared to the triplet lifetime of 20 μ s this high spin polarization is retained during the lifetime of the triplet state.

In the NOVEL experiment the composite microwave pulse is applied immediately following the laser flash resonant with the high-field transition. After the polarization transfer the triplet state decays to the singlet ground state with a time constant of 20 μ s. This sequence is repeated at a rate of 50 Hz (the repetition rate of the N_2 laser) during 3 minutes and the resulting nuclear polarization is measured via its NMR signal. Note that the accumulation time is short compared with the spin-lattice relaxation time of 40 minutes of the proton spins.

The dependence of the resulting nuclear polarization on the amplitude of the microwave field is presented in Fig.4 and it shows that a maximum occurs at a value where ω_{eff} is close to the proton Zeeman frequency of 15 MHz. With the amplitude of the microwave field fixed we then adjusted the phase shift to its optimum setting $\phi = \pi/2$. With B_1 and ϕ set at these optimum values we then measured the proton spin polarization as a function of the duration of the locking pulse τ_L . The result is shown in Fig.5 The complementary decrease of the electron spin polarization as a function of τ_L is obtained from the intensity of the free induction decay signal after the locking pulse. This FID was made visible by applying a π -pulse 0.5 μ s after the locking pulse and detecting the ensuing echo height. The result is shown in Fig. 6.

From the results presented in Fig.5 and Fig.6 it appears that the transfer of the electron spin polarization takes place in the order of a few hundred ns. More interestingly it is seen that the cross-relaxation exhibits an oscillatory behaviour. In a separate paper we have demonstrated that this time-dependent behaviour of the cross-relaxation process is caused by a dominant value in the spectrum of eigen frequencies of the dipolar interactions between the triplet spin of the pentacene molecule and the proton spins of the neighbouring naphthalene molecules [6].

The result of the fulfilled NOVEL experiment shows that once the resonance condition for cross-relaxation is fulfilled the polarization transfer occurs very rapidly on a time scale determined by the size of the dipolar interactions. The drawback is that only a fraction of the electron spins participate and that the final enhancement is limited to a factor of a few hundred. A great improvement is achieved by applying the ISE technique. This experiment was performed on the same high-field transition and by applying a strong microwave pulse accompanied by a fast magnetic field sweep immediately following the laser flash. By repeating this sequence at a repetition rate of 50 Hz during 60 minutes a maximum enhancement of a factor of 15 000 was achieved almost two orders of magnitude higher than the enhancement obtained with the NOVEL method.

CONCLUSION

We have demonstrated that a fast transfer can be achieved of the optically pumped electron spin polarization of a triplet state guest molecule to the nuclear spin system of a host crystal. The transfer rate is determined by the dipolar interactions between the triplet spins and the protons of the surrounding host molecules. The Integrated Solid Effect appears to be an efficient process because it uses all electron spins in the inhomogeneous EPR line. A great attraction is that it allows us to take advantage of the very large, optically induced electron spin polarization of short-lived photo-excited triplet state molecules, to enhance the polarization of nuclear spins to values that cannot be reached with systems that are paramagnetic in the ground state.

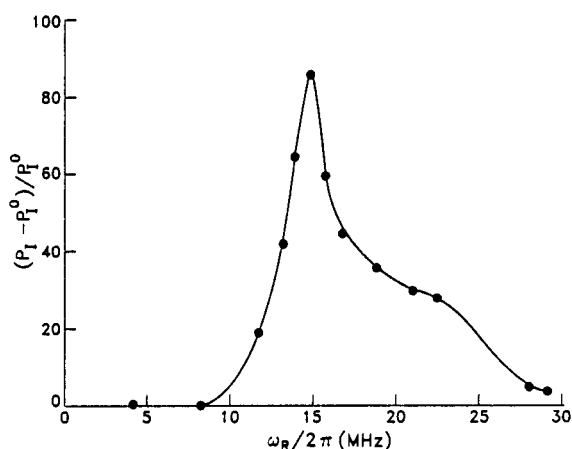


Figure 4. The dependence of the enhancement of the nuclear spin polarization on the Rabi frequency ω_R in a NOVEL experiment.

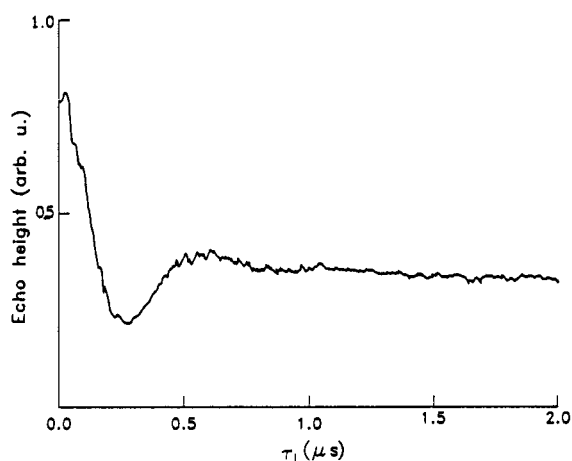


Figure 6. The intensity of the ESE signal induced by a π -pulse following the locking pulse. This signal is proportional to the electron spin polarization at the end of the locking pulse.

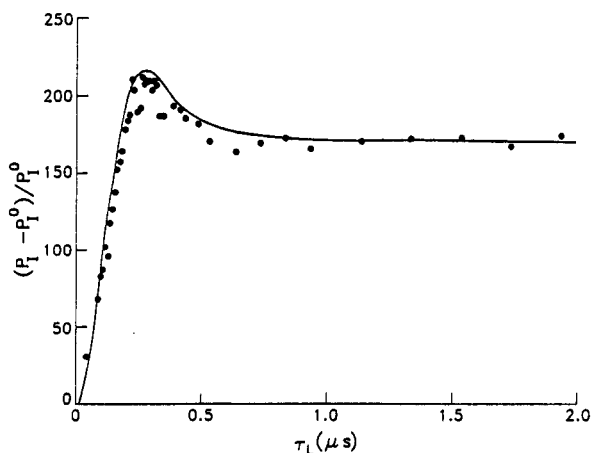


Figure 5. The enhancement of the nuclear spin polarization as a function of the length τ_L of the locking pulse in a NOVEL experiment. The points represent the experimental findings. The drawn line is the result of a theoretical model in which the dipolar interaction between the triplet electron spins and the nuclear spins is considered [13].

Acknowledgements

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