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Development and research of X-band dynamic nuclear polarization system

Y. Fujii[1], S. Mitsudo[1], M. Toda[1], H. Ito[2], S. Minami[2], Y. Ishiguro[2] and M. Chiba[2]

[1]*Research Center for Development of Far-Infrared Region, University of Fukui (FIR FU), 3-9-1 Bunkyo, Fukui-shi 910-8507, Japan*
[2]*Department of Applied Physics, University of Fukui, 3-9-1 Bunkyo, Fukui-shi 910-8507, Japan*

Abstract

In order to investigate the experimental technique and the high magnetic field effect in the dynamic nuclear polarization (DNP) experiments, the X-band ^{1}H-DNP experiments have been performed on a organic solution of α,γ-bisdiphenylene-β-phyenylallyl (BDPA) radical at room temperature. Because BDPA-doped toluene solution evaporated immediately during sub-THz irradiation, we tried DNP experiments with changing the solvent from toluene to benzene. As a result, we obtained similar DNP effects on the two solutions. We can expect that benzene solution is an appropriate sample for sub-THz DNP experiments. Further, we performed DNP measurements with degassed sample in order to avoid the relaxation due to oxygen in the sample solution. DNP enhancement observed in our measurements is well interpreted in terms of Overhauser effect.

1. Introduction

Dynamic nuclear polarization (DNP) is a variation of the double resonance technique in NMR spectroscopy, which has a history of more than 50 years. DNP results from transferring spin polarization from electrons to nuclei. Since electron spin polarization is much larger than nuclear one, NMR signal intensity can be largely enhanced by DNP effect. NMR has been widely applied to chemistry, biology, medical science, etc. as well as physics. Thus, DNP is considered as a promising method in near future in the research field of NMR.

In order to cause DNP, it is necessary to deviate electron spin polarization from its thermal equilibrium. This is why a high power light source is necessary for DNP. Most of DNP experiments have been performed at very low temperatures, where the power is required less than 0.1 W. Such a power level is achievable even by a Gunn oscillator. At higher temperatures (room temperature), on the other hand, much higher power is often required (especially for solid-state materials) because of short relaxation time of electron magnetic moment. Further, we need a millimeter/submillimeter wave above 100 GHz for DNP under the magnetic field of several teslas. So far, a gyrotron is the only watt-class high-power light source which has been used for DNP experiments in the power gap region of millimeter/submillimeter wave. [1]

We started from development of an X-band DNP system in order to accumulate techniques of DNP experiments and to enable to study in wide frequency range. [2]

2. Experimental

Schematic diagram of the X-band DNP system is shown in Fig. 1. This system consists of a conventional 5-to-400 MHz NMR instruments, an X-band ESR system with a TE011 cylindrical cavity ($Q \sim 10^4$), a sample shuttle system, and a 2 T electromagnet. As for the microwave source of ESR, we have used an yttrium-iron-garnet (YIG) oscillator and a traveling-wave tube amplifier (TWTA). The output from a TWTA is in the frequency range of 8 $\sim$ 12.4 GHz, and the maximum output power is more than 15 W. In order to avoid interference between copper coil for NMR and the cylindrical cavity, the NMR coil is positioned outside and adjacent to the cavity resonant space. The sample shuttle system is made with a programmable logic controller (PLC) and a pneumatic cylinder actuator (what is called, air piston). The sample is put in a glass tube, and transported between the NMR coil and the resonant cavity center within $\sim$ 0.1 s.

3. Experimental results and discussion

3.1 BDPA-doped toluene solution

As a test sample, we used a solution of an organic radical BDPA (BDPA = α,γ-bisdiphenylene-β-phyenylallyl). Figure 2 shows the microwave power dependence of
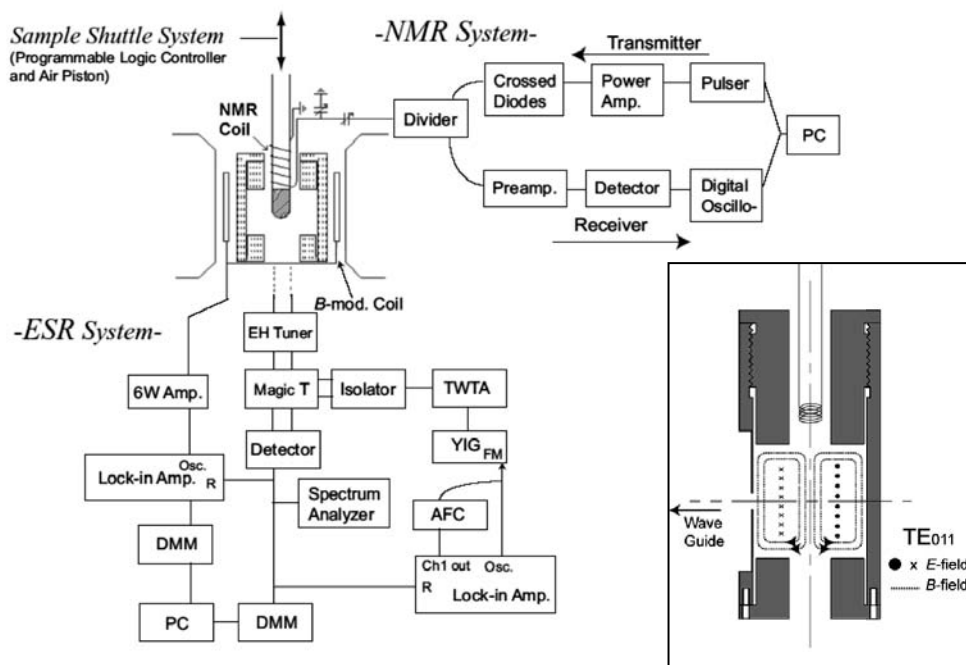
Figure 1: Schematic diagram of the X-band DNP system and a cross section of TE011 cylindrical cavity.

the ^{1}H-NMR spin echo signal of the BDPA-doped toluene with approximately 0.1 mol/L. ESR and NMR frequency was 11.3 GHz and 17.3 MHz, respectively. As the microwave power was increased, the intensity of spin echo signal first decreased, and then largely increased to the negative direction. The effect of microwave irradiation seemed to saturate around 0.7 W. The results indicate the existence of the Overhauser effect of the dipolar interaction origin. Note that the values of the power are different from those reported in ref. [2], because the microwave power irradiated *on the sample* were re-calibrated by bead-pull method. [3,4] One may feel that the value seems small, but the output power of TWTA is about ten times as large as the power irradiated on the sample. This is why we need TWTA.

Our goal is to develop DNP system in the millimeter/submillimeter region. However, as we reported previously [2], when the high power sub-THz wave (299 GHz) out of a gyrotron was irradiated on the BDPA-doped toluene in order to confirm the evidence of DNP, the sample has evaporated due to the electromagnetic wave heating. This may be because of electric dipole moment of toluene molecule. Then, we measured DNP by changing solvent from toluene to a nonpolar molecule benzene, and obtained qualitatively the same results, which is already reported (in Japanese) last year. [4]
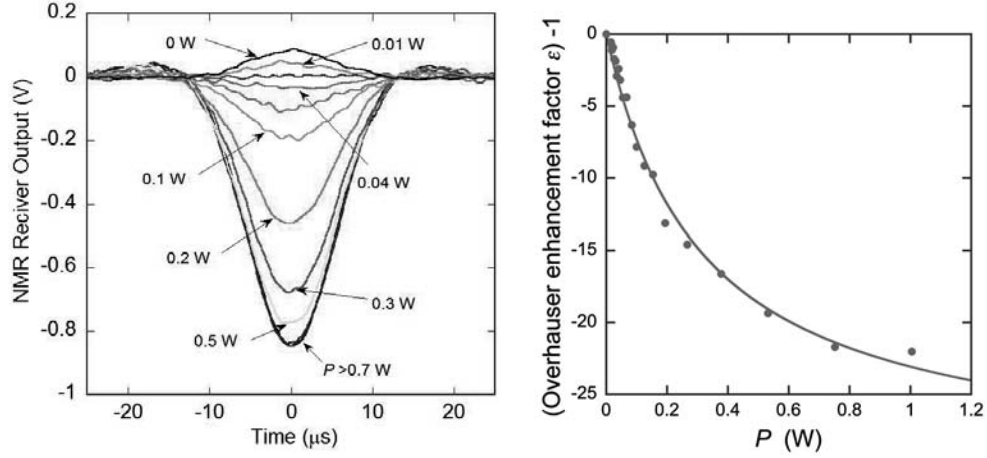
Figure 2: Microwave power dependence of the ^{1}H-NMR spin echo signal (left) and its intensity (right) of the BDPA-doped toluene with approximately 0.1 mol/L. The solid line in the right panel represents the best fit of eq. (1).

3.2 Overhauser effect

Here we define the Overhauser enhancement factor as $\varepsilon = \langle I_z \rangle / \langle I_0 \rangle$, where $\langle I_z \rangle$ and $\langle I_0 \rangle$ are nuclear polarization when the microwave irradiation is on and off, respectively. Overhauser enhancement factor ε is given by, [5]

$$1 - \varepsilon = \rho f s \gamma_e / \gamma_n. \tag{1}$$

In this equation, ρ is the coupling factor on the basis of dipole-dipole coupling between electron and nuclear spins, γ_e and γ_n are the gyromagnetic ratio of electron and proton, respectively. The leakage factor $f = (T_1^{-1})_{\mathrm{II}} / ((T_1^{-1})_0 + (T_1^{-1})_{\mathrm{II}})$, where $(T_1^{-1})_0$ is nuclear relaxation rate of solvent and $(T_1^{-1})_{\mathrm{II}}$ is that of BDPA-doped solution. The saturation factor s depends on the power of the irradiation microwave P, and it can be approximated as

$$s = \gamma_e^2 B_1^2 T_{1e} T_{2e} / (1 + \gamma_e^2 B_1^2 T_{1e} T_{2e}) = \beta P / (1 + \beta P), \tag{2}$$

where B_1 is the amplitude of the oscillating B-field, T_{1e} and T_{2e} are the spin-lattice relaxation time and the spin-spin relaxation time of electron, respectively, and we have put $T_{1e} T_{2e} \gamma_e^2 B_1^2 = \beta P$.

3.3 Degassed BDPA-doped benzene solution

All of our results mentioned above are well interpreted in terms of Overhauser effect with maximum enhancement factor about -20. In order to avoid the effect of oxygen in the sample, we further performed DNP measurements with degassed BDPA-doped benzene solution (~ 0.1 mol/L before degassing). Figure 3 shows the results. The absolute
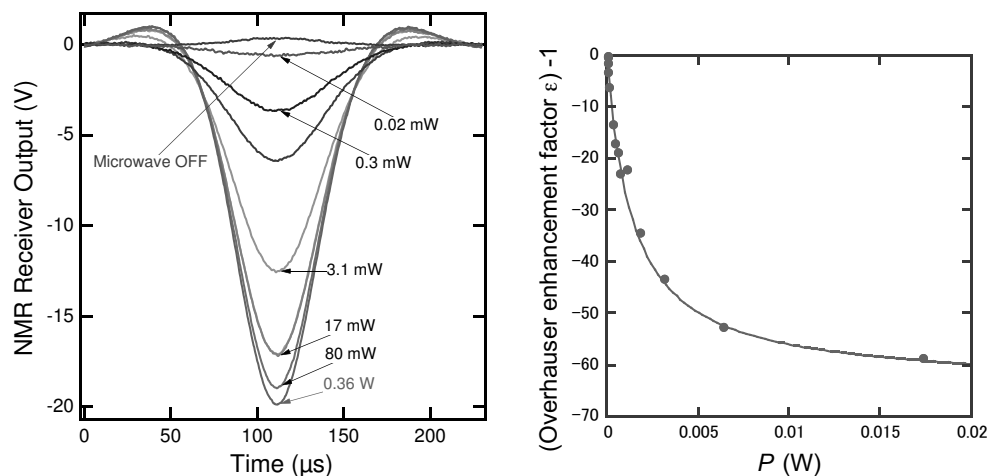
Figure 3: Microwave power dependence of the ^{1}H-NMR spin echo signal (left) and its intensity (right) of the degassed BDPA-doped benzene solution with approximately 0.1 mol/L. The solid line in the right panel represents the best fit of eq. (1).

value of the enhancement factor increased approximately three-fold as compared to that for non-degassed sample, which suggests increase of the leakage factor f. The dependence on the power P is well reproduced by eq. (1), being qualitatively the same as above cases. The fitting parameter β in the saturation factor s increased largely, though the reason for it is unclear at present. We found that the degassing was effective to perform DNP.

4. Summary

As a basic study of dynamic nuclear polarization (DNP) effect, we have performed DNP experiments at X-band at room temperature with liquid state samples. All results are well interpreted in terms of Overhauser effect. We found that benzene solution of BDPA is a candidate sample for DNP with millimeter/submillimeter wave from a gyrotron.

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