Microwave Induced Nuclear Polarization

K. H. Hausser

Max-Planck-Institut
Abteilung Molekulare Physik
6900 Heidelberg
West Germany

The polarization of nuclear spin I = 1/2 is defined by

$$p_n = (N_+ - N_-)/(N_+ + N_-)$$

where the population of the Zeeman energy levels N_+ and N_- is determined by the Boltzmann factor

$$N_- = N_+ e^{-\Delta E/kT}.$$

A larger nuclear polarization p_n is desirable for several reasons:

1) In NMR the quantity to be measured is the absorbed radiofrequency energy. Since transitions from the higher to the lower level (induced emission) are induced with the same a priori probability as those from the lower to the higher level, the net absorption and hence the signal-to-noise ratio of an NMR experiment is linearly proportional to the polarization p_n.

2) Many experiments in nuclear physics require targets in which nuclei are polarized as much as possible.

3) The interesting phenomenon of nuclear ordering as studied by Abragam and his group requires a very high nuclear polarization p_n as well.

The classical method to increase the nuclear spin polarization is the "solid effect" mainly developed by Abragam and Jeffries, where the Boltzmann polarization of unpaired electrons present in the sample is transferred to the nuclei by inducing forbidden transitions which flip one nucleus and one electron simultaneously (1,2).

A different method is the optical nuclear polarization (ONP) which we discovered in 1967. In this method the nuclear spins are polarized by their interaction with the unpaired electrons of an excited triplet state in a molecular crystal (3). It could be shown that the selection rules of spin-orbit coupling combined with the mixing of states in the triplet manifold by the hyperfine coupling results in different population (s_i) and decay rates (k_i) and hence in different equilibrium populations N_i of the electronic nuclear sublevels (4). This type of ONP produces an appreciable nuclear spin polarization p_n only in the level anticrossing (LAC) region of the external magnetic field.

More recently we have combined the ONP with the solid effect, i.e., the induction of forbidden transitions between the electronic nuclear sublevels. The polarization of nuclei with this mechanism, which was termed Microwave Induced Optical Nuclear Polarization (MI-ONP), is the subject of this paper.

The energy levels and the relevant parameters of an excited triplet state are shown in Figure 1. The three sublevels T_x, T_y, and T_z are non-degenerate even in zero field due to the dipolar interaction between the two triplet electrons. This zero-field splitting

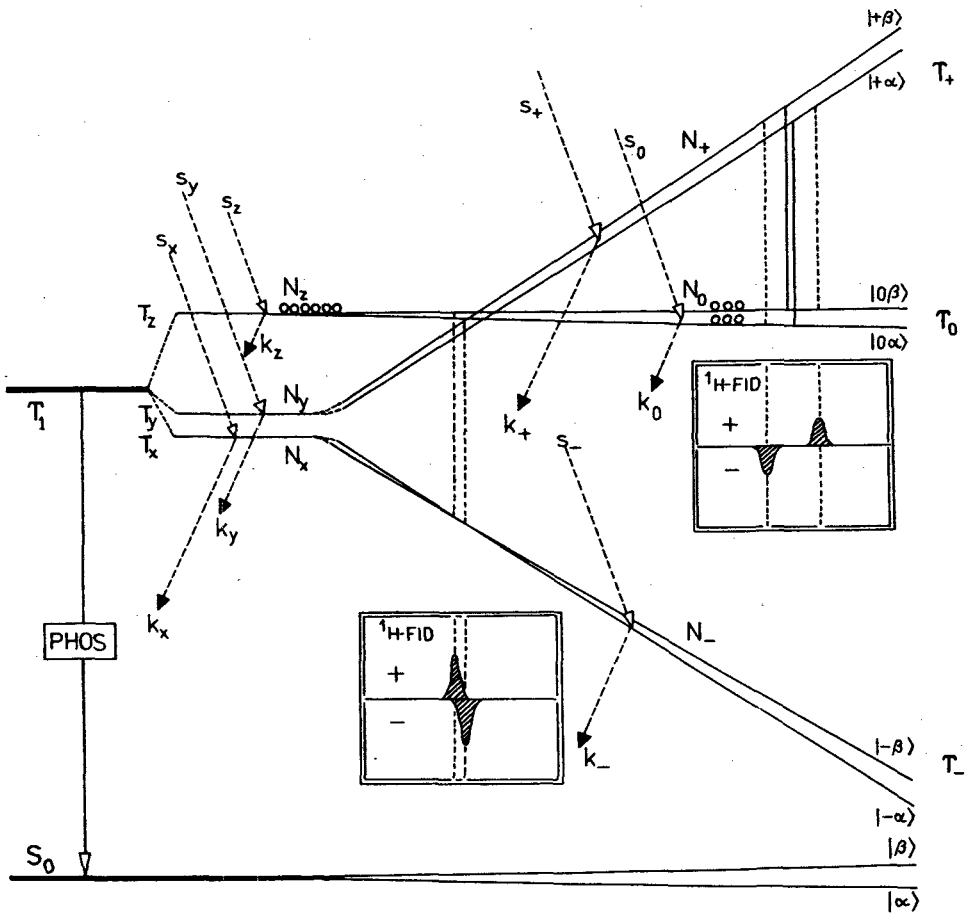

Figure 1. Energy levels of the first excited triplet state of an aromatic molecule in zero field and in an external magnetic field H_0 together with the population rate constants s_i, the depopulation rate constants k_i, and the steady-state population N_i. α,β = nuclear spin states, —— allowed ODMR transitions, ---- forbidden transitions.

is not negligible even at magnetic fields of a few Tesla and results in different energy differences between T_+ and T_0 and between the T_0 and T_- electronic substates. The population rates s_i, the depopulation rates k_i, and the equilibrium population constants N_i of the electronic triplet sublevels are not equal but subject to the selection rules of spin-orbit interaction.

We have performed our experiments in host-guest single crystals with a guest concentration of the order of 100-1000 ppm. We assume for simplicity reasons that the spin S = 1 is coupled with one proton with spin I = 1/2, and that the linewidth is smaller than the distance of the forbidden satellites from the allowed ESR transition so that they are completely separated, a situation which is termed "resolved solid state effect." We further assume that the highest level is exclusively populated in zero field, and hence in high field the T_0 level is populated, N_0 = 100%, while the upper and the lower levels are empty, $N_+ = N_- = 0$. Under this condition the induction of the allowed

transitions $\Delta m_S = \pm 1$, $\Delta m_I = 0$, produce the ordinary ODMR signal by changing the population of the levels involved. Induction of the forbidden transitions $\Delta m_S = \pm 1$, $\Delta m_I = \pm 1$, on the other hand, for instance at the high field side of the high field line, $|0\ \beta\rangle \rightarrow |+\ \alpha\rangle$, depopulates the β spin state and results in a positive polarization in the ground state S_0; note that the decay into the ground state does not affect the nuclear spins and conserves their orientation. In analogy, the forbidden transition at the low field side of the high field line produces a negative polarization.

The main difference of MI-ONP with respect to the solid effect with doublet states is twofold:

1) The selective population of the three electronic triplet sublevels is a consequence of the selection rules of the spin-orbit coupling *operator and is not proportional* to the magnetic field in contrast to the Boltzmann factor.

2) The second and perhaps most important advantage of using excited triplet states instead of doublet ground states is their short lifetimes of the order of milliseconds to a few seconds. If the exciting light is switched off, the unpaired triplet electrons vanish and leave a diamagnetic crystal with polarized nuclei which preserve their polarization for many hours or days due to the, in most cases, very long nuclear spin-lattice relaxation times T_1^n of spins I = 1/2 in diamagnetic samples at very low temperatures.*

---

*Recently van Kesteren et al. (5) have reported a nuclear polarization experiment with excited triplet states with short electronic relaxation times T_1^e in which they have used the electonic Botlzmann equilibrium. From this point of view their experiment is identical with the traditional solid effect, but it also has the important advantage number 2, i.e., the disappearance of the unpaired electrons

In the next section I shall discuss the favorable conditions for obtaining a high nuclear spin polarization. In principle, there are two possibilities, i.e., a steady-state experiment in which both the light for exciting the triplet state and the microwaves are irradiated continuously (6) and a time-resolved experiment where both light and microwaves are irradiated in short pulses (7).

Let us consider the two upper levels since the third one is not in resonance with the irradiated microwaves at a given external magnetic field and can hence be neglected. We have discussed above an idealized case where the T_0 level is exclusively populated and the T_+ level is empty; in practical cases we must look for a molecule where the population difference in the steady state is as high as possible $N_+ \ll N_0$ or $N_+ \gg N_0$, since this limits the maximum obtainable nublear spin polarization p_n.

However, in most cases the steady-state population difference is not very high, $N_+ \simeq N_0$ This is due to the fact that the selection rules of spin-orbit interaction for the population rates s_i of the triplet sublevels which are based on the admixture of some singlet character to one particular triplet sublevel are usually valid for the depopulation rates k_i as well. Let us assume that $s_0 \gg s_+$ and $k_0 \gg k_+$ with the result that $N_+ \simeq N_0$. In this situation it is obviously more promising to use a time-resolved MI-ONP, i.e., a short laser pulse, duration 10^{-8} s, and at the same time a microwave pulse of a time t_m which should be long enough to induce the forbidden transition, but short as compared to the lifetime τ^1 of the short-lived triplet sublevel (7), Figure 2. In this manner the effective population difference is proportional to the ratio of s_+/s_0 rather than of N_+/N_0. However, if the decay constants are very different, for instance, $k_0 \gg k_+$, another version of time-resolved MI-ONP may be applied: if the microwave pulse is applied after a decay time of

---

after switching off the light.

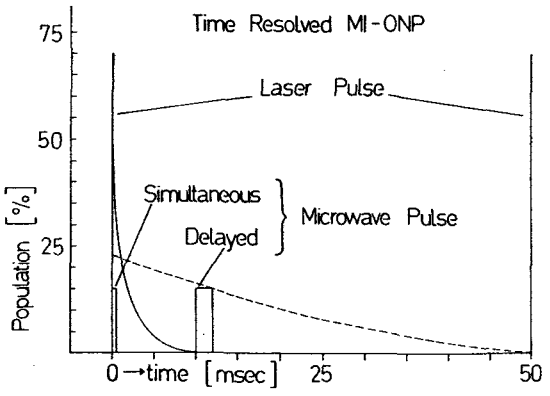

Figure 2. Time resolved MI-ONP with a laser pulse and simultaneous or delayed microwave pulse, schematic.

about five times τ^1, the short-lived triplet sublevel N_0 will be empty and the nuclear spin polarization obtained in this manner could in principle be complete, $p_n = 1$. In both cases this procedure must, of course, be repeated many times.

However, there is an additional aspect which we have not considered so far. When irradiating into the triplet exciton band of the host, the mobile excitons do not contribute to the MI-ONP because they are out of resonance with the applied microwave frequency, but they contribute to the nuclear spin-lattice relaxation; as a matter of fact, the interaction of the nuclei with the triplet excitons is their predominant relaxation mechanism compared to which the nuclear relaxation in the dark is negligible. The maximum obtainable nuclear polarization depends, of course, on the equilibrium between the MI-ONP and the nuclear relaxation. Hence we expect the maximum nuclear polarization with a system in which the first excited singlet state of the guest possesses a lower energy than the triplet exciton band of the host. In this case it is possible to excite the triplet state of the guest without exciting the triplet excitons in the host.

The last point I would like to discuss before showing experimental results is the time and light intensity required for MI-OPN. The size of our crystal was about 3X2X2 mm which corresponds with a specific weight of about 1.8 to 20 mg or to about $3X10^{20}$ protons. The intensity of the irradiation which we used with the mercury lamp was about 100 mW corresponding to about $2X10^{17}$ photons per second in the frequency range of 29000 cm^{-1}. When using a cw-laser the intensity was the same in order to avoid overheating the sample; in the case of the pulse laser the intensity was the same, i.e., 5 mJoule per pulse with a repetition rate of 20 s^{-1}. Assuming that 10% of the irradiated photons created an excited triplet state, the rest being lost due to imcomplete absorption and a quantum yield below one, we calculate that in 2 min 1% of the protons could be polarized which corresponds to an enhancement with respect to the nuclear Boltzmann polarization of a factor of 100. The maximum nuclear polarization which can be obtained depends, of course, on the equilibrium between the polarization and the nuclear relaxation; we estimate that this equilibrium will be reached after a time of the order of a few hours.

Let us now look at the experimental results. With the first system investigated, p-dichlorobenzene in p-dibromobenzene, we obtained under steady-state conditions an enhancement of the nuclear spin polarization p of about a factor of 10. A much higher polarization was obtained with the system benzophenone (BPh) in dibromodiphenylether (DDE), concentration about 1000 ppm. The population and depopulation rates of this system were investigated by several authors (8,9). The absolute values as given by Hochstrasser et al. (8) for the lifetime of the short-lived triplet sublevels are $\tau_0^1 \simeq 1.7$ ms and for the two long-lived triplet sublevels $\tau_+^1 \simeq \tau_-^1 \simeq 25$ ms, which corrsponds to decay rate constants $k_0 \simeq 580\ s^{-1}$ and $k_+ \simeq k_- \simeq 40\ s^{-1}$ or, in terms of percentage of the total decay, $k_0 \simeq 88\%$ and $k_+ \simeq k_- \simeq 6\%$. The relevant parameters are compiled in Table I. The numbers for the $S_0 \rightarrow S_1$ excitation in the guest BPh are taken from Hochstrasser et al. (8) who used a mercury arc for excitation, while those for $S_0 \rightarrow T_1$

Table I. Relevant Parameters of the Excited Triplet State of Benzophenone (BPH) in Dibromdiphenylether (DDE) for Different Excitation, in Percentage

Type of Excitation	Decay Rate Constants, $k_0 = 88\%, k_+, k_- = 6\%$							
	Population Rate Constant		Steady-State Population			First Msec Average Population		
	S_0	S_+, S_- (%)	N_0	N_+, N_- (%)	P_E (%)	N_0	N_+, N_- (%)	P_E (%)
$S_0 - S_1$ (BPh)	85	7.5	28	36	12.5	50	7.5	74
$S_0 - T_1$ (DDE) (YAG-Laser)	54	23	7	46.5	74	40	22.5	28

excitation into the triplet exciton band of the host DDE were measured in our laboratory using a YAG-laser with 28200 cm^{-1}; they differ slightly from those given in (8) with the same $S_0 \rightarrow T_1$ excitation but using a mercury lamp. Note that the equilibrium population N_0 of the triplet sublevel T_0 depends on the ratio s_0/k_0; hence due to the much larger decay constant k_0 the T_0 level is less populated in the steady state than the others in spite of its higher population rate constant s_0. Using the equation given in the beginning for the polarization p_e for the two-level system N_0 and N_+ with the numbers for $S_0 \rightarrow T_1$ excitation into the triplet band of the host DDE $p_e \simeq 74\%$ and for $S_0 \rightarrow S_1$ excitation in the guest BPh, $p_e \simeq 12\%$.

Figure 3 shows in the upper part the low field ODMR line in a magnetic field B_0 parallel to the z-axis of BPh and in the lower part the corresponding nuclear polarization p_n. The maximum enhancement which we have obtained with this system is about a factor of 840 which corresponds to a spin temperature of about 1.4 mK at a lattice temperature of about 1.2 K or to an absolute nuclear polarization of $p_n = 11\%$ (10).

In the next section we shall discuss the time resolved MI-ONP of Figure 2. As mentioned before, the experiment may be done in two ways: either the laser pulse and the microwave pulse are applied simultaneously, or the latter is applied after a certain time delay of the order of several τ_0^1, the lifetime of the short-lived sublevel. For the first case of simultaneous laser and microwave irradiation the excitation of the triplet sublevel T_0 should

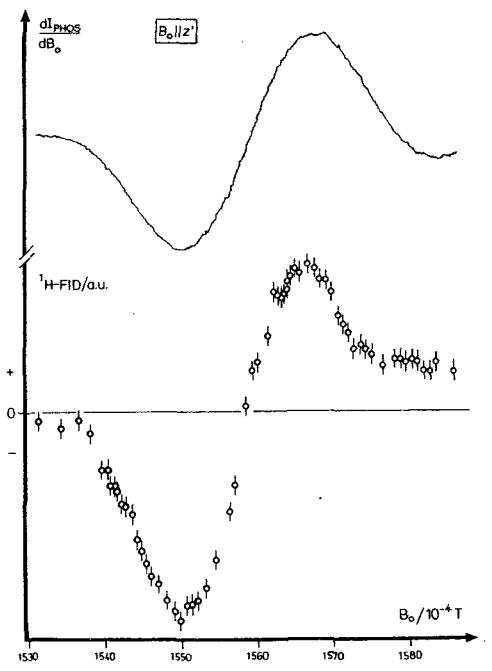

Figure 3. Low field ODMR line of benzophenone (BPh) in dibromodiphenylether (DDE) with the external magnetic field B_0 parallel to the C-O bond. Below the corresponding MI-ONP in arbitrary units.

be as selective as possible, $s_0 >> s_+ \simeq s_-$. For our system BPh in DDE this condition is best fulfilled using a laser frequency of 26000 cm^{-1} which excites the $S_0 \rightarrow S_1$ transition of the guest BPh, Table I. Note that the s_i given in the table do not add up to 100% because the lifetime τ_0^1 of T_0 is not short as compared to the microwave pulse, and we have therefore averaged N_0 over the first ms. Nevertheless, we expect an electronic polarization of the order of 75% in this case. For the other type of MI-ONP where the microwave pulse is irradiated after a delay of several τ_0^1, as much as possible of the excitation should go into the long-lived sublevel s_+, s_-. We learn from Table I that this occurs when using a laser frequency of about 29000 cm^{-1} which excites mainly $S_0 \rightarrow T_1$, the triplet state of the host, although the lower energy $S_0 \rightarrow S_1$ transition of the guest BPh is, of course, excited as well. However, this mixed excitation is already taken into account in the numbers given in the table.

We have carried out both experiments with a mixed crystal of BPh in DDE, concentration about 1000 ppm, a laser pulse of about 5 mJoule, duration 10^{-8} s, repetition rate 20 s^{-1}, and a microwave pulse of about 10 W and a pulse length of about .5 ms for the simultaneous irradiation and several ms for the irradiation with a delay of 10 ms. In both experiments we obtained a strong enhancement of the nuclear polarization, but this polarization remained hitherto below the 10% obtained with the stead-state experiment.

Let me conclude with the following remarks:

1. We have shown that it is possible to obtain a considerable nuclear polarization with the method of MI-ONP. Since the unpaired electrons vanish with the lifetime of the triplet state within seconds, the method provides a diamagnetic crystal with polarized nuclei for hours due to the very long spin-lattice relaxation time of nuclei with spin I = 1/2 at low temperature.

2. With the system of benzophenone in dibromodiphenylether we have reached a nuclear polarization of about 10% under steady-state conditions. Since we have studied only a few systems so far, this is probably not the most favorable system.

3. Theoretical considerations led to the conclusion that time resolved MI-ONP with short laser and microwave pulses could produce still appreciably higher nuclear polarizations. We have shown experimentally that the method is feasible but in the early stage of our experiments we have not yet reached higher nuclear polarizations than the 10% obtained under steady-state conditions. However, I am convinced that in principle this is possible with time resolved MI-ONP

REFERENCES

[1] A. Abragam and W. G. Proctor, Comt. Rend. *246*, 2253 (1958); A. Abragam, J. Combrisson, and I. Solomon, Compt. Rend. *247*, 2237 (1958); A. Abragam and M. Goldman, Rep. Prog. Phys. *41*, 395 (1978).

[2] C. D. Jeffries, Phys. Rev. *106*, 164 (1957); C. D. Jeffries, *ibid.* *117*, 1056 (1960); C. D. Jeffries, Dynamic Nuclear Polarization, Interscience, 1963.

[3] G. Maier, U. Haeberlen, H. C. Wolf, and K. H. Hausser, Phys. Lett. *25*, 384 (1967).

[4] J. P. Colpa, K. H. Hausser, and D. Stehlik, Z. Naturforsch., *A 26*, 1793 (1971).

[5] H. W. van Kesteren, W. Th. Wenkebach, J. Schmidt, and N. J. Poulis, Chem. Phys. Lett. *87*, 67 (1982).

[6] M. Deimling, H. Brunner, K. P. Dinse, K. H. Hausser, and J. P. Colpa, J. Magn. Reson. *39*, 185 (1980).

[7] K. H. Hausser, Laser Chem., in press.

[8] R. M. Hochstrasser, G. W. Scott, and A.H. Zewail, Mol. Phys. *36*, 475 (1978).

[9] S. Yamauchi and D. W. Pratt, Mol. Phys. *37*, 541 (1979).

[10] P. Bachert, Thesis, Heidelberg University, 1983.