TIME-RESOLVED MICROWAVE INDUCED OPTICAL NUCLEAR POLARIZATION

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The nuclear polarization p of a system of spins I = 1/2 is usually expressed as the difference of the population of the two Zeeman levels divided by the total number of nuclear spins $N = N^+ + N^-$

$$p = (N^+ - N^-)/N$$

Many NMR-experiments in molecular crystals suffer from an insufficient signal to noise ratio S/N. Since S/N is directly proportional to the nuclear polarization p_n, an increase of p_n is in general desirable. The interesting phenomenon of nuclear ordering requires a very high nuclear polarizationas well.

It was shown that a higher nuclear polarization can be achieved by transferring the high population differences of the electronic sublevels of photo-excited triplet states in molecular crystals to the nuclear spin system /1/. This transfer occurs in the level anti-crossing area of an external magnetic field B_0 /2/ or with simultaneous irradiation of light and microwave, a method which was termed microwave induced optical nuclear polarization (MI-ONP) /3/. The main advantage of the MI-ONP as compared to the classical method for obtaining high nuclear polarizations by transferring the Boltzmann polarization of the unpaired electrons of doublet ground states, e.g. free radicals, to the nuclei, termed solid effect, originates from the short lifetimes of the excited triplet states of the order of a few milliseconds to a few seconds. When polarizing the nuclei by their interaction with doublet ground states, the unpaired electrons are always present within the sample and may have undesirable effects in most experiments to be performed with the polarized nuclei. On the other hand, when polarizing the nuclei by their interaction with the unpaired electrons of photo-excited triplet states, the unpaired electrons vanish with the lifetime of the triplet states and leave a diamagnetic crystal with polarized nuclei which preserve their polarization for many hours due to the in most cases very long nuclear spin lattice relaxation time T_1 of spins I = 1/2 in diamagnetic solids at very low temperatures.

The population differences of the electronic sublevels of the excited triplet states which are transferred to the nuclei are in our case due to the in general very selective population rate s_i and the depopulation rates k_i which originate from the selection rules of spin orbit coupling. Note that van Kesteren et al. /4/ have reported a nuclear spin polarization experiment with excited triplet states in which they have used the electronic Boltzmann equilibrium in a magnetic field of 2.55 Tesla.

We have carried out our experiment with mixed crystals of Benzophenone or several 4,4'-substituted Benzophenones in the host 4,4'-Dibromodiphenylether (DDE), typical guest concentration a few thousand ppm. I shall concentrate the discussion here on 4,4' Dichlorobenzophenone (DCBP). Fig. 1 shows the energy level diagram, the excitation path of the excited triplet state of this system as well as the electronic sublevels of the excited triplet state of the guest in zero field and in external magnetic field B_0; note that the energy differences between these levels, right part of the figure, are largely enhanced as compared to the left part.

In this figure we assume for simplicity that the spin S = 1 is coupled to one proton with spin I = 1/2 and that we have the case of complete resolution,
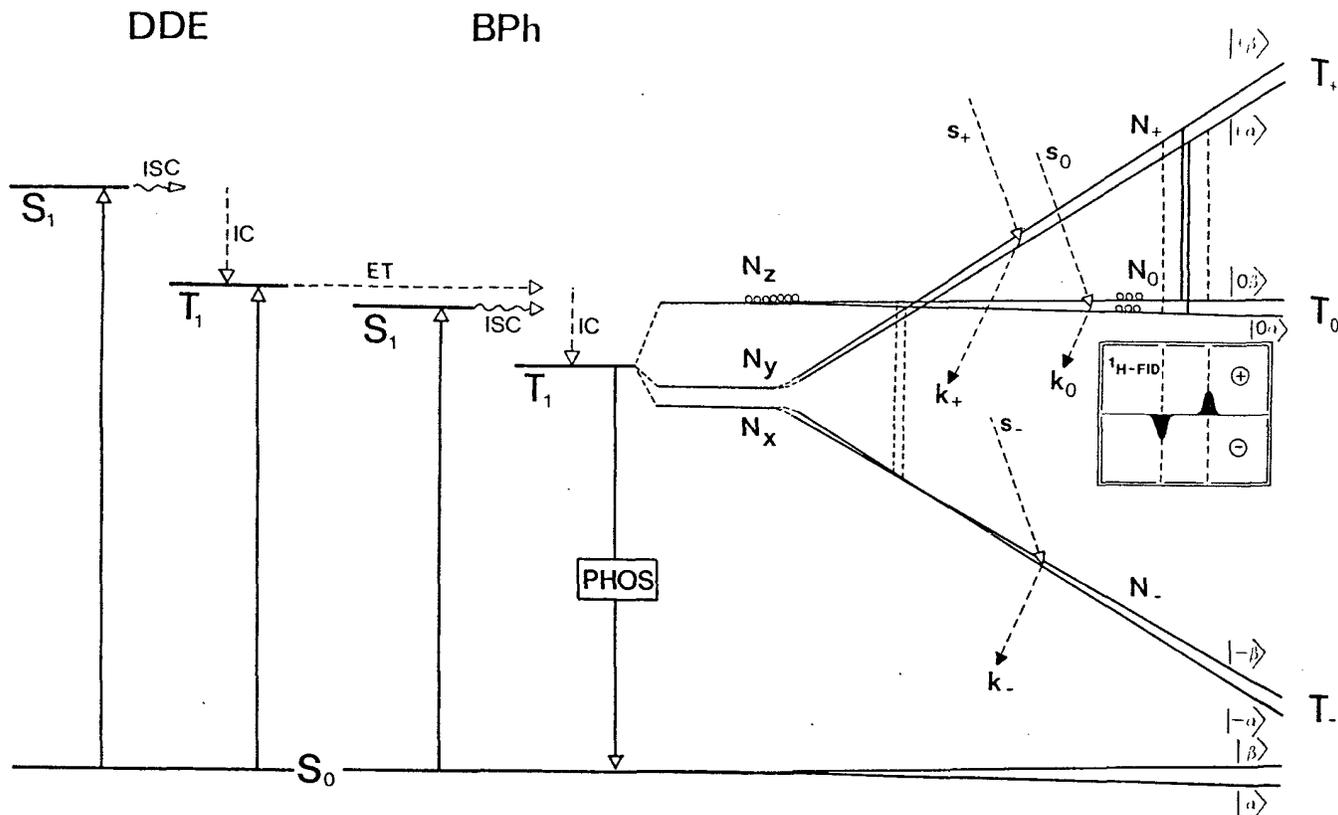
Fig. 1: Energy level diagram of 4,4'-Dichlorobenzophenone (DCBP) in
4,4-Dibromodiphenylether. Details see text.

i.e. that the linewidth is smaller than the distance of the forbidden satellites from the allowed transsitions.

In reality, not only one proton interacts with the unpaired triplet electrons, but eight protons in the DCBP-molecule and a certain number of protons in the neighbouring host molecules as well. This leads to the "differential solid effect", but it does not affect the principle of MI-ONP. At an arbitrary orientation of the ZFS-tensor axes with respect to the external magnetic field, all spin functions would be mixed by the field and any selectivity of the population would be averaged out. However, if one of the ZFS-tensor axes - which coincides in our system with the molecular z-axis - is oriented parallel to the magnetic field B_O, only the two other spin functions are mixed by the field and the T_z-level which becomes the T_O-level in high field might not be populated at all, $s_O = 0$, or is populated exclusively, $s_O = 100$ %.

We make the latter assumption and the even more simplifying assumption that in the steady state the T_O-level is exclusively populated, $N_O = 100$ %, while the upper and the lower levels are empty, $N_+ = N_- = 0$. In this case 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 two levels. On the other hand, induction of the forbidden transitions $\Delta m_S = \pm 1, \Delta m_I = \pm 1$, f.i. at the high field side of the high field line $|0\beta\rangle - |+1\alpha\rangle$, causes nuclear spins to be flipped from the ß-spin state to the α-spin state and hence produces a positive nuclear polarization. Similarly the induction of the forbidden transition at the low field side of the high field line produces a negative polarization. Note that the orientation of the nuclear spins is not affected by the decay to the ground state.

I have explained that a necessary condition for this mechanism is that one of the main axes of the ZFS-tensor which is determined by the molecular axis system is oriented parallel to the magnetic field B_O. In most molecular

crystals there are at least two or more non-equivalent molecules in the unit cell with different orientations of the molecular axis x,y,z with respect to the crystalline axis a,b,c; hence this condition can never be fulfilled for more than half (or less) of the molecules in the crystal. In the special situation of the DDE crystal the z-axis which is the twofold symmetry axis of the DDE molecules is parallel to the crystalline c-axis for all molecules. Furthermore, the x- and y-axis of the two inequivalent molecules form an angle of only $\pm$ 1°40' with the crystalline b-axis. The same is true for the DCBP-guest molecules since they enter the DDE-crystal substitutionally. This rare property renders the DDE-crystal particularly suitable for MI-ONP experiments.

The triplet state of the guest may be excited in two ways, i.e. by $S_o - T_1$ absorption in the host followed by energy transfer to the guest T_1-state or by $S_o - S_1$ absorption in the guest followed by intersystem crossing to the T_1-state. In our system the S_1-state of the guest has a lower energy as compared to the T_1-state of the host in distinction to most mixed crystals. Hence the T_1-state of the guest can be excited separately which has two important consequences both of which render our system favourable for MI-ONP. Firstly, excitation via one excitation path only produces a higher selectivity of the population rates s_i; for DCBP s_z = 96 %, while s_x = s_y = 2 % /5/. Seondly, the maximum obtainable polarization is always an equilibrium between the polarization with the rate $\dot{p}$ and the nuclear relaxation with the total rate constant $w_t = 1/T_1$. The latter is the sum of the relaxation in the dark with the rate constant w_d and the rate constant w_l

$$w_t = w_d + w_l$$

The relaxation rate w_d is very small and can hence be neglected. The relaxation rate w_l depends strongly on the frequency of the exciting light. If the frequency of the irradiating light cor-

responds to the $S_o - S_1$ transition of the guest, Fig. 1, one excites via intersystem crossing the localized T_1-triplet states only which are much less efficient in relaxing the nuclei then the mobile triplet excitons which are excited with a light frequency corresponding to the $S_o - T_1$ transition of the host or higher.

The maximum enhancement with respect to the Boltzmann polarization which we have obtained with a steady state experiment with the system BPh in DDE is about a factor 800 which corresponds to a spin temperature of about 1.4 mK at a lattice temperature of 1.3 K or to an absolute nuclear polarization of about 10 %, p_n = 0.1 /6/.

From the very selective population constants s_i one may expect considerably higher nuclear polarizations. However, in the steady state experiment the maximum obtainable nuclear polarization depends on the population differences between the energy levels $N_i - N_j$ in the steady state which are in general much lower than the differences in the population rates $s_i - s_j$. The main reason why it is so is the fact that the selection rules of spin orbit interaction for the population of the triplet sublevels, i.e. the admixture of some singlet character to one particular triplet sublevel, are usually valid for the selection rules for the depopulation as well. Hence we expect a higher polarization if we can design an experiment where the maximum obtainable polarization is proportional to the differences of the population rate constants $s_{i,j}$ rather than to the differences of the steady state populations $N_{i,j}$. This can be achieved with the method of time-resolved MI-ONP /7/ the principle of which is shown schematically in Fig. 2. The triplet states are excited with a short laser pulse, duration 10^{-8} sec, repetition rate about 10 per second. Simultaneously with the laser pulse a microwave pulse is applied for a time t_m short compared to the lifetime of the short-living triplet sublevel but long enough to induce the forbidden transition $\Delta m_S = \pm 1$,
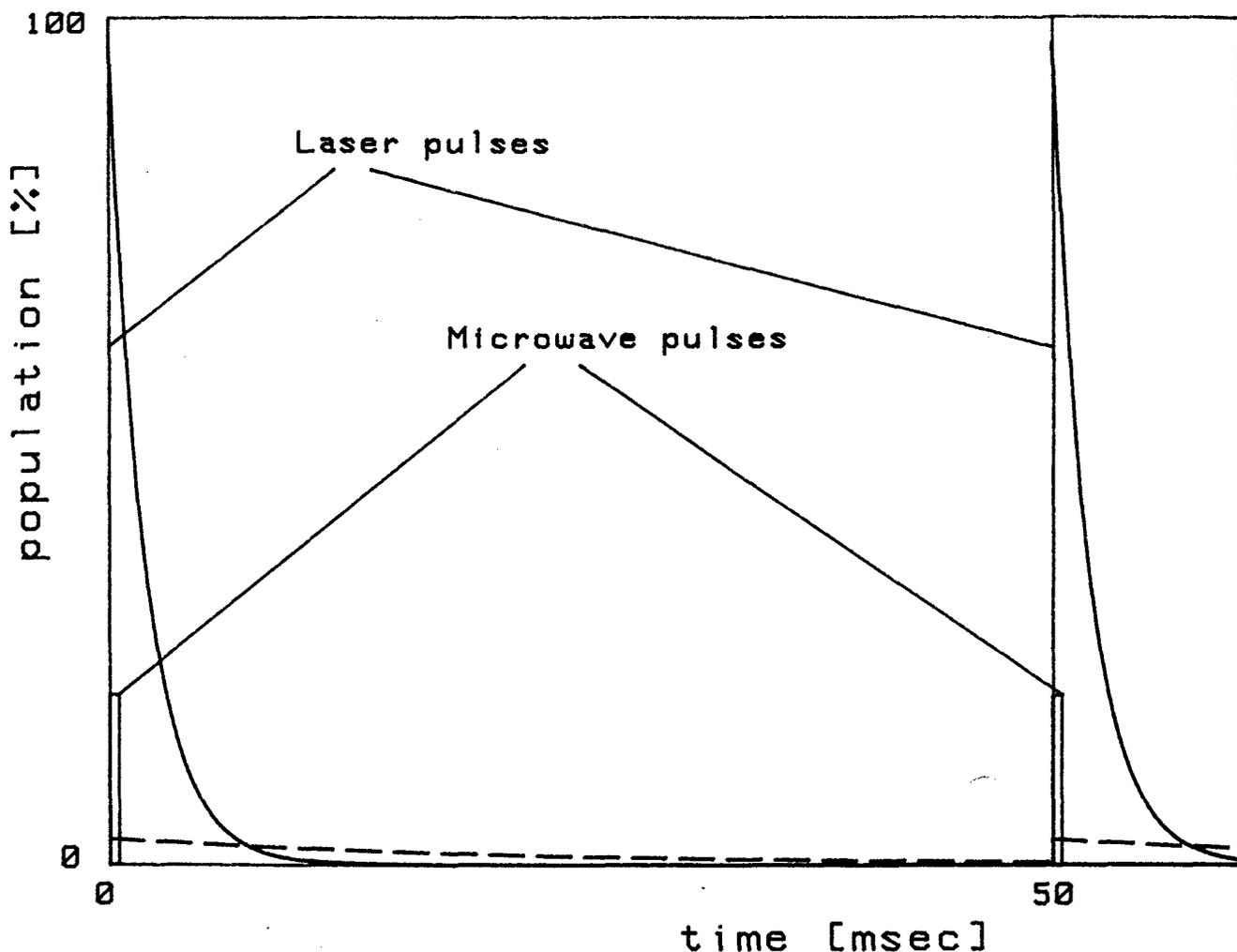
Fig. 2: Time resolved MI-ONP of 4,4'-Dichlorobenzophenone in DDE. Excitation via $S_o - S_1$ (DCBPh). Full and broken lines: Decay of the short-living and of the long-living electronic triplet substate, resp.

$\Delta m_I = \pm 1$ which depends, of course, on the microwave power. The full line marks the decay of the short-living sublevel and the broken line marks the decay of the long-living sublevel.

The best results, i.e. the highest polarization p_n which we have obtained so far with the time-resolved MI-ONP is $p_n = 0.33$ or 33 % compared to about 10 % with a steady state experiment. Although this polarization is more than a factor three higher than the one obtained with the steady state experiment, it is still about a factor two below the one expected on the basis of the high selectivity of the population states s_i. This is due to the fact mentioned above that the

maximum polarization p_{max} is determined by an equilibrium between the polarization rate $\dot{p}$ and the total relaxation rate w_t. The relevant relaxation rate w_t with $S_o - S_1$ excitation in the guest was found to be of the order of $5 \cdot 10^{-5}$ sec^{-1} corresponding to a relaxation time $T_1 = 2 \cdot 10^4$ sec $\approx$ 5 h. The measured polarization p_n after one minute was about 0.3 - 0.6 % corresponding to an initial polarization rate $\dot{p} = 5 \; 10^{-5}$ to 10^{-4}sec^{-1} at time t = 0. The range in which these numbers vary is considerably larger than the accuracy of each experiment which is partially due to the different quality of the crystals investigated; another reason for the variation of the results seems to

be the not sufficiently constant intensity of the laser beam – both effects require further experiments.

The numbers given above show that both quantities, i.e. the initial polarization rate $\dot{p}$ and the total relaxation rate w_t are of the same order of magnitude. Since the maximum polarization p_{max} depends critically on the ratio of the polarization rate $\dot{p}$ to the relaxation rate w_t, an increase of the former by increasing the intensity of the laser beam seems to be indicated. However, we operate near the upper limit of the irradiating intensity above which the crystal is damaged. Nevertheless, we are optimistic that a more detailed understanding of the mechanisms of both processes would enable us to increase the p/w_t ratio by a factor two with a corresponding increase of the maximum polarization p_{max}.

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