Cross Polarization in Electron Nuclear Double Resonance by Satisfying the Hartmann-Hahn Condition

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The polarization of electronic spins \(S\) is transferred to nuclear spins \(I\) by cross relaxation in an electron nuclear double resonance experiment. The cross relaxation becomes very efficient with a time constant \(T_{cr}\) of about 0.5 microseconds if the Hartmann-Hahn condition is satisfied for electronic spins spin-locked to the microwave field \(B_{1,5}\) in the rotating frame and for proton spins \(I\) in the static magnetic field \(B_0\).

We have performed a double resonance experiment in which the high polarization of electronic spins \(S\) of excited triplet states is transferred to nuclear spins \(I\) by cross relaxation. The essence of the experiment is that the cross relaxation becomes very efficient by satisfying the Hartmann-Hahn condition \([1]\) for electronic spins \(S\) spin-locked in the rotating frame by a microwave field \(B_{1,5}\) and the nuclear spins \(I\) in the laboratory frame; in this case the Hartmann-Hahn condition must be written in the form

\[
\omega_{1,5} = C \cdot \gamma_S B_{1,5} = \gamma_I B_0 = \omega_I, (1)
\]

where \(\gamma = [S(S + 1) - m(m - 1)]^{1/2}\) (see \((4)\) and \((81)\) in \([1]\); for \(S = 1\) \(\gamma = \sqrt{2}\). \(C\) must be added to take the anisotropic coupling of the electronic spins to the \(B_{1,5}\)-field into account. The phenomenon will be described in terms of the nuclear polarization \(p_\parallel = (N_+ - N_-)/(N_+ + N_-)\), where \(N_+\) and \(N_-\) are the populations of the nuclear Zeeman levels and the electronic polarization \(p_\parallel\) defined analogously with the populations of the two electronic triplet sublevels used in the experiment. It may as well be described in terms of Redfield's concept of spin temperature in the rotating frame \([2]\). The very low spin temperature of the electronic spins \(S\) in the rotating frame is very efficiently transferred to the nuclear spins \(I\) when switching on the coupling between the electronic and nuclear spins by satisfying \((1)\). A detailed theoretical treatment was given more recently by Vega et al. \([3]\).

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Our system was 4,4'-Dichlorobenzophenone (DCBP) in 4,4'-Dibromodiphenylether (DDE). The \(S\)-spins were the electronic spins of the excited triplet states of DCBP and the \(I\)-spins were protons. In this particular mixed single crystal at a canonical orientation with the molecular symmetry axis parallel to the magnetic field \(B_0\), and with an X-band microwave frequency of about 9 GHz, resonance transitions \(\Delta m_I = 1\) occur at low field at about 1900 G and at high field at about 5000 G \([4]\). Hence in order to fulfill \((1)\), the \(B_{1,5}\)-field must be about 2 G when spin-locking the electrons at the low field transition and correspondingly about 5.5 G at the high field transition. The set-up we used is a combination between an ESR-pulse-spectrometer and a conventional NMR-pulse-spectrometer. The crucial part is the probe which permits to perform a double resonance experiment at 1.3 K. It consists of a new type of resonator \([5]\) of very small volume and hence very high energy density. Furthermore, the resonator has a low \(Q\)-value of about 600 in order to reduce the dead time after a microwave pulse. A \(B_{1,5}\)-field strength of approximately 2 G was produced by about 2 W incident power, after attenuation by various microwave components, from a Hughes TWT-amplifier with nominal 20 W output power. After having finished the polarization transfer, the \(B_0\)-field was always set to the same value of 3340 G and the nuclear magnetization \(M_\perp\) was measured at a fixed frequency of 14 MHz in the same manner described previously \([6]\); the receiving RF-coil is included in the probe as well. The triplet states were excited with an excimer-dye-laser (Lambda-Physik EMG 101/FL 2001), which limited the repetition rate to about 10 Hz.

If the electronic magnetization \(M_\parallel\) would initially be at Boltzmann equilibrium in the magnetic field \(B_0\), the spin temperature of the electronic spins in the rotating frame would be reduced by a factor \(\omega_B/\omega_{1,5}\). However, when exciting a triplet state, the electronic sublevels are in most cases very selectively populated \([7]\); in the case of DCBP at the orientation given above the \(T_1\)-level is populated to 96% and the \(T_2\) and \(T_{2r}\)-levels are equally populated to 2% each \([4]\). Hence the electronic magnetization \(M_\parallel\) is even much higher and the spin temperature much lower than it would be if starting the experiment with the electronic spin system being in Boltzmann equilibrium in the static magnetic field \(B_0\).

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If the resonance condition \( \omega_s = \gamma_{s,\text{eff}} B_0 \) was exactly satisfied, any contribution of microwave induced optical nuclear polarization vanished [6, 8] and the observed polarization of the protons was entirely due to electron nuclear cross relaxation. This was also verified in an experiment where in order to spin-lock the \( S \)-spins the phase of the \( B_{1,S} \)-field was changed electronically by \(-90^\circ\) instead of \(+90^\circ\), resulting in an antiparallel instead of a parallel orientation of the electronic magnetization \( M_S \) with respect to the \( B_{1,S} \)-field. In this case the nuclear polarization \( p_1 \) was inverted as well with respect to the static magnetic field \( B_0 \).

In Fig. 1 the nuclear polarization \( p_1 \) is plotted as a function of the spin-locking time \( T_{SL} \) of the \( S \)-spins, i.e., the time during which cross relaxation occurs. For each data point the nuclear polarization \( p_1 \) built-up with 3000 cross polarization cycles was measured. The enhancement factor of the nuclear polarization \( p_1 \) as compared to the Boltzmann polarization \( p_{1,0} \) in the same magnetic field \( B_0 \) is estimated to be about 100.

The electron nuclear cross relaxation time \( T_{1,e} \) estimated from Fig. 1 is about 0.5 microseconds. This is in good agreement with the hyperfine interaction between the electronic spins \( S \) and the protons in DCBP, being of the order of several MHz. The slowing down of the increase of \( p_1 \) in Fig. 1 after several hundred nanoseconds is most likely due to the relaxation of the electronic spins in the rotating frame with the time constant \( T_{1,e} \). The predominant mechanism of this relaxation is in our system the electronic nuclear cross relaxation. In other words, if most electronic spins \( S \) which were excited with one laser pulse have undergone flip-flop-processes with protons, the electronic spin system is warmed up and does not cool down the nuclear spin temperature anymore. A more detailed paper will be published elsewhere.

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