

Adiabatic transfer of net electron polarization to nuclear polarization

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(Received 15 June 1995; revised version accepted 11 July 1995)

A new type of spin chemical experiment is suggested which utilizes adiabatic reversion of a low magnetic B_0 field for an efficient transfer of net electron spin polarization, as arising from some CIDEP mechanism, to the nuclear polarization of radicals. After trapping the radicals in diamagnetic products and transferring the sample to a NMR probe, the adiabatic polarization transfer effect can be measured as induced CIDNP, as in the recently established SNP method. The optimum conditions concerning delay time and duration of the B_0 field switching, as well as the trapping rate constant are analysed quantitatively for a radical with one nuclear spin $I = 1/2$. Owing to their efficiency and some parameters that can be controlled in the experiment, adiabatic polarization transfer effects should have clear advantages over experiments relying on DNP effects due to the Overhauser mechanism.

1. Introduction

A great variety of magnetic field and spin effects in chemical reactions have been discovered and studied in the past twentyfive years and the research field of spin chemistry has been established [1, 2]. The most prominent and most intensely studied of these effects occur with photo and radiation induced radical reactions in liquid solutions. The combined chemical, diffusional and spin dynamics of spin correlated radical pairs are of central importance here, and have been explored in stationary and time-resolved ESR experiments (CIDEP) [1], and by magnetic field dependent detection of product yield and transient kinetics (MARY) [3]. Concerning the effects of external magnetic fields, the behaviour of spin correlated radical pairs has been controlled by steady magnetic fields or by steady plus resonant radio or microwave fields. The latter situation is characteristic of the family of RYDMR spectroscopy methods [4], wherein the magnetic resonance spectra of the radical pairs are measured by monitoring the yield of some reaction product as a function of the radiofrequency or the field strength of the steady magnetic field. The recently developed stimulated nuclear polarization (SNP) [5] method is a variant of the RYDMR method where the 'yield' is detected by monitoring the nuclear spin polarization collected in some diamagnetic product of the radical reaction. In usual RYDMR applications the resonant B_1 field is applied throughout the lifetime of the radical pair. However, for obtaining time-resolved information, it also may be switched on, or off, or pulsed with variable delay during the radical pair lifetime [6].

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Recently, another variant of magnetic field variation was proposed, consisting of the fast switching of the *steady* magnetic field B_0 during the lifetime of radical pairs. First experiments of this kind were performed by Lavrik and Khmelinsky [7, 8] in a study of the magnetic field dependence of exciplex fluorescence originating from radical-ion pair recombination. More recently, Bagryanskaya and co-workers [9] applied fast switching of the B_0 field (field inversion, or stepwise changes of the field) to modulate CIDNP signal intensities originating from radical pairs in low magnetic fields. In these experiments the field changes (of the order of 20 G) were achieved during about 2 ns. It is these conditions of fast switching that are considered in a previous theoretical treatment by Doktorov and co-workers [10], who investigated the situation of infinitely fast (sudden) switching of the magnetic field.

In the present communication we want to show that the opposite extreme, i.e., *adiabatic* switching of the B_0 field, may be of great practical interest, too. It will be shown that adiabatic switching of the magnetic field can lead to efficient transfer of electron spin polarization, to nuclear polarization, so that one can monitor the CIDEP effects through the observation of CIDNP in the diamagnetic products of radical reactions, as in the SNP method [11].

2. Theory

In the course of a photochemical reaction, chemically induced electron spin polarization (CIDEP) may arise through two main mechanisms, the triplet mechanism and the radical pair mechanism. If triggered by a short laser pulse, the maximum of CIDEP intensity may be reached on the time scale of nanoseconds, i.e., at the resolution limit of time-resolved ESR. The subsequent decay of ESR intensity is determined by the decay of spin polarization through relaxation and by the decay of the radicals through radical recombinations or scavenging. Let us consider a situation (figure 1) where, in the presence of a constant magnetic field $B_{0,a}$ radical pairs have been produced by a short laser pulse applied at $t = 0$, and full CIDEP intensity has developed before $t = t_0$. Then, the magnetic field shall be reversed using a linear field gradient during a time interval τ which is supposed to be short on the

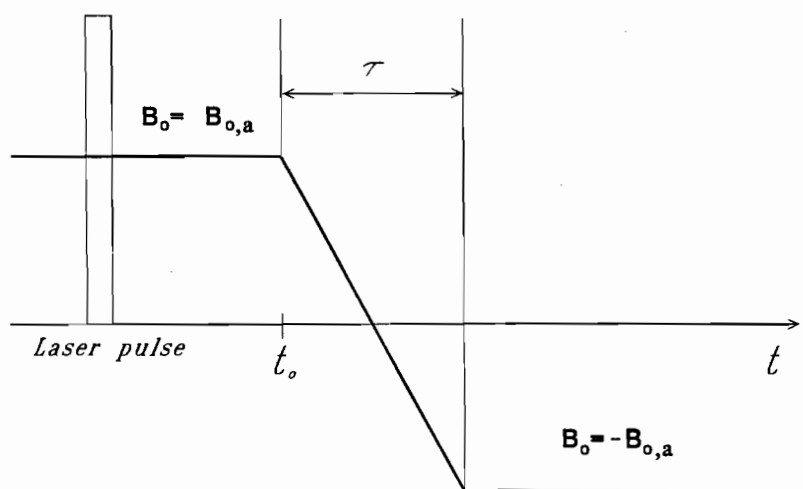


Figure 1. Time profile of magnetic field switching.

time scale of electron spin relaxation, but long enough to correspond to an adiabatic change of the spin Hamiltonian. Explicitly, the time dependence of the external magnetic field will be assumed to be given by

$$\begin{aligned} B_0(t) &= B_{0,a} & 0 \leq t \leq t_0 \\ &= B_{0,a} \left(1 - \left[\frac{2(t-t_0)}{\tau} \right] \right) & t_0 \leq t \leq t_0 + \tau \\ &= -B_{0,a} & t \geq t_0 + \tau. \end{aligned} \quad (1)$$

Let us consider how the polarization of a radical is affected by this field switching if, for convenience, we assume that the radical has only one nuclear spin with $I = 1/2$. For this purpose we have to know the eigenvalues and eigenstates of the spin Hamiltonian as a function of the external magnetic field. The spin Hamiltonian $\hat{\mathcal{H}}$ is given by

$$\hat{\mathcal{H}}(t) = g_e \beta_e B_0 \hat{S}_z - g_n \beta_n B_0 \hat{I}_z + A \vec{I} \vec{S} \quad (2)$$

Here, the terms $g_e \beta_e B_0 \hat{S}_z$ and $g_n \beta_n B_0 \hat{I}_z$ describe the Zeeman interaction of electron and nuclear spin, respectively, with time dependent (during the switching) external magnetic field B_0 ; g_e , β_e and g_n , β_n are the g factors and magnetons of electron and nucleus, respectively. The term $A \vec{I} \vec{S}$ describes the isotropic hyperfine interaction between electronic and nuclear spins; A is the hyperfine coupling constant.

In the field region where $B_0 > 0$ and $|B_0| \gg A$, the eigenstates and eigenvalues are given by

Case I

$$\left. \begin{aligned} |1\rangle &= \alpha_e \alpha_n; & E_1 &= \frac{1}{2}(g_e \beta_e - g_n \beta_n) B_0 + \frac{1}{4} A \\ |2\rangle &= \alpha_e \beta_n; & E_2 &= \frac{1}{2}(g_e \beta_e + g_n \beta_n) B_0 - \frac{1}{4} A \\ |3\rangle &= \beta_e \beta_n; & E_3 &= -\frac{1}{2}(g_e \beta_e - g_n \beta_n) B_0 + \frac{1}{4} A \\ |4\rangle &= \beta_e \alpha_n; & E_4 &= -\frac{1}{2}(g_e \beta_e + g_n \beta_n) B_0 - \frac{1}{4} A. \end{aligned} \right\} \quad (3)$$

Here, as usual, α and β denote the spin states with projections $S_z = 1/2$ and $S_z = -1/2$, respectively.

At $t = t_0 + \tau/2$ when $B_0 = 0$, the eigenstates are

Case II

$$\left. \begin{aligned} |1\rangle &= \alpha_e \alpha_n; & E_1 &= \frac{1}{4} A \\ |2\rangle &= \frac{1}{\sqrt{2}} (\alpha_e \beta_n + \beta_e \alpha_n); & E_2 &= \frac{1}{4} A \\ |3\rangle &= \beta_e \beta_n; & E_3 &= \frac{1}{4} A \\ |4\rangle &= \frac{1}{\sqrt{2}} (\alpha_e \beta_n - \beta_e \alpha_n); & E_4 &= -\frac{3}{4} A. \end{aligned} \right\} \quad (4)$$

Finally, for $B_0 < 0$, $|B_0| \gg A$,

Case III

$$\left. \begin{aligned} |1\rangle &= \beta_e \beta_n; & E_1 &= -\frac{1}{2}(g_e \beta_e - g_n \beta_n) B_0 + \frac{1}{4} A \\ |2\rangle &= \beta_e \alpha_n; & E_2 &= -\frac{1}{2}(g_e \beta_e + g_n \beta_n) B_0 - \frac{1}{4} A \\ |3\rangle &= \alpha_e \alpha_n; & E_3 &= \frac{1}{2}(g_e \beta_e - g_n \beta_n) B_0 + \frac{1}{4} A \\ |4\rangle &= \alpha_e \beta_n; & E_4 &= \frac{1}{2}(g_e \beta_e + g_n \beta_n) B_0 - \frac{1}{4} A. \end{aligned} \right\} \quad (5)$$

Note that, independent of the polarity of the B_0 field, the basis states α, β in all of equations (3)–(5) are defined with respect to the initial orientation and polarity of the z axis. For all values of the magnetic field B_0 , $\alpha_e \alpha_n$ and $\beta_e \beta_n$ are eigenstates of $\hat{\mathcal{H}}$. So, in passing from situation I to III, the state of highest energy $|1\rangle$ moves linearly down to state $|3\rangle$, whereas state $|3\rangle$ in situation I moves linearly up to state $|1\rangle$ in situation III. At $B_0 = 0$ the corresponding levels cross without mixing of the states. It should be noted, however, that this is true only if the B_0 field really passes through zero [12], which is not exactly the case if some constant transverse component of a steady magnetic field, e.g., the earth's magnetic field, is present (cf. insert in figure 2). Whether a state mixing will become effective in passing the crossing region depends on the ratio of the residual field and the rate of passage through this region. The anticrossing effect of a residual field can be neglected if the rate of passage through the crossing region is in the non-adiabatic limit. Below, we shall estimate the conditions for a non-adiabatic passage through the residual field region.

For $\alpha_e \beta_n$ and $\beta_e \alpha_n$ there is a well defined anticrossing at $B_0 = 0$, with a splitting energy of A . Thus, in an adiabatic passage through the anticrossing region, $\alpha_e \beta_n$ is transferred to $\beta_e \alpha_n$ and $\beta_e \alpha_n$ to $\alpha_e \beta_n$, implying a full exchange of polarization between electronic and nuclear spin.

Such an efficient adiabatic polarization transfer (APT) may be of great interest to exploit experimentally. It could be detected as a strong CIDNP signal after trapping the nuclear spin polarized radicals in diamagnetic products. For such applications it would be required that the radicals be trapped before nuclear

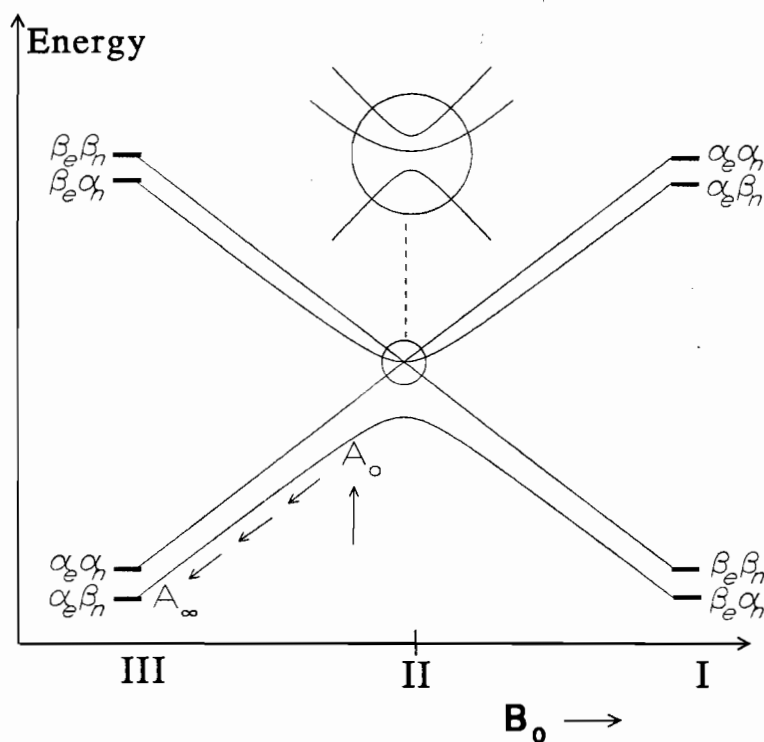


Figure 2. Schematic energy correlation diagram with varying external field strength for a two-spin electron–nuclear system with $S = 1/2$, $I = 1/2$. The state labels (electron–nuclear spin function products) refer to basis states quantized along the positive B_0 direction. The trajectory $\rightarrow A_0 \rightarrow \rightarrow A_\infty$ refers to a comparison with the ALTADENA effect (see text).

relaxation takes place (cf. below). This requirement sets an upper limit to the switching time τ of the magnetic field. On the other hand, a lower limit to τ is due to the condition that the time-dependent behaviour of the spin system should remain within the adiabatic limit.

An estimation of this lower bound to τ can be given on the basis of Landau-Zener theory [13]. For example, starting out from spin state $\alpha_e\beta_n$ at $t = 0$, when $|B_0| \gg |A|$ (state $|2\rangle$ of case I), the Landau-Zener probability W_{22} to reach $\beta_e\alpha_n$ when $B_0 < 0$, and $|B_0| \gg |A|$ (state $|2\rangle$ of case III) is given by

$$W_{22} = 1 - \exp\left(-\frac{\pi\gamma_e^2 A^2}{2h_0}\right), \quad (6)$$

with

$$h_0 = \gamma_e \frac{dB_0(t)}{dt} = \frac{2\gamma_e B_{0,a}}{\tau}. \quad (7)$$

Thus, the adiabatic limit (i.e., $W_{22} \rightarrow 1$) is characterized by the criterion

$$\frac{dB_0(t)}{dt} \ll \gamma_e A^2. \quad (8)$$

If, for example, we choose $A = 5$ G

$$\frac{dB_0(t)}{dt} \ll 0.44 \text{ G ns}^{-1}; \quad (9)$$

i.e., for $B_{0,a} = 10$ G we require

$$\tau \gg \frac{2B_{0,a}}{\gamma_e A^2} = 45 \text{ ns}. \quad (10)$$

On the other hand, from relation (8) we can derive the condition for essentially non-adiabatic passage of the crossing region in the presence of a small residual transversal field $B_r = 1$ G. Substituting B_r for A we obtain

$$\frac{dB_0(t)}{dt} \gg 0.018 \text{ G ns}^{-1}, \quad (11)$$

i.e., for $B_{0,a} = 10$ G the switching time for field inversion should be shorter than 1100 ns, which clearly is compatible with condition (10).

3. Discussion

To see the concrete effects that can be achieved by the adiabatic switching technique, we will consider initial electron spin polarization due to two characteristic mechanisms: the triplet mechanism and the $T_0 - S$ radical pair mechanism. In the former case, electron spin polarization is independent of nuclear spin. An example of a CIDEP spectrum corresponding to enhanced absorption is shown in figure 3. On adiabatic switching of B_0 the electron polarization disappears completely while, according to the correlation diagram (figure 2), the polarization is transferred fully to the nuclear spin. The CIDEP spectrum has collapsed but, after trapping the radicals, the diamagnetic product will show CIDNP emission due to a preponderance of β nuclear spins.

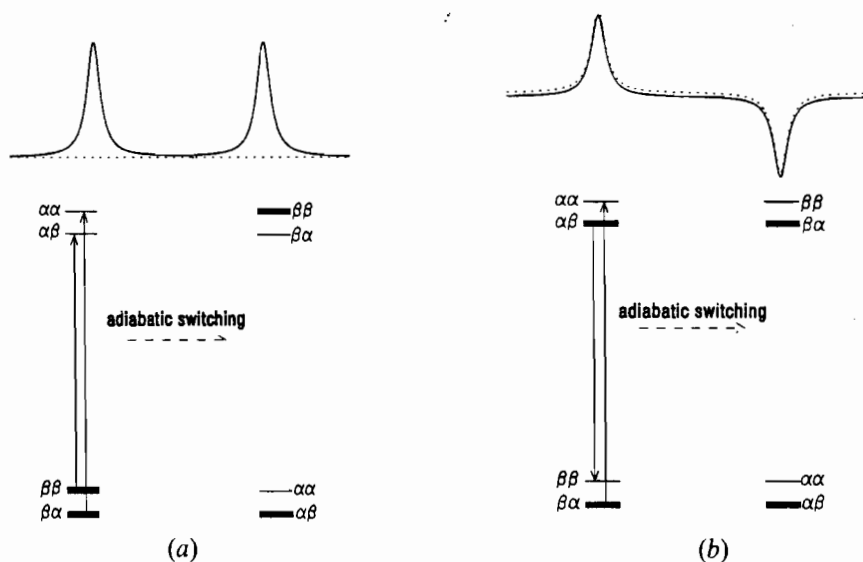


Figure 3. Polarization patterns and CIDEP spectra before and after adiabatic polarization transfer: (a) initial spin polarization due to the triplet mechanism, and (b) initial spin polarization due to T_0 -S radical pair mechanism. The solid and dotted curves in the upper half represent the CIDEP spectra before and after the polarization transfer, respectively.

In the case of the T_0 -S CIDEP mechanism in radical pairs, the two hyperfine lines in the CIDEP spectrum show opposite polarization. In this case, however, adiabatic polarization transfer during B_0 switching will reproduce exactly the initial level population pattern, i.e., the CIDEP spectrum will be unaffected and no extra CIDNP will be seen in the scavenged diamagnetic products of the radicals. Thus, we note that the adiabatic switching method is selective for transforming net electron spin polarization into nuclear spin polarization. It must be pointed out, though, that in the case of multiplet type CIDEP net electron spin polarization can still be achieved through microwave saturation of the emissive or absorptive part of the hyperfine structure. Thus, experiments with a combination of resonant pumping and APT could be carried out, whereby the microwave pumping should be applied during the generation of the radical pair and continue until a maximum of CIDEP has been developed. Then the microwave irradiation should be switched off and the net electron spin polarization can be transferred to net nuclear polarization by adiabatically reversing the B_0 field.

Apart from the triplet mechanism, the S - T_+ mechanism in radical pairs and the T - D mechanism in triplet-doublet pairs should be considered as potential sources of net electron spin polarization. For enhancing the effects of all of the pair mechanisms one can take advantage of the micellar supercage effect. That electron spin polarization can arise with radicals produced at low fields has been demonstrated in recent work from the Novosibirsk group [11].

Next, let us consider in more detail how short, in fact, the switching time τ can be made before significant deviations from adiabatic limit behaviour will occur and to what extent at $B_0 = 2A$ the high-field approximation used in the last section is valid. To this end we investigated the exact numerical solution of the Liouville equation for the Landau-Zener problem considered above. Examples of the results with $B_0 = 10$ G and $A = 5$ G are shown in figure 4. Here, an ensemble of radicals

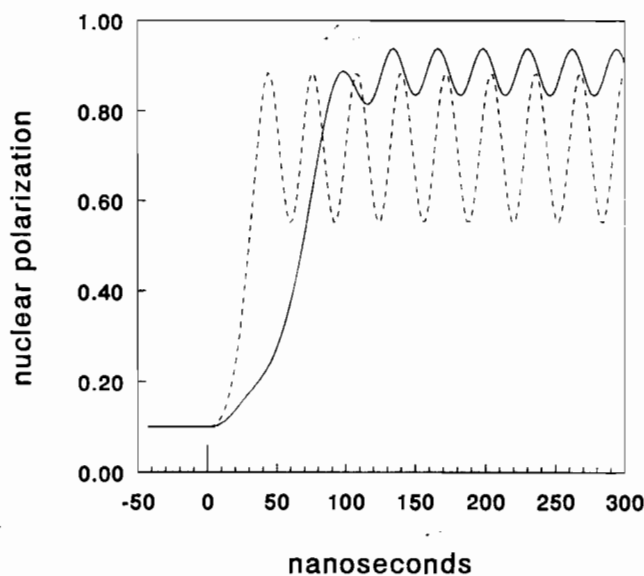


Figure 4. Exact time dependence of nuclear polarization after B_0 field switching during 45 ns (dotted curve) and 135 ns (solid curve). $B_{0,a} = 10$ G, $A = 5$ G. The initial polarization corresponds to the maximum of stationary α polarization of the electron spin and the minimum of stationary α polarization of the nuclear spin in the given magnetic field (see text).

is considered starting out from a polarization state which corresponds to the maximum of stationary electron spin polarization and, at the same time, the minimum of stationary nuclear spin polarization. Note that in situations when the external field B_0 is not much larger than the hyperfine coupling constant A , a situation with an electron spin polarization of 1 and nuclear spin polarization of 0 (or, in other words, a high-field energy eigenstate) is not stationary. Averaging over a full oscillation period of such a situation yields the stationary ensemble considered in our numerical example. If the switching time τ corresponds to 45 ns, the characteristic time according to inequality (9), the nuclear polarization rises from 0.1 to an average of 0.7 (note that, after switching, the polarization is non-stationary, the beat amplitude amounting to about 0.2). For $\tau = 130$ ns the mean value of the final polarization is close to 0.9, and the beat amplitude has been reduced to about 0.05. Thus, a switching time about 3 times the critical value of inequality (9) may be considered already close to the adiabatic limit. Concerning the lower limit of the switching time in cases where the radicals are produced in higher B_0 fields, we want to point out that for fields $B_0 \gg A$ there is no theoretical restriction for the switching time. Thus, in order to achieve adiabatic electron–nuclear polarization transfer, the field may be decreased rapidly, to a value where B_0 approaches the order of several times A and then only this small field has to be reversed adiabatically. Thus, a total switching time of about 150 ns seems feasible for APT even for radicals created in fields of several 100 G.

In order to conserve the nuclear polarization created through APT in the radicals, they have to be converted into diamagnetic species before nuclear relaxation takes place. This can be achieved through some scavenging reaction consisting of the transfer of an electron or atom from, or to, a diamagnetic scavenger. Degenerate electron exchange is a special case of such a reaction. Since the scavenging reaction is a bimolecular process, the time scale of scavenging can be optimized by suitably

adjusting the concentration of the scavenger. In organic radicals, anisotropic electron–nuclear dipolar interaction leading to cross relaxation is one of the main mechanisms and determines the time scale on which the radicals should be trapped. Under conditions of fast isotropic rotational diffusion the decay of nuclear spin polarization is described by:

$$P_n = \frac{1}{2} \left(\exp\left(-\frac{3\omega t}{4}\right) + \exp\left(-\frac{\omega t}{4}\right) \right), \quad (12)$$

whereby some of this polarization is partially transferred to the electron spin (inverse Overhauser effect), the time dependence of which is described by

$$P_e = -\frac{1}{2} \left(\exp\left(-\frac{3\omega t}{4}\right) - \exp\left(-\frac{\omega t}{4}\right) \right). \quad (13)$$

The characteristic rate constant w is given by

$$w = \frac{1}{3}\tau_c \sum_{i=1}^3 t_{\alpha\alpha}^2 \quad (14)$$

where the $t_{\alpha\alpha}$ are the components of the anisotropic part of the hyperfine coupling tensor and τ_c is the rotational correlation time. With the typical values of $\tau_c = 10^{-10}$ s and $\sum t_{\alpha\alpha}^2 = 50 \text{ G}^2$ one obtains $w = 0.5 \times 10^6 \text{ s}^{-1}$.

In figure 5 a possible time sequence of an APT experiment is depicted. Here it is assumed that electron spin polarization radicals are created, e.g., through the triplet mechanism, during a short laser pulse. If no switching of the magnetic field is applied (figure 5(a)) some nuclear polarization will arise through the Overhauser effect (described by equations (12) and (13) with the roles of electron and nuclear spins interchanged). At a delay time of typically several microseconds, about 20% of the initial electron spin polarization will be reached. (In order to avoid confusion, note that the sign of spin polarization is defined here in correspondence with the ratio $(N_\alpha(t) - N_\beta(t))/(N_\alpha(0) + N_\beta(0))$ for both electrons and nuclei, not in terms of absorption and emission.)

In figure 5(b), B_0 is switched from $B_{0,a}$ to $-B_{0,a}$ during the time window from $t_0 = 45$ ns to $t_0 + \tau = 175$ ns after the laser pulse. Thereby, APT from electrons to nuclei takes place with almost 100% efficiency. Note that the sign of nuclear spin polarization is opposite for APT and the Overhauser process. Hereafter, nuclear polarization in the radicals decays as described by equation (12).

In figure 5(c) the effect of radical scavenging and trapping of nuclear polarization in diamagnetic products is shown. Kinetically, the scavenging process is of pseudo first order, i.e., exponential. It is shown that, with a trapping constant of $k_{tr} = 2.5 \times 10^6 \text{ s}^{-1}$, 60% of the initial electron spin polarization can be transferred into nuclear spin polarization of the diamagnetic products. In figure 5(d) the result of an exact solution of the Liouville equation is shown for the situation, which in figure 5(c) is represented in an idealized way. Apart from the quantum beats arising as a result of the finite time during which electron spin polarization is created and the imperfect adiabaticity of the field switching, the results closely correspond to those of the simplified treatment. In particular, the final nuclear spin polarization of 67.2% collected in the diamagnetic product is close to the result of 64.7% arrived at in figure 5(c).

If the trapping rate constant is optimized (for the values of t_0 , τ , w used above,

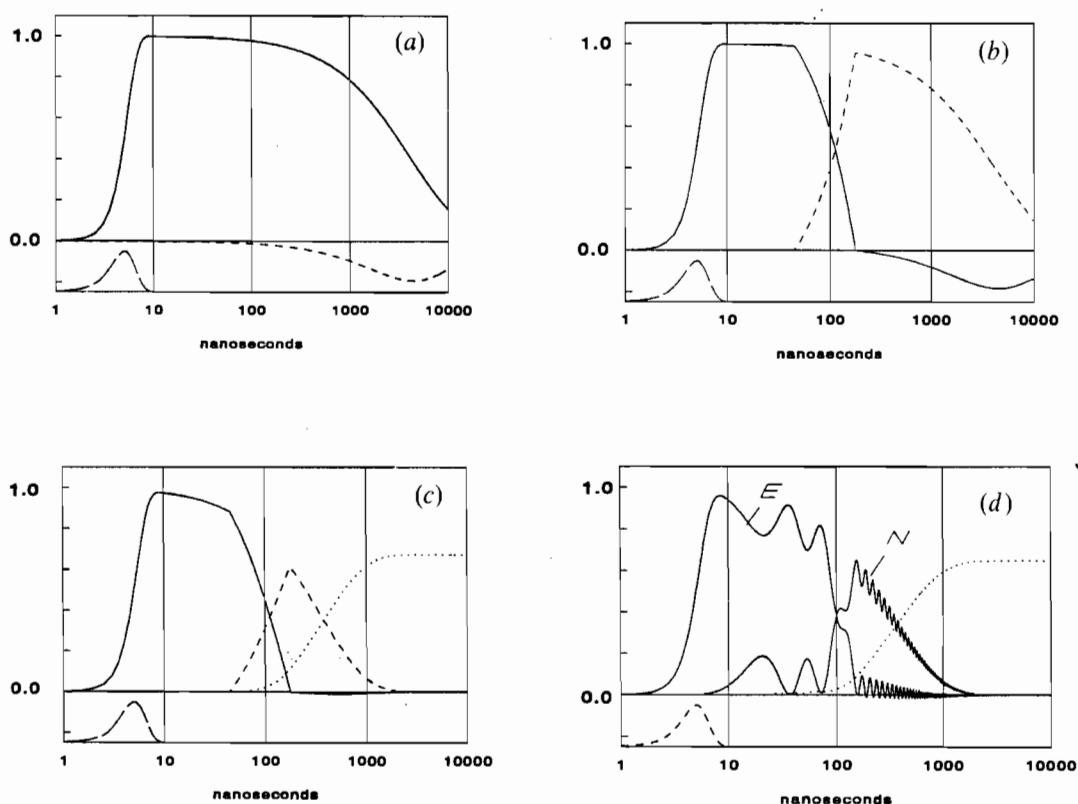


Figure 5. (a–c) Idealized time dependence of electron spin polarization (solid curve), nuclear spin polarization in radicals (dashed curve) and in scavenged diamagnetic product (dotted curve). The time profile of the laser is given on the bottom line. Radicals produced by laser photolysis are assumed to originate with net electron spin polarization of a relative amplitude of 1. (a) Electron–nuclear cross relaxation only; (b) additional adiabatic switching of B_0 from $B_{0,a}$ at $t_0 = 45$ ns to $-B_{0,a}$ at $t_0 + \tau = 175$ ns; (c) additional scavenging of radicals with a rate constant $k_{sc} = 2.5 \times 10^6$ s $^{-1}$; and (d) time profiles according to an exact calculation. E is electron spin polarization, and N is nuclear spin polarization in radicals.

the optimum trapping rate constant would be $k_{tr} = 1.3 \times 10^6$ s $^{-1}$) a conversion efficiency of electron to nuclear polarization of 71% can be achieved. This value should be compared with a maximum value of –13%, achievable by exploiting the Overhauser effect only; however, an optimum trapping rate constant for this case is about 0.2×10^6 s $^{-1}$, so that the time to recover the maximum nuclear polarization in the diamagnetic product is about 6 times longer and the efficiency is about 5 times smaller than with the method of adiabatic polarization transfer by switching B_0 .

In the literature, adiabatic transfer of spin polarization has been considered in some detail in connection with low-field CIDNP experiments [14], where nuclear spin polarization is created in an auxiliary magnet of desired field strength and thereafter the sample is transferred adiabatically to the high field of a conventional FT-NMR spectrometer. To interpret the corresponding results correctly in terms of the spin polarization mechanism effective at low field, one has to analyse the corresponding energy correlation diagrams of the nuclear spin system.

It is of interest to note that the so-called ALTADENA effect [15] of nuclear spin polarization has some formal similarity to the APT method described in this paper. In the former, the singlet spin correlation of a pair of hydrogen nuclei chemically

introduced into some olefinic double bond by addition of *para*-hydrogen in a low magnetic field is converted to an $\alpha\beta$ spin polarized state of this pair of hydrogen nuclei by adiabatically transferring the sample to a high magnetic field. Actually, this adiabatic passage is analogous to a section of the adiabatic $\beta_e\alpha_n \rightarrow \alpha_e\beta_n$ trajectory in the case of the electron–nuclear spin system considered by us (cf. figure 2). The difference is that in the ALTADENA effect the adiabatic trajectory does not include the field inversion. The nuclear spin system is created in the low field region (cf. point 'A₀' in figure 2) as an eigenstate which is essentially a spin singlet. While the absolute value of the field is increased (in terms of figure 2 this means going to more negative fields) the spin character changes adiabatically to $\alpha_n\beta_n$ (corresponding to position 'A_x' in figure 2). In the ALTADENA effect the corresponding energy trajectory ($\rightarrow A_0 \rightarrow \rightarrow A_x$) followed by the nuclear spin system runs above the T_{n-} curve. The order of energies of the corresponding curves is reversed in our case because of the great difference in Zeeman energies of nuclear and electronic spin.

Spin polarization transfer by level crossing techniques has been utilized extensively in nuclear quadrupole double resonance (cf. [16]). One of these methods, termed 'spin mixing by level crossing' and developed by Koo and Hahn [17], is particularly interesting to compare with the experiment suggested by us. The former deals with two sorts Q and P of nuclei in a solid environment: nuclei Q with electric quadrupole moment, weak Zeeman splitting and present in low abundance, and nuclei P, e.g., with spin 1/2, strong Zeeman splitting and present in high abundance. The experiment involves field cycling, starting with thermalization of the spin systems at high magnetic field B_0 , followed by adiabatic removal of the sample to a region with zero magnetic field. Thereby the levels of the Q nuclei change little because they are mainly determined by the quadrupolar splitting. However, the Zeeman splitting of the P spins decreases linearly with the field. Since the process is adiabatic the level population of P and Q is unchanged. On the other hand, the spin temperature of the P spin system decreases linearly with B_0 while that of the Q spin system changes very little. As the Zeeman splitting of the P spin system continues to decrease it will pass through situations of resonance with some of the quadrupole splittings. At these level crossing points dipolar interaction between nearest neighbour Q and P spins causes energy exchange between the two spin systems, which according to the established gradient in spin temperature will lead to net energy flow from the Q to the P spin system. The same type of process will occur when the sample is adiabatically returned to the initial field B_0 after transitions between Q levels have been pumped at zero field by resonant radiation with some frequency ω_Q . The effect of such twofold energy transfer from Q spins to P spins, whereby the possibility of energy transfer in the rising field depends on whether ω_Q had been at resonance with the Q system or not, will be detected as a loss of polarization of the P system (higher spin temperature) probed after the system has returned to the initial B_0 field.

The analogy with our experiment lies in the transfer of spin polarization from one spin system to another using adiabatic passage through a level crossing region. However, beyond the obvious difference that in our case the initial polarization is non-thermal and due to chemical pumping, there are more basic differences between the two cases that need to be emphasized. In our case, both spin systems comprise exactly the same number of spins and, whereas in Koo and Hahn's case the Q and P spins are of different numbers and are coupled in a random fashion, in our case they are coupled in an exclusive pairwise fashion of isolated Q–P pairs. Using the language of spin thermodynamics, the effect of level crossing is an equilibration of

spin temperatures of the two subsystems, connected with a net increase of entropy in an irreversible approach to thermodynamic equilibrium in the Hahn and Koo experiment, but corresponds to a mere exchange of entropy between the two subsystems with no net entropy production, i.e., it is fully reversible in our case.

4. Conclusion

We have described a new method for the rapid transfer of net electron spin polarization in radicals to nuclear polarization of diamagnetic products by adiabatically switching the static magnetic field in which the electron spin polarization of the radicals was created. In combination with a variation of the delay time t_0 of switching, or of the switching time τ , a method whereby various nuclei may be differentiated according to their hyperfine coupling strength, this technique may prove particularly useful for studying electron spin polarization in low magnetic fields without the need for an ESR spectrometer. The actual detection can take place in a high-field NMR spectrometer to which the scavenged diamagnetic product has to be transferred. The latter has become a routine procedure in low-field CIDNP or in SNP experiments. Favourable conditions for collecting high efficiencies of transferred nuclear spin polarization have been demonstrated.

We thank Dr Keith McLauchlan, for drawing our attention to the nuclear level crossing experiments of Koo and Hahn. The grant of an Alexander von Humboldt fellowship to N.L. and support of this research by the International Association for the Promotion of Cooperation with Scientists from the Independent States of the Former Soviet Union (INTAS, grant No. 93-1626) are gratefully acknowledged.

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