TIME-DOMAIN ZERO-FIELD MAGNETIC RESONANCE WITH FIELD PULSE EXCITATION

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An improved technique of time-domain zero-field magnetic resonance is proposed which employs a pair of short magnetic field pulses for excitation and detection of free precession.

1. Introduction

The principal attraction of magnetic resonance in zero field is the isotropy of space which allows one to record high-resolution spectra even for powder samples. This extends the domain of magnetic resonance to systems of which large single crystals cannot be grown.

Normally, sensitivity considerations do not permit direct observation of zero-field resonance and special high-sensitivity procedures must be applied. Numerous procedures have been proposed to detect resonance indirectly by field cycling techniques [1–7] consisting of three phases: (i) prepolarization in high magnetic field, (ii) resonance in zero field, and (iii) observation in high field This scheme has led to high-sensitivity techniques for the detection of low-abundance nuclei. Field cycling has become one of the standard procedures for deuterium, nitrogen-14, and oxygen-17 quadrupole resonance [5–7].

All these techniques are conceived as spectral methods determining the zero-field spectrum point by point. Recently an alternative real-time Fourier technique has been introduced by Pines and co-workers [8,9] where the zero-field free induction decay is indirectly sampled and Fourier-transformed to obtain the spectrum. This technique features high resolution and high sensitivity. The procedure used so far employs a very fast jump to zero field in order to create a non-equilibrium state which precesses under the zero-field Hamiltonian. By the sudden application of a magnetic field, it is then possible to spin-lock part of the mag-

netization for the final detection in high magnetic field.

We propose in this Letter an alternative technique of zero-field resonance, employing an adiabatic transfer of spin order between high field and zero field and vice versa. The non-equilibrium state is created and sampled by a pair of short magnetic field pulses which set the time interval for free precession. The proposed technique has advantages insofar as the technical realization is simpler, and numerous variants are feasible in view of further refinements of zero-field spectroscopy.

2. Field pulse procedure

The proposed technique uses the experimental scheme shown in fig. 1. The sample is polarized in high magnetic field for a time long compared to T_1 and then rapidly transported to zero field by a gas pressure system. During this transfer process, the initial high-field density operator σ_0^{HF} follows adiabatically the change of the Hamiltonian and reaches a state σ_0^{HF} which is diagonal in the eigenbase of the zero-field Hamiltonian. A magnetic field pulse of amplitude B_p and duration τ_p is then applied to create a non-equilibrium state $\sigma^{ZF}(t_1 = 0)$ which precesses under the zero-field Hamiltonian $\mathcal{H}^{ZF}$. At time t_1, a second magnetic field pulse samples the coherence. Components which do not commute with the zero-field Hamiltonian decay rapidly, leaving a stationary
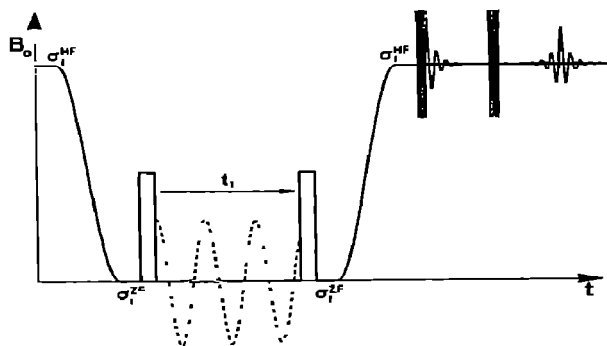
Fig. 1. Scheme of pulsed zero-field magnetic resonance. The initial density operator σ_i^{ZF} is created by an adiabatic transfer of the sample to zero field. The free precession during t_1 is initiated and terminated by a pair of magnetic field pulses. The detection by an echo sequence follows the adiabatic transfer of the sample to high field.

density operator. While the sample is transferred back to the high magnetic field, the density operator undergoes another adiabatic change. Finally, the recovered magnetization is detected by the application of an echo sequence using composite $\pi/2$ pulses [10].

This procedure can be applied for dipolar spectra as well as for nuclear quadrupole resonance. We restrict the discussion to the case of pure nuclear quadrupole resonance. Fig. 2 compares two deuterium zero-field spectra of a powder sample of perdeuterated malonic acid. One was recorded with the standard field-jump technique, the other one with the proposed field-pulse method. It can be inferred that the two techniques are comparable with regard to resolution and sensitivity although in the field-pulse method only a very short field pulse of 2.0 μs duration had to be applied while the field-jump experiment required the application of the switched field for at least 10 ms. The resolution of the two spectra is determined by the dipolar couplings among the deuterons.

The zero-field spectrum of malonic acid reflects the non-equivalence of the four deuterons. The two doublets at 135 and 138 kHz correspond to the two carboxylic deuterons. The doublet splittings of 9.2 and 10.2 kHz, respectively, are due to the asymmetry parameter η. The two methylene resonances near 125 kHz exhibit incompletely resolved doublets with smaller asymmetry parameters. In addition, each deuteron gives rise to a low-frequency transition $\omega = \frac{2}{3}\omega_q\eta$ with the two carboxylic lines near 10 kHz and the two methylene lines near 2 kHz. Finally, there is a contribution at zero frequency originating from those components which are not affected by the field pulses (this contribution was partially suppressed by a baseline correction of the free induction decay).

A full description of the apparatus will be presented elsewhere. The high magnetic field is provided by a 5.2 T superconducting Bruker 9 cm bore magnet. Deuterium resonance is detected at 33.8 MHz. The sample of 160 mm^3 volume is shuttled by compressed air within 100 ms over a distance of 70 cm to a field
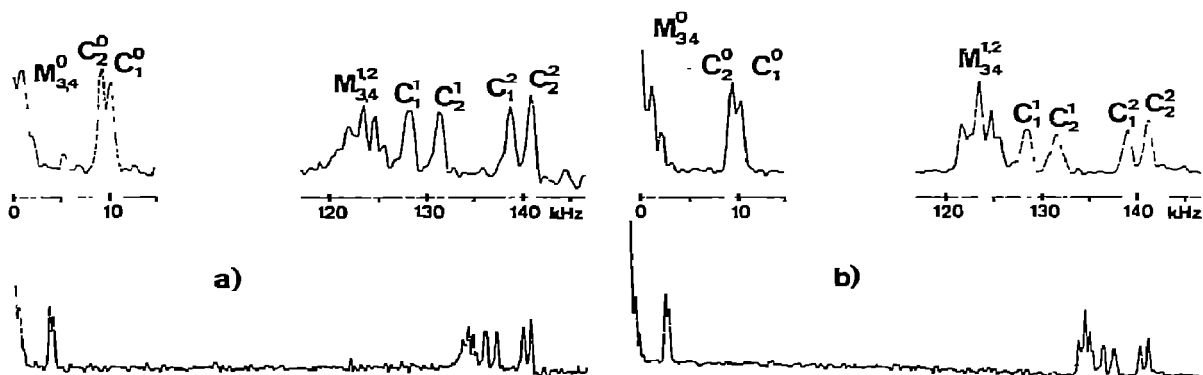

Fig. 2. Deuterium nuclear quadrupole zero-field spectra of a powder sample of perdeuterated malonic acid, (a) obtained with the proposed field pulse technique, (b) recorded with the conventional field-jump method. The resonance lines are labelled in the blow-up using the deuterium assignment of ref. [11]. The lines C_1^0, C_1^1, C_1^2 and C_2^0, C_2^1, C_2^2, can be assigned to the two carboxylic deuterons while the resonances $M_{3,4}^0$ and $M_{3,4}^{1,2}$ belong to the two methylene deuterons.

that is smaller than 10^{-5} T. This is achieved by ferromagnetic shielding and by a simple system of gradient correction coils. The magnetic field pulses use an amplitude of 30 mT and have a characteristic time constant of 1.2 μs.

3. Analysis of the procedure

The Hamiltonian describing an isolated spin $I = 1$, written in the principal-axis system of the quadrupole coupling tensor, is

$$\mathcal{H} = \omega_q [(I_z^2 - \tfrac{2}{3}) + \tfrac{1}{3}\eta(I_x^2 - I_y^2)]$$

$$+ \omega_0 [I_z \cos\theta + \sin\theta (I_x \cos\phi + I_y \sin\phi)] , \quad (1)$$

where ω_q is the quadrupole coupling constant, η the asymmetry parameter, $\omega_0 = -\gamma B_0$ the Larmor frequency, and the angles θ and ϕ define the orientation of the magnetic field B_0. The three eigenvalues of this Hamiltonian are

$$E_k = 2(\alpha/3)^{1/2} \cos[\delta - 2\pi k/3] , \quad k = 1,2,3, \quad (2)$$

with

$$\cos(3\delta) = \frac{b/2}{(a^3/27)^{1/2}} ,$$

$$a = \tfrac{1}{3}\omega_q^2(\tfrac{1}{3}\eta^2 + 1) + \omega_0^2 ,$$

$$b = \omega_q \{\omega_0^2 [\tfrac{1}{3}\eta \sin^2\theta \cos(2\phi) - \tfrac{1}{3} + \cos^2\theta]$$

$$- \tfrac{2}{27}\omega_q^2(1 - \eta^2)\} .$$

After the system has been prepolarized at high magnetic field the experiment starts with the density operator

$$\sigma_1^{HF} = I_z' = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{bmatrix} , \quad (3)$$

diagonal in the eigenbasis of the high-field Hamiltonian (disregarding unimportant constants). The adiabatic transfer depends on the course of energy levels and eigenfunctions when the magnetic field strength is lowered to zero. This course is determined by the relative orientation of magnetic field and quadrupole
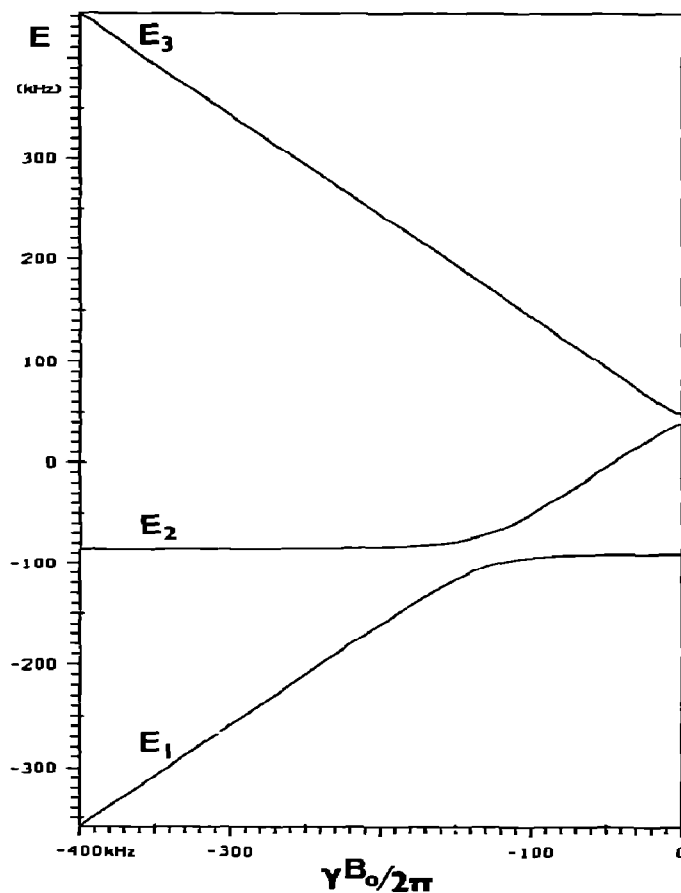

Fig. 3. Course of the energy levels during the transfer to zero-field for an isolated spin $I = 1$ with a quadrupolar coupling tensor with $\omega_q/2\pi = 135$ kHz and $\eta = 0.1$. The magnetic field is at the orientation $\theta = 10°$, $\phi = 20°$ with respect to the principal axes of the quadrupolar coupling tensor. The three eigenvalues, given by eq. (2), are plotted as functions of the external field amplitude $\gamma B_0/2\pi$.

coupling tensor and by the asymmetry parameter η. An example of such a field dependence is shown in fig. 3. It has been found that only for a negligible number of orientations does a crossing of energy levels occur. Under the adiabatic transfer, the density operator remains diagonal in the momentary eigenbasis of the changing Hamiltonian $\mathcal{H}$. The populations do not change, so that at zero field the density operator takes the form

$$\sigma_i^{ZF} = -\tfrac{3}{2}(I_z^2 - \tfrac{2}{3}) - \tfrac{1}{2}(I_x^2 - I_y^2) = I_z''$$

$$= \begin{bmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -0 \end{bmatrix} \tag{4}$$

where the operator I_z'' and its matrix representation refer to the zero-field eigenbasis with the eigenfunctions $\psi_1 = |0\rangle$, $\psi_2 = 2^{-1/2}(|1\rangle - |-1\rangle)$, $\psi_3 = 2^{-1/2} \times (|1\rangle + |-1\rangle)$, and with the corresponding eigenvalues $E_1 = -\tfrac{2}{3}\omega_q$, $E_2 = \tfrac{1}{3}\omega_q(1 - \eta)$ and $E_3 = \tfrac{1}{3}\omega_q(1 + \eta)$. The functions $|1\rangle, |0\rangle, |-1\rangle$ are the eigenfunctions of I_z in the principal-axis frame of the quadrupole tensor.

The magnetic field pulse, applied after the adiabatic transfer, induces a rotation $R(\beta, \theta, \phi)$ by the angle β about the magnetic field direction at the orientation (θ, ϕ) with respect to the principal-axis frame of the quadrupole coupling tensor. For an arbitrary orientation, all three coherences with the frequencies $\omega_{12} = \omega_q(1 - \tfrac{1}{3}\eta)$, $\omega_{13} = \omega_q(1 + \tfrac{1}{3}\eta)$ and $\omega_{23} = \tfrac{2}{3}\omega_q \eta$ are excited. However, the following special orientations with the magnetic field along one of the principal axes may be noted:

$$R(\beta, 0, 0) = \exp(-2i\beta I_x^{(23)''}), \quad B_0 \parallel z\text{-axis},$$

$$R(\beta, \tfrac{1}{2}\pi, 0) = \exp(-2i\beta I_x^{(13)''}), \quad B_0 \parallel x\text{-axis},$$

$$R(\beta, \tfrac{1}{2}\pi, \tfrac{1}{2}\pi) = \exp(2i\beta I_y^{(12)''}), \quad B_0 \parallel y\text{-axis}, \tag{5}$$

where R acts as a selective pulse of double rotation angle and excites only a single transition. The double-primed single transition operators [12,13] refer to the eigenbasis of the zero-field Hamiltonian. Maximum efficiency is achieved for $\beta = \tfrac{1}{4}\pi$. With these particular transformations, a general rotation β about an arbitrary direction (θ, ϕ) is easily expressed in the eigenbasis of the zero-field Hamiltonian:

$$R(\beta, \theta, \phi) = R(\phi, 0, 0) R(\theta, \tfrac{1}{2}\pi, \tfrac{1}{2}\pi) R(\beta, 0, 0)$$

$$\times R(\theta, \tfrac{1}{2}\pi, \tfrac{1}{2}\pi)^{-1} R(\phi, 0, 0)^{-1}. \tag{6}$$

After free precession for a time t_1, the second field pulse converts part of the coherences back into populations which are modulated by the free precession frequencies as a function of t_1. The remaining coherences will decay rapidly.

The following adiabatic transfer to high field leaves again the populations invariant and an applied radiofrequency pulse leads finally to a free induction decay of which the x-component is measured by an echo experiment.

Formally, the signal amplitude after the detection pulse may be described by the expression

$$\langle I_x \rangle (t_1) = \mathrm{Tr}\{I_x' \, T\hat{\tilde{D}}[R(\beta, \theta, \phi) E(t_1) R(\beta, \theta, \phi) \, \sigma_i^{HF}$$

$$\times R(\beta, \theta, \phi)^{-1} E(t_1)^{-1} R(\beta, \theta, \phi)^{-1}] T^{-1}\}. \tag{7}$$

The operator $T = \exp\{-i\alpha I_y'\}$ represents the radiofrequency pulse in the high-field frame with rotation angle α, the diagonal part projector $\hat{D}$ destroys off-diagonal elements, and the operator $E(t_1) = \exp(-i\mathcal{H}_{ZF} t_1)$ describes the time evolution in zero field.

The full response observed in the experiment is obtained by averaging the angles θ and ϕ over an isotropic distribution on the unit sphere.

4. Conclusions

The proposed zero-field experiment with field pulse excitation features the technical advantage of requiring only very short magnetic field pulses of a few μs length while the standard procedure [8,9] demands magnetic field pulses of several ms duration. This allows one to increase the feasible field amplitude and to observe wider spectra than was previously possible. It should be noted, however, that even with this improved experiment it is difficult to detect zero-field spectra with a width exceeding about 1 MHz. This limits its applicability to spectra with moderately wide spread, such as ^{1}H and ^{2}D resonance, and to spectra with reduced quadrupole splittings due to motional averaging. It is however feasible to excite semi-selectively by means of low-frequency pulses a part of a spectrum which is too wide to be fully covered by a dc pulse.

The field pulse technique can be extended in various ways. Special effects can be achieved by proper selection of the pulse rotation angle $\beta = -\gamma B_p \tau_p$. For example, it is possible to distinguish different nuclear species: Noting that β is proportional to the gyromagnetic ratio γ the rotation angle is set to $2n\pi$ for the species to be suppressed. The entire armory of com-

posite pulses [14] is at one's disposal to improve the properties of an experiment. Field pulses can also serve to induce homonuclear or heteronuclear coherence or polarization transfer and to refocus the evolution under a specific Hamiltonian. The experiment conforms to the general scheme of two-dimensional spectroscopy [15,16] and extensions to a two-dimensional data display are straightforward.

Field cycling techniques, in general, require long spin—lattice relaxation times ($T_1 \gtrsim 0.1$ s) in order to allow the physical transport of spin order. Nevertheless numerous interesting applications have so far been treated by traditional field-cycling techniques [6,7], and it is expected that pulsed zero-field magnetic resonance has also a wide field of potential applications on systems with sufficiently long spin—lattice relaxation times.

After completion of this work we became aware of similar developments in the research group of Pines [17].

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