

RADIOFREQUENCY-PULSE EXCITATION IN TIME-DOMAIN ZERO-FIELD MAGNETIC RESONANCE

R. KREIS, D. SUTER and R.R. ERNST

Laboratorium für Physikalische Chemie, Eidgenössische Technische Hochschule, 8092 Zurich, Switzerland

Received 16 October 1985

Time-domain zero-field magnetic resonance is extended by applying radiofrequency pulses for the initiation and termination of precession at zero field. Radiofrequency-pulse excitation is suitable for observing resonance in wide quadrupolar spectra and for the design of more elaborate pulse experiments.

1. Introduction

We propose in this Letter a modification of the basic scheme of time-domain zero-field magnetic resonance [1–4] which should further extend its range of application. Remote detection of zero-field resonance at high magnetic fields has been used for many years to enhance the sensitivity of pure quadrupolar resonance [5–9]. In contrast to magnetic resonance in high magnetic fields, zero-field experiments require no single crystals for achieving highly resolved spectra. More recently Pines and co-workers [1,2] proposed time-domain experiments as alternatives to the conventional continuous-wave zero-field experiments. Time-domain experiments feature the advantage of improving the resolution further as no saturation broadening is possible. In addition, they are admissible to all the trickery of modern pulse spectroscopy [10].

The first proposal of time-domain zero-field resonance [1,2] employed a sudden field jump to zero field for initiating free precession. The termination of precession at the end of the evolution period was effected by a reverse field jump locking one component of the coherence along the magnetic field. As an alternative, it has been suggested recently [3,4] to lower the magnetic field adiabatically to zero and to employ two short dc magnetic field pulses for the initiation and termination of free precession at zero field. Apart from the greater flexibility in the design of experiments, this procedure has the advantage of reduc-

ing the power duration of the rapidly switched dc field by as much as three orders of magnitude. The reduced power requirements ease the coverage of wide frequency ranges. However, even this improved technique has still its limitations when applied to very wide spectra as the length τ_p of the dc pulses must fulfil the condition

$$\tau_p < 1/f_{\max},$$

where f_{\max} is the maximum frequency of the zero-field spectrum to be covered. In practice f_{\max} may easily exceed 1 MHz for quadrupolar spins such as ^{14}N , thus requiring extremely short high-amplitude dc field pulses.

In many situations it is sufficient or even preferable to excite only part of the zero-field spectrum. This can be achieved by replacing the dc field pulses by radiofrequency pulses with the proper carrier frequency. The resulting modified pulse scheme is shown in fig. 1. After prepolarization at high magnetic field B_0 , the sample is transported adiabatically into a region of zero field. The populations of the high-field eigenstates are thereby transferred adiabatically to the zero-field eigenstates. The first rf pulse creates coherence on the selected transitions which starts precessing under the zero-field Hamiltonian. A second rf pulse reconverts part of this coherence into populations. The following adiabatic transfer of the sample to high field renders again Zeeman magnetization, which can be measured as usual by means of a spin echo or spin-echo sequence experiment.

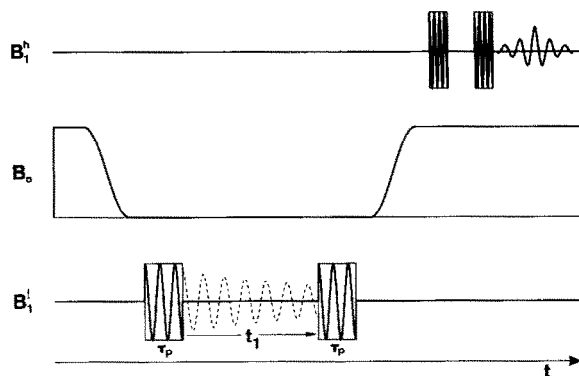


Fig. 1. Timing diagram of time-domain zero-field magnetic resonance with rf pulse excitation. The adiabatic transfer of the sample between high field and zero field is indicated by the time course of the field B_0 . The low-frequency rf pulses B_i^l initiate and terminate the precession of coherence in zero field. The high-frequency rf pulses B_i^h are needed for the detection of resonance at high field.

2. Efficiency of rf pulse excitation

The discussion is limited to the selective excitation of non-connected transitions, a situation fulfilled in many selective excitation experiments. It is then sufficient to consider a two-level subsystem which can be described in terms of single transition or virtual spin-1/2 operators [10–12].

We further restrict the calculations to a purely quadrupolar system with $I = 1$. The Hamiltonian in the principal axis (PA) frame of the quadrupolar tensor takes the form

$$\mathcal{H}^{\text{PA}} = \omega_q \left[(I_z^2 - \frac{2}{3}) + \frac{1}{3} \eta (I_x^2 - I_y^2) \right] + \omega_1(t) \times [I_z \cos \theta + \sin \theta (I_x \cos \phi + I_y \sin \phi)], \quad (1)$$

where ω_q is the quadrupolar coupling constant, η the asymmetry parameter, and $\omega_1(t)$ the oscillating amplitude of the applied rf field, $\omega_1(t) = \omega_1 \cos(\omega_{\text{rf}} t)$, with $\omega_1 = -\gamma B_1^0$. The orientation of the magnetic field with respect to the quadrupolar principal axis frame is indicated by the polar angles θ and ϕ .

For the description of the selective excitation, it is of advantage to transform the full Hamiltonian into the eigenbase (EB) of the unperturbed quadrupolar Hamiltonian. Following ref. [3], we define the eigenvalues and eigenfunctions in the order of increasing energy, leading to the eigenfunctions $\psi_1^{\text{EB}} = |m=0\rangle$,

$\psi_2^{\text{EB}} = 2^{-1/2}(|1\rangle - |-1\rangle)$, $\psi_3^{\text{EB}} = 2^{-1/2}(|1\rangle + |-1\rangle)$. In terms of the single transition operators $I_{x,y,z}^{(kl)}$ [11], we obtain (see also eq. (5) of ref. [3]):

$$\mathcal{H}^{\text{EB}} = -\omega_q \left(1 + \frac{1}{3} \eta \right) I_z^{(13)} - \omega_q (1 - \eta) (2I_z^{(13)2} - \frac{1}{3}) + 2\omega_1 \cos(\omega_{\text{rf}} t) [\cos \theta I_x^{(23)} + \sin \theta \cos \phi I_x^{(13)} - \sin \theta \sin \phi I_y^{(12)}]. \quad (2)$$

We assume selective excitation of transition (1,3) so that we can drop all terms referring to other transitions as well as the unity operator of transition (1,3). This leads to the reduced Hamiltonian

$$\mathcal{H}^{(13)} = -\omega_q \left(1 + \frac{1}{3} \eta \right) I_z^{(13)} + 2\omega_1 \cos(\omega_{\text{rf}} t) \sin \theta \cos \phi I_x^{(13)}. \quad (3)$$

The effective field acting on transition (1,3), expressed in the frame rotating with the frequency ω_{rf} , is then

$$\omega_1^{\text{eff}}(\theta, \phi) = \Omega e_z + \omega_1 \sin \theta \cos \phi e_x, \quad (4)$$

where Ω is the resonance offset,

$$\Omega = -\omega_q \left(1 + \frac{1}{3} \eta \right) - \omega_{\text{rf}}. \quad (5)$$

Eq. (4) demonstrates that the effective field depends on the direction of the applied rf field with respect to the orientation of a particular microcrystallite in the powder sample.

The signal observed at high field is finally obtained by averaging the response over the isotropic powder distribution. We discuss in the following the dependence of the signal amplitude on the flip angle of the rf pulses for two different experiments.

2.1. Application of a single rf pulse at zero field

Observing the effect of a single rf pulse while the sample is at zero field, can be used for calibrating the rf field strength. This reduced experiment shows some characteristic features of zero-field resonance. The signal $S_{1p}^{(13)}(\tau_p)$ detected at high field after applying one selective pulse of length τ_p at zero field to transition (1,3) measures the residual unperturbed population difference $\Delta P^{(13)}$ at zero field. It is given by the powder average

$$S_{1p}^{(13)}(\tau_p) \propto \frac{1}{4\pi} \int_0^{2\pi} d\phi \int_0^\pi \sin\theta d\theta \{ \cos^2\xi + \sin^2\xi \cos[\omega_1^{\text{eff}}(\theta, \phi)\tau_p] \}, \quad (6)$$

where ω_1^{eff} is the amplitude and ξ the orientational angle of the effective field ω_1^{eff} , and

$$\omega_1^{\text{eff}} = [(\omega_1 \sin\theta \cos\phi)^2 + \Omega^2]^{1/2},$$

$$\tan\xi = \omega_1 \sin\theta \cos\phi / \Omega.$$

For exact on-resonance irradiation, $\Omega = 0$, the power average can be evaluated analytically:

$$S_{1p}^{(13)}(\tau_p) \propto \sin(\omega_1\tau_p) / \omega_1\tau_p. \quad (7)$$

The signal decays according to a sinc-function when increasing the pulse length τ_p . This dependence implies that the effective rf fields ω_1^{eff} across the powder sample possess a rectangular distribution of uniform probability within the limits $-\omega_1 \leq \omega_1^{\text{eff}} \leq \omega_1$.

For off-resonance irradiation, the expression for $S_{1p}^{(13)}(\tau_p)$ becomes more complicated and has been integrated numerically. In fig. 2a, the results for a particular set of conditions are compared with the experimental signal amplitudes obtained for deuterium resonance of a fully deuterated malonic acid powder sample. Qualitatively, the off-resonance behavior is similar to the on-resonance sinc-dependence.

2.2. Application of a pair of rf pulses

We discuss the flip angle dependence of the signal amplitude as observed in the proposed experiment of fig. 1. Both pulses are assumed to be of equal length τ_p , and the flip angle dependence enters twice, once upon excitation and once upon termination. We indicate an analytical result for on-resonance irradiation, where we obtain the following intensity of the transition (1,3):

$$S_{2p}^{(13)}(\tau_p) \propto \frac{1}{4\pi} \int_0^{2\pi} d\phi \int_0^\pi \sin\theta d\theta \sin^2[\omega_1^{\text{eff}}(\theta, \phi)\tau_p] = \frac{1}{2} [1 - \sin(2\omega_1\tau_p) / 2\omega_1\tau_p]. \quad (8)$$

Comparing with eq. (7), we find

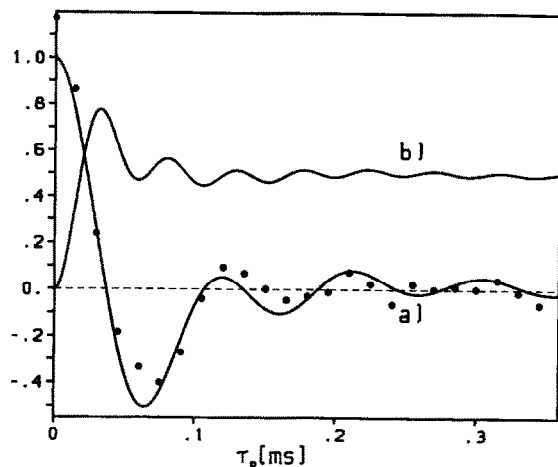


Fig. 2. Dependence of the signal $S^{(13)}(\tau_p)$ on the rf pulse length τ_p in a time-domain zero-field magnetic resonance experiment. (a) Using the timing diagram of fig. 1, modified by suppressing one of the low-field rf pulses. The experimental values stem from a selective excitation of the transition (1,3) in a powder sample of fully deuterated malonic acid using a resonance offset of 1.2 kHz and a rf field strength of 5.2 kHz. The full curve has been calculated by a numerical integration of eq. (6). The effects of rf field inhomogeneity and dipolar line broadening have been taken into account by an exponential damping of the signal as a function of τ_p with a time constant of 400 μ s. (b) Calculated signal intensity for the two-pulse experiment of fig. 1. The same parameters have been used as in (a). The pulse separation τ_1 is supposed to be sufficiently short to allow the neglect of relaxation and precession.

$$S_{2p}^{(13)}(\tau_p) = \frac{1}{2} [1 - S_{1p}^{(13)}(2\tau_p)]. \quad (9)$$

This relation still holds for off-resonance irradiation, $\Omega \neq 0$, provided that in successive experiments one of the two pulses is phase-alternated and the results are alternately added and subtracted. This procedure eliminates undesired dc components as well as one of the two quadrature components precessing at zero field.

The dependence of the signal amplitude on the pulse length τ_p is visualized in fig. 2b for the same conditions as for fig. 2a. It is apparent that the signal rapidly increases and starts to oscillate about the equilibrium value 1/2 approached for long pulses $\tau_p \rightarrow \infty$. This behavior is in contrast to the well known sinusoidal dependence in high-field resonance. It is obviously due to the distribution of effective rf field strengths. As a consequence notions like " $\pi/2$ " and

" π -pulse" lose their strict significance for selective irradiation in powder samples at zero field.

3. Experimental example

The practical performance of the proposed scheme of fig. 1 is demonstrated on fully deuterated malonic acid which contains four non-equivalent deuterons, each leading to three resonance lines. Fig. 3a shows for reference the entire zero-field spectrum as obtained with the dc field pulse technique [3]. The result of a selective rf pulse experiment is presented in fig. 3b. The two resonance lines visible correspond to the (1,3) transitions of the two non-equivalent carboxyl deuterons C_1 and C_2 .

Because of the distribution of effective rf fields and effective flip angles some stationary spin order will remain after the initial rf pulse irrespective of the pulse length. To eliminate the resulting background signal (leading to a δ -function peak at $\Delta\omega = 0$) the phase alternation scheme mentioned in section 2.2 was applied.

The experiments used a pneumatic transport for

transferring the sample between the shielded zero-field area and the high-field region provided by a 5.2 T superconducting Bruker magnet. The sample contained in a Kel-F container was shuttled within 100 ms across the 70 cm between the zero- and high-field areas.

The rf field pulses were applied at 145 kHz with an amplitude of 5.2 kHz, using a solenoidal transmitter coil tuned to the carrier frequency. An input power of 0.25 W was sufficient for producing the required rf field strength.

4. Discussion

Although the scheme of fig. 1 allows the investigation of systems with wide zero-field spectra, limitations may arise due to the employed high-field detection process: In the case of extremely wide zero-field spectra, the decay times of the signals at high field may become very short, requiring excessively strong rf pulses and leading to poor sensitivity. In this situation it is advantageous to transfer adiabatically the spin order to a second nuclear spin species with a nar-

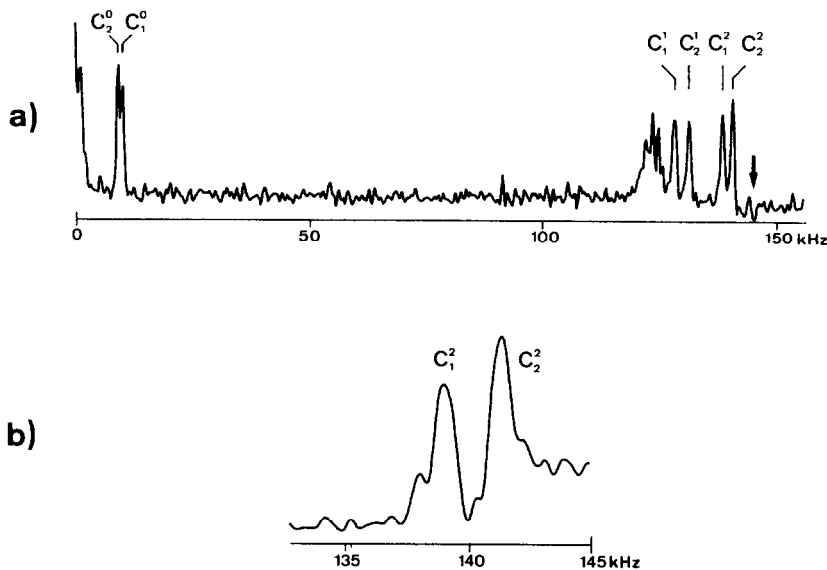


Fig. 3. Deuterium nuclear quadrupole zero-field spectra of a powder sample of fully deuterated malonic acid. (a) Full spectrum obtained with the dc field pulse method [3] featuring three resonance lines C^0 , C^1 and C^2 for each of the two carboxylic deuterons C_1 and C_2 . The remaining lines originate from the two methylene deuterons. (b) Partial spectrum obtained by selective excitation and detection using a pair of rf pulses with a frequency of 145 kHz (arrow in fig. 3a), an amplitude of 5.2 kHz and a pulse length $\tau_p = 35 \mu\text{s}$.

row high-field spectrum and with inherently high receptivity, such as protons [4]. Indirect detection via a second spin species allows high-sensitivity detection irrespective of the width of the indirectly observed zero-field spectrum.

In some situations, it is possible to take advantage of the two additional degrees of freedom that rf pulses possess in comparison to dc pulses: the free selection of phase and frequency. The availability of a phase variable permits the design of quadrature phase experiments extending the frequency range by a factor of two [10], and it renders feasible the design of composite pulses requiring quadrature phases [13]. Although not impossible, such experiments are more difficult to be realized with dc pulses. Heteronuclear decoupling experiments may be conceived that use zero-field rf pulse irradiation for eliminating the heteronuclear dipolar broadening of half integer quadrupolar spins. In the case of integer spins, heteronuclear dipolar interactions are normally quenched when $\eta \neq 0$ [14].

In summary, it is expected that radiofrequency pulse excitation extends the applicability of time-domain zero-field magnetic resonance. Its use seems particularly appropriate in the case of wide quadrupolar zero-field spectra and when more elaborate experiments requiring selective excitation are envisaged.

Acknowledgement

This research has been supported by the Swiss

National Science Foundation. RK acknowledges a scholarship by the Swiss Chemical Industry. The manuscript has been edited by Miss. I. Müller.

References

- [1] D.P. Weitekamp, A. Bielecki, D. Zax, K. Zilm and A. Pines, *Phys. Rev. Letters* 50 (1983) 1807.
- [2] A. Bielecki, J.B. Murdoch, D.P. Weitekamp, D.B. Zax, K.W. Zilm, H. Zimmermann and A. Pines, *J. Chem. Phys.* 80 (1984) 2232.
- [3] R. Kreis, D. Suter and R.R. Ernst, *Chem. Phys. Letters* 118 (1985) 120.
- [4] J.M. Millar, A.M. Thayer, A. Bielecki, D.B. Zax and A. Pines, *J. Chem. Phys.* 83 (1985) 934.
- [5] R.L. Trombotne and E.L. Hahn, *Phys. Rev.* 133A (1964) 1616.
- [6] R.E. Slusher and E.L. Hahn, *Phys. Rev. Letters* 12 (1964) 246; *Phys. Rev.* 166 (1968) 332.
- [7] D.T. Edmonds and P.A. Speight, *Phys. Letters* 34A (1971) 325.
- [8] R. Blinc, *Advan. Nucl. Quadrupole Reson.* 2 (1975) 71.
- [9] D.T. Edmonds, *Phys. Rept.* 29 (1977) 233; *Intern. Rev. Phys. Chem.* 2 (1982) 103.
- [10] R.R. Ernst, G. Bodenhausen and A. Wokaun, *Principles of nuclear magnetic resonance in one and two dimensions* (Oxford Univ. Press, Oxford), to be published.
- [11] A. Wokaun and R.R. Ernst, *J. Chem. Phys.* 67 (1977) 1752.
- [12] S. Vega, *J. Chem. Phys.* 68 (1978) 5518.
- [13] M.H. Levitt, *Progr. NMR Spectry.*, to be published.
- [14] G.W. Leppelmeier and E.L. Hahn, *Phys. Rev.* 141 (1966) 724.