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### Authors

Yen, Y.S.

Weitekamp, D.P.

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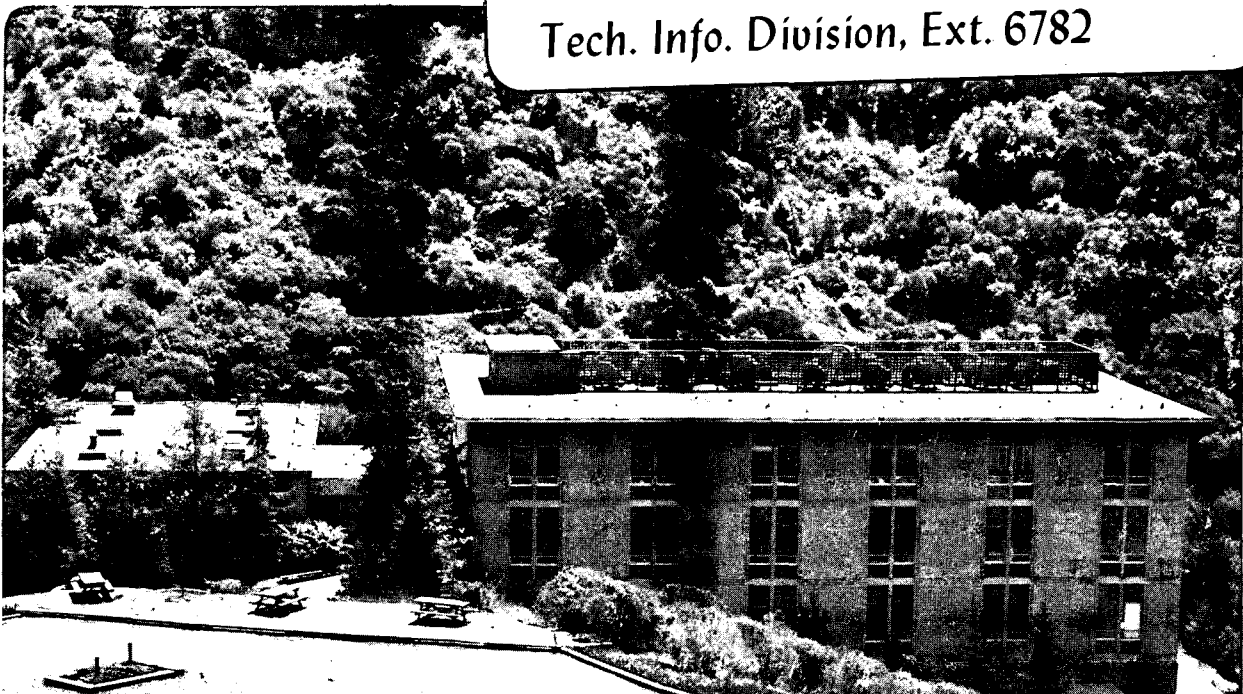
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QUANTUM COHERENCE IN LIQUIDS

Y.S. Yen and D.P. Weitekamp

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INDIRECT DETECTION OF SPIN 1 DOUBLE  
QUANTUM COHERENCE IN LIQUIDS

Y. S. Yen and D. P. Weitekamp  
Department of Chemistry and  
Lawrence Berkeley Laboratory, University  
of California, Berkeley CA 94720

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Indirect Detection of Spin 1 Double  
Quantum Coherence in Liquids

ABSTRACT

Using only the magnetization of bound protons,  $^{14}\text{N}$  double quantum coherence is observed with high sensitivity in isotropic solution. Spin echoes were used to obtain the homogeneous double quantum spectrum and to suppress a large  $\text{H}_2\text{O}$  solvent signal.

## INTRODUCTION

Time domain multiple quantum (MQ) NMR has been demonstrated in a variety of systems (1) to offer higher resolution, and more information on relaxation dynamics than single quantum (SQ) methods. Although  $S = 1$  nuclei in anisotropic systems were among the early applications of time domain double quantum (DQ) NMR, (2, 3, 4) it is only recently that the interesting problem has been raised of observing these transitions in isotropic solution, where the quadrupole coupling vanishes. Prestegard and Miner (5) recognized that the usual preparation sequence using two  $\pi/2$  pulses (6, 7) on the S spins ( $^{14}\text{N}$ ) does not excite DQ coherence, even when the spectrum shows resolved J coupling to neighboring heteronuclei. They demonstrated that augmentation of this sequence by spin tickling of bound protons ( $I = 1/2$ ) did allow S spin DQ coherence to be prepared from and mixed to S spin magnetization.

In this work we demonstrate that the S DQ coherence can be excited and detected using only the I spin magnetization and simple hard pulses at both I and S frequencies. This is an example of heteronuclear coherence transfer (8, 9) and is an extension of heteronuclear MQ techniques already demonstrated for  $I = S = 1/2$  in liquids (10) and in liquid crystals (11), and for  $I = 1/2$ ,  $S = 1$  in liquid crystals (12) and solids (13, 14, 15).

This indirect method of observation of  $S = 1$  DQ coherence benefits from the signal enhancement (10, 12) which comes from using only proton magnetization as the initial and final conditions. In addition, we employ spin echoes and time proportional phase incrementation (TPPI) (7, 16) to separate orders and a form of coherence transfer echo (9, 17) to suppress large zero quantum interference.

In discussing the various coherences possible in a heteronuclear system, it is useful to label them with a pair of quantum numbers  $(n^I, n^S)$  which are conserved under free evolution. For any coherent superposition  $|i\rangle\langle j|$  of two eigenstates these are defined by the relations

$$[I_z, |i\rangle\langle j|] = n_{ij}^I |i\rangle\langle j| \quad [1a]$$

$$[S_z, |i\rangle\langle j|] = n_{ij}^S |i\rangle\langle j| \quad [1b]$$

These are just the differences in Zeeman quantum numbers for the

states connected:  $n_{ij}^I = m_i^I - m_j^I$ ,  $n_{ij}^S = m_i^S - m_j^S$ .

#### THEORY

Shown in Fig. 1 are two pulse sequence variations for observation of various orders of coherence  $(n^I, n^S)$  using only I spin magnetization. Perfect rf pulses of negligible duration are assumed. We consider here the case of a group of equivalent I spins identically coupled to a single  $S = 1$  spin. The unperturbed rotating frame Hamiltonian is

$$\mathcal{H} = -\Delta\omega_I I_z - \Delta\omega_S S_z + J' I_z S_z \quad [2]$$

where  $J' = 2\pi J$  is the scalar heteronuclear coupling in radians/sec

and  $I_z = \sum_i I_{z_i}$ . For the preparation sequence  $(\pi/2)_x(I) - \tau/2 - (\pi)_x(I, S) - \tau/2 - (\pi/2)_x(I, S)$  the propagator is

$$\begin{aligned} U(\tau) &= \exp(i\pi/2(I_x + S_x)) \exp(-iJ'\tau/2) \exp(i\pi(I_x + S_x)) \exp(-iJ'\tau/2) \exp(i(\pi/2)I_x) \\ &= \exp(-i\tau J' I_y S_y) \exp(i\pi S_x) \end{aligned} \quad [3]$$

The simultaneous  $\pi$  pulses remove the dependence on the offset terms in the Hamiltonian of Eq. [2] making the propagator even quantum selective (4,10,18) and dependent only on the variable  $J'\tau$ .

The density operator at the end of the preparation period is  $\rho(\tau) = U(\tau)\rho(0)U^{-1}(\tau)$ . Neglecting the term proportional to the identity this is given by

$$\begin{aligned}\rho(\tau) &= \exp(-i\tau J' I_y S_y)(b I_z) \exp(i\tau J' I_y S_y) \\ &= b [I_z \cos(J'\tau S_y) + I_x \sin(J'\tau S_y)] \\ &= b \{ I_z [1 + S_y^2 (\cos J'\tau - 1)] + I_x S_y \sin J'\tau \}\end{aligned}\quad [4]$$

In the last step, the identities

$$\cos(\theta S_y) = 1 + S_y^2 (\cos\theta - 1) \quad [5a]$$

$$\sin(\theta S_y) = S_y \sin\theta \quad [5b]$$

appropriate to  $S = 1$  have been used. The initial equilibrium spin density operator proportional to  $S_z$  is not included in the expression, since it does not yield DQ coherence nor will it lead to an eventual signal in the proton channel. Eq. [4] can be written using the fictitious spin 1/2 operators (19, 20) for the S operators:

$$\rho(\tau) = b \{ I_z [1 + (2/3 - S_x^{1-3} - 1/3 (S_z^{1-2} - S_z^{2-3})) (\cos J'\tau - 1)] + \sqrt{2} I_x (S_y^{1-2} + S_y^{2-3}) \sin J'\tau \} \quad [6]$$

This expansion shows that  $S_y^2$  consists of zero quantum and DQ operators. The coefficient of the operator  $I_z S_y^2$ , and thus of the  $(n^I = 0, n^S = \pm 2)$  coherence  $I_z S_x^{1-3}$ , is maximized by setting  $\tau = 1/2J$  sec, where J is in Hz.

The prepared coherences evolve during  $t_1$ . Since only  $(n^I = \pm 1, n^S = 0)$  coherences can freely evolve into proton transverse magnetization, the



$\pi/2$  pulses at the end of  $t_1$  are needed to convert MQ coherence into such SQ coherence. For each increment in  $t_1$ , only the peak of the MQ spin echo at  $t_2 = \tau$  was sampled in the proton channel. The resulting heteronuclear MQ interferogram as a function of the evolution time  $t_1$  is the autocorrelation function of  $\rho(\tau) = \rho(\tau, t_1 = 0)$ . Neglecting relaxation and with  $\Delta_1 = \Delta_2 = 0$  (Fig. 1), this is

$$\begin{aligned}
 S(t_1) &= \text{Tr}\{\rho(\tau, 0)\rho(\tau, t_1)\} \\
 &= \text{Tr}\{\rho(\tau, 0)\exp(-it_1 J' I_z S_z)\rho(\tau, 0)\exp(it_1 J' I_z S_z)\} \\
 &= \sum_{i,j} |\rho(\tau, 0)|_{i,j}^2 \exp(-i\omega_{ij} t_1)
 \end{aligned} \tag{7}$$

where  $\omega_{ij} = \omega_i - \omega_j$  and  $\omega_i = \langle i | J' I_z S_z | i \rangle$ .

Evaluation of the matrix elements of  $I_z S_x^{1-3}$  (Eq. 6) for the case of four equivalent  $I_1 = 1/2$  spins shows that the DQ spectrum is a quintet with line separation of  $2J$  and line amplitude of

$$\begin{aligned}
 A(m^I) &= \frac{1}{4}(\cos J'\tau - 1)(\cos J't_2 - 1)(m^I)^2 g(m^I) \\
 &= \begin{cases} (\cos J'\tau - 1)(\cos J't_2 - 1) & , \quad m^I = \pm 2 \\ (\cos J'\tau - 1)(\cos J't_2 - 1) & , \quad m^I = \pm 1 \\ 0 & , \quad m^I = 0 \end{cases}
 \end{aligned} \tag{8}$$

Note that the central line of the quintet has zero amplitude. The degeneracies  $g(m^I)$  are 1, 4, 6 for  $m^I = \pm 2, \pm 1, 0$ , respectively.

The fixed time delays  $\Delta_1$  and  $\Delta_2$  are included to selectively echo the desired order for detection. The scheme is similar to pulsed field gradient methods (17), except that here the static field inhomogeneity and a longer time delay are used for the dephasing and selective rephasing. Advantage is taken of the proportionality of the

dephasing rate to  $n^I \gamma_I + n^S \gamma_S$ , thereby allowing separation of various MQ echoes. Sampling at the peak of the desired MQ echo results in detection of the selected order and suppression of the other orders. In our experiments, the  $^{14}\text{N}$  DQ coherence dephases at a rate proportional to  $2\gamma_S$  in  $\Delta_1$  and rephases as proton SQ coherence at a rate proportional to  $\gamma_I$  in  $\Delta_2$ . To observe the  $^{14}\text{N}$  DQ coherence echo as proton transverse magnetization,  $\Delta_2$  must be set at:

$$\Delta_2 = \frac{2\gamma_S}{\gamma_I} \Delta_1 \quad [9]$$

This scheme can be viewed as a coherence transfer echo filtering (CTEF) process. The desired DQ signal is a small oscillation on top of a large signal originating from coherences not of DQ nature, the largest being from the  $\text{H}_2\text{O}$  solvent. Fluctuations in the large signal due to instrumental instability appear in the Fourier transform as noise at all values of  $\omega_1$ . Because this  $t_1$  noise can be comparable to the DQ signal, it is desirable to eliminate it by "filtering" out the large signal. In addition, the dynamic range requirements of the spectrometer are reduced, since the largest signals never reach the receiver.

Pulse sequence B differs from A only in the way the separation of MQ orders is accomplished. Because of the tensorial properties of MQ operators expressed in Eq.[1], the center of the order  $(n^I, n^S)$  is at  $n^I \Delta\omega_I + n^S \Delta\omega_S$ . Pulse sequence A requires a real resonance offset, whereas pulse sequence B creates an artificial offset by TPPI (7,16). The  $\pi$  pulses in  $t_1$  remove all real resonance offset terms and thus field inhomogeneity. The phase incrementation of the S rf pulses in the preparation period for each incrementation in  $t_1$  effects an apparent S frequency offset in the observing frame. TPPI yields a spectrum

that is free of inhomogeneous broadening and yet retains separation of MQ orders.

## RESULTS AND DISCUSSION

Spectra were obtained at 27°C of an 8 molar  $\text{NH}_4\text{NO}_3$  aqueous solution acidified to pH 1 to slow down proton exchange with the solvent. The spectrum in Fig. 2 was obtained using pulse sequence A with the  $^{14}\text{N}$  carrier frequency offset by 0.85 kHz from  $\text{NH}_4^+$  resonance and the proton carrier frequency on resonance at 185 MHz. The time delays  $\Delta_1$  and  $\Delta_2$  were set according to Eq. [9]. The central peak at  $\Delta\omega = 0$  arises predominantly from imperfect CTEF of the longitudinal proton magnetization of the solvent  $\text{H}_2\text{O}$  present during evolution. Other contributions are from the zero quantum portion of  $I_z S_y^2$  and from  $I_z$  of the ammonium protons, both of which terms are present in  $\rho(\tau)$  even when DQ coherence is maximized (Eq. [4-6]). The multiplet corresponds to the DQ coherence transfer spectrum of  $^{14}\text{N}$ . Its center is offset by 1.70 kHz which is twice the carrier frequency offset, the splitting is  $2J$ , and the linewidth is twice that of  $^{14}\text{N}$  SQ inhomogeneous linewidth - all of which are indicative of  $^{14}\text{N}$  DQ transitions.

Figure 3 shows the improvement in resolution of the multiplet using pulse sequence B with the same parameter settings. The spectrum is a quintet with relative amplitudes of 1 : 1 : 0 : 1 : 1 and splittings of  $2J$ , in agreement with the calculations (Eq. [8]). The splitting is  $105 \pm 1$  Hz; the homogeneous absorption linewidth (full width at half maximum) is  $7 \pm 1$  Hz as compared with the inhomogeneous linewidth of 70-80 Hz in Fig. 2.

Also of importance is the comparison of the homogeneous  $^{14}\text{N}$  DQ and SQ linewidths. Through a conventional  $^{14}\text{N}$  detected spin echo sequence, with a simultaneous  $\pi$  pulse applied to the protons to preserve the

J coupling, the absorption linewidth of  $^{14}\text{N}$  SQ coherence was measured to be  $6.4 \pm 0.5$  Hz. To within the measurement error, the  $^{14}\text{N}$  DQ and SQ homogeneous linewidths are the same.

In both Figs. 2 and 3, the magnitude spectra are displayed. The lines of the quintet can in principle be observed in phase (Eq. [7]), but were not because of the use of CTEF. The insertion of the time delay  $\Delta_1$  in  $t_1$  necessitates that the heteronuclear MQ interferogram is first sampled not at  $t_1 = 0$  but at  $t_1 = \Delta_1$ . During the extra time  $\Delta_1$ , the lines accumulate phase at different rates resulting in a large phase shift linear in  $\omega_1$ .

To demonstrate the sinusoidal dependence of the  $I_z S_x^{1-3}$  operator on preparation time (Eq. [6]), pulse sequence B was employed with  $t_2$  held constant for different values of  $\tau$ . With  $t_2$  fixed, the line amplitude varies with  $\tau$  as  $(\cos J\tau - 1)\exp(-\tau/T_2)$ , where now  $T_2$  refers to the  $n^I = 1$  homogeneous decay time. Figure 4 shows the integrated line amplitude of the quintet as a function of  $\tau$ . A least squares analysis gave  $T_2 = 80 \pm 11$  ms.

In summary, DQ transitions in  $^{14}\text{N}$ , a quadrupolar nucleus of spin  $S = 1$ , is made possible through the J coupling to the protons. Sensitivity is greatly improved by indirectly detecting the quadrupolar nuclei through the protons. Using TPPI and a spin echo in the evolution period, the inherently higher resolution of the DQ spectrum is realized.

#### ACKNOWLEDGEMENT

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1. G. Bodenhausen, Prog. NMR Spectros. 14, 137 (1981).
2. S. Vega and A. Pines, J. Chem. Phys. 66, 5624 (1977).
3. S. Hsi, H. Zimmerman and Z. Luz, J. Chem. Phys. 69, 4126 (1978).
4. D. Wemmer, Ph.D. Thesis, University of California, Berkeley (1978).
5. J. H. Prestegard and V. W. Miner, 22nd Experimental NMR Conference (1981); V. W. Miner and J. H. Prestegard, J. Am. Chem. Soc. 103, 5979 (1981)
6. W. P. Aue, E. Bartholdi and R. R. Ernst, J. Chem. Phys. 64, 2229 (1976).
7. G. Drobny, A. Pines, S. Sinton, D. P. Weitekamp and D. Wemmer, Faraday Symp. Chem. Soc. 13, 49 (1979).
8. A. A. Maudsley and R. R. Ernst, Chem. Phys. Lett. 50, 368 (1977).
9. A. A. Maudsley, A. Wokaun and R. R. Ernst, Chem. Phys. Lett. 55, 9 (1978).
10. L. Müller, J. Am. Chem. Soc. 101, 4481 (1979).
11. D. P. Weitekamp, J. R. Garbow and A. Pines, submitted to J. Chem. Phys.
12. A. Minoretti, W. P. Aue, M. Rheinhold and R. R. Ernst, J. Mag. Res. 40, 175 (1980).
13. S. Vega, T. W. Shattuck and A. Pines, Phys. Rev. A 22, 638 (1980).
14. P. Brunner, M. Rheinhold and R. R. Ernst, J. Chem. Phys. 73, 1086 (1980).
15. M. Rheinhold, P. Brunner and R. R. Ernst, J. Chem. Phys. 74, 184 (1980).
16. G. Bodenhausen, R. L. Vold and R. R. Vold, J. Mag. Res. 37, 93 (1980).
17. A. Bax, P. G. de Jong, A. F. Mehlkopf and J. Smidt, Chem. Phys. Lett. 69, 567 (1980).
18. W. S. Warren, D. P. Weitekamp and A. Pines, J. Chem. Phys. 73, 2084 (1980).
19. A. Wokaun and R. R. Ernst, J. Chem. Phys. 67, 1752 (1977).
20. S. Vega, J. Chem. Phys. 68, 5518 (1978).

## FIGURE CAPTIONS

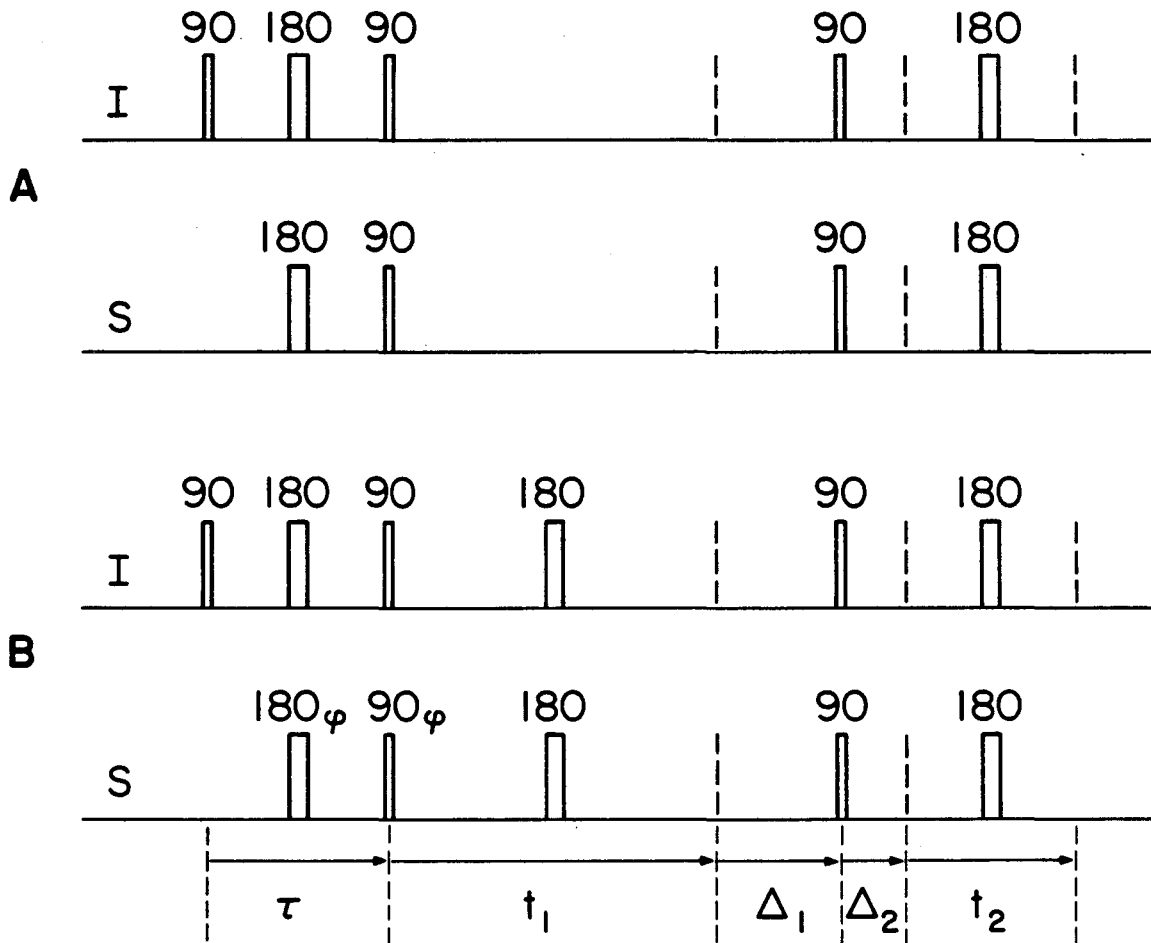
Fig. 1: Pulse sequences used for observing heteronuclear MQ coherence.

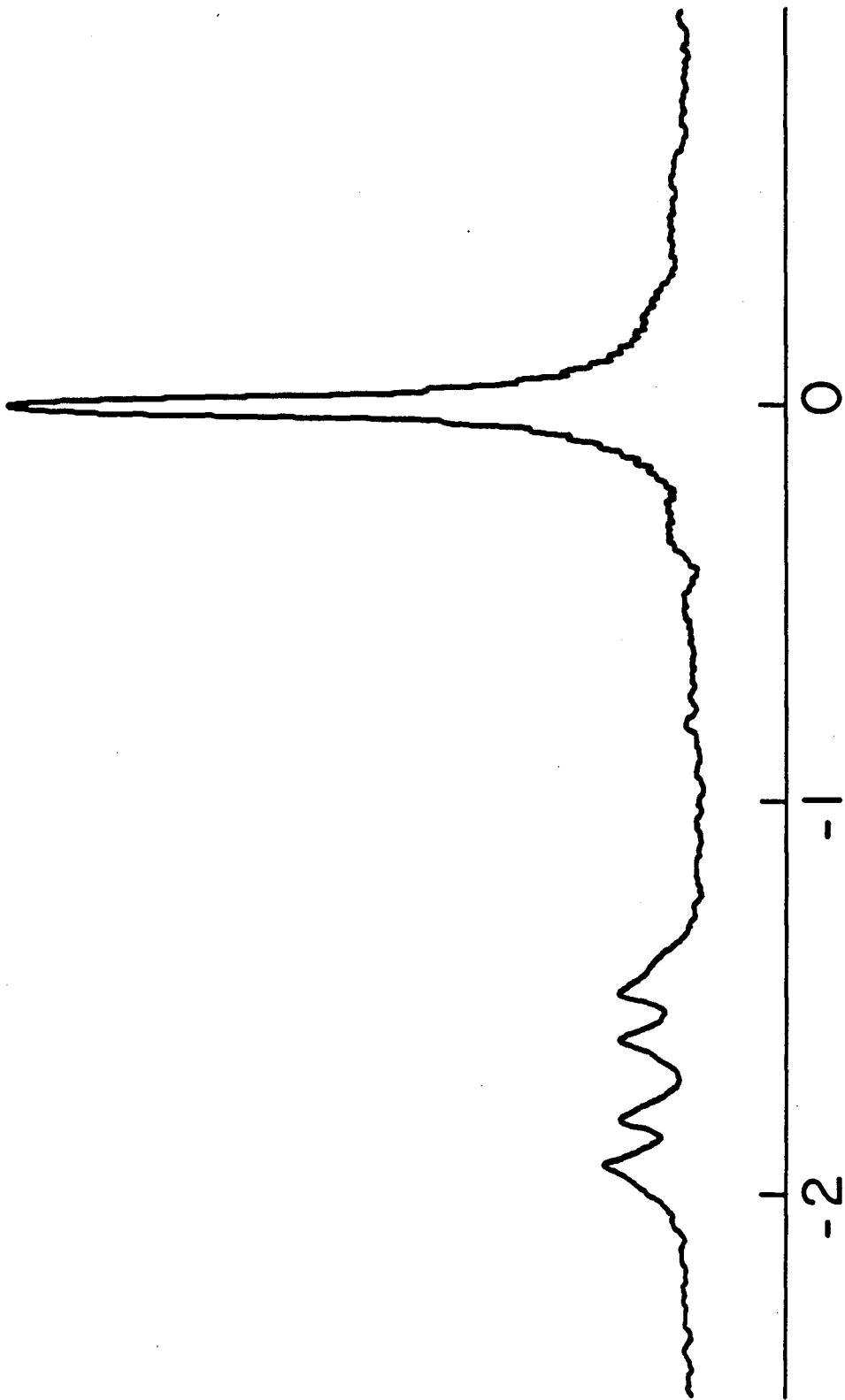
The I spin FID is monitored at  $t_2 = \tau$ . Pulse sequence B has the first two S spin rf pulses phase shifted by  $\phi = \Delta\omega t_1$  (TPPI). All other rf pulses of a given frequency may be of the same phase. The delays  $\Delta_1$  and  $\Delta_2$  allow suppression of the signal from all but one order of coherence.

Fig. 2: Proton detected heteronuclear MQ magnitude spectrum of acidified 8 molar  $\text{NH}_4\text{NO}_3$  aqueous solution observed at 185 MHz. The spectrum is obtained using pulse sequence A in Fig. 1 with  $^{14}\text{N}$  carrier frequency offset from  $\text{NH}_4^+$  resonance by  $\Delta\omega_S = 0.85$  kHz,  $\tau = t_2 = 9.6$  ms,  $t_1$  increment = 200  $\mu\text{s}$ ,  $\Delta_1 = 11.327$  ms and  $\Delta_2 = 1.618$  ms. The incompletely suppressed on-resonance line arises predominantly from longitudinal  $\text{H}_2\text{O}$  magnetization present during  $t_1$ . The multiplet with the center offset by 1.70 kHz is the  $^{14}\text{N}$  DQ spectrum.

Fig. 3: Proton detected  $^{14}\text{N}$  DQ magnitude spectrum using pulse sequence B in Fig. 1 with  $^1\text{H}$  and  $^{14}\text{N}$  carrier frequencies on resonance.  $\tau = t_2 = 10$  ms; all other parameter settings are the same as in Fig. 2. The spectrum is a quintet with 1 : 1 : 0 : 1 : 1 amplitude ratio and 105 Hz peak separation.

Fig. 4: Normalized  $^{14}\text{N}$  DQ line amplitude as a function of the preparation time  $\tau$ . The experimental points are compared with the solid theoretical curve of  $(\cos J\tau - 1)\exp(-\tau/T_2)$ .

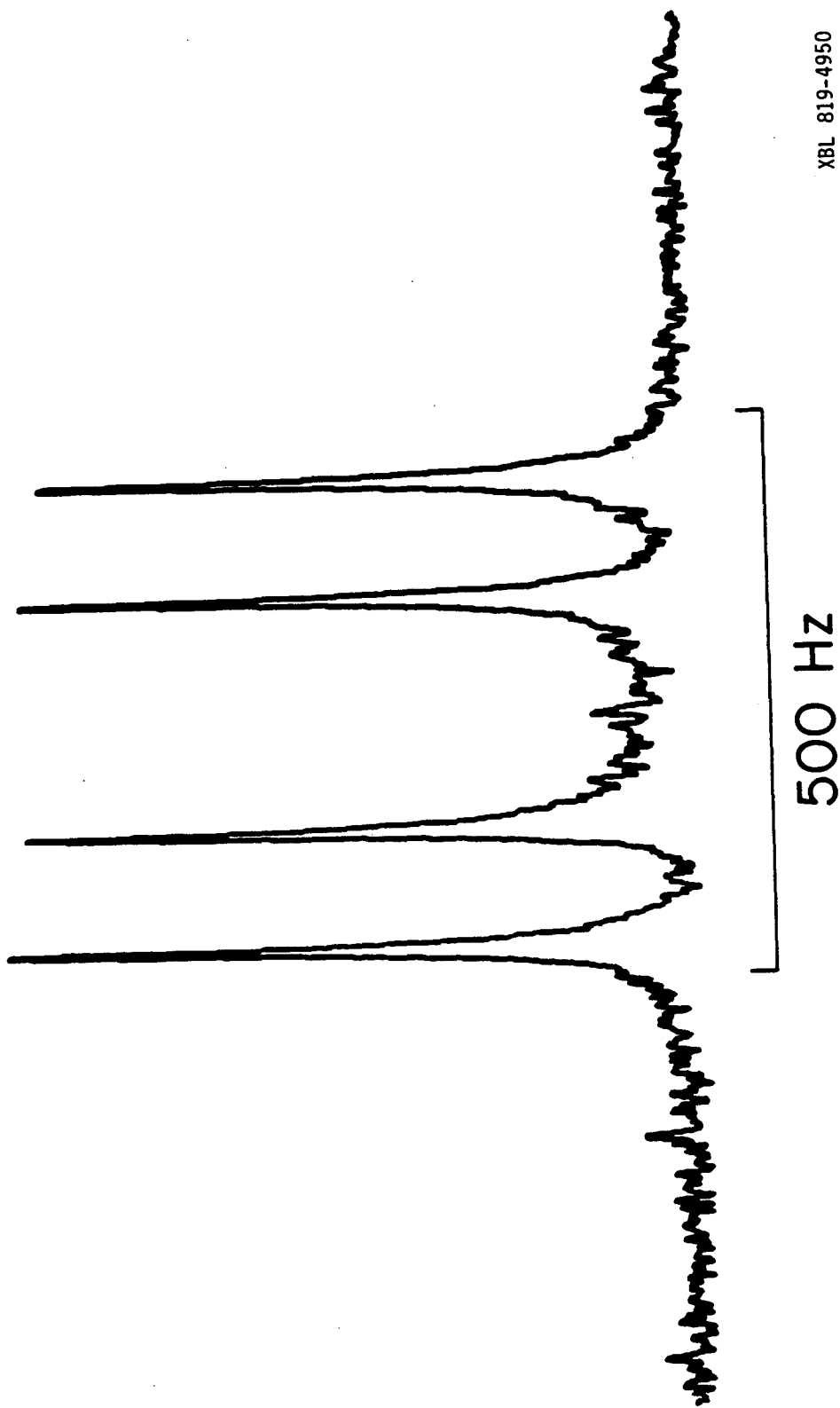


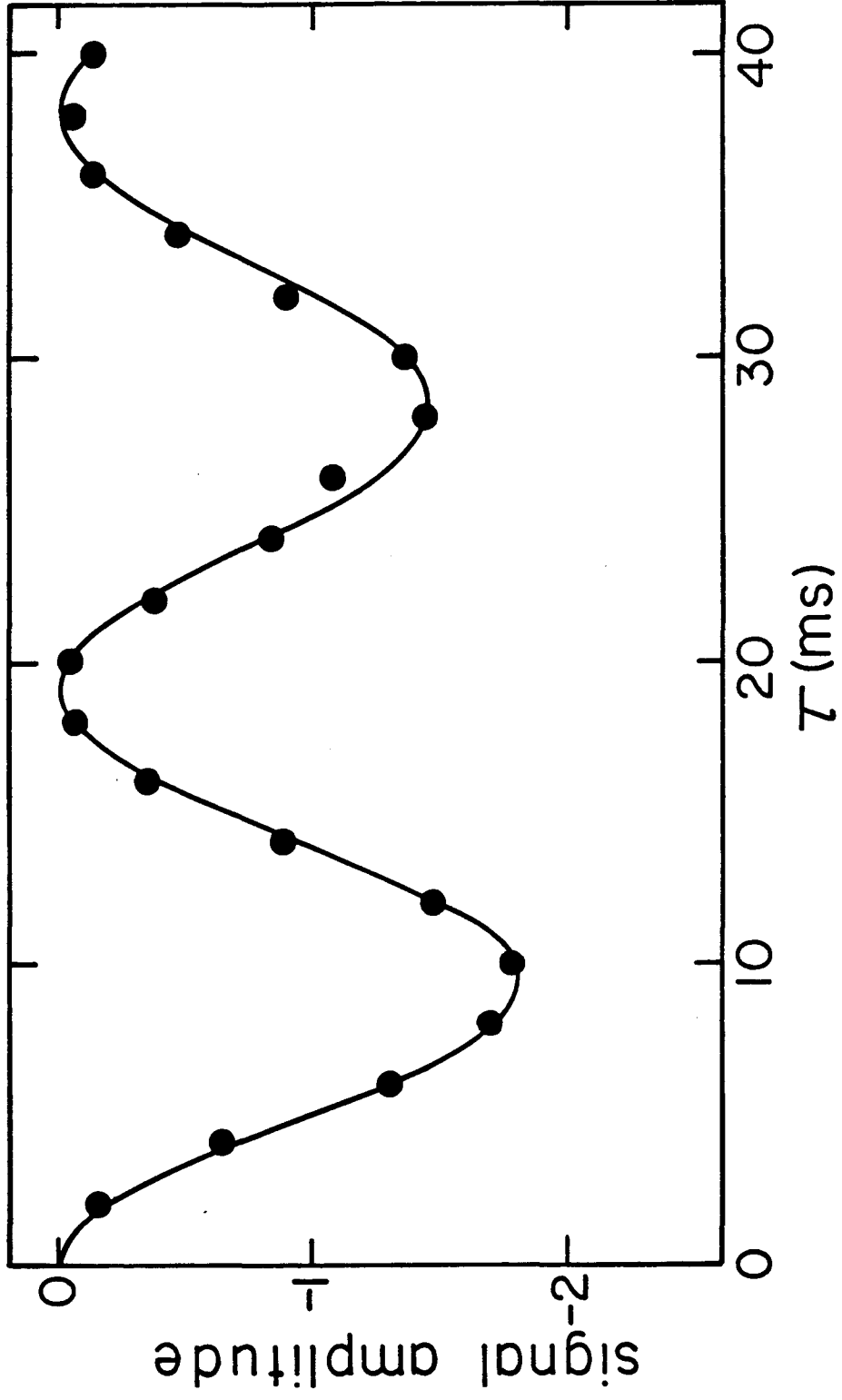


$\Delta\omega$  (kHz)

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