# SUPPRESSION OF THE ZERO FREQUENCY PEAK IN ZERO FIELD NMR

T.P. JARVIE, K. TAKEGOSHI, D. SUTER, A. PINES

*Department of Chemistry, University of California, Berkeley,*
*and Material and Chemical Science Division, Lawrence Berkeley Laboratory, Berkeley, CA 94720, USA*

and

D.B. ZAX

*Department of Isotope Research, Weizmann Institute of Science, Rehovot 76100, Israel*

In zero field NMR, a peak at zero frequency arising from nonevolving magnetization often obscures low-frequency lines. An indirect observation of second-rank order time evolution in zero field enables suppression of the zero frequency peak. This opens the possibility for resolution of previously marked low-frequency lines.

The time domain zero field NMR spectrum for a pair of spins-1/2, such as protons in polycrystalline $Ba(ClO_3)_2 \cdot H_2O$, consists of three lines [1–3]. One of the lines, which appears around zero frequency, arises from spins that do not evolve or evolve very slowly. Indeed Kubo and Toyabe have previously shown that, in a system of random dipole–dipole couplings and in powdered materials, one third of the total magnetization prepared is nonevolving [4]. The two other lines in the zero frequency spectrum appear at frequencies of $\pm \frac{3}{2}\omega_D = \gamma^2 \hbar / r^2$, where $\gamma$ is the gyromagnetic ratio and $r$ is the interproton distance. As $\omega_D$ depends strongly on $r$, zero field NMR provides a means of determining distances in polycrystalline samples [5]. However, when an interproton distance is greater than about 4 Å, the separation between the peaks at $\pm \frac{3}{2}\omega_D$ becomes too small to be resolved from the zero frequency peak. Further, low-frequency lines which arise from small-amplitude motions [6,7] are often similarly hidden. In this paper we demonstrate a simple way of suppressing the zero frequency peak and illustrate its application to several samples.

Two possible procedures for suppression of the zero frequency peak are schematically shown in fig. 1. In each case the spin system is prepolarized in a large

applied magnetic field, manipulated so as to reveal the spin couplings in the absence of those fields, and finally returned to the large applied field where the evolved magnetization is sampled. This cycle is repeated for a number of values of $t_1$. The resulting data array $S(t_1)$ may then be Fourier transformed and will reveal the zero field evolution frequencies. Details concerning the implementation of both such field cycles are found elsewhere [1–3,8].

In isolated spin systems, and in the absence of relaxation, the signals predicted from the two variations of the experiment shown in fig. 1 are identical (to within a possible change of sign). As the spin temperature hypothesis is inappropriate for spin systems where the zero field spectrum consists of discrete absorption frequencies, the initial condition achieved after slow demagnetization, or the final condition achieved after remagnetization is not generally known. Considerable insight, however, into the basic physical phenomenon can be obtained by considering an ideal three-level system such as might be represented by a spin-1 nucleus or the triplet sublevel of two dipolar coupled spins-1/2.

A theoretical basis for analyzing such sequences and a number of relevant calculations appear elsewhere [9]. For concreteness, and because of several
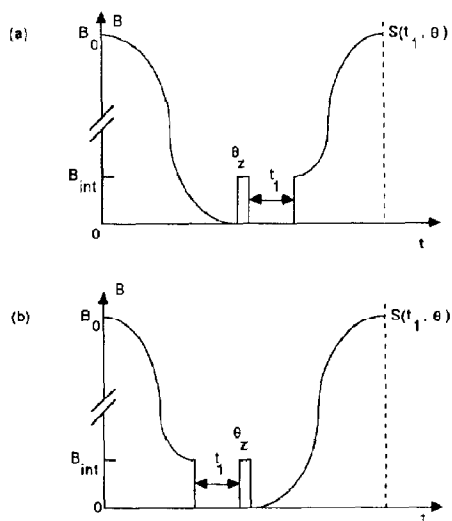
Fig. 1. Schematic field cycles for the zero frequency suppression experiment which correlates dipolar magnetization with higher-rank tensor operators. (a) The sample is slowly removed from high field (4.2 T) to zero field. A dc magnetic field pulse of angle $\theta_z$ initiates evolution which proceeds for a time $t_1$. Termination of the evolution is caused by the sudden reapplication of an intermediate field (0.01 T) along the z-axis. The sample is slowly remagnetized to high field where the signal as a function of $t_1$ is measured. The maximum signal is achieved when $\theta_z$ is 50°. (b) Similar to (a) except the sequence in low field is reversed. The sudden transition initiates evolution which proceeds for a time $t_1$. Evolution is terminated by the application of a dc field pulse.

inherent experimental advantages, we concentrate in what follows on the sequence illustrated in fig. 1a. While the subject of this paper is primarily of use in dipolar coupled systems, calculations are most efficiently performed by using the analogy between the triplet state of two coupled homonuclear spins-1/2 and the three-level system of eigenstates which characterize a spin-1 nucleus (such as $^2$H) conventionally designated as $|x\rangle$, $|y\rangle$, and $|z\rangle$. Throughout we shall use the notation appropriate to pure nuclear quadrupole resonance of spin-1 [10] which applies equally well (with minor notational differences) to pure nuclear dipole resonance of a pair of spins-1/2.

Computer simulations and simple arguments appealing to the adiabaticity condition [8,9,11,12] have shown that when an isolated three-level system is adiabatically demagnetized from a large applied field to zero field, the populations are transferred (essentially completely) directly to eigenstates of the zero

field Hamiltonian. Thus, given a density operator $\rho$ consisting of only populations $\rho_{ii}$ in a large external field, under slow demagnetization (and ignoring relaxation) the same numbers $\rho_{ii}$ characterize $\rho$ in zero applied field, where $\rho$ is consistently defined for each crystallite in a local frame of reference.

In a three-level system there are two constants of the motion (two diagonal operators which commute with the Hamiltonian). In high field, where the effective quadrupolar Hamiltonian is

$$H_{hf} = -\delta_\omega I_z - 0.5\omega_q[(3\cos^2\theta - 1)$$
$$+ \eta\sin^2\theta\cos 2\phi](3I_z^2 - I^2) ,$$

the constants of the motion are Zeeman order (proportional to $I_z$) and quadrupolar order (proportional to $3I_z^2 - I^2$). In zero field, where the effective Hamiltonian is

$$H_{zf} = \omega_q[(3I_z^2 - I^2) + \eta(I_x^2 - I_y^2)] ,$$

the constants of the motion are quadrupolar order and "eta-order" (proportional to $I_x^2 - I_y^2$). For pairs of dipolar coupled spins, the same is true if we everywhere replace "quadrupolar" with "dipole–dipole" and allow for $\eta \neq 0$, a motionally induced asymmetry parameter [6,7].

For the three-level system, equilibrium in high field corresponds to a Zeeman ordered state (dipolar magnetization). After adiabatic demagnetization all nuclear spin order is conserved but no dipolar magnetization remains because $\rho$ is diagonal in a local frame only. After demagnetization, evolution is initiated by a dc magnetic field pulse of strength $\theta = 2\pi Bt$ (where $\theta$ is the flip angle, $B$ the magnetic field strength and $t$ the duration of the pulse) along a laboratory axis. Following evolution, a large static magnetic field is applied which freezes the evolution and newly developed dipolar magnetization. Only for freezing fields aligned parallel to the excitation pulse can signal be observed. This result is well known from more traditional NQR studies [13].

For the initial condition described above (all populations uniformly carried over to the corresponding spin eigenstates in zero field) we find

$$S(t_1, \theta) \propto (2\sin 2\theta + \sin \theta)$$
$$\times [5(\sin \omega_{yz}t + \sin \omega_{zx}t) + 4\sin \omega_{xy}t] ,$$

where $\omega_{\alpha\beta}$ is the frequency between levels $\alpha$ and $\beta$.

In an isolated three level system the magnetization produced after a $\theta$ pulse is always proportional to $2 \sin 2\theta + \sin \theta$. This holds independent of the initial condition as long as the demagnetized operator $p$ is independent of orientation. Note that the signal grows in as the sines of the evolution frequencies, as is appropriate for an experiment which interrogates cross correlations [14]. Only spins which can support either quadrupolar and/or multispin dipole–dipole order, and whose evolution frequencies are nonzero, can contribute to the macroscopic magnetization returned to high field at the end of $t_1$. Kreis et al. [12] have developed an alternative, phase cycling approach, which allows for suppression of $\nu_0$ or $\nu_+$ and $\nu_-$ lines by using low-frequency pulses.

These conclusions, derived with specific reference to the three-level system only, can be easily generalized to other systems and Hamiltonians, $H$. In zero field, $H$ is a sum over second-rank tensors, and $p$ commutes with $H$ only if it is comprised of even-rank time-independent tensor operators. A short field pulse transforms populations of $p$ into coherences, and time evolution under $H$ creates some odd-rank tensor operators (including magnetization, a first-rank tensor operator). A trapping field then freezes that portion of the spin order which projects onto magnetization pointing along the axis of the field pulse. Nonevolving operators, or spin systems which cannot support the multispin operators characteristic of higher-order tensors, cannot contribute to the observed cross-correlation signal.

Figs. 2a and 2b show the zero field NMR spectra of the protons in polycrystalline $Ba(ClO_3)_2 \cdot H_2O$ obtained by using the conventional sudden experiment [1–3] and the suppression sequence shown in fig. 1a, respectively. In the latter the zero frequency peak appears to be effectively suppressed. A series of experiments performed by varying $\theta$ confirm the intensity dependence predicted in the equation for $S(t_1, \theta)$. Experiments utilizing the sequence in fig. 1b were less successful in suppressing the zero frequency peak, probably because this field cycle is more sensitive to distortions which may arise from less than ideal demagnetization/remagnetization during the field cycle. As the slow remagnetization occurs after $t_1$, the signal measured in high field may suffer from different distortions for each point in $t_1$.
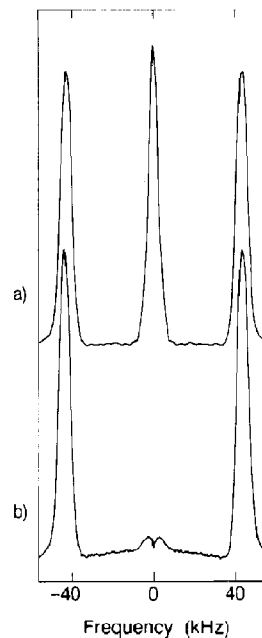
The system illustrated in fig. 3 corresponds to the



Fig. 2. (a) Experimental spectrum of polycrystalline $Ba(ClO_3)_2 \cdot H_2O$ obtained by the conventional sudden experiment. Here the zero frequency peak is equal in intensity to the peaks at $\pm \frac{3}{2}\omega_D$. (b) Phase-corrected experimental spectrum of polycrystalline $Ba(ClO_3)_2 \cdot H_2O$ obtained by the suppression scheme shown in fig. 1a. Here $\theta_2$ is between 40 and $60°$.

two spin-1/2 $^1H$ atoms undergoing correlated exchange in $p$-toluic acid dimer [6]. Due to the motion, the dipole–dipole interaction becomes asymmetric and a low-frequency peak is expected in the spectrum. Residual $^1H$ atoms with no near neighbors in the lattice (the sample is 60% deuterated at the acid sites and 98% deuterated elsewhere) contribute to the large zero frequency peak observed in the normal zero field NMR experiment (fig. 3a). Where we monitor instead the cross-correlation spectrum (fig. 3b), the previously masked low-frequency line is clearly observed.

Although the theory here is relevant to a proton pair, the underlying idea for the suppression experiment, that is, observation of only those coherences which correspond to correlations between multispin order created in the demagnetization to zero field and trapped by the sudden reapplication of a large magnetic field, does work for larger spin systems as shown in fig. 4. Figs. 4a and 4b show the conventional and suppressed zero field NMR spectra, respectively, for
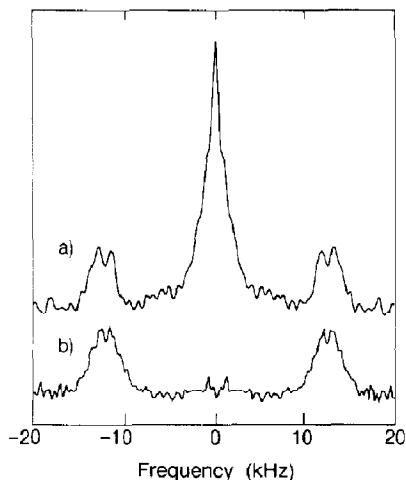
Fig. 3. (a) Conventional sudden experiment spectrum of poly-crystalline p-toluic acid. The splitting between the peaks at 11.8 and 12.8 kHz arises from the correlated motion of the H-bonded carboxyl protons in p-toluic acid dimers. The difference peak predicted to be observed at 1.0 kHz is hidden under the broad line arising from residual protons with no near neighbors in the lattice. (b) Experimental spectrum of polycrystalline p-toluic acid obtained with the suppression technique in fig. 1a. Suppression of the peak due to nonevolving magnetization allows us to observe the weak difference frequency line.
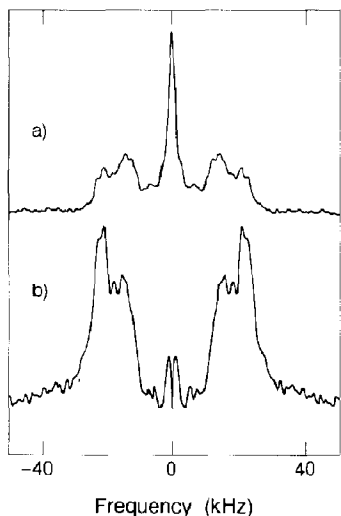


Fig. 4. (a) Sudden experiment spectrum of 1,2,3,4-tetrachloro-naphthalene bis-(hexachlorocyclopentadiene) adduct, a sample which can be treated as relatively isolated four-proton groups. (b) Suppression spectrum of the adduct obtained with the field cycle in fig. 1a. Here the zero frequency peak is suppressed leading to improved dynamic range in the rest of the spectrum. One can see, however, that the amplitudes of the peaks are not preserved in the four-proton system.

an approximately isolated four-proton system in 1,2,3,4-tetrachloronaphthalene bis-(hexachloropentadiene) adduct [2]. Suppression of the intense zero frequency peak (fig. 4b) leads to improved dynamic range for the remainder of the spectrum, which contains information about the dipole–dipole couplings and structure of the four-proton system.

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