

HETERONUCLEAR ZERO-FIELD NMR

D.B. ZAX, A. BIELECKI, K.W. ZILM[‡] and A. PINES

Department of Chemistry and Materials and Molecular Research Division, Lawrence Berkeley Laboratory, University of California, Berkeley, California 94720, USA

Received 2 March 1984

The NMR spectra of polycrystalline solids are often best resolved in the absence of applied magnetic fields. Additionally, heteronuclear spin systems in zero field display features not observed in homonuclear systems. In this letter, spectra are presented and analyzed for the cases of heteronuclear spin pairs in ¹³C-enriched β-calcium formate (solid) and in diethyl phosphite (liquid).

1. Introduction

In zero-field NMR [1,2], a sample is subjected to a time-dependent magnetic field which cycles between a high value, B_0 , and zero field. The B_0 field is useful for preparation and high-sensitivity detection of the spins. Evolution occurs for a variable time t_1 in zero field. This yields sharp crystal-like NMR spectra from polycrystalline samples, where ordinarily only powder patterns are observed. Examples have been shown for groups of coupled protons in solids [1], as well as Fourier-transform pure NQR of ²D, ⁷Li [2], and ²⁷Al [3].

An interesting situation arises if the coupled spins are inequivalent; that is, their natural resonance frequencies differ widely due to chemical shifts or because the nuclei are of different species (e.g. the heteronuclear pair $I = {}^1\text{H}$, $S = {}^{13}\text{C}$). Consider, in fact, a single I - S spin pair coupled by a dipolar interaction*

$$\mathcal{H}_{IS} = \omega_{IS}^D(I \cdot S - 3I_z S_z), \quad (1)$$

where $\omega_{IS}^D = \gamma_I \gamma_S \hbar / r_{IS}^3$.

In zero field, the eigenstates of the zero-field hamiltonian (1) (singlet and triplet manifolds) are

[‡] Present address: Department of Chemistry, Yale University, 225 Prospect Street, P.O. Box 6666, New Haven, Connecticut 06511, USA.

* Note that this definition of the dipolar coupling constant, ω_{ij}^D , differs from that of ref. [1]. In addition, that ω_{ij}^D incorrectly includes a factor of $1/\pi$.

identical to the homonuclear case ($I = S$) [1] because (1) is invariant to the exchange of I and S . However, unlike the equivalent-spin case, at high field the effective hamiltonian is

$$\mathcal{H}_{IS}^{(0)} = -\omega_I I_z - \omega_S S_z + \omega_{IS}^D(1 - 3\cos^2\theta)I_z S_z$$

and I and S spins can be manipulated independently. This allows the preparation of initial zero-field conditions which are not possible for equivalent spins. As a consequence of this inequivalence, additional zero-field transitions arise; by suitable preparation, particular subsets of transitions can be enhanced or eliminated. These factors should be valuable in disentangling zero-field spectra arising from different functional groups.

2. Eigenstates and transitions

Fig. 1 summarizes the relevant eigenstates and possible transitions for I - I and I - S pairs at high and zero fields. Assume we begin the experiment in B_0 with an initial state of polarization. In the high-temperature approximation, the density matrix is given by

$$\rho = 1/Z_I + a_I I_z + 1/Z_S + a_S S_z, \quad (2)$$

where

$$a_I = -\frac{1}{Z_I} \frac{\gamma_I \hbar B_0}{kT}, \quad a_S = -\frac{1}{Z_S} \frac{\gamma_S \hbar B_0}{kT}$$

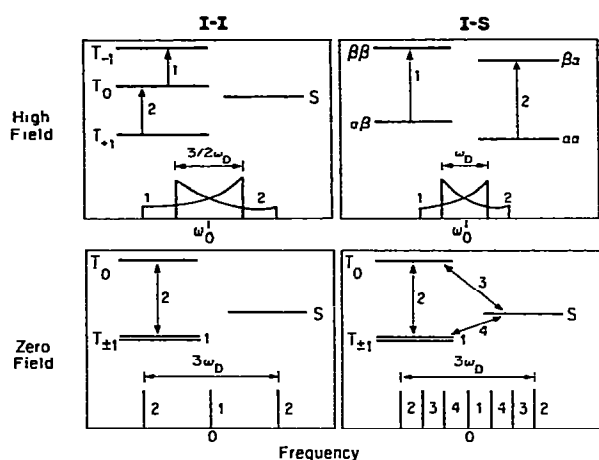


Fig. 1. Energy-level diagrams for homonuclear ($I-I$) and heteronuclear ($I-S$) dipolar coupled spin pairs in high and zero applied magnetic field. The allowed transitions are indicated by arrows between states. In high field the transition frequencies are orientation dependent and fall in a broad range. In zero field, the transition frequencies are orientation independent and appear as sharp lines at characteristic frequencies. The high-field eigenstates are quantized along the applied field; the zero-field eigenstates along the internuclear vector. In the direct product basis set $T_1 = \alpha\alpha$, $T_0 = \frac{1}{2}(\alpha\beta + \beta\alpha)$, $T_{-1} = \beta\beta$, $S = \frac{1}{2}(\alpha\beta - \beta\alpha)$.

and the Z s represent partition functions. As the constant parts of eq. (2) commute with all rotations, the portion of the density matrix of interest in an NMR experiment is given by the reduced density matrix

$$\rho_0 = a_I J_z + a_S S_z \quad (3)$$

Upon sudden switching of the field to zero the initial density matrix at $t_1 = 0$ is then given by eq. (3) which we rewrite as:

$$\rho_0^{(0)} = \frac{1}{2}(a_I + a_S)(I_z + S_z) + \frac{1}{2}(a_I - a_S)(I_z - S_z) \quad (4)$$

The last, antisymmetric term is peculiar to the heteronuclear (or inequivalent) spin pair. Calculating the evolution in t_1 of the magnetization represented in eq. (4) we find

$$\begin{aligned} M_z(t_1) = & \frac{1}{3} \left[\frac{1}{2}(a_I + a_S) \right] \\ & + \frac{2}{3} \left[\frac{1}{2}(a_I + a_S) \right] \cos\left(\frac{3}{2}\omega_{IS}^D t_1\right) \\ & \pm \frac{2}{3} \left[\frac{1}{2}(a_I - a_S) \right] \cos\left(\frac{1}{2}\omega_{IS}^D t_1\right) \\ & \pm \frac{1}{3} \left[\frac{1}{2}(a_I - a_S) \right] \cos(\omega_{IS}^D t_1), \end{aligned} \quad (5)$$

where \pm refer to $M = I$ or $M = S$ spin magnetization, respectively. The first two terms correspond to the homonuclear case and connect states only within the triplet manifold. The last two terms arise from the initial polarization difference and correspond to transitions between singlet and triplet states. In all, the Fourier transform of eq. (5) should exhibit seven lines, one at zero frequency and 3 pairs. Identical frequencies appear whichever nucleus is observed in high field.

3. Experimental

All seven lines can be seen in fig. 2, where we present spectra of β -calcium formate enriched to 90% in ^{13}C . The initial condition corresponds to equilibrium ^1H magnetization and complete depolarization of the ^{13}C magnetization. For this initial state, the intensities predicted by eq. (5) are $2 : 2 : 1 : 2$ for the lines at 0 , $\pm\frac{1}{2}\omega_{IS}^D$, $\pm\omega_{IS}^D$, and $\pm\frac{3}{2}\omega_{IS}^D$. The measured ω_{IS}^D corresponds to a C-H bond distance of $1.11 \pm 0.02 \text{ \AA}$. This

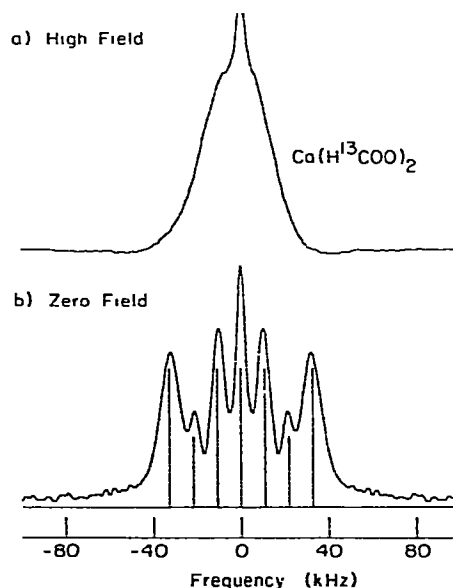


Fig. 2. Spectra of polycrystalline β - $\text{Ca}(\text{H}^{13}\text{COO})_2$. (a) High-field proton spectrum. The sharp spike at the center of the spectrum is due to adsorbed water. (b) Zero-field spectrum and intensity simulation. The ^{13}C nuclei are depolarized prior to the field cycle, and the proton magnetization sampled at $5 \mu\text{s}$ increments of the zero-field interval, t_1 .

is in close agreement with previous NMR measurements on this molecule and neutron-diffraction data [4].

The relative intensities of these lines are determined by the initial preparation of the spin system. The polarizations a_I and a_S can be manipulated either in high field with standard radio-frequency (rf) techniques, or in zero field, where eq. (5) predicts a regular oscillation of magnetization between the I and S systems \ddagger .

We illustrate the effect of different preparation sequences in fig. 3. Carbon spin-lattice relaxation times

\ddagger Similar effects appear in high-field NMR spectroscopy under suitable conditions of radio-frequency pulses. See ref. [5].

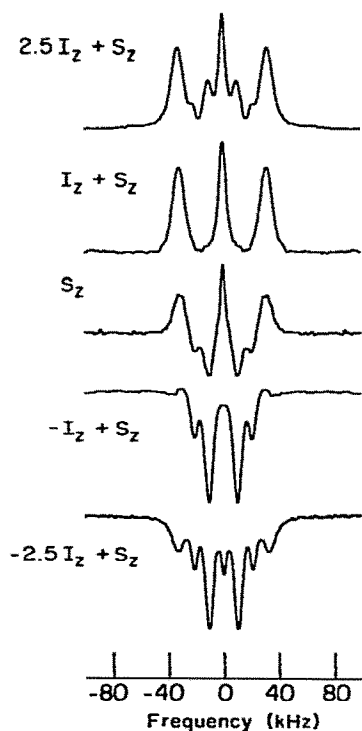


Fig. 3. Spectra of β -Ca(H¹³COO)₂ as a function of preparation sequence. The relative initial magnetizations are indicated at left. The ¹³C nuclei are polarized as described in the text. Immediately prior to the field cycle, a radio-frequency pulse is applied to the protons. The preparation pulse lengths are: 0°, 66°, 90°, 114°, and 180°. The proton magnetization is sampled at 5 μ s increments in the zero-field interval, t_1 . Spectral intensities vary in the regular manner predicted by eq. (5).

(T_1 s) in solids are quite long (typically minutes) and calcium formate is no exception. Therefore, it is advantageous to initially prepare the combined ¹H-¹³C spin system in a long-lived non-equilibrium state using a zero-field interval of fixed duration. This efficiently transfers magnetization from ¹H to ¹³C nuclei in times comparable to the proton T_1 s, normally much shorter than ¹³C T_1 s. To perform this preparation on the calcium formate spin system, the following steps precede each cycle of the zero-field experiments:

- (1) Depolarization in zero field for 10 ms.
- (2) Repolarization of the protons in high field.
- (3) Transfer of magnetization from ¹H to ¹³C with a fixed zero-field interval of 32 μ s.
- (4) Repolarization of the protons in high field.

This four-step sequence creates equilibrium proton magnetization, and a persistent ¹³C magnetization 60% larger than equilibrium ($a_I/a_S = 2.5$). Finally, a resonant rf pulse may be applied to the protons, which destroys or inverts some of the initial proton magnetization. The intensities of all lines vary in the manner predicted by eq. (5).

4. Zero-field NMR in liquids

The high-field inequivalence of I and S spins allows for the possibility of zero-field NMR in J -coupled liquids. While the J coupling is isotropic in space and its magnitude is unaffected by the application of a magnetic field, the antisymmetric components of the initial density operator oscillate at the coupling frequency in zero field. For a heteronuclear J -coupled pair

$$M_Z(t) = \frac{1}{2}(a_I + a_S) \pm \frac{1}{2}(a_I - a_S) \cos(J_{IS}t). \quad (6)$$

Since most line-broadening mechanisms are averaged away by the rapid, isotropic motion in liquids, the observed linewidths are sensitive to the effects of residual magnetic fields. The experiment is done precisely the same way for liquids as for solids. The sample is prepared in high field, shuttled to a small field (≈ 0.01 T) which is rapidly switched to zero. At a time t_1 the field is switched back and the sample returned to high field for detection. Fig. 4 shows the ³¹P detected zero-field interferogram and spectrum of neat diethyl phosphite ((C₂H₅O)₂PHO). The narrow lines and absence of Zeeman splittings illustrate the ability of our apparatus to accurately create a region of negligible residual magnetic fields.

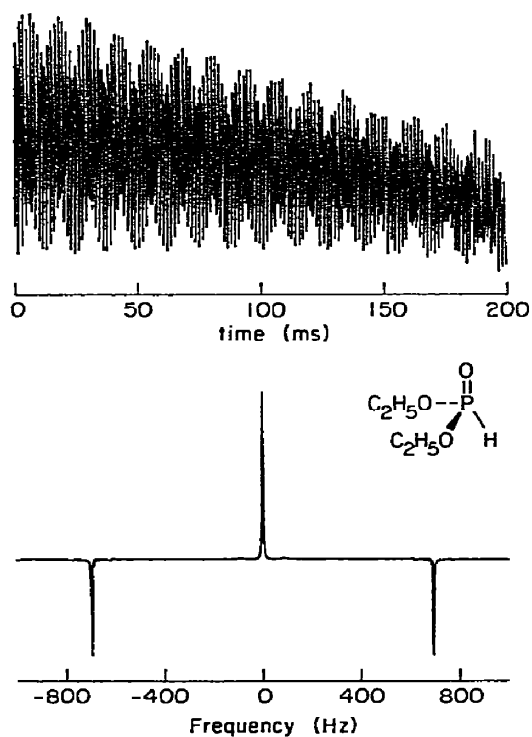


Fig. 4. Phosphorus detected zero-field free-precession interferogram and Fourier-transform spectrum of neat diethyl phosphite ((C₂H₅O)₂PHO). Both spin systems (³¹P and ¹H) equilibrate in high field. Immediately prior to the field cycle, a 180° pulse is applied to the protons. This enhances the amplitude of the transition at the coupling frequency (see eq. (6)). Only the coupling between the phosphorus and the directly bound proton is resolved ($J = 692 \pm 1$ Hz), however, the relatively weak couplings between the phosphorus and the methylene protons are expected to have a slight effect on the observed splitting. For purposes of display the spectral lines are artificially broadened.

5. Summary

We have shown that zero-field spectra of heteronuclear systems can be influenced by preparation of

the spin system in large magnetic fields. This variability should prove useful in the disentanglement of spectral patterns arising from different functional groups (e.g. CH, CH₂, and CH₃). Furthermore, the zero-field period can be used to transfer polarization from protons to heteronuclear spins. This should be of particular value for very low γ nuclei where high-field cross-polarization [6] requires unreasonably high radio-frequency power levels. This sensitivity enhancement is applicable to liquids as well.

Acknowledgement

One of us (DBZ) acknowledges support by a National Science Foundation graduate fellowship and another of us (KWZ) by an IBM postdoctoral fellowship. This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Sciences Division of the U.S. Department of Energy under Contract No. DE-ACO3-76SF00098.

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.*, to be published.
- [3] D.B. Zax, A. Bielecki, K.W. Zilm and A. Pines, in preparation.
- [4] M.G. Munowitz, Ph.D. thesis, Harvard University (1982); M. Matsui, T. Watanebi, N. Kamijo, R. Lapp and R.A. Jackson, *Acta Cryst. B* 36 (1980) 1081.
- [5] D.P. Weitekamp, J.R. Garbow and A. Pines, *J. Chem. Phys.* 77 (1982) 2870; L. Braunschweiler and R.R. Ernst, *J. Magn. Reson.* 53 (1983) 521; P. Caravatti, L. Braunschweiler and R.R. Ernst, *Chem. Phys. Letters* 100 (1983) 305.
- [6] A. Pines, M.G. Gibby and J.S. Waugh, *J. Chem. Phys.* 59 (1973) 569.