Coherent Response Signals of Dipolar-coupled Spin Systems

B. M. Fung, V. L. Ermakov, and A. K. Khitrin[a]

Department of Chemistry and Biochemistry, University of Oklahoma, Norman,
Oklahoma 73019-3051, USA
[a] Department of Chemistry, Kent State University, Kent, Ohio 44242-0001, USA

Reprint requests to Prof. A. K.; E-mail: akhitrin@kent.edu

Z. Naturforsch. **59a,** 209 – 216 (2004); received January 31, 2004

Recently, it has been demonstrated that long pulses of a weak radio-frequency field can generate long-lived coherent NMR signals in bulk liquid crystals, which are systems of dipolar-coupled spins with unresolved conventional spectra. Here we describe this phenomenon in more detail and present results of new experimental investigations and computer simulations. It is shown that such response signals can also be excited when the initial spin state of a system corresponds to dipolar ordering. In addition, results of the application of weak pulses on liquid crystalline systems with heteronuclear dipolar couplings are presented, and the role of overlapping peaks is explored.

Key words: Spin System; NMR; Coherent Response; Dipolar Coupling.

1. Introduction

Recently we have demonstrated that the application of long and weak pulses of a radio-frequency field to some dipolar-coupled nuclear spin systems with broad and unresolved conventional ^{1}H NMR spectra can produce rather narrow peaks [1 – 5]. The phase of the signal excited by a “soft” pulse is opposite to the phase of a signal excited by a “hard” 90° pulse. The process of excitation is non-linear, and experiments with two consecutive weak pulses, the second one having a 90° phase shift, show a very unusual behavior [2]. The uncommon features of these coherent response signals are not well understood yet. On the other hand, possible interesting applications of this type of signals, such as the storage and processing of binary information at the molecular level [1 – 4], suggest that a more detailed study of the phenomenon is needed.

Our initial experiments were performed with nematic liquid crystals [1 – 4], where there are strong intra-molecular dipole-dipole interactions due to orientational order of the molecules, but the intermolecular spin-spin interactions are averaged out by fast translational motions. Subsequently, it was found that certain organic solids with rapid molecular motions behave similarly [5], and the absence of intermolecular interactions is not a requirement for the observation of the coherent response signals. Nevertheless, even if intermolecular dipolar coupling is not taken into account, the dynamical complexity of spin clusters increases very rapidly with the number of coupled spins. In the case of high-field NMR, for N spins 1/2 coupled by dipole-dipole interactions, there are up to $C_{2N}^{N+1} \sim 2^{2N}$ allowed single quantum transitions between 2^N quantum levels. For any practical value of N, the spin dynamics is too complicated for a complete theoretical analysis. In such cases, a thermodynamic approach based on the concept of spin temperature [6] is sometimes used. The most successful example is Provotorov’s saturation theory [7], which describes the interaction of a spin system with a weak excitation field and explains various phenomena in solid-state NMR. The spin-temperature approach is based on the assumption that, if a system with the Hamiltonian H_0 deviates from equilibrium in its initial state, it would evolve to the equilibrium state, which is described by

$$\rho_{\mathrm{eq}} = Z^{-1}\exp(-H_{\mathrm{o}}/kT) = Z^{-1}\exp(-\beta H_{\mathrm{o}}), \quad (1)$$

where ρ_{eq} is the equilibrium density matrix, $Z = \mathrm{Tr}\{\exp(-H_0/kT)\}$, k is the Boltzmann constant, T is the equilibrium spin temperature, and $\beta = 1/kT$. The characteristic time of this evolution is the characteristic time of spin-spin interactions T_2. In the case of several additive integrals of motion, the equilibrium can be described by several different spin temperatures. If, after an initial excitation, the system approaches the equilibrium (1) with the characteristic time T_2, it automatically means that any response signal also decays with the same characteristic time because a system at equilibrium cannot produce any detectable signal. Therefore, the corresponding spectrum (Fourier transform) would have a width of about $1/\pi T_2$.

However, there are experimental indications that the situation is not so unambiguous. In a classic time-reversal NMR experiment [8], a response signal was refocused after a duration which was several times longer than T_2. It has also been demonstrated that the spin diffusion in a system of dipolar-coupled nuclear spins can be reversed [9]. More recently, with computer simulations, an unusual type of spin polarization localization has been discovered in one-dimensional chains of dipolar-coupled spins [10, 11], and its presence has been confirmed experimentally [12]. This kind of behavior has been studied analytically and with computer simulations for simple spin systems [13, 14]. For dilute systems of electron spins, it has been demonstrated that the homogeneous width of spin packets can be significantly smaller than the statistical dipolar linewidth [15]. Our recent experiments show that ^{1}H NMR peaks three orders of magnitude narrower than the dipolar width can be observed with weak excitation [1–5].

In this work, a theoretical argument on the general features of the response of a dipolar-coupled system to a weak external radio-frequency (rf) field is introduced first. Then, new experimental results and computer simulations are presented. This paper contains three aspects. (a) A theoretical argument is given to contend that it is possible to tailor the spectrum of a large coupled spin system to a desired shape. (b) Experimental results and computer simulations of the response to a weak external rf field are presented for a homonuclear dipolar-coupled system in a dipolar-ordered initial state. (c) The responses of heteronuclear dipolar-coupled systems to weak rf pulses are discussed.

2. Theoretical Considerations

In this part we give an argument that, in the absence of spin-lattice relaxation, it is theoretically possible to excite arbitrarily long response signals in a cluster of coupled spins and to tailor the corresponding response spectrum to a specific shape. The idea is to select, in a density matrix, only those elements which contribute to desired regions of the spectrum.

Let us consider the high-temperature initial state

$$\rho_{\text{in}} = (1/\text{Tr}\mathbf{1})\{\mathbf{1} - \beta \int \text{d}\omega \text{f}(\omega)(S_\omega + S_{-\omega})/2\}, \quad (2)$$

where $\text{f}(\omega)$ is an arbitrary function of ω, S_ω is the Fourier component (in the interaction representation) of $S_x(t)$, and S_x is the x-component of the total spin:

$$S_x = \int \text{d}\omega\, S_\omega, \quad (3)$$

$$S_x(t) = \exp(iH_0 t)\, S_x \exp(-iH_0 t) = \int \text{d}\omega\, S_\omega \exp(i\omega t), \quad (4)$$

and the following commutation relation is valid:

$$[H_0, S_\omega] = \omega S_\omega. \quad (5)$$

At $\text{f}(\omega) \equiv 1$ the initial state (2) corresponds to a uniform polarization along the x-axis: $\rho_{\text{in}} = (1/\text{Tr}\mathbf{1})\{\mathbf{1} - \beta S_x\}$. If the observable is S_x, for the initial condition (2) one gets the following expression for the response signal:

$$\begin{aligned} \langle S_x(t)\rangle &= \text{Tr}\{S_x(t)\rho_{\text{in}}\} \\ &= 2^{-N}(\beta/2) \iint \text{d}\omega \text{d}\omega' \text{f}(\omega) \exp(i\omega' t) \\ &\qquad \cdot \text{Tr}\{(S_\omega + S_{-\omega})S_{\omega'}\} \\ &= 2^{-N}\beta \int \text{d}\omega \text{f}(\omega) \cos(\omega t) \text{Tr}(S_\omega S_{-\omega}) \\ &= \beta \int \text{d}\omega \text{f}(\omega) \text{g}(\omega) \cos(\omega t), \end{aligned} \quad (6)$$

where $\text{g}(\omega) = 2^{-N}\text{Tr}(S_\omega S_{-\omega})$ is the conventional linear-response spectrum. In deriving (6), the following property of the traces has been used:

$$\text{Tr}(S_\omega S_{\omega'}) = \delta(\omega + \omega')\text{Tr}(S_\omega S_{-\omega}). \quad (7)$$

It can be seen that, by choosing the function $\text{f}(\omega)$ in the initial state (2), one can get a specified response spectrum within the shape $\text{g}(\omega)$. As an example, when $\text{f}(\omega)$ is the δ-function, the response signal (6) oscillates without decay, and the corresponding spectrum has also a shape of the δ-function. Therefore, initial conditions of the form (2) can be used for producing long-lived response signals. However, the above discussion does not suggest any practical means of preparing such spin states.

The ability to create a large amount of distinguishable shapes of the response signal means that the "output" signal can carry a large bulk of information. As an example, it has been demonstrated experimentally [2] that the NMR signal of a cluster of 19 nuclear spins contained more than one kilobit of information.

Now let us discuss an excitation by a weak monochromatic external field. The Hamiltonian during the excitation period is ($\hbar = 1$):

$$H = 2\Omega\cos(\omega_{\text{ex}}t)S_x + H_0, \tag{8}$$

where 2Ω is the amplitude (in frequency units) of the external field, applied in the x-direction, and ω_{ex} is the frequency of excitation. Before the excitation is applied, the system is supposed to be in the equilibrium state. For simplicity, we will use the high-temperature approximation, at which (1) becomes

$$\rho_{\text{eq}} = 2^{-N}(\mathbf{1} - \beta H_0). \tag{9}$$

In the interaction representation

$$\rho'(t) = \exp(-iH_0t)\rho(t)\exp(iH_0t)$$

the equation for the density matrix is

$$\begin{aligned} \mathrm{d}\rho'(t)/\mathrm{d}t &= -i[2\Omega\cos(\omega_{\text{ex}}t)S_x(t), \rho'(t)] \\ &= -i\Omega\big[\exp(i\omega_{\text{ex}}t) + \exp(-i\omega_{\text{ex}}t) \\ &\quad \cdot \int \mathrm{d}\omega S_\omega \exp(i\omega t), \rho'(t)\big]. \end{aligned} \tag{10}$$

Solving this equation by iterations, starting with the initial state (9), one can get

$$\begin{aligned} \rho'(t) - \rho_{\text{eq}} = {} & -i2^{-N}\beta\Omega \int_0^t \mathrm{d}t' \left[\int \mathrm{d}\omega S_\omega \left\{\exp((\omega + \omega_{\text{ex}})t') + \exp((\omega - \omega_{\text{ex}})t')\right\}, H_0\right] \\ & - 2^{-N}\beta\Omega^2 \int_0^t \mathrm{d}t' \int_0^{t'} \mathrm{d}t''[\ldots,[\ldots,H_0]] + \ldots . \end{aligned} \tag{11}$$

With the commutation relation (5), this can be rewritten as

$$\begin{aligned} \rho'(t) - \rho_{\text{eq}} = {} & i2^{-N}\beta\Omega \int_0^t \mathrm{d}t' \int \omega \mathrm{d}\omega S_\omega \left\{\exp((\omega + \omega_{\text{ex}})t') + \exp((\omega - \omega_{\text{ex}})t')\right\} \\ & + 2^{-N}\beta\Omega^2 \int_0^t \mathrm{d}t' \int_0^{t'} \mathrm{d}t'' \left[\int \mathrm{d}\omega S_\omega \left\{\exp((\omega + \omega_{\text{ex}})t') + \exp((\omega - \omega_{\text{ex}})t')\right\},\right. \\ & \left. \int \omega \mathrm{d}\omega S_\omega \left\{\exp((\omega + \omega_{\text{ex}})t'') + \exp((\omega - \omega_{\text{ex}})t'')\right\}\right] + \ldots . \end{aligned} \tag{12}$$

By neglecting the fast oscillating terms with $|\omega \pm \omega_{\text{ex}}| \gg \Omega$, one can see that at $\Omega \ll \|H_0\|$ only narrow bands of frequencies near $\pm\omega_{\text{ex}}$ are important, and the factors ω inside the integrals over ω can be replaced by the constants $\pm\omega_{\text{ex}}$. Therefore, the intensity of the excited signal will be proportional to the excitation frequency ω_{ex} and to the inverse spin temperature β.

In the above discussion, the effect of relaxation is neglected. At present, the role of spin-lattice relaxation in the observation of long-lived response signals is not clear. Our computer simulations show that in comparatively small clusters of dipolar-coupled spins the signals can be generated in the absence of spin-lattice relaxation. However, an important condition for the presence of long-lived signals in systems with unrestricted networks of dipolar couplings is the existence of rapid motions of at least some of the molecular segments, as in the cases of a number of tetraalkylammonium salts and some compounds containing tertiary butyl groups [5]. The rapid motions render the relaxation behavior quite different from solids with only small-amplitude vibrations, so that the effect of a prolonged weak rf irradiation would not be completely negated by fast spin-spin relaxation.

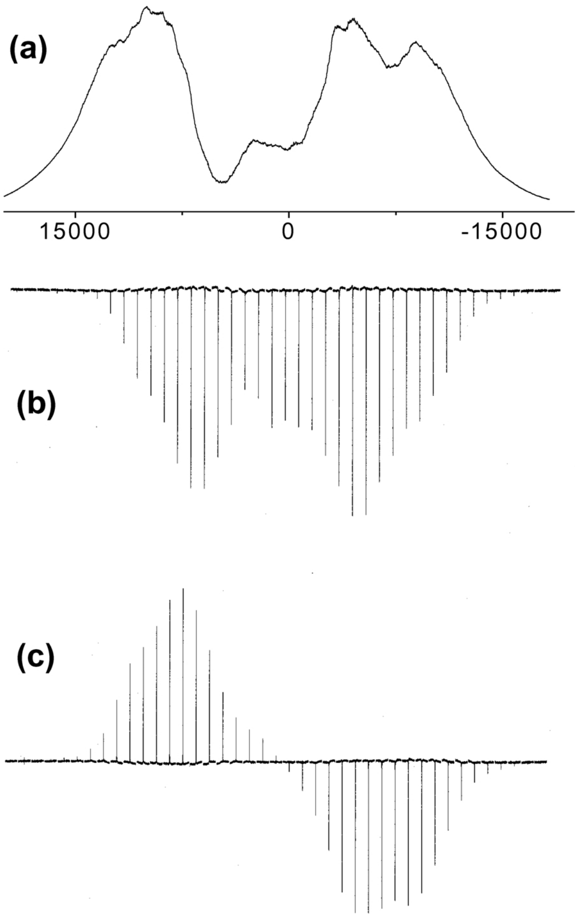

Fig. 1. (a) Conventional ^{1}H NMR spectrum of the nematic liquid crystal 4'-*n*-pentyl-4-biphenylcarbonitrile (5CB) obtained by the application of a 5 μs "hard" 90° pulse. (b) An array of spectra obtained by applying a "soft" pulse with the Zeeman initial state; the amplitude $(\gamma B_1/2\pi)$ of the rf field is 7.7 Hz, and the pulse width was 0.1 s. The rf frequencies of the irradiation were shifted by 1 kHz stepwise. (c) Profile of excitation by the same set of "soft" pulses with the dipolar initial state, created by a two-pulse sequence $(90^\circ - \tau - 45^\circ;\ \tau = 20\ \mu\text{s})$.

3. Experimental Results for Different Initial States of a Homonuclear Dipolar-coupled System

The experiments were carried out on a Varian Unity/Inova 400 MHz NMR spectrometer at 20 °C, using a liquid crystalline sample of 4′-*n*-pentyl-4-biphenylcarbonitrile (5CB). The intermolecular spin-spin interactions in this liquid crystal are averaged by rapid translational motions, but the 19 proton spins of each molecule are coupled to one another by dipole-dipole interactions. The conventional proton NMR spectrum, obtained by Fourier-transforming the free-induction decay following the application of a "hard" 90° pulse, is shown in Figure 1a. This unresolved spectrum has a width of about 30 kHz, a result of extensive intramolecular dipole-dipole couplings between the proton spins.

The excitation profile for a long and weak "soft" pulse is presented as an array of spectra, each of which recorded in a separate experiment (Fig. 1b). The excitation frequency in successive experiments was increased by 1 kHz, and the array of spectra is plotted in such a way that the position of each peak corresponds to the frequency of the applied "soft" pulse. The width of individual peaks is about 15 Hz. By comparing the two plots in Figs. 1a and 1b, it can be seen that the excitation profile of a soft pulse approximately mimics the conventional NMR spectrum.

For the spectra in Figs. 1a and 1b, the initial spin state of the system corresponds to equilibrium magnetization in an external magnetic field. In the initial density matrix (9), the major term of the Hamiltonian H_0 is the Zeeman interaction $-\omega_0 S_z$ and the excitation frequencies $\omega_{\text{ex}} \approx \omega_0 = \text{constant}$.

To gain another perspective of the interaction between a weak radio-frequency field and a dipolar coupled spin system, a different initial state was studied. With the two-pulse Jeener-Broekaert sequence $(90^\circ - \tau - 45^\circ;\ \tau = 20\ \mu\text{s}$ in our experiments) [16], the initial state with dipolar ordering can be prepared. This state, represented by $H_0 = H_{\text{dz}}$ in (9), corresponds to a thermal equilibrium in the rotating frame where the strong polarizing magnetic field is absent. Since the excitation frequency is close to $\omega_{\text{ex}} = 0$, according to (12), the intensities of the peaks excited by soft pulses should have an explicit dependence on the excitation frequency. In the experimental results obtained for the dipolar-ordered initial spin state (Fig. 1c), if the overall spectral profile of the system (Fig. 1a) is considered to be a constraint, the peak intensities are indeed approximately proportional to the excitation frequency ω_{ex}, including its sign.

4. Numerical Simulations

To simulate the dynamics of the system of 19 coupled proton spins of the 5CB molecule, a very substantial effort of numerical computations must be performed, and the use of massive parallel processors would be required [17]. As an alternative, we used a desk-top computer (with a Pentium 1.5 GHz proces-

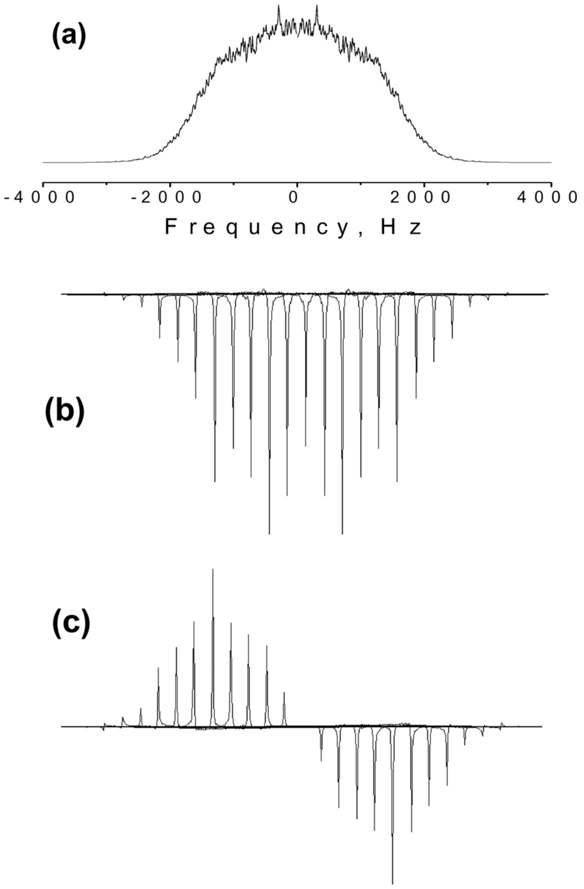

Fig. 2. (a) Simulated conventional spectrum (excitation with a "hard" pulse) of a cluster of 10 spins with random dipolar coupling constants. (b) A series of simulated spectra obtained by applying a 1 s "soft" pulse to the Zeeman initial state; the amplitude ($\gamma B_1/2\pi$) of the rf field is 4.0 Hz. The rf frequencies of the irradiation were shifted by 200 Hz stepwise, and all the spectra are superimposed on each other. (c) Simulated profile of excitation with the same "soft" pulse applied to the dipolar initial state of the spin cluster.

sor) to carry out simulations for a cluster of only ten dipolar-coupled spins as a model system. In the simulation, the chemical shifts of all spins were set to zero, leaving only the dipolar interaction terms in the Hamiltonian. In order to render the number of peaks in the spectrum a maximum, each of the 45 constants of the dipole-dipole interaction was chosen at random to avoid any symmetry; the values were set in the range of -792 to 792 Hz; the root mean square scaling factor turned out to be 0.564. The simulated conventional spectrum of this system is shown in Figure 2a. A line-broadening factor of 12 Hz is used to display all simulated spectra.

To simulate the response of the spin system to a weak pulse, the amplitude of the rf field was set at $\gamma B_1/2\pi = 4$ Hz, and the pulse width was set at 1 s. A set of simulations was performed by incrementing the excitation frequency in steps of 200 Hz in a spectral range from -3000 to $+3000$ Hz. Each simulation took 3.15 hours. Every simulated spectrum shows a narrow peak at the excitation frequency, with some broadening near the baseline. The broadening is due to the presence of neighboring peaks close to the irradiation frequency; the patterns are not the same for different excitation frequencies because the peaks are not evenly distributed throughout the whole spectral range. The complete sets of spectra are displayed in Figs. 2b and 2c. Fig. 2b illustrates the excitation profile for the Zeeman initial condition, and Fig. 2c shows the excitation profile for the dipolar-ordered initial spin state. Both sets of simulated spectra reproduce the basic features of the experimental results shown in Figure 1.

Although the high-temperature approximation is adequate for our experiments and has been used in (9) and subsequent expressions, additional simulations were carried out by varying the spin temperature of the initial state to gain some qualitative insight to the temperature dependence. The results show that at high spin temperatures, for which $\beta\|H\| \ll 1$, the signals grow proportionally to the inverse temperature β, in agreement with (12). At $\beta\|H\| \approx 1$ the signal intensities stop growing. At further decrease of the spin temperature (or increase of interactions), there appear small spectral regions in which the applied rf does not produce corresponding peaks. These regions become larger when the spin temperature decreases. This reflects a gradual freezing of the degrees of freedom of the spin system, as its dynamics becomes simpler and the number of peaks in the spectrum becomes smaller at lower temperatures.

5. Experimental Results for Heteronuclear Dipolar-coupled Systems

In order to further explore the origin of the unusual response of coupled spin systems to weak rf excitation, we have studied several liquid crystalline samples with heteronuclear dipolar couplings.

The "normal" proton-coupled ^{13}C spectrum of a bulk liquid crystal (with a single ^{13}C labeling [18]) has a linewidth of about 3 kHz due to unresolved dipolar coupling with the protons, which are extensively coupled themselves (Fig. 3a). Applying a weak ^{13}C pulse,

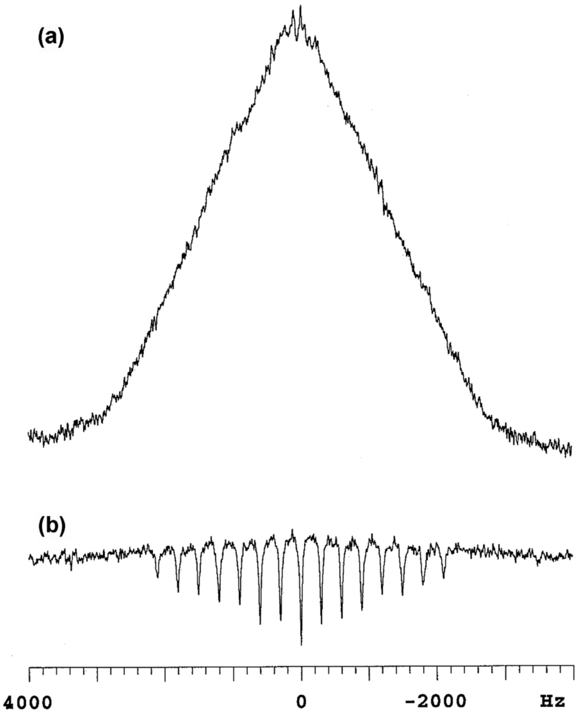

Fig. 3. Proton-coupled ^{13}C NMR spectra of 4'-cyano-4-biphenyl hexanoate-1-^{13}C at 100.6 MHz and 55 °C. (a) Spectrum obtained by using a strong $\pi/2$ pulse ($\gamma B_1/2\pi =$ 25 kHz). (b) Spectrum obtained by applying a weak 15-frequency pulse (total $\gamma B_1/2\pi = 157$ Hz) for a duration of 60 ms. Each spectrum had 100 scans and was processed with an exponential multiplication factor of 10 Hz.

either single-frequency or multi-frequency, produces inverted narrow peaks (Fig. 3b) just like in homonuclear dipolar-coupled systems. The excitation profile also mimics the lineshape of the normal spectrum.

The ^{2}H spectrum of a monodeuterated liquid crystal [19–21] shows a doublet due to deuterium quadrupole splitting. Without proton decoupling, each half of the doublet has a linewidth of about 1.6 kHz; when weak ^{2}H pulses are applied, inverted peaks having linewidths two orders of magnitude less are produced.

These experiments show that a single "rare" nucleus coupled to a proton cluster responds to prolonged weak rf irradiation similar to the response of abundant proton nuclei. Heteronuclear dipole-dipole interactions involve only z-components of nuclear spins. It is interesting to note that this simple uniaxial interaction is sufficient to organize a collective response of a system: rare nucleus + cluster of protons, when only the rare nucleus is coupled to the external rf field.

For small solute molecules dissolved in liquid crystalline solvents, NMR spectra are usually well resolved. The ^{19}F spectrum of 1-fluorotoluene dissolved in a commercial liquid crystal mixture E7 (EM Chemicals, Hawthorne, New York) is shown in Figure 4. The ^{1}H spectrum is also well resolved and covers a range of 20 kHz, but the effect of applying weak pulses was not studied because the responses of the solvent and solute cannot be easily separated. For selective excitation of the ^{19}F peaks, the results are shown in Figure 5. When the rf field strength is larger than the linewidth, all peaks exhibit normal damped sinusoidal oscillations as a function of increasing pulse width (Fig. 5, column I). However, when the rf field strength is comparable to the linewidth, the negative parts of the sinusoidal oscillations dampen slower than the positive parts (Fig. 5, column II,a and b). When there are overlapping peaks so that the overall linewidth is larger than the rf field strength, prolonged irradiation produces only negative peaks (Fig. 5, column II,c). For bulk liquid crystals, the spectra are unresolved due to the presence of numerous overlapping peaks [22], and the results in Figs. 1b and 3b can be considered as extreme cases of Fig. 5, IIc. It is quite likely that the presence of densely overlapping signals throughout the whole spectral range of a bulk liquid crystal is responsible for the production of a narrow peak at the frequency of a weak rf irradiation. The irradiation not only acts on the peak(s) at exact resonance, but its effect (including amplitudes and phases) on the peaks slightly off-resonance [23] must also be considered; the overall signal is, of course, a sum of the contributions from all the peaks being affected. The array of spectra shown in Fig. 5, IIc, is an illustration of this effect. Detailed studies of systems having resolvable spectra but with more overlapping peaks are being carried out.

Another feature of selective excitation is that the periodicity of oscillation is different for different peaks (Fig. 5, column I), which results from the fact that single-quantum transitions corresponding to different peaks have different amplitudes of the transition matrix elements.

6. Conclusion

The results presented in Fig. 1c demonstrate that it is possible to excite long-lived coherent response signals with soft pulses when the initial spin state of a system is dipolar-ordered, illustrating the difference between

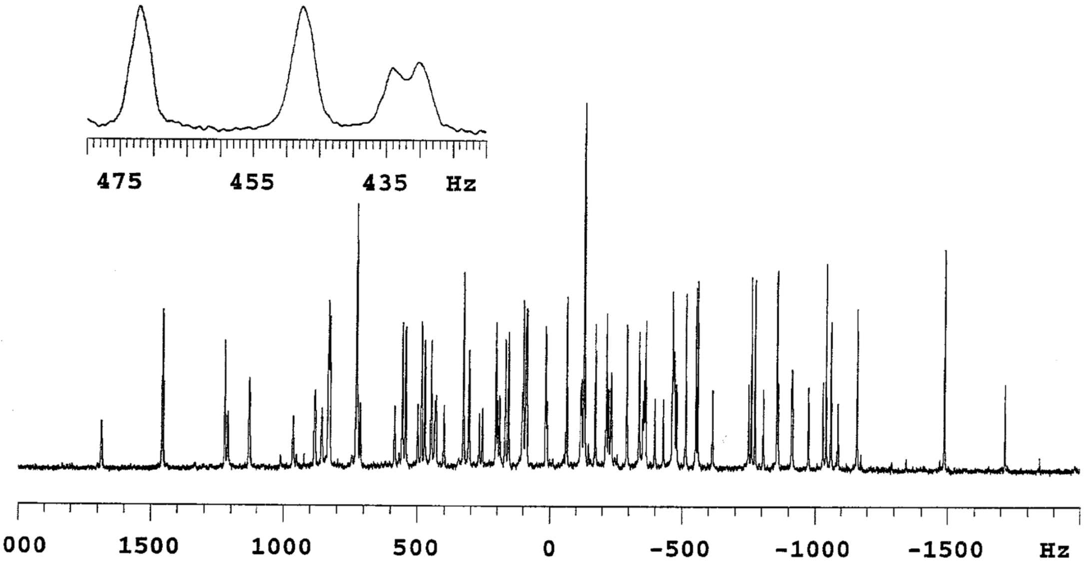

Fig. 4. ^{19}F NMR spectrum of 8% 1-fluorotoluene in E7 at 376.3 MHz and 21 °C, obtained by using a strong $\pi/2$ pulse ($\gamma B_1/2\pi = 70$ kHz). The center of the spectrum (0 Hz) corresponds to a chemical shift of -113 ppm with respect to external $CFCl_3$. The inset shows a small portion of the spectrum.

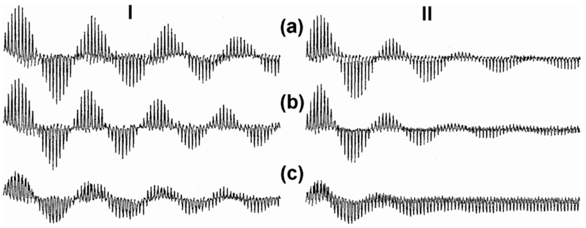

Fig. 5. Arrays of ^{19}F NMR spectra of 8% 4-fluorotoluene in E7 at 376.3 MHz and 21 °C, obtained by using weak pulses (column I: $\gamma B_1/2\pi = 20$ Hz; column II: $\gamma B_1/2\pi = 5.0$ Hz). Each array contains 80 spectra with successively increasing pulse widths (column I: 0.0025, 0.0050, ….. 0.20 s; column II: 0.01, 0.02, …0.80 s). Different rows of spectra were obtained by setting the radio-frequency at the centers of different peaks shown in the inset of Fig. 4: (a) 472 Hz; (b) 448 Hz; (c) 431 Hz. The spectral width of each plot in every array is 16 Hz.

this type of excitation and the selective excitation of an inhomogeneously broadened spectrum. In inhomogeneously broadened systems, the existing longitudinal magnetization is converted into the observable transverse signal, while for the dipolar-coupled spins the initial ordering with internal interactions is sufficient. This phenomenon may have a more general nature and can perhaps be observed in other types of physical systems. If other physical systems are to be considered for possible generation of this type of coherent dynamics, the best candidates would have the strength of internal interactions $||H|| \approx kT$ (for example clusters of electronic spins in a paramagnetic region). In this case, the intensity of the coherent response signals will be near the maximum while the excitation profile is still rich.

The simulated results presented in Fig. 2 are in good qualitative agreement with the experimental observations obtained for 5CB, including both the thermal equilibrium initial state and the dipolar-ordered initial state. However, the ten-spin cluster used for our numerical simulations is too small to reproduce all the features of collective coherent response signals. For example, the unusual behavior observed in experiments with two consecutive weak pulses, the second one, having a 90° phase shift [2], was not reproduced in our simulations. It should be noted that the simulations presented in this work do not account for the effect of relaxation; instead, a common line-broadening factor is used in the step of Fourier transform to yield frequency domain spectra. The results presented in Fig. 5, column II, show that the inherent linewidths of the peaks, especially when they overlap, are an important factor in determining the response of the spin system to weak rf irradiation. Further studies are being carried out to understand the unusual results of the response of homogenously broadened spin systems to weak pulses.

The work of BMF was supported by the National Science Foundation under grants numbers DMR-9809555 and DMR-0090218.

[1] A. K. Khitrin, V. L. Ermakov, and B. M. Fung, Chem. Phys. Lett. **360**, 161 (2002).
[2] A. K. Khitrin, V. L. Ermakov, and B. M. Fung, J. Chem. Phys. **117**, 6903 (2002).
[3] A. K. Khitrin, V. L. Ermakov, and B. M. Fung, Phys. Rev. Lett. **89**, 277902 (2002).
[4] B. M. Fung and V. L. Ermakov, J. Magn. Reson., in press.
[5] B. M. Fung and V. L. Ermakov, The Presence of Long-lived Spin States in Organic Solids with Rapid Molecular Motions, to be published.
[6] M. Goldman, Spin Temperature and Nuclear Magnetic Resonance in Solids, Clarendon Press, Oxford 1970.
[7] B. N. Provotorov, Zh. Eksperim. i Teor. Fiz. **41**, 1582 (1961).
[8] W. K. Rhim, A. Pines, and J. S. Waugh, Phys. Rev. B **3**, 684 (1971).
[9] S. Zhang, B. H. Meier, and R. R. Ernst, Phys. Rev. Lett. **69**, 2149 (1992).
[10] R. Brueschweiler and R. R. Ernst, Chem. Phys. Lett. **264**, 393 (1997).
[11] J. S. Waugh, Mol. Phys. **95**, 731 (1998).
[12] A. K. Khitrin and B. M. Fung, J. Chem. Phys. **111**, 7480 (1999).
[13] M. G. Rudavets and E. B. Fel'dman, JETP Letters **75**, 635 (2002).
[14] E. B. Fel'dman, R. Bruschweiler, and R. R. Ernst, Chem. Phys. Lett. **294**, 297 (1998).
[15] V. A. Atsarkin, G. A. Vasneva, and V. V. Demidov, Sov. Phys. JETP **64**, 898 (1986).
[16] J. Jeener and P. Broekaert, Phys. Rev. **157**, 232 (1967).
[17] J. Niwa, K. Matsumoto, and H. Imai, Phys. Rev. A **66**, 062317 (2002).
[18] C. Tan and B. M. Fung, J. Phys. Chem. A **107**, 3966 (2003).
[19] C. Canlet and B. M. Fung, J. Phys. Chem. B **104**, 6181 (2000).
[20] C. Canlet and B. M. Fung, Liq. Cryst. **28**, 1863 (2001).
[21] C. Tan, C. Canlet, and B. M. Fung, Liq. Cryst. **30**, 611 (2003).
[22] Y. Yu and B. M. Fung, Mol. Phys. **94**, 863 (1998).
[23] M. L. Martin, J.-J. Delpeuch, and G. J. Martin, Practical NMR Spectroscopy, p. 108, Heyden & Son Ltd., London 1980.