

DYNAMICS OF SPIN DECOUPLING IN CARBON-13-PROTON NMR

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In solids containing two nuclear spin species I and S , the magnetic dipolar coupling causing broadening of the S NMR line is partially averaged due to I spin flip-flop motion due to I - I coupling. This paper shows that the effects we observed previously in AgF (Abragam and Winter) are also present in ^{13}C - ^1H systems in organic solids.

1. Introduction

It was demonstrated recently [1], that the flip-flop spin motion of abundant spins (I) can be varied experimentally over a wide dynamical range, resulting in NMR line broadening and line narrowing effects of rare spins (S), which are dipolar coupled to abundant spins (I). This effect comes about by the scaling of the corresponding dipolar hamiltonian between I spins caused by the application of strong rf fields in the rotating frame [2]. The flip-flop rate of the abundant I spins may therefore be scaled at the experimenters discretion, leading to exchange motionally narrowed lineshapes similar to lattice motion [3-5]. The effect is essentially a slowing down of spin fluctuations by means of a radiofrequency field, i.e. the spin space analog of freezing of molecular motion by the lowering of temperature or motional narrowing by raising of temperature.

In this communication we want to demonstrate that these effects are also observed in a ^{13}C - ^1H system, and are thus important in the application of proton-enhanced NMR to solids [5].

2. Spin fluctuations and lattice motion in adamantane

As a representative example for a ^{13}C - ^1H system we choose adamantane ($\text{C}_{10}\text{H}_{16}$) whose NMR properties have been studied in great detail [6-10]. The molecular crystal has face centered cubic (fcc) structure at room temperature and is composed of globular-shaped molecules which reorient rapidly above 200 K. Intramolecular dipolar interaction among the protons and carbons is therefore averaged to zero, leaving only the intermolecular interactions among different molecules of the fcc lattice. The protons and carbons of each molecule are viewed as being located at the center of the molecule. Intermolecular interaction is treated by taking the average hamiltonian over the motion, i.e. the average of $P_2(\cos \vartheta_{ij}) r_{ij}^{-3}$ over the molecular motion has to be calculated, where $P_2(\cos \vartheta_{ij})$ is the Legendre polynomial and r_{ij} is the distance of two nuclear spins i and j and where ϑ_{ij} is the angle between r_{ij} and the magnetic field H_0 .

However we find it a good enough approximation to average over r_{ij}^{-3} alone resulting in [11]

$$\langle r_{ij}^{-3} \rangle = r_{0ij}^{-3} (1 - \epsilon^2)^{-1}, \quad (1)$$

with

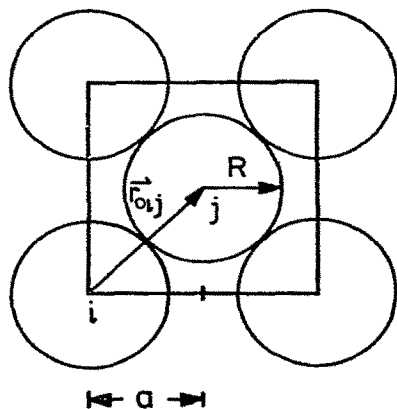


Fig. 1. (010) plane of the fcc unit cell of adamantane at room temperature with the lattice constant $a = 4.725$ Å. The globular shaped molecules of adamantane ($C_{10}H_{16}$) are approximated by spheres of radius $R = 3.34$ Å. Two different molecules i and j are connected by the vector r_{0ij} which makes the angle ϑ_{ij} with the magnetic field H_0 .

$$\epsilon = R/r_{0ij},$$

and where R is the effective radius of the globular shaped molecule and r_{0ij} is the distance between the center of two molecules i and j (see fig. 1).

Since at room temperature reorientation of the molecules is very rapid even compared with the Larmor period, the average secular dipolar interactions $\mathcal{H}_{II}^{(0)}$ and $\mathcal{H}_{IS}^{(0)}$ can be considered essentially as being static, with

$$\mathcal{H}_{II}^{(0)} = \sum_{i < j} A_{ij} (3I_{zi}I_{zj} - I_i \cdot I_j), \quad (2)$$

$$A_{ij} = -\gamma_I^2 \hbar \langle r_{ij}^{-3} \rangle P_2(\cos \vartheta_{ij}) \quad (3)$$

and

$$\mathcal{H}_{IS}^{(0)} = \sum_j B_j I_{zj} S_z, \quad (4)$$

$$B_j = -2\gamma_I \gamma_S \hbar \langle r_j^{-3} \rangle P_2(\cos \vartheta_j), \quad (5)$$

where the I spins are considered to be the abundant protons and the S spins are the dilute ^{13}C of natural abundance (1.1%). There are two magnetically inequivalent ^{13}C in each molecule of adamantane in the rotor phase [9]. The excess linewidth (full width at half height) of the ^{13}C spectrum broadened by di-

polar interaction with the protons of neighboring molecules will be discussed in the following, when strong rf irradiation at the proton resonance frequency is applied. Basically this broadening may be thought of as being described by the second moment of the I - S interaction, which results in

$$M_2^{IS} = 3.141 \times 10^7 \text{ s}^{-2}$$

for adamantane powder, using eqs. (1)–(5) with $a = 4.725$ Å for the lattice constant of adamantane and $R = 3.34$ Å. Assuming a gaussian lineshape for the I - S interaction, and using the above value of M_2^{IS} , would result in an excess linewidth $\Delta\nu = 2105$ Hz, whereas $\Delta\nu = 1050$ Hz is observed. This type of discrepancy has long been noticed in other cases and was first discussed by Abragam and Winter [4], who realized that the ^{109}Ag - ^{19}F interaction in AgF is influenced by the flip-flop motion of the fluorine spins.

The same arguments hold albeit more meanelly in the case of ^{13}C - ^1H system as is demonstrated here. Moreover, the NMR line-broadening effect due to slowing down of the spin fluctuations, which was demonstrated recently [1], is clearly visible in ^{13}C - ^1H systems too.

The protons are irradiated by a strong rf field close to their Larmor frequency, resulting in the following secular hamiltonian in the doubly tilted rotating (DTR) frame [2], where couplings among the S spins are being neglected

$$\mathcal{H} = \mathcal{H}_{II} + \mathcal{H}_{IS}, \quad (6)$$

with

$$\mathcal{H}_{II} = P_2(\cos \vartheta_I) \mathcal{H}_{II}^{(0)}, \quad (7)$$

$$\mathcal{H}_{IS} = \cos \vartheta_I \mathcal{H}_{IS}^{(0)}, \quad (8)$$

where ϑ_I is the angle between the static magnetic field H_0 and the effective field in the rotating frame of the I spins. At the "magic angle" $P_2(\cos \vartheta_I) = 0$ and the flip-flop motion of the I spins is quenched. The full dipolar linewidth due to the I - S interaction is thus observed, however scaled by a factor $\cos(54^\circ 44') = 3^{-1/2}$ [12]. The NMR lineshape may be calculated by Fourier transformation of the free induction decay (fid), which can be calculated rigorously at the "magic angle" by [13, 14] ($I = 1/2$)

$$G(t) = \prod \cos(3^{-1/2} B_j t / 2). \quad (9)$$

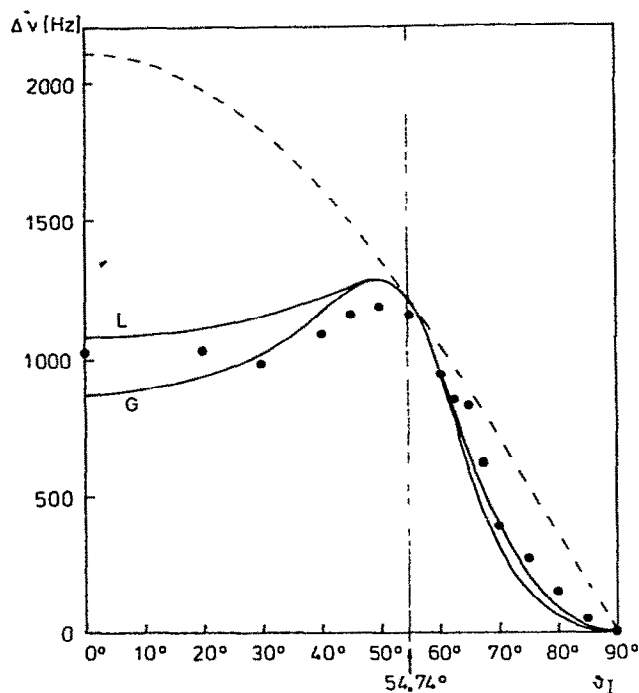


Fig. 2. Excess linewidth $\Delta\nu$ of the ^{13}C NMR signal versus the angle ϑ_I of the effective field applied in the rotating frame of the proton resonance. The data points were obtained experimentally as described in the text, whereas the theoretical lines (L: lorentzian, G: gaussian approximation of $K_{II}(t)$, eq. (16)) were calculated by using the mixed memory function approach. Note the increase of the linewidth at the magic angle. The dashed line indicates what would happen if the proton flip-flop spin motion had no effect on the ^{13}C line. Notice, that agreement between the two approaches exists at the magic angle $\vartheta_I = 54.7^\circ$.

Lineshapes generated for different orientations of the magnetic field by using eq. (9), were averaged to obtain the linewidth for a powder sample of adamantane. The calculated value of $\Delta\nu = 1205$ Hz agrees quite well with the measured value of 1200 Hz.

For smaller values ϑ_I than the "magic angle" the flip-flop motion of the proton spins increases and starts to narrow the ^{13}C spectrum. For larger values of ϑ_I , approaching $\vartheta_I = 90^\circ$ the I - S interaction is scaled drastically as compared with the I - I interaction, leading to an even further narrowing of the ^{13}C spectrum by rapid proton spin flip-flops (see fig. 2). An exact theory covering both regions does not exist and amounts to solving a many body problem involving some 10^{21} spins. However approximation schemes

are known to exist in many body theories and the particular useful approach of the memory function formalism has been applied to the problem discussed here [14, 15].

3. Lineshape theory and experiments

We give a brief outline of the memory function approach used to calculate the excess linewidth $\Delta\nu$ over the full range of ϑ_I values. A more detailed discussion may be found in ref. [14].

The S spins are thought to be excited by a 90° pulse in the y -direction of their rotating frame at time $t = 0$, resulting in a free induction decay signal of the S spins as given by

$$\langle S_x(t) \rangle = \langle S_x | \rho(t) \rangle / \langle S_x | \rho(0) \rangle, \quad (10)$$

where $\rho(t)$ is the time dependent spin density matrix in the rotating frame and $\rho(0)$ its value immediately after the application of the rf pulse. We use here the notation [14]

$$\langle A | B \rangle \stackrel{\text{def}}{=} \text{Tr} \{ A^\dagger B \}, \quad (11)$$

where A^\dagger is the adjoint of A . The I spins are thought to be continuously irradiated at the angle ϑ_I in their rotating frame by a strong rf field H_{1I} . Employing the "high temperature approximation" we can rigorously derive the following integro-differential equation for the free induction decay of the S spins [14]

$$d\langle S_x(t) \rangle / dt = - \int_0^t dt' K(t') \langle S_x(t-t') \rangle, \quad (12)$$

with the memory function [14]

$$K(t') = \frac{\langle S_x | \hat{\mathcal{H}}_{IS} \exp \{ -it' [\hat{\mathcal{H}}_{II} + (1-P) \hat{\mathcal{H}}_{IS}] \} \hat{\mathcal{H}}_{IS} | S_x \rangle}{\langle S_x | S_x \rangle}, \quad (13)$$

where the projection operator

$$P = | S_x \rangle \langle S_x | / \langle S_x | S_x \rangle$$

and the definition

$$\hat{\mathcal{H}} = [\mathcal{H}, \dots]$$

have been used together with the hamiltonians \mathcal{H}_{II} and \mathcal{H}_{IS} as defined in eqs. (7) and (8).

If the memory function $K(t)$ is known whether exactly or in some degree of approximation, the NMR lineshape may be calculated by Laplace inversion, as [14, 15]

$$\zeta(\omega) = K'(\omega) / \{[\omega - K''(\omega)]^2 + K'^2(\omega)\}, \quad (14)$$

with

$$K'(\omega) = \int_0^{\infty} dt K(t) \cos \omega t,$$

$$K''(\omega) = \int_0^{\infty} dt K(t) \sin \omega t.$$

Normally $K(t)$ cannot be calculated exactly because of the many body character of the interaction. A simple assumption about the functional form of $K(t)$ however, fitted to the correct values for the second moment and for $K(0)$ is usually sufficient to demonstrate the overall behavior of the lineshape, covering all values of ϑ_I . Notice however, that at the "magic angle" the lineshape $J_{IS}(\omega)$ and correspondingly $K_{IS}(t)$ is known exactly. Neglecting cross correlations of higher order, we are therefore led to try [14]

$$K(t) = K_{II}(t) K_{IS}(t), \quad (15)$$

with

$$K_{II}(t) = \frac{\langle S_x | \hat{\mathcal{H}}_{IS} \exp(-it \hat{\mathcal{H}}_{II}) \hat{\mathcal{H}}_{IS} | S_x \rangle}{(\hat{\mathcal{H}}_{IS} | \hat{\mathcal{H}}_{IS})} \quad (16)$$

and

$$K_{IS}(t) = \frac{\langle S_x | \hat{\mathcal{H}}_{IS} \exp[-it(1-P) \hat{\mathcal{H}}_{IS}] \hat{\mathcal{H}}_{IS} | S_x \rangle}{\langle S_x | S_x \rangle}. \quad (17)$$

The memory function $K_{II}(t)$ governs the cross relaxation processes in dipolar coupled spin systems and has been investigated to a high degree of approximation [16]. For our purpose it is sufficient to take the approach of McArthur et al. [17] who showed that their data in CaF_2 agree with a lorentzian shape for $K_{II}(t)$, namely

$$K_{II}(t) = [1 + (t/\tau_c)^2]^{-1}, \quad (18)$$

with

$$\tau_c^{-2} = N_2/2,$$

where N_2 is the second moment of $K_{II}(t)$ and where

in the case of adamantane $M_4^{HIS}/(M_2^{IS})^2 = 6.2$ has been calculated from the lattice constants, with M_4^{HIS} being the fourth moment due to the $II-IS$ interaction. The lorentzian character of $K_{II}(t)$ has been confirmed in other systems [9, 14] too, especially adamantane, so that it can be considered as a reasonable assumption. However we have investigated a gaussian functional form of $K_{II}(t)$ too for comparison. $K_{IS}(t)$ and the second moment N_2 of $K_{II}(t)$ have been calculated numerically for all orientations of the magnetic field H_0 in the case of adamantane for each value of ϑ_I . The NMR lineshape according to eq. (14) was then calculated by the mixed memory function approach (eqs. (15)–(18)) where the correct second moment N_2 for adamantane powder was used by evaluating the corresponding lattice sums numerically. The theoretical linewidth obtained by using both a lorentzian or a gaussian form for $K_{II}(t)$ is compared with the experimentally determined excess linewidth for different values of ϑ_I in fig. 2.

The experimental linewidth of adamantane was obtained from the experimental spectra by deconvolution with the totally decoupled spectrum. Fig. 2 shows a fairly good agreement between theory and experiment. Notice that the full range of ϑ_I is covered, including the "magic angle" where a "line broadening" is observed. Also for comparison we have plotted a line calculated from $\Delta\nu = 0.3756 (M_2^{IS})^{1/2} \cos \vartheta_I$, which is the behavior expected for a gaussian line if the $I-I$ couplings were absent, i.e. there was no initial narrowing of the ^{13}C NMR line without proton irradiation. The ratio of the last line to the observed one indicates that the "self-decoupling" caused by the $I-I$ couplings is quite significant.

We have applied this theory also to the case of AgF discussed earlier [1]. This and a more detailed treatment will be published elsewhere.

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