A simple model for the influence of motion on the NMR line shape.

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Introduction

A problem as old as NMR is that of the influence of motion on the shape of the NMR absorption signal, or equivalently the shape of the FID. Although it is known that motion means narrowing, only two limiting cases are well defined.

In the rigid solid, one has a clean theoretical expression for the FID function, in terms of the secular part $\mathcal{H}_{SS}$ of the spin-spin interactions, most of the time essentially dipolar (1). This is insufficient to know the FID shape, nor that of its Fourier transform, the absorption f signal, but one can compute the first few moments of the latter and obtain reasonably good value for its frequency width $\Delta\omega_0$ (1-3).

The other extreme is that of a fast motion whereby the spin-spin interactions have a vanishing average value and are modulated at a rate τ_C^{-1} which is fast on the time scale of the solid-state FID decay rate $\Delta\omega_0$:

$$\Delta\omega_0 \tau_C << 1 \qquad [1]$$

In that case, relaxation theory predicts that the transverse magnetization decay is exponential, with a relaxation time T_2 related in a precise way to the magnitude of the spin-spin interactions and the nature of the motion (1,4). The absorption line is then Lorentzian, and its half-width at half intensity T_2^{-1} is of the order of:

$$\Delta\omega \approx (\Delta\omega_0)^2 \tau_C \qquad [2]$$

Things are much more confuse in the intermediate case, that is for motions rates for which $\Delta\omega_0 \tau_C \approx 1$. In that domain there exists only qualitative models of the Anderson-Weiss (5) or of the Kubo-Tomita type (6), which are admittedly very crude and whose sole ambition is to provide a general physical feeling of how the signals are evolving from slow to fast motion.

In this article, we attempt to correlate the FID shape under intermediate rate motion to that of the rigid solid. We use for that purpose a simple-minded model that is not new: it is the so-called Strong Collision Model (7). It has been used in particular for μSR studies (8) but in conjunction with other approximation. This is at variance with our approach, which treats the rigid lattice FID as an empirical information. This model is not

rigorous either, but it fits remarkably well the experimental results, as will be shown later.

The theoretical model

The scenario of the Strong Collision Model is the following. Let us consider a spin system whose FID signal is $G_r(t)$ when it is rigid, with the usual normalization:

$$G_r(0)=1 \qquad [3]$$

This system undergoes sudden motions at random time intervals with probability λ per unit time. After each motion, the FID starts anew with the same shape as initially, but with an initial value equal to G_r immediately before the jump. In other words all correlations developed in the system by its previous evolution are lost, and the only "memory" left is that of the transverse polarization at the time of the sudden motion. This results in a FID signal $G_m(t)$ (where m stands for motion) which is the weighted average of all possible random successions of initial rigid-state FID's.

A pulse being applied at time 0, the possibilities at time t are:

i) No jump between 0 and t. This corresponds to a FID signal shape $G_r(t)$ and its probability to occur is equal to $\exp(-\lambda t)$. Its contribution to $G_m(t)$ is then:

$$G_r(t)\exp(-\lambda t)$$

ii) One jump only at a time between t_1 and t_1+dt_1. The corresponding probability is:

$$\exp(-\lambda t_1)\times\lambda dt_1\times$$

$$\times\exp\left[-\lambda(t-t_1)\right]=\lambda\exp(-\lambda t)dt_1$$

and the signal at time t is then:

$$G_r(t_1)\times G_r(t-t_1)$$

By integrating over the time t_1 we obtain the contribution to $G_m(t)$:

$$\lambda\exp(-\lambda t)\int_0^t G_r(t_1)G_r(t-t_1)dt_1$$

iii) Two jumps between 0 and t. By an extension of the preceding argument, the contribution to $G_m(t)$ is:

$$\lambda^2\exp(-\lambda t)\int_0^t G_r(t_1)dt\times$$

$$\times\int_0^{t-t_1} G_r(t_2)G_r(t-t_1-t_2)dt_2$$

etc...

By taking the Laplace transforms:

$$\theta(z)=\int_0^\infty G(t)\exp(-zt)dt \qquad [4]$$

we obtain:

$$\theta_m(z)=\theta_r(z+\lambda)+\sum_{n=0}^{\infty}\lambda^n\theta_r^{n+1}(z+\lambda) \qquad [5]$$

that is:

$$\theta_m(z)=\frac{\theta_r(z+\lambda)}{1-\lambda\theta_r(z+\lambda)} \qquad [6]$$

which is identical with Eq.(18) of ref.(8).

The same result can be obtained much more simply by noting that after a jump the subsequent FID is that of the mobile system normalized to the transverse polarization at the time of the jump. The two possibilities being no jump between 0 and t, or at least one jump, we obtain :

$$G_m(t)=G_r(t)\exp(-\lambda t)+ \qquad [7]$$

$$+\lambda\int_0^t G_r(t')\exp(-\lambda t')G_m(t-t')dt'$$

whence the following relations between Laplace transforms :

$$\theta_m(z)=\theta_r(z+\lambda)+\lambda\theta_r(z+\lambda)\theta_m(z) \qquad [8]$$

from which Eq.[6] follows.

The advantage of the first treatment is to make explicit use of the assumption that each partial FID between jumps has the same shape. The simplest way of interpreting Eq.[6] is through the consideration of memory functions (2,3,9). The memory function K of a function $G(t)$ is defined through:

$$\frac{d}{dt}G(t) = -\int_0^t K(t-t')G(t')dt' \qquad [9]$$

This form yields remarkably simple expressions for the Laplace transforms. That of the left-hand side is equal to: $z\theta(z) - G(0) = z\theta(z) - 1$, where we have used Eq.[3], and that of the right-hand side is equal to $-\varphi(z)\theta(z)$, where $\varphi(z)$ is the Laplace transform of $K(t)$:

$$\varphi(z) = \int_0^\infty K(t)\exp(-zt)dt \qquad [10]$$

Then, Eq.[9] yields:

$$z\theta(z) - 1 = -\varphi(z)\theta(z) \qquad [11]$$

Now, Eq.[6] yields:

$$\frac{1}{\theta_m(z)} = \frac{1}{\theta_r(z+\lambda)} - \lambda \qquad [12]$$

or else:

$$\frac{1}{\theta_m(z)} - z = \frac{1}{\theta_r(z+\lambda)} - z - \lambda \qquad [13]$$

whence, according to Eq.[11]:

$$\varphi_m(z) = \varphi_r(z+\lambda) \qquad [14]$$

This corresponds to the following relations between memory functions:

$$K_m(t) = K_r(t)\exp(-\lambda t) \qquad [15]$$

We obtain the remarkably simple result that in the Strong Collision Model, the rate of decay of the "memory" shows up simply by an extra exponential decay of the memory function.

Constraints and limitations to the model

The most questionable assumption underlying the model is that following a motion, everything is lost but the transverse magnetization. This will be discussed in a forthcoming article.

A key assumption in the formulation of the model is that the shape of the rigid-state FID is not modified by a motion, which implies that the motions do not change the form of the spin-spin interactions. This is only possible if the nuclear environment of each individual spin is the same after as before a motion, the only change being that it is not the same nuclei that occupy the same relative sites. This case corresponds to atomic or molecular motion induced by the diffusion of vacancies at low concentrations in a single crystal. One must make the distinction, first introduced by Eisenstadt and Redfield (10), between a jump and an encounter. A given portion of the crystal experiences the sudden arrival of a vacancy, which performs many jumps before disappearing for away (This is the standard expression. It is evident that it is the atoms, or molecules, that jump into vacant sites.). The whole process is sudden, in the sense that it takes place in a time too short for the spin system to undergo any significant evolution. That portion of the crystal was vacancy-free at the end of the encounter, so that the form of the spin-spin interactions is indeed the same. The motions referred to in describing the model are in fact encounters, and not individual jumps.

In a powder, each crystallite obeys the relation [15], but with different rigid-lattice memory functions $K_r(t)$. The motion rate λ being independent of crystal orientation, we have on the average:

$$\overline{K_m(t)} = \overline{K_r(t)}\exp(-\lambda t) \qquad [15']$$

and:

$$\overline{\varphi_m(z)} = \overline{\varphi_r(z+\lambda)} \qquad [14']$$

These relations being linear, it seems that we might use powder samples, and not solely single crystals to test the model. Unfortunately, this is not the case because all one can observe in a powder is the average FID (or average absorption signal). We have, in place of Eq.[8]:

$$\overline{\theta_m(z)} = \overline{\theta_r(z+\lambda)} + \lambda\overline{\theta_r(z+\lambda)\theta_m(z)} \quad [8']$$

This is a non-linear relation, and we have in general:

$$\overline{\theta_r(z+\lambda)\theta_m(z)} \neq \overline{\theta_r(z+\lambda)} \times \overline{\theta_m(z)} \quad [16]$$

It is therefore impossible to test the model with powders.

Experimental study

We have tested the model with a single crystal of Hexamethylethane (HME) which is the most symmetrical octane molecule.

Single crystals of HME are obtained from the liquid state by the Stockbarger method. Due to the high vapour pressure of the solid, the crystal is enclosed in a sealed tube.

This molecular crystal experiences a first-order phase transition at 152.5 K whereby the molecules undergo rapid reorientation up to the melting point at 374 K. As a consequence, the inter-molecular dipolar interactions average to zero, whereas the average dipolar interactions between protons of different molecules are the same as if each proton was located at the centre of gravity of its molecule. These centres form a body centred cubic structure with a unit cell of size 7.69 Å.

NMR relaxation measurements reveal the existence in this phase of a thermally activated translational diffusion of the molecules through the motion of vacancies (11). Analysis of these measurements yields the value of the average time τ between successive motions, as a function of temperature (12).

The proton FID's were observed at 91 MHz with a home-made pulse spectro-meter. We have used 0.5 µs pulses with a repetition time of 0.3 sec. The FID signal were sampled in 2048 channels with a time of 0.3µs per channel. The FID signals were extrapolated back to the origin through a fourth-order Taylor expansion approxi-mation:

$$G(t) = 1 - \frac{M_2}{2}t^2 + \frac{M_4}{4!}t^4$$

The main test consists in checking whether the model is actually able to account for the variation of the FID shape with temperature. This is done with the help of Eq.[6] for $z = i\omega$. The results of the fits are given Figure 1.

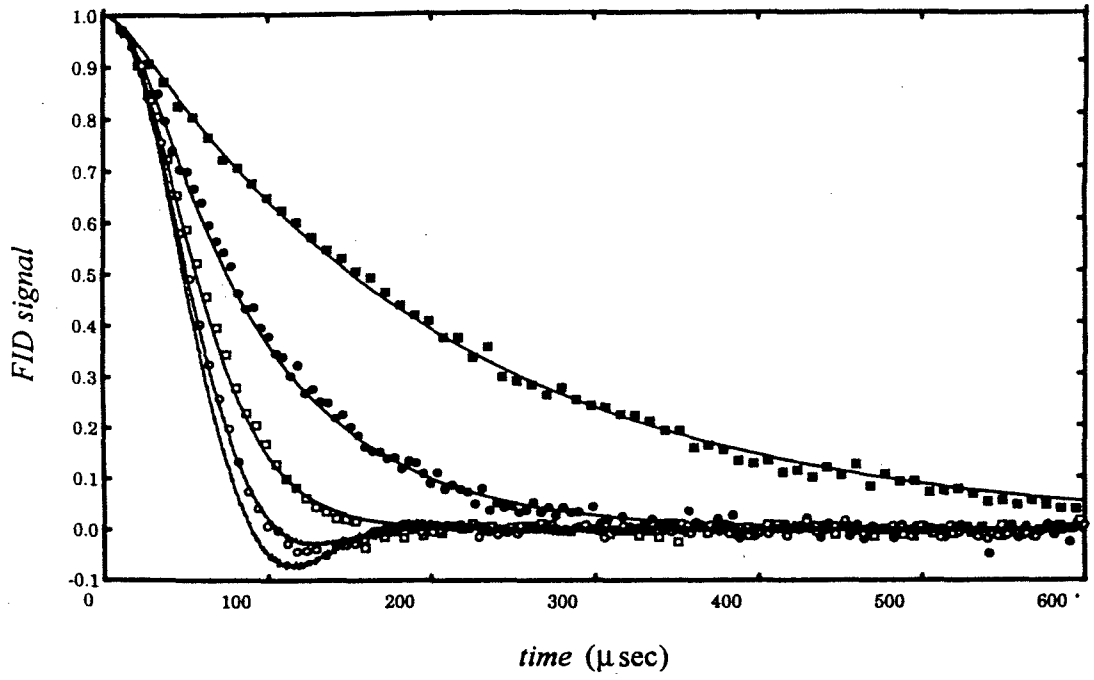

figure 1: Free Induction Decay Signals at different temperatures: open circles: 283 K, open squares : 292.5 K, full circles: 303 K, full squares : 311.3 K. Solid curves are calculated with our model.

The only fit parameter is λ. The values of λ are plotted as a function of 1/T in figure 2, together with values of $1/\tau$ taken from ref.(12) . It is seen that both λ and $1/\tau$ obey an Arrhenius law with the same activation energy.

The ratio $(\lambda\tau)^{-1} \approx 1.6$ is compatible with λ being equal to the decay rate of the secular dipolar auto-correlation function.

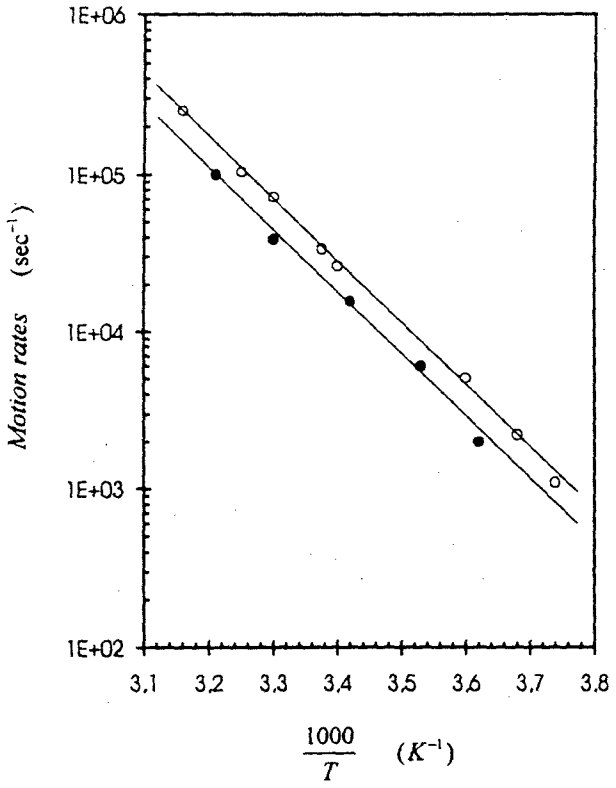

figure 2 : Memory decay rates λ (white circles, present work) and average jump rates τ^{-1} (black circles, deduced from ref. (12)).

Conclusion

The naïve strong collision model is remarkably successful in accounting for the variation of the FID with motion of intermediate rate. There is however a surprising and unexplained fact : the rate λ entering eq.[7] is smaller than the average rate between encounters. This rate λ is found approximately equal to the rate of decay of the dipolar auto-correlation function, which is well known from theory to involve several encounters (13).

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