CONF-801124--49

NEW METHOD FOR THE DETERMINATION OF DIFFUSION CONSTANTS
FROM
PARTIALLY NARROWED NMR LINES

by

D. Wolf

Prepared for

Materials Research Society Symposium
on
Nuclear and Electron Resonance Spectroscopies
Applied to Materials Science

Boston, Massachusetts

November 17-20, 1980

UofC-AUA-USDOE

ARGONNE NATIONAL LABORATORY, ARGONNE, ILLINOIS

Operated under Contract W-31-109-Eng-38 for the
U. S. DEPARTMENT OF ENERGY

NEW METHOD FOR THE DETERMINATION OF DIFFUSION CONSTANTS FROM PARTIALLY NARROWED NMR LINES*

D. WOLF
Materials Science Division, Argonne National Laboratory, Argonne, IL 60439

ABSTRACT

The effect of atomic and molecular motions on the NMR free-induction decay (FID) and lineshape is investigated theoretically in the intermediate temperature range in which the NMR line is only partially narrowed. It is shown that the FID may be decomposed into the weighted sum of a rigid-lattice (background) contribution and an exponentially decaying part containing all the information on the diffusive or reorientational motions in the crystal in terms of the spin-spin relaxation time T_2.

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*Work supported by the U.S. Department of Energy.

INTRODUCTION

In contrast to spin-lattice relaxation processes, spin-spin relaxation is most effective in the absence of atomic or molecular motions. The result is a background ("rigid-lattice") free-induction decay (FID) or linewidth which prohibits the investigation of internal motions in crystals if the mean time τ between consecutive jumps of an atom or molecule, τ, is longer than the inverse of the rigid-lattice second moment, $\Delta\omega^{RL}$.

Owing to the complexity of NMR lineshape theories in solids, it has been difficult in the past to extract quantitative information (such as the diffusion coefficient) from the relatively simple FID or lineshape measurements in the intermediate temperature range in which the NMR line is neither Lorentzian (as in the motionally-narrowed region) nor practically Gaussian (as in the rigid-lattice region).

In this article it is shown that the rigid-lattice (RL) and motional FID or linewidth contributions are simply additive and that, therefore, the information on the atomic motions is extracted rather easily by subtracting the experimentally measuable RL background contribution from the actual FID or linewidth in the intermediate region. For simplicity, the following discussion is couched in terms of the FID. As is well known, the lineshape is obtained by a simple Fourier transform of the FID.

BASIC THEORY

As discussed in some detail in Ref. 1, for NMR purposes the Hamiltonian H of a crystal is subdivided into a "lattice" Hamiltonian, H_L, a Hamiltonian, H_S, of the completely isolated spin system embedded in the crystal, and the spin-lattice coupling Hamiltonian, H_{SL}, according to

$$H = H_S + H_{SL} + H_L \quad . \tag{1}$$

By definition, $[H_S,H_L] = 0$. In general, H_S includes internal (rigid-lattice) spin-spin interactions inside the isolated spin system (such as the direct dipolar interaction Hamiltonian, H_D^{RL}), as well as Zeeman interaction Hamiltonians with externally applied time-independent (H_Z) and time-dependent $[H_1(t)]$ magnetic fields, $\vec{h}_0$ and $\vec{h}_1(t)$, respectively; hence, considering only internal dipole-dipole interactions,

$$H_S = H_D^{RL} + H_Z + H_1(t) \quad . \tag{2}$$

The "lattice"-induced fluctuations of H_{SL} are governed by the expression [1]

$$H_{SL}(t) = e^{i/\hbar\, H_L t}\, H_{SL} e^{-i/\hbar\, H_L t} = H_D(t) - H_D^{RL} \, , \tag{3}$$

where it was observed that, by definition, $[H_D^{RL},H_L] = 0$.

According to Eqs. (1) - (3),

$$H(t) = e^{i/\hbar\, H_L t}\, H\, e^{-i/\hbar\, H_L t} = H_o + H_L + H_1(t) + H_{SL}(t)\ , \qquad (4)$$

where $H_o = H_Z + H_D^{RL}$; i.e., H(t) is explicitely time-dependent due to the time variation of the external field $\vec{h}_1(t)$ and implicitely time dependent due to the fluctuations in the crystal (such as diffusive motions).

The time evolution of the density matrix σ of the spin system (averaged over all "lattice" degrees of freedom) satisfies the Von Neumann-Liouville equation (see, e.g., Refs. 1-7)

$$\frac{d\sigma}{dt} = -\frac{i}{\hbar}\left[H_o + H_1(t) + H_{SL}(t),\ \sigma(t)\right]\quad , \qquad (5)$$

with the initial condition that for $t \to -\infty$ the spin system is at thermal equilibrium with itself and with the "lattice" at temperature θ_L:

$$\sigma(t \to -\infty) = \sigma_{eq} = \frac{e^{-H_o/k\theta_L}}{\mathrm{Tr}\left(e^{-H_o/k\theta_L}\right)}\quad , \qquad (6)$$

where k denotes Boltzmann's constant.

Within the framework of the Bloch-Wangsness-Redfield theory [1,2,7] $H_{SL}(t)$ in Eq. (5) is considered as a perturbation while $H_1(t) \equiv 0$. For that reason the theory is restricted to the motionally-narrowed region.

In the linear-response theory of Kubo and Tomita [1,4,8] $H_1(t)$ is treated as the small perturbation, thus enabling the calculation of the FID and NMR lineshape even in a rigid lattice in which by definition, $H_{SL}(t) \equiv 0$.

In contrast to both theories, we now consider both $H_1(t)$ and $H_{SL}(t)$ simultaneously as weak perturbations on the spin system. In the usual manner Eq. (5) may thus be solved recursively by applying an iterative perturbation-type procedure. The "fast" time variation in Eq. (5) due to H_o is readily removed by defining the Heisenberg operators

$$H^{*}_{SL}(t) = e^{i/\hbar\, H_o t} H_{SL}(t) e^{-i/\hbar\, H_o t}\ ;\ \vec{\mu}(t) = e^{i/\hbar\, H_o t}\, \vec{\mu}\, e^{-i/\hbar\, H_o t}\quad , \qquad (7)$$

where $\vec{\mu} = \Sigma_i\, \vec{\mu}_i = \gamma\hbar\, \Sigma_i\, \vec{I}_i$ is the magnetic-moment operator (γ = gyromagnetic ratio, $\vec{I}$ = nuclear spin vector operator), wich $H_1(t) = -\vec{\mu}\,\vec{h}_1(t)$. If $H_{SL}(t)$ is assumed to be a random stationary operator with vanishing ensemble average and if we realize that the time variations of $H_{SL}(t)$ and $H_1(t)$ are not correlated, it may be shown after a straightforward calculation (compare, e.g., Ref. 3) that in the linear-response limit for $H_1(t)$ and in the second-order perturbation limit for $H_{SL}(t)$ the solution to Eq. (5) may be written as follows:

$$\sigma(t) = \sigma_{eq} + \sigma^{RL}(t) + \sigma^{SL}(t) \quad , \tag{8}$$

with

$$\sigma^{RL}(t) = \frac{i}{\hbar} \int_{-\infty}^{t} dt' \, \vec{h}_1(t') \, \overline{[\vec{\mu}(t'-t), \sigma_{eq}]} \tag{9}$$

and

$$\sigma^{SL}(t) = -\frac{1}{\hbar^2} \int_{-\infty}^{t} dt' \int_{-\infty}^{t'} dt'' \, \overline{[H^{*}_{SL}(t'-t), [H^{*}_{SL}(t''-t), \sigma_{eq}]]} \, , \tag{10}$$

where the bar indicates an ensemble average. Note that $\sigma^{SL}(t)$ is essentially governed by $H_{SL}(t)$ while $\sigma^{RL}(t)$ contains rigid-lattice properties only. Equations (8) - (10) may be applied to determine the time variation of the expectation value $\langle Q \rangle = \mathrm{Tr}(\sigma(t)Q)$ of any operator Q associated with the spin system, such as the energy $\langle H_S \rangle$ or the magnetization $\vec{M} = \langle \vec{\mu} \rangle$.

FID IN THE PRESENCE OF NUCLEAR MOTIONS

From Eq. (8) the relaxation equation for the macroscopic magnetization in the x direction (perpendicular to $\vec{h}_o$, with $M_x^{eq} = 0$) becomes:

$$M_x(t) = M_x^{RL} + M_x^{SL}(t) \quad . \tag{11}$$

Completely analogous to the theory of Kubo and Tomita [8], $\vec{h}_1(t)$ in Eq. (9) may be identified with a step function perturbation associated, say, with the sudden removal of $\vec{h}_1$ at $t = 0$. Also, applying the classical dissipation-fluctuation theorem [4] and limiting ourselves to spin systems containing one sort of nuclei only, after a straightforward calculation identical to that of Abragam [9], we obtain (with $\omega_o = \gamma H_o$)

$$M_x^{RL}(t) = \frac{\cos \omega_o t}{2\mathrm{Tr}(\sigma_{eq} \mu_x^{2})} \mathrm{Tr}(\sigma_{eq} [\mu_x^{RL}(t), \mu_x]) \tag{12}$$

with

$$M_x^{RL}(t) = e^{i/\hbar \, H_D^{(0)RL} t} \, \mu_x \, e^{-i/\hbar \, H_D^{(0)RL} t} \quad , \tag{13}$$

where $H_D^{(0)}$ denotes the secular part of the dipole Hamiltonian. We are thus restricting ourselves to the adiabatic lineshape (i.e., to temperatures well below the T_1 minimum due to the nuclear motions). Equation (12) is identical with the usual starting equation for the explicit determination of the rigid-lattice FID and lineshape [3,8,9]. Hence, in the rotating reference frame (index r) Eq. (12) may formally be written as follows:

$$M_{xr}^{RL}(t) = M_{xr}^{RL}(0)\ F^{RL}(t) \quad , \tag{14}$$

where $F^{RL}(t)$ is the normalized rigid-lattice FID function.

In a similar manner, starting from Eq. (10) $M_x^{SL}(t)$ may be determined. After a calculation similar to that of Abragam [2] it is found that in the high-field limit (in which $H_o >> H_L$, where H_L is the dipolar local field)

$$M_{xr}^{SL}(t) = M_{xr}^{SL}(0)\ e^{-t/T_2} \quad , \tag{15}$$

with the usual expression for T_2 in the adiabatic limit (Ref. 2):

$$\frac{1}{T_2} = \frac{3}{8}\ \gamma^4 \hbar^2\ I(I + 1)\ J^{(0)}(0) \quad , \tag{16}$$

where $J^{(0)}$ is the spectral density function associated with fluctuations of the secular dipole Hamiltonian. For self diffusion in crystals, $J^{(0)}(0) = A\tau$ where τ denotes the mean time between successive jumps of an atom, while the constant A depends on the diffusion mechanism [1].

Combining Eqs. (11), (14) and (15) we thus obtain:

$$M_{xr}(t) = M_{xr}(0)F(t) = M_{xr}^{RL}(0)F^{RL}(t) + M_{xr}^{SL}(0)e^{-t/T_2} \quad . \tag{17}$$

As is well known [3,8,9], the calculation of $F^{RL}(t)$ and hence of the actual FID function F(t) in the presence of nuclear motions is a very difficult problem. However, to use FID's to investigate atomic motions (via T_2) it is sufficient, according to Eq. (17), to measure $F^{RL}(t)$ rather than calculate it.

INVESTIGATION OF ATOMIC MOTIONS FROM THE ONSET OF MOTIONAL NARROWING

The remaining problem in applying Eq. (17) to determine T_2 arises from the temperature-dependent prefactors in the weighted sum in Eq. (17). Since, by definition, $F^{RL}(0) = 1$, for $t = 0$ Eq. (17) yields:

$$M_{xr}(0) = M_{xr}^{RL}(0) + M_{xr}^{SL}(0) \quad . \tag{18}$$

Note that $M_{xr}(0)$ is determined experimentally by the actual FID in the intermediate temperature range. To determine $M_{xr}^{RL}(0)$ and $M_{xr}^{SL}(0)$ independently, another relationship is needed.

According to Eq. (17), two types of spins may be distinguished, namely those performing at least one jump during a time of the order of T_2^{RL} (defined as the inverse of the RL second moment, $\Delta\omega^{RL}$) and those which do not jump during that time. The probability $w_o(T_2^{RL},\tau)$ that an atom does not perform any jumps in time T_2^{RL} if the mean time between successive jumps of a given atom is τ, is [1]

$$w_o(T_2^{RL},\tau) = \exp\left(-T_2^{RL}/\tau\right) \quad . \tag{19}$$

Since $M_{xr}(0)$ is proportional to the total number of spins, we may write

$$M_{xr}^{RL}(0) = M_{xr}(0)\; w_o(T_2^{RL},\tau) \quad . \tag{20}$$

Hence, with Eq. (18) we find that

$$M_{xr}^{SL}(0) = M_{xr}(0)\; \left[1 - w_o\left(T_2^{RL},\tau\right)\right] \quad . \tag{21}$$

Combining Eqs. (17) - (21) we finally obtain for the FID shape function in the intermediate temperature region:

$$F(t) = e^{-T_2^{RL}/\tau}\, F^{RL}(t) + \left(1 - e^{-T_2^{RL}/\tau}\right) e^{-t/T_2} \quad . \tag{22}$$

For thermally activated processes $\tau = \tau_o \exp(E/kT)$, where E is the activation energy. This enables F(t) in Eq. (22) to be expressed in terms of the absolute temperature T.

DISCUSSION

As pointed out above, for an assumed diffusion mechanism T_2^{-1} may be expressed in terms of τ with no adjustable parameters. Hence, Eq. (22) relates the actual FID shape function F(t), for example, to the diffusion constant $D = \ell^2/6\tau$, where ℓ is the jump distance of the atoms. The normalized rigid-lattice FID function, $F^{RL}(t)$, may be determined from an FID measurement at a lower temperature. Therefore, Eq. (22) contains only one parameter, namely, the mean residence time τ. From a fit of Eq. (22) to the experimental FID, F(t), in the intermediate temperature range, τ and hence D may be extracted in a rather straightforward manner.

Another, perhaps more interesting way to extract the diffusional contribution to F(t) in Eq. (22) may be the use of a multiple-pulse sequence. This technique takes advantage of the idea that the part of the FID associated with $F^{RL}(t)$ is reversible (and may thus be refocussed by means of a proper pulse sequence) while the contribution arising from the nuclear motions (T_2) is irreversible.

Finally, it is pointed out that the Fourier transform of Eq. (22) yields the interesting result that the actual NMR lineshape under conditions of partial motional narrowing is a weighted average of the rigid-lattice (low-temperature) and the motionally-narrowed Lorentzian (high-temperature) lineshape.

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