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A. M. Albano

Peter A. Beckmann

Bryn Mawr College, pbeckman@brynmawr.edu

M. E. Carrington

F. A. Fusco

A. E. O'Neill

See next page for additional authors

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Authors

A. M. Albano, Peter A. Beckmann, M. E. Carrington, F. A. Fusco, A. E. O'Neill, and M. E. Scott

LETTER TO THE EDITOR

A general NMR spectral density and its experimental verification

A M Albano, P A Beckmann, M E Carrington†, F A Fusco‡, A E O'Neill§ and M E Scott

Department of Physics, Bryn Mawr College, Bryn Mawr, Pennsylvania 19010, USA

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Abstract. We develop a new general spectral density for use in interpreting nuclear spin-lattice relaxation measurements in molecular solids where molecular and/or intramolecular reorientation is responsible for the relaxation. We show that the simplest case of the general theory fits both the temperature and Larmor frequency dependence of some very complicated relaxation measurements which could not be previously fitted using several standard spectral densities. The relationship of the spectral density to a distribution of molecular potentials is briefly outlined.

Nuclear spin relaxation (NSR) is a valuable tool in the study of molecular and intramolecular reorientation in molecular solids. A serious problem in the subject is the need for realistic spectral densities (i.e. the power spectrum of the local magnetic field) which characterise the molecular motion. There are two theoretical approaches used in the temperature dependence of the nuclear spin-lattice relaxation rate (R versus T) is not explained by a simple lorentzian spectral density $j(\tau, \omega) = 2\tau/(1 + \omega^2\tau^2)$ with correlation time τ and Larmor angular frequency ω (Abragam 1961). One method is to employ a non-exponential correlation function (whose Fourier transform is $j(\tau, \omega)$) and the other is to employ a distribution of correlation times τ each of which is characterised by an exponential correlation function $g(\tau, t) = \exp(-|t|/\tau)$ (Lindsey and Patterson 1980). In this Letter we introduce a new spectral density which adopts the latter approach.

A major goal is to exploit NSR experiments to learn about the molecular environment of the nuclear spins. It is this environment that determines the molecular motion which modulates the appropriate interaction and causes the relaxation. In many molecular solids, particularly organic solids which may exhibit hydrogen bonding, there are a variety of such environments even though on a single molecule basis the nuclei of interest are chemically equivalent. This situation can be described by a continuous distribution of inter- and intramolecular potentials. For NSR, it is convenient to relate the correlation time which characterises the molecular and/or intramolecular reorientation to an 'acti-

† Present address: Department of Physics, State University of New York at Stony Brook, Stony Brook, New York 11794, USA.

‡ Present address: Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, USA.

§ Present address: 930 Woodlea Court, Birmingham, Michigan 48009, USA.

vation' energy E via an Arrhenius relationship:

$$\tau = \tau_{\infty} \exp(E/kT) \quad (1)$$

where the relationship between E , the temperature-independent parameter τ_{∞} and the appropriate molecular potentials depends on the magnitudes of these parameters and the model employed (Brot 1969). A more detailed understanding of this link is a very important problem which we leave for the present. For NSR the environment is conveniently characterised by a distribution of activation energies $\Gamma(E)$, where $\Gamma(E) dE$ is the fraction of molecules with activation energies in the range from E to $E + dE$. These molecules will be characterised by a correlation time τ , and if $\Lambda(\tau)$ is the distribution of the τ corresponding to $\Gamma(E)$ then it follows from equation (1) that

$$\Lambda(\tau) = \Gamma(E) dE/d\tau = (kT/\tau) \Gamma(E).$$

We adopt the approach that a general spectral density can be defined via a linear combination of lorentzian spectral densities:

$$j(\omega, \tau_c) = \int_0^{\tau_c} \Lambda(\tau) \frac{2\tau}{1 + \omega^2\tau^2} d\tau. \quad (2)$$

It is assumed that as $E \rightarrow 0$, $\Gamma(E) \rightarrow 0$, and $\tau \rightarrow \tau_{\infty}$ which is very small so the lower limit of the integral in equation (2) may be taken as zero. It is also assumed that Λ depends on T only through τ . The cut-off τ_c corresponds to a cut-off activation energy E_c for $\Gamma(E)$ via equation (1): $\tau_c = \tau_{\infty} \exp(E_c/kT)$. The physical interpretation of the cut-off E_c is not clear and requires further justification. We introduce the dimensionless variable $z = (\tau/\tau_c) - 1$ and rewrite equation (2):

$$j(\omega, \tau_c) = \frac{\tau_c^2}{1 + \omega^2\tau_c^2} h(\omega\tau_c) \quad (3)$$

$$h(x) = \int_{-1}^0 \left[\frac{\Lambda(z)(1+z)}{1 + \left(\frac{x^2}{1+x^2}\right)(2z+z^2)} \right] dz \quad (4)$$

where $x = \omega\tau_c$. In principle, $j(\omega, \tau_c)$ can be determined for a given distribution function $\Lambda(\tau)$.

We wish to place limitations on $h(x)$ based on experimental results. In a large class of systems, the observed low- and high-temperature slopes in $\ln R$ versus T^{-1} are different and this means that a simple lorentzian spectral density is insufficient. Also, the frequency dependence of R in the long correlation time limit is often not $R \propto \omega^{-2}$ predicted by a lorentzian spectral density (Abragam 1961).

The points raised above are demonstrated in figure 1, where we show $\ln R$ versus T^{-1} at two frequencies in 3,5-di-t-butylphenol whose phenolic hydrogen has been deuterated (3,5-DTBp-OD). The data at 30 MHz have been reported previously by Aronson *et al* (1981) and the present measurements at 8.5 MHz were made using the standard $\pi-t-\pi/2-T$ pulse sequence with $T > 8R^{-1}$. Sample preparation and specific deuteration have been discussed previously by Aronson *et al* (1981), although it should be noted that much of the scatter in the earlier 30 MHz experiments is due to thermal history effects which have now been essentially eliminated in the newly reported 8.5 MHz data. These matters will be addressed further in another paper. The 18 protons whose motion modulates the proton dipole-dipole interaction and thus causes the relaxation are in six

chemically equivalent methyl groups. The two t-butyl groups reorient at the same rate as their constituent methyls and thus a single maximum in R versus T is observed (i.e. $\omega\tau_c \sim 1$ occurs only once), as discussed by Beckmann (1981).

To determine conditions which $h(x)$ in equation (3) must satisfy based on the experiments, we note that $R \propto j$ and that $\ln R$ versus T^{-1} is linear at high and low temperatures. Thus we require that $\partial(\ln j)/\partial(T^{-1})$ equals E_c/k in the short correlation time limit

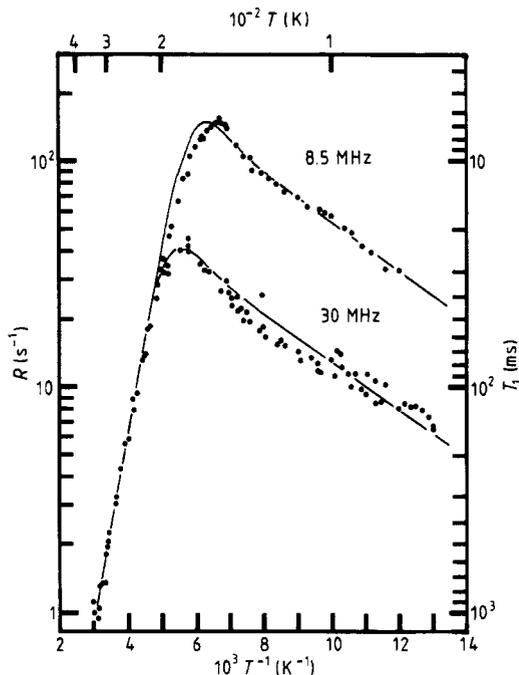


Figure 1. The proton spin-lattice relaxation rate $R = T_1^{-1}$ as a function of temperature T at 8.5 and 30 MHz. The full curves are discussed in the text.

$\omega\tau_c \ll 1$ (high temperature) and $-\gamma E_c/k$ with $0 < \gamma < 1$ in the long correlation time limit (low temperature). For solid 3,5-DTBP-OD, the high-temperature data yields $E_c/k = 1.81$ kK and the ratio of the two limiting slopes yields $\gamma = 0.134$. These conditions applied to equation (3) require

$$\frac{\partial \ln h(x)}{\partial x} = -\frac{1}{x} \{1 + \rho(x)(\gamma - 1)\} \tag{5}$$

$$\lim_{x \rightarrow 0} p(x) = 0$$

$$\lim_{x \rightarrow \infty} p(x) = 1. \tag{6}$$

Many classes of functions $p(x)$ will satisfy equation (6) and here we pursue the following:

$$p(x) = \sum_{i=1}^{\infty} a_i \left(\frac{x^n}{1 + x^n} \right)^i \tag{7}$$

with the condition $\sum_i a_i = 1$. Equation (7) can be inserted in equation (5) and the result integrated to find $h(x)$. We shall present this general solution in a future paper but here we note that the simplest form of equation (7) fits the data very well. If only the first term of equation (7) is taken it follows that

$$j(\tau_c, \omega) = \frac{2\tau_c}{1 + \omega^2\tau_c^2} \{1 + \omega^n\tau_c^n\}^{(1-\gamma)/n}. \quad (8)$$

This reduces to the well known lorentzian spectral density $2\tau_c/(1 + \omega^2\tau_c^2)$ in the limit $\gamma \rightarrow 1$. For $\omega\tau_c \ll 1$ (high temperatures) $j(\tau_c, \omega) = j(\tau_c, 0) = 2\tau_c$ which is frequency independent and indistinguishable from the lorentzian spectral density. For $\omega\tau_c \gg 1$ (low temperatures) $j(\tau_c, \omega) = 2/(\tau_c^\gamma\omega^{1+\gamma})$. As discussed previously, this gives limiting slopes for $\ln(j)$ versus T^{-1} of E_c/k and $-\gamma E_c/k$ for $\omega\tau_c \ll 1$ and $\omega\tau_c \gg 1$ respectively. The spectral density is independent of n in these two limiting regions. In the region $\omega\tau_c \sim 1$, the effect of n is to increase j (smaller n) or decrease j (larger n).

We note there are two factors which complicate the relationship between the observed R in Solid 3,5-DTBP-OD and the theoretical $j(\tau_c, \omega)$. Firstly, since dipole-dipole interactions are responsible for the relaxation, both single and double spin flips are involved and the combination $j(\tau_c, \omega) + 4j(\tau_c, 2\omega)$ enters into R . Secondly, the methyl reorientation is superimposed on t-butyl reorientation and this leads to terms in $\tau_c/2$ as well as τ_c since the superposition frequency $\tau_c^{-1} + \tau_c^{-1} = 2\tau_c^{-1}$ enters the relaxation as well as just τ_c^{-1} (Beckmann 1980). The detailed calculation of R is given by Beckmann (1981) and the result is

$$R = A \left[j(\tau_c, \omega) + 4j(\tau_c, 2\omega) + j\left(\frac{\tau_c}{2}, \omega\right) + 4j\left(\frac{\tau_c}{2}, 2\omega\right) \right]. \quad (9)$$

These details do not affect any of the properties under discussion and if we had assumed $R = Aj(\tau_c, \omega)$ the resulting fit would be virtually indistinguishable from that obtained using equation (9): only the parameters A and $\tau_{c\infty}$ would change. Equations (9) and (8) with $n = 1$ give the fit shown in figure 1. The low- and high-temperature slopes give $E_c/k = 1.81$ kK and $\gamma = 0.134$ as discussed previously and the two intercepts yield $\tau_{c\infty} = 4.1 \times 10^{-13}$ s and $A = 6.6 \times 10^8$ s $^{-2}$.

There are several important points here. Firstly, this data cannot be fitted with a variety of standard spectral densities (Beckmann 1981), whereas the one presented here is quite successful. Secondly, the ratio of the high- to low-temperature slopes of $\ln R$ versus T^{-1} gives γ independently for each frequency and that the additional prediction $R \propto 1/\omega^{1+\gamma}$ for $\omega\tau_c \gg 1$ is also correct for the two frequencies is an additional check on the spectral density. Thirdly, it is interesting that such a good fit occurs for $n = 1$. The relaxation is independent of n at both high and low temperatures and the physical origins of the parameter n are not yet understood. We are presently investigating this. Fourthly, R in the region of $\omega\tau_c \sim 1$ (where n plays a role) is significantly greater than that obtained from the intersection of the high- and low-temperature straight lines. To put it more plainly, this spectral density with $n = 1$ leads to a 'bump' in the vicinity of the maxima in R . This bump can be raised ($n < 1$) or lowered ($n > 1$) without effect on the high- and low-temperature limits.

We are now investigating the physical origins of this simple yet successful spectral density by studying the distributions of correlation times and activation energies which give rise to it. At the same time, we are experimentally measuring spin-lattice relaxation rates in a series of molecular solids.

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