ANISOTROPIC NUCLEAR SPIN RELAXATION OF $^{13}$C IN SOLID BENZENE

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The resolved chemical shielding anisotropy of $^{13}$C in solid benzene allows a study of nuclear spin relaxation for benzene molecules with different orientations. As expected from a simple theory, the relaxation is strongly orientation dependent due to the strongly anisotropic motion of the benzene molecule (which consists of reorientation about the hexad axis). Preliminary data are presented which exhibit quantitative agreement between theory and results for the $^{13}$C anisotropic nuclear spin–lattice relaxation and for the $^{13}$C anisotropic nuclear Overhauser enhancement on saturation of the proton resonance.

1. Introduction

Elementary molecular motions leading to nuclear spin–lattice relaxation are usually anisotropic, and so should be expected in principle to lead to an anisotropy in $T_1$. Such anisotropies are not seen in liquids because they are isotropic on a time scale comparable to $T_1$. Even in solids the anisotropy is often largely or completely suppressed: a variety of elementary interactions with different correlation times or different angle dependences may be present, and even when they are not there may be dipolar broadening and spin diffusion which partially short-circuits the distinguishability of molecules having different orientations. We report here an illustrative study of solid benzene, expected to display anisotropy in $T_1$ because of the dominance of molecular rotation about the hexad axis [1–4], which overcomes these difficulties.

Fig. 1 shows a proton-enhanced nuclear induction spectrum [5] of natural abundance $^{13}$C in benzene at $-50^\circ$C. The spectrum reflects a pseudooxial symmetry in the chemical shielding tensor due to rapid motion about the hexad axis [1]; comparison with a theoretical unBroadened powder pattern [6] in the same figure demonstrates the uncharacteristically high resolution for a solid state nmr spectrum and the lack of any distortion. The anisotropy ($\Delta \sigma$) is $180 \pm 2$ ppm in agreement with the value reported by

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Yannoni and Bleich [7]. Experiments on the other aromatic compounds [8] indicate that a departure from axial symmetry of ≈ 80 ppm is expected when the benzene molecules are rigid (< 40°K).

The fact that we have a resolved chemical shielding anisotropy without dipolar broadening presents us with a unique opportunity for a dynamical study. Since each portion of the spectrum corresponds to benzene molecules with a particular orientation, we can carry out a study of orientation-dependent behavior of relaxation processes without resorting to single-crystal experiments. Moreover the $^{13}$C spin relaxation is expected to be dominated by intramolecular interactions and is thus related directly to the orientation and motion of a single molecule [9]; this is not true of proton spin relaxation [4].

2. Simple relaxation theory

The analysis is simplified by the following observations:

(i) relaxation of the $^{13}$C nucleus ($S$) is dominated by dipolar interaction with the single proton ($I$) immediately bonded to it at distance $r^*$. 

(ii) The molecular motion consists of random jumps with correlation time $\tau_c$ among equivalent orientations about the $C_6$ axis, which makes a fixed angle $\beta$ with the external magnetic field \[2\].

We proceed from the usual coupled rate equations for $I$ and $S$ magnetizations \[10\]. The rate coefficients, evaluated by perturbation theory with suitable averaging over the six equivalent orientations of the benzene ring, are found to be

\[
\frac{1}{T_{1}^{SS}} = \frac{3\gamma_S^2\gamma_I^2I(I+1)}{16r^6} \left\{ \frac{y_0(\beta)}{1 + (\omega_S^2 - \omega_I^2)^2 r_c^2} + \frac{y_1(\beta)}{1 + \omega_S^2 r_c^2} \right\} + \frac{y_2(\beta)}{1 + (\omega_S^2 + \omega_I^2)^2 r_c^2}, \tag{1}
\]

where

\[
y_0(\beta) = \sin^4 \beta, \]
\[
y_1(\beta) = 2 \sin^2 \beta (1 + \cos^2 \beta), \]
\[
y_2(\beta) = 1 + 6 \cos^2 \beta + \cos^4 \beta. \tag{3}
\]

Two special cases are of experimental interest:

(i) If the $S$ spins ($^{13}$C) alone are disturbed from equilibrium, the polarization $I_0$ of the protons remains near its equilibrium value $I_0$ because the $S$ spins are dilute, and the spin–lattice relaxation is exponential with the time constant $T_{1}^{SS}$ given in (1).

(ii) If the $I$ spins are saturated, $I_I = 0$, the system approaches with time constant $T_{1}^{SS}$ a steady state characterized by an Overhauser enhancement $1 + \eta$ in the $S$ polarization, with

\[
\eta = \gamma_1 T_{1}^{SS}/\gamma_S T_{1}^{SI}. \tag{4}
\]

The angle dependences of both $T_{1}^{SS}$ and $\eta$ can be studied through differential behavior of different parts of the powder pattern of fig. 1. Instead of the angle $\beta$ it is convenient to use the experimental abscissa $\sigma$ in expressing the results:

\[
\cos^2 \beta = (\sigma - \sigma_\perp)/(\sigma_\parallel - \sigma_\perp). \tag{5}
\]

Notice that the anisotropies expressed in (1)–(4) are in some cases quite large, and moreover depend strongly on the correlation time. In particular the anisotropy in $T_{1}^{SS}$ changes sign as one goes from one side of the $T_{1}^{1}$ minimum to the other: at low temperatures the right-hand side of the pattern relaxes more slowly than the left-hand side, whereas at high temperatures the reverse is true.

3. Results

Fig. 2. shows representative spectra on the low-
These spectra are susceptible to quantitative analysis through eqs. (1)–(4). Moreover the temperature dependence of $t_c$ is known through previous studies of isotropic deuteron relaxation [4], so the full analysis can be carried out with no adjustable parameters:

$$t_c = 9.2 \times 10^{-15} \exp \left(-\frac{4200}{RT} \right).$$

Fig. 3 is an example of the $T_1$ anisotropy at $-80^\circ$C, which is above the $T_1$ minimum, showing excellent agreement with the value of $\omega S C = 0.075$ predicted by (6). Fig. 4 shows the experimental Overhauser distortion factors for two temperatures, one above and one below the $T_1$ minimum, again showing quantitative agreement with (6).

![Fig. 2. Effects of anisotropic motion of the $^{13}$C nuclear spin relaxation. (a) Normal proton-decoupled Fourier transform $^{13}$C spectrum in solid benzene. These experiments were done on a sample with $\approx 4\%$ abundance of $^{13}$C to enhance sensitivity since no proton-enhancement was used. (b) Same but with the protons saturated by a $\approx 1$G field, showing the anisotropic nuclear Overhauser enhancement. The lineshape is predicted quantitatively by theory (see fig. 4) and depends strongly on temperature. (c) Fourier transform spectrum after inverting the $^{13}$C resonance by a resonant 180° pulse and waiting 50 msec. $^{13}$C nuclei in molecules with $\beta = \pi/2 (\sigma = \sigma_\perp)$ relax much more rapidly ($=7X$) to equilibrium than those with $\beta = 0 (\sigma = \sigma_\parallel)$. Again agreement with theory is good; behavior changes markedly with temperature – for example at $-80^\circ$C (which is above $T_{1,\text{min}}$ for all orientations) the $T_1$ behavior is reversed (see fig. 4) and much less anisotropic ($\approx 2:1$).

The direct study of anisotropic spin—lattice processes, through the spectroscopy of rare spins decoupled from their abundant-spin surroundings, offers a number of advantages for the analysis of molecular dynamics. While this fact has been illustrated here with an example in which the dynamics were already understood, the same should be true of other cases. We have already studied the relaxation of $^{13}$C in adamantane [5], which shows the expected more rapid relaxation of those $^{13}$C nuclei having two rather than one directly bound protons, and an
Fig. 4. Example of dependence of the $^{13}$C nuclear Overhauser enhancement on orientation of the benzene molecule for two temperatures. The theoretical lines were calculated using eqs. (1)-(4). The experimental points were obtained by comparing the spectrum of fig. 2a with spectra like that of fig. 2b. The Overhauser enhancement is a much less sensitive quantitative test of $t_0$ than is the spin–lattice relaxation time.

Overhauser enhancement approximating the "normal" value $1 + \eta = 3$. These data, and a more extensive analysis of benzene including the dynamics of the cross-polarization process [5], will be presented elsewhere.

The experiments were performed on a homebuilt double-resonance spectrometer using rf fields of $\approx 10$ G for protons and 40–50 G for $^{13}$C. The $^{13}$C resonance frequency was 24.46 MHz. The proton-enhanced nuclear induction spectrum was obtained from natural abundance $^{13}$C while the remaining experiments employed a benzene sample enriched to $\approx 4\%$ in $^{13}$C.

References

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