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.

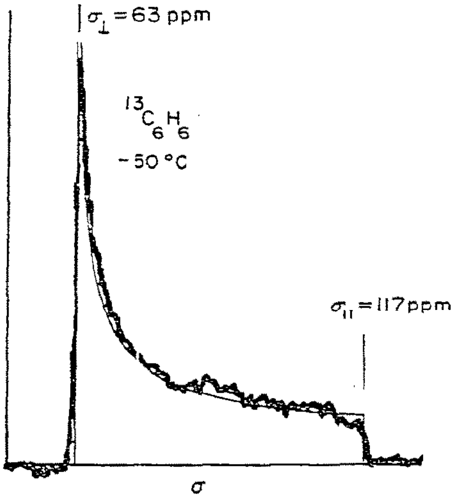

Fig. 1. Proton-enhanced nuclear induction spectrum of natural abundance ^{13}C in ≈ 200 mG of benzene at − 50°C. The smooth line is the expected absorption lineshape for a chemical shielding tensor with axial symmetry. The spectrum was obtained in ≈ 50 sec using a single shot version of the cross-polarization technique [5].

Fig. 1 shows a proton-enhanced nuclear induction spectrum [5] of natural abundance ^{13}C in benzene at − 50°C. The spectrum reflects a pseudoaxial 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 ± 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 an 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 t_c among equivalent orientations about the C_6 axis, which makes a fixed angle β 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

$$\frac{1}{T_1^{\mathrm{SS}}} = \frac{3\gamma_S^2\gamma_I^2\hbar^2 I(I+1)\,t_c}{16r^6} \times \left\{\frac{y_0(\beta)}{1+(\omega_S-\omega_I)^2t_c^2} + \frac{y_1(\beta)}{1+\omega_S^2t_c^2} + \frac{y_2(\beta)}{1+(\omega_S+\omega_I)^2t_c^2}\right\}, \tag{1}$$

$$\frac{1}{T_1^{\mathrm{IS}}} = \frac{3\gamma_S^2\gamma_I^2\hbar^2 S(S+1)\,t_c}{16r^6} \times \left\{-\frac{y_0(\beta)}{1+(\omega_S-\omega_I)^2t_c^2} + \frac{y_2(\beta)}{1+(\omega_S+\omega_I)^2t_c^2}\right\}, \tag{2}$$

where

$$\begin{aligned} y_0(\beta) &= \sin^4\beta\,, \\ y_1(\beta) &= 2\sin^2\beta(1+\cos^2\beta)\,, \\ y_2(\beta) &= 1+6\cos^2\beta+\cos^4\beta\,. \end{aligned} \tag{3}$$

Two special cases are of experimental interest:

(i) If the S spins (^{13}C) alone are disturbed from equilibrium, the polarization $\langle I_z\rangle$ 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, $\langle I_z\rangle = 0$, the system approaches with time constant T_1^{SS} a steady state characterized by an Overhauser enhancement $1+\eta$ in the S polarization, with

$$\eta = \gamma_I T_1^{\mathrm{SS}}/\gamma_S T_1^{\mathrm{SI}}\,. \tag{4}$$

The angle dependences of both T_1^{SS} and η can be studied through differential behavior of different parts of the powder pattern of fig. 1. Instead of the angle β it is convenient to use the experimental abscissa σ 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 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-

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[*] This is justified by field-dependence studies in the liquid (see ref. [9]).

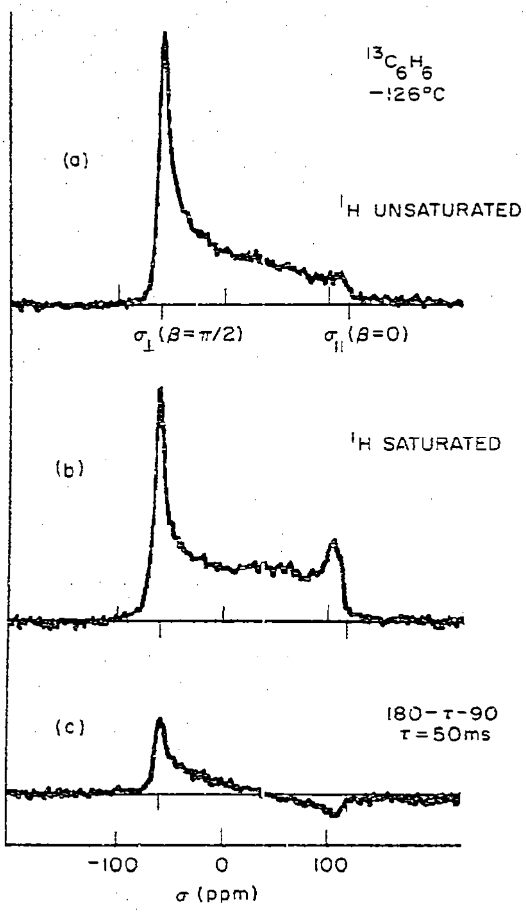

Fig. 2. Effects of anisotropic motion of the ^{13}C nuclear spin relaxation. (a) Normal proton-decoupled Fourier transform ^{13}C spectrum in solid benzene. These experiments were done on a sample with ≈ 4% abundance of ^{13}C to enhance sensitivity since no proton-enhancement was used. (b) Same but with the protons saturated by a ≈ 1G 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°C (which is above $T_{1,\mathrm{min}}$ for all orientations) the T_1 behavior is reversed (see fig. 4) and much less anisotropic (≈2:1).

temperature side of the T_1 minimum. Fig. 2b exhibits a remarkable and characteristic Overhauser distortion of the normal pattern (fig. 2a). Fig. 2c is a representative spectrum obtained by the inversion-recovery technique [11] showing differential effects in T_1^{SS}.

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*:

$$t_\mathrm{c} = 9.2 \times 10^{-15} \exp(-4200/RT)\,. \qquad (6)$$

Fig. 3 is an example of the T_1^{SS} anisotropy at −80°C, which is above the T_1 minimum, showing excellent agreement with the value of $\omega_S t_\mathrm{c} = 0.075$ 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).

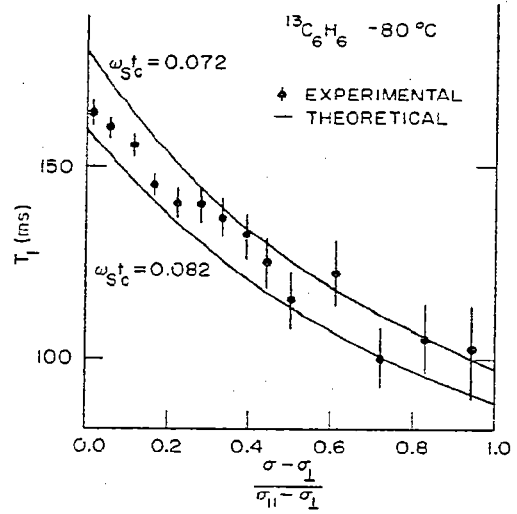

Fig. 3. Examples of dependence of ^{13}C T_1 on orientation of the benzene molecules [see eq. (5)]. The theoretical curves were calculated using eq. (1) with r = 1.085 Å. The experimental points were obtained by analysis of the time dependence of spectra like that in fig. 2c.

Evidently 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

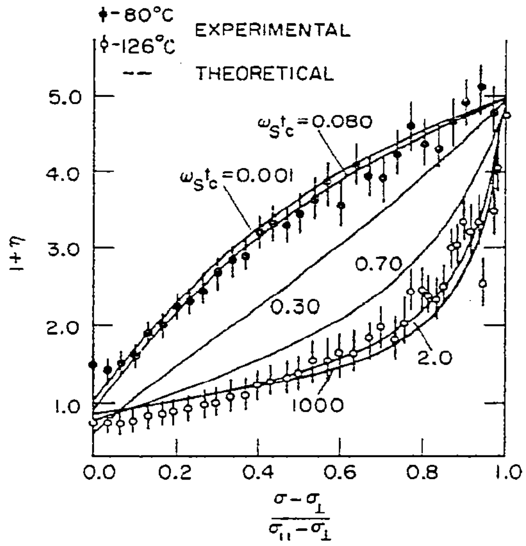

Fig. 4. Example of dependence of the ^{13}C nuclear Overhauser enhancement on orientation of the benzene molecule for two temperatures. The theoretical lines were calculated using eqs. (1)–(4). The experimental points were obtained by comparing the spectrum of fig. 2a with spectra like that of fig. 2b. The Overhauser enhancement is a much less sensitive quantitative test of t_c 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 ≈ 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 ≈ 4% in ^{13}C.

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