

^{15}N AND ^{13}C SPIN LATTICE RELAXATION IN NEAT LIQUIDS AT HIGH MAGNETIC FIELDS

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Abstract. General features of ^{15}N spin lattice relaxation in nitrobenzene, pyridine and triethanolamine are discussed and compared with ^{13}C relaxation mechanisms.

General features of ^{15}N spin lattice relaxation are probably best discussed in comparison with ^{13}C , where a lot of experimental material has been collected in the past few years. For ^{13}C usually two relaxation mechanisms are predominant: intramolecular dipole dipole interaction (DDI) between the nuclear spins of the carbon and directly bound protons and spin rotation interaction (SRI), since spin rotation constants for ^{13}C are relatively large. On the other hand, relaxation due to anisotropic chemical shift (ACS) could be demonstrated for ^{13}C only in a few cases ^{1.)} and intermolecular DDI can be neglected almost completely.

For ^{15}N the first two relaxation mechanisms are also important as was shown by Lippmaa et al. ^{2.)}, e.g., in aniline and nitrobenzene. We shall demonstrate that for ^{15}N relaxation due to ACS and intermolecular DDI can also be significant by combining ^{15}N and ^{13}C spin lattice relaxation rate measurements in the same molecule as a function of frequency and temperature. The relaxation measurements provide information about correlation times for both nuclei as well as values for the anisotropy of the chemical shift and the spin rotation constants for ^{15}N ^{3.)} These values can be compared with those obtained independently from the powder spectra of the frozen liquids.

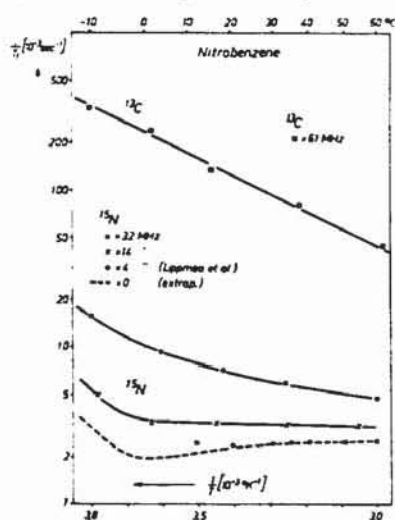


fig. 1

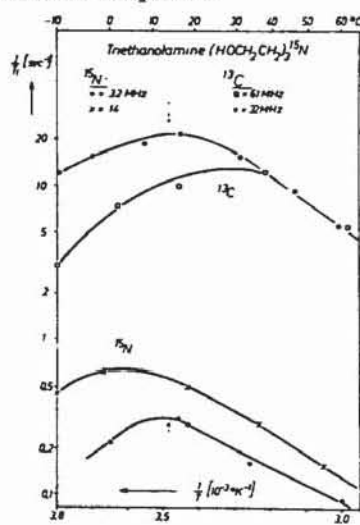


fig. 2

In fig. 1 the relaxation rates $1/T_1$ of ^{15}N and ^{13}C in nitrobenzene are shown. It can be seen that at 32 MHz (equivalent to a magnetic field of about 75 kG) the relaxation due to ACS is predominant and even at $+60^\circ\text{C}$ still accounts for about half of the total relaxation rate of the ^{15}N . With correlation times τ_c obtained from the ^{13}C relaxation rates (fig. 1) (^{13}C relaxation rates for aromatic ring carbons are solely determined in a good approximation by intramolecular DDI in this temperature range) we could determine a value $|\Delta\sigma| = |\sigma_{\parallel} - \sigma_{\perp}| = 400$ ppm for the ACS of the ^{15}N from the T_1 measurements. We also measured $\Delta\sigma$ directly in the powder by FT-NMR at -105°C . The $\hat{\sigma}$ -tensor is found

to be almost axially symmetric with $\Delta\sigma = -398 \pm 20$ ppm^{4.)}. From the shift components measured in the solid one can calculate the ^{15}N spin rotation constants: $C_{xx} = 11.4 \pm 1.5$ KHz, $C_{yy} = 1.6 \pm 0.5$ KHz, and $C_{zz} = 1.1 \pm 0.5$ KHz. Here the x-direction coincides with the twofold symmetry axis of nitrobenzene. Spin rotation constants we obtained independently from the relaxation measurements in the liquid agree remarkably well with those given above^{4.)}.

Similarly for pyridine a significant frequency dependence of the ^{15}N relaxation rate was observed^{3.)}. The frequency independent part of the relaxation rate is dominated by SRI at high temperatures (above 0°C). Below -30°C the major contribution to this rate is given by DDI, which is about 90 o/o due to intermolecular DDI^{3.)}. The reason is that the non-bonding orbital of the nitrogen can interact with protons of neighbouring molecules. Again $|\Delta\sigma|$ can be obtained from our T_1 data giving $|\Delta\sigma| = 710$ ppm. From the powder spectrum we obtained for ^{15}N : $\Delta\sigma = 672 \pm 20$ ppm, $C_{xx} = 16.5 \pm 1$ KHz, $C_{yy} = 11.5 \pm 1$ KHz, and $C_{zz} = 0.6 \pm 1$ KHz. Here the z-direction coincides with the direction perpendicular to the molecular plane of the pyridine.

In triethanolamine (HOCH_2CH_2)₃N the nitrogen atom has a non-bonding orbital as in the case of pyridine. From a molecular model, however, it can be seen that in this case the nitrogen atom is more or less shielded by the surrounding atoms of the molecule^{5.)}. Therefore, relaxation due to intermolecular DDI might be small. The results of the relaxation rate measurements for ^{15}N and ^{13}C are shown in fig. 2. Here the frequency dependence is opposite to that of ^{15}N in nitrobenzene (fig. 1) and pyridine because in triethanolamine the correlation times are much longer so that $\omega\tau_c \approx 1$. From the maximum of the relaxation rate we get the correlation times τ_c . With those τ_c the relaxation rates for the ^{13}C as well as for the ^{15}N can be completely accounted for by intramolecular DDI^{5.)}. The nature of the motion of the carbons and the nitrogen must be the same because we find the relaxation rate maxima at 32 MHz for C and N at the same temperature. This also means that the relaxation is caused by reorientation of the molecule as a whole.

These examples show that for ^{15}N intramolecular as well as intermolecular DDI, SRI and ACS can be important relaxation mechanisms depending on the system and experimental conditions. Consequently, a considerable amount of information can be gathered from ^{15}N relaxation studies.

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