

HIGH RESOLUTION NMR OF ^{15}N IN SOLIDS*

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^{15}N NMR spectra, obtained in the solid state by transfer of polarization from protons, are reported for $(\text{NH}_4)_2\text{SO}_4$, NH_4NO_3 , and glycine.

NMR chemical shifts and electron coupled interactions of nitrogen hold considerable intrinsic interest because of the role played by the N atom in peptide bonds, nucleotides, and other compounds, but they have been little studied. The abundant ^{14}N isotope suffers from small gyromagnetic ratio $\gamma(^{14}\text{N}) = 1.934 \times 10^3$ A sec/G and from quadrupole relaxation broadening of many of its resonances. ^{15}N , while of spin 1/2, also has a small magnetic moment $\gamma(^{15}\text{N}) = -2.712 \times 10^3$ A sec/G and is of low natural isotopic abundance (0.365%). It also often displays inconveniently slow spin-lattice relaxation [1]. Thus most workers who have studied ^{15}N have resorted to isotopic enrichment [2], although recently some Fourier-transform spectra have been obtained in natural abundance [3].

A recently introduced double resonance method [4] offers a considerable improvement in this situation when the rare ^{15}N spins (S) are coupled to abundant spins (I), usually protons. When the rotating frame relaxation time $T_{1\rho}(I)$ of the abundant spins is long, a limiting gain in power signal-to-noise ratio (i.e., a saving in time) of

$$G = N_I \gamma_I^2 I(I+1) / N_S \gamma_S^2 S(S+1)$$

is obtained. For ^{15}N in typical organic compounds,

$G > 10^5$ is not atypical, though $T_{1\rho}(I)$ will rarely be long enough to take advantage of this full improvement. Fig. 1 shows a spectrum obtained in 10 min from the naturally occurring ^{15}N in 150 mg of $(\text{NH}_4)_2\text{SO}_4$ at room temperature in a field H_0 of 22 800 G. Because $T_{1\rho}(H)$ is relatively short in this compound, the protons were repolarized every 8 sec and only 25 I - S contacts were made per polarization. Thus $G \approx 10^3$, but this still represents a substantial saving in time by comparison with conventional Fourier techniques [3].

A line width of ≈ 150 Hz arises primarily from dipolar coupling with ^{14}N in the (solid) sample: this could be reduced by further decoupling at the ^{14}N frequency or by sample rotation about the magic axis [5]. The latter would also destroy information concerning the anisotropy of the chemical shift.

The spectrum of fig. 1a shows no such anisotropy anyway, the site symmetry being very high. A more typical situation is that of the nitrate ion in NH_4NO_3 (fig. 1b). This spectrum was obtained from an isotopically enriched (30%) powder sample at room temperature, where the crystal structure is orthorhombic with C_{2v} site symmetry at the nitrate nitrogen [6], one N-O bond being 0.02 Å shorter than the other two. Note that the chemical shielding tensor displays a perceptible departure from axial symmetry, betraying a distortion of the local distribution away from the D_{3h} symmetry which would be exhibited by a free NO_3^- ion.

Measurements of chemical shielding anisotropies could be of great value to the study of proteins, nucleic

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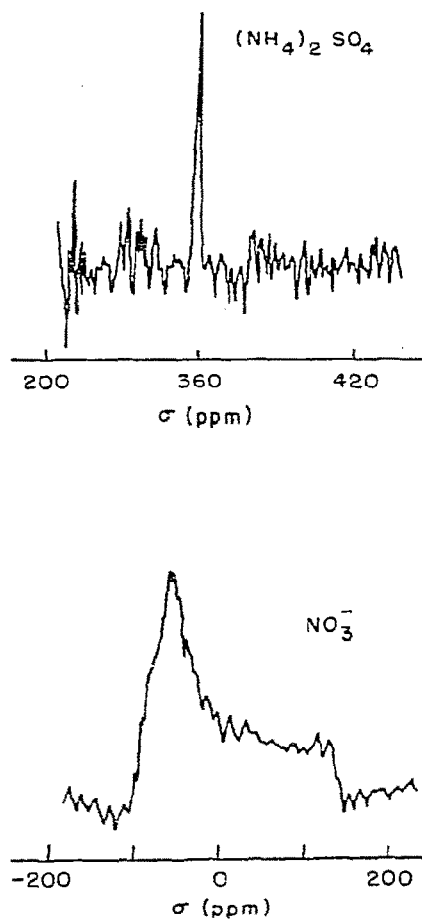


Fig. 1. Proton-enhanced nuclear induction spectra of ^{15}N obtained at room temperature, $H_0 = 22.8$ kG. (a) The result of a 10-min accumulation on natural abundance $(\text{NH}_4)_2\text{SO}_4$. (b) Chemical shielding anisotropy powder pattern of the nitrate ion in NH_4NO_3 . The spectrum was obtained from a 30% enriched sample; the single line due to NH_4^+ at 352 ppm is not shown. Principal elements of the chemical shift tensor, referenced to NO_3^- in $5\text{MnH}_4\text{NO}_3 - 2\text{MnHO}_3$ aqueous solution, are -83 , -57 and $+140$ ppm.

acids, and other substances of biological importance. A preliminary measurement of glycine shows, interestingly enough, that the ^{15}N shift has *no* detectable anisotropy, and that within our experimental resolution its shift is identical to that of NH_4^+ in $(\text{NH}_4)_2\text{SO}_4$ and NH_4NO_3 .

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