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Application of the Sideband Technique to Wide-Line NMR Spectra

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at 9196 A, a region of rapidly decreasing plate sensitivity. No anti-Stokes lines have been observed.

The addition of these alkali metal Raman lamps to those already available extends further the wide range of electrodeless annular Raman sources.

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Application of the Sideband Technique to Wide-Line NMR Spectra

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THE solution of the Bloch macroscopic equations of motion for a magnetic dipole subject to a sinusoidally modulated magnetic field[1–6] has been applied successfully in high-resolution NMR spectra, while in wide-line NMR, as well as in ESR, the derivative method[7] is still in use. The purpose of this note is, therefore, to point out the advantages of directly recording the absorption spectra and eliminating the broadening due to a finite modulation amplitude which arises, in the derivative method,[8] when the modulation frequency ω_M is set such that $\omega_M T_1$, $\omega_M T_2 \gg 1$. Under these conditions and for a slow passage the time dependent resonance signal is given by[1–6]

$$F(t)=\sum_{n,k=-\infty}^{+\infty}\varphi_n J_k(\beta)\,J_n(\beta)\,\exp i(n-k)\omega_M t, \qquad (1)$$

where

$$\varphi_n=\frac{[-\,|\,\gamma\,|\,H_1 M_0 T_2(1-iT_2\Delta_n w)]}{[1+T_2^2(\Delta_n w)^2+\gamma^2 T_1 T_2 J_n^2(\beta)H_1^2]},$$

J_n = Bessel functions of the first kind,

$$\Delta_n w=(|\,\gamma\,|\,H_0-w+n\omega_M),$$

$\beta=|\,\gamma\,|\,H_M/\omega_M$, and $F=v+iu$ in the notation of (1). φ_n is of the same form as the resonance signal in the static case, except for the saturation parameter which is now reduced by the factor $J_n^2(\beta)$ for the nth harmonic. This only affects the saturation experiments since ordinarily in order to avoid undesirable distortion effects, H_1 is set so small that $\gamma^2 H_1^2 T_1 T_2 \ll 1$.

In the lock-in detector,[9] $F(t)$ is mixed with a reference signal $S(t)=\cos(\omega_M t-\phi)$ in such a way that the integral over a cycle ($t=0$, $2\pi/\omega_M$) gives the dc output. This means that in Eq. (1) only the terms with $(n-k)=\pm 1$ will contribute to the dc signal which is a function of the reference phase angle ϕ and is given by

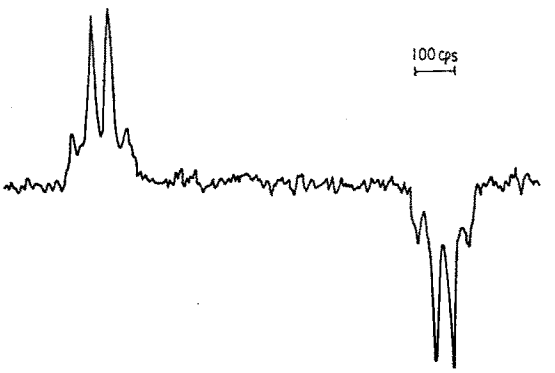

FIG. 1. Nitrogen NMR resonance (v_1 and v_{-1}) of liquid ammonia at $w=3.076$ Mc/sec, $\omega_M=392$ cps, and $\beta=1.24$.

$$F(\phi)=\oint F(t)\,S(t)\,dt$$

$$=\sum_{n=-\infty}^{+\infty}\varphi_n J_n(\beta)\left[\frac{2n}{\beta}J_n(\beta)e^{-i\phi}+2iJ_{n-1}(\beta)\sin\phi\right]. \qquad (2)$$

The real and imaginary components of φ_n, the absorption and dispersion modes, respectively, are isolated by setting $\phi=0$ or 90°:

$$F(0)=\sum_{n=-\infty}^{+\infty}a_n(\beta)\varphi_n, \qquad [a_n(\beta)=2n/\beta J_n^2(\beta)],$$

$$F(90°)=\sum_{n=\infty}^{+\infty}b_n(\beta)\varphi_n,$$

$$\{b_n(\beta)=2i[-n/\beta J_n^2(\beta)+J_n(\beta)\,J_{n-1}(\beta)]\}. \qquad (3)$$

The measurement of the NMR spectra with the natural line widths is carried out with $\gamma^2 H_1^2 T_1 T_2 \ll 1$. Therefore in this case the optimum conditions are obtained when $\phi=0$ with $|\,a_1\,|_{\max}=0.42$ for $\beta=1.5[J_1(\beta)/J_0(\beta)]=1.35$ and when $\phi=90$ with $|\,b_0\,|_{\max}=0.68$ for $\beta=[(\beta^2+\frac{1}{2})^{\frac{1}{2}}-\frac{1}{2}]J_0(\beta)/J_1(\beta)=1.08$. The value of β is determined directly from the spectra when the saturation parameter is negligible by comparing the amplitude of the different sidebands, $a_n(\beta)$ or $b_n(\beta)$.

The coupling constant for liquid ammonia was determined with a Varian wide-line NMR spectrometer operating at 3.076 Mc/sec in a field of 10^4 oe with $|\,\gamma\,|\,H_1 \ll \omega_M=392$ cps. The center band was set manually to zero amplitude by adjusting the reference phase, as shown in Fig. 1.

The value obtained for $|\,J_{\mathrm{NH}}\,|$, 40 ± 1 cps, is higher than the one reported by Ogg and Ray.[10] However, the preparation difficulties reported by the above authors were not encountered. The compressed ammonia from a cylinder tank was first dried with sodium metal and then distilled under vacuum to a sample tube which had been first aged in dilute HCl, passed through cleaning solution, then steamed and dried in the absence of dust.

Here, by phasing out the center band, very good resolution is obtained when the total width of the

spectrum is approximately one third of the modulation frequency. Since modulation frequencies of 100 kc/sec can easily be obtained, the absorption signal of lines which are several kc/sec should be measured by the sideband technique. This is a distinct advantage over the derivative method where the maximum voltage deflection is given by[7]

$$|\gamma H_M H_1 (d\Delta v/d\Delta w)|_{\max} = (3^{\frac{3}{2}}/8) M_0 |\gamma| H_1 T_2 (|\gamma| H_M T_2), \quad (4)$$

and where, in order to obtain a reliable measurement, the modulation amplitude must be set so that $|\gamma| H_M T_2 \ll 1$.

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Electron Spin Resonance Study of γ-Irradiated Single Crystals of *dl*-Isovaline*

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SINGLE crystals of *dl*-isovaline were initially exposed at room temperature to x-irradiation from a source operated at 40 kv and 4.5 ma for 24 hr. The radiation damage was examined at room temperature in a 3-cm electron spin resonance (ESR) spectrometer

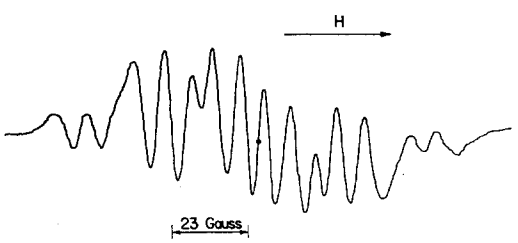
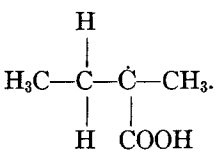


FIG. 1. The 3-cm ESR spectrum of γ-irradiated *dl*-isovaline observed at room temperature. The center of the spectrum, indicated by the dot, is located at $g=2.0043\pm0.0004$.

Only a weak ESR signal was observed. However, room temperature exposure of the crystal to $6.3\times10^6 r$ of γ-irradiation from a Co^{60} source resulted in an intense, stable ESR spectrum.

Although the crystal structure of *dl*-isovaline is unknown, its crystalline form is monoclinic. By taking ESR spectra at several orientations of the crystal in the magnetic field, it was determined that more than one radical site exists in the unit cell. Interpretation of the spectra indicates that irradiation results in the abstraction of the NH_2 group from the molecule, leaving the stable radical product



To test this interpretation single crystals of deuterated *dl*-isovaline were grown in a vacuum dessicator by five recrystallizations from heavy water. In this way deuterons were substituted for the protons of the amino group. ESR examination of the radiation damaged deuterated single crystal showed no difference, at any orientation, from the ESR spectrum observed in the undeuterated material. This result is therefore believed to confirm the interpretation of NH_2 abstraction produced by the radiation damage process.

The ESR spectrum observed at one orientation is shown in Fig. 1. The simplicity of this spectrum suggests that all radicals in the unit cell are magnetically equivalent at this particular orientation. Interpretations of ESR spectra at several orientations indicate isotropic hyperfine splittings of 65 ± 3 Mc resulting from each of the protons in the methyl group bonded to the carbon atom on which the unpaired electron is principally localized. Slightly anisotropic hyperfine interactions were associated with the methylene protons. The hyperfine interval for one of the methylene protons was observed to vary between 22 and 31 Mc, and that for the other proton, between 106 and 112 Mc. The contribution of the protons of the methyl group attached to the methylene carbon was negligible. These results are similar to those observed in the methyl radical,[1] urea,[2] and *dl*-aspartic acid.[3]

The different hyperfine splittings resulting from the two methylene protons indicate that these protons are chemically distinct, as observed in *dl*-aspartic acid.[3] The isotropic hyperfine interaction, b_N, of a π proton has been expressed as:[4]

$$b_N = \rho_N B \cos^2\theta, \quad (1)$$

where ρ_N is the spin density on the neighboring carbon atom on which the unpaired electron is principally localized, $B=112$ Mc (for $(CH_3)_2\dot{C}OH$), and θ is the angle between the π orbital and the projection of the π-proton C—H bond along the C—C bond onto the