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THE SIDEBAND TECHNIQUE IN A VARIABLE FREQUENCY NMR SPECTROMETER

J. V. Acrivos

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J. V. Acrivos

Lawrence Radiation Laboratory

University of California, Berkeley 4, California

The purpose of this Note is to point out the advantages of the sideband technique [1,2,3] over the derivative method [4] in wideline NMR spectroscopy. In the sideband technique the absorption spectrum is recorded directly and the modulation amplitude is no longer a determining factor in the resolution. Here, the resonance condition when the external magnetic field is sinusoidally modulated is satisfied for

$$w = |\gamma| H_O + n\omega_M, \qquad n = 0, \pm 1, \pm 2, \cdots \tag{1}$$

where ω_M is the modulation frequency.

The Block [5] macroscopic equations of motion for a sinusoidally modulated magnetic field are given by

$$\dot{F} + [i(|\gamma| H_z(t) - w) + 1/T_2]F + |\gamma| M_z H_1 = 0 \tag{2}$$

$$\dot{M}_z - |\gamma| H_1 v + \frac{M_z - M_O}{T_1} = 0$$

where

$$F = v + iu$$

$$H_z(t) = H_0 + H_M \cos \omega_M t$$

Under conditions of slow passage and,

$$\omega_M T_1, \omega_M T_2 >> 1 \tag{3}$$

the solution to equation 2 is [6,7,8]

$$F(t) = -\gamma H_1 M_z T_2 \sum_{n,\, k=-\infty}^{+\infty} \left[J_k(\beta) J_n(\beta) \; e^{i(n-k)\omega_M t} \right] \frac{(1 - iT_2 \Delta_n w)}{1 + T_2^2 \Delta_n^2 w}$$

$$M_z = M_0 \left[1 + \gamma^2 H_1^2 T_1 T_2 \sum_{n=-\infty}^{+\infty} \frac{J_n^2(\beta)}{1 + T_2^2 \Delta_n^2 w} \right] \tag{4}$$

where $J_n(\beta)$ are the Bessel functions of the first kind and,

$$\Delta_n w = [|\gamma| H_0 - (w - n\omega_M)]$$

$$\beta = \frac{|\gamma| H_M}{\omega_M}$$

The lock-in detector [9] responds only to the fundamental frequency ω_M which means that in equations 4 only the terms with $(n - k) = \pm 1$ will contribute to the signal. The dc output of the lock-in detector is therefore given by

$$F(\emptyset) = -|\gamma| H_1 M_0 T_2 \sum_{n=-\infty}^{+\infty} J_n(\beta) \left[\frac{2n}{\beta} J_n(\beta) e^{-i\emptyset} + 2iJ_{n-1}(\beta) \sin \emptyset \right]$$

$$\times \frac{[1 - iT_2 \Delta_n w]}{1 + T_2^2 \Delta_n^2 w + \gamma^2 T_1 T_2 J_n^2(\beta) H_1^2} \tag{5}$$

where $\emptyset$ is the reference phase in the lock-in detector. The best conditions are obtained when $\emptyset$ is set equal to zero, i.e.

$$F(0) = -|\gamma| H_1 M_0 T_2 \sum_{n=-\infty}^{\infty} a_n(\beta) \frac{[1 - iT_2 \Delta_n w]}{1 + T_2^2 \Delta_n^2 w + \gamma^2 T_1 T_2 J_n^2(\beta) H_1^2}$$

$$a_n(\beta) = \frac{2n}{\beta} J_n^2(\beta).$$

Under these conditions the center band has zero amplitude and for $\gamma H_1 \quad \omega_M$ the first sidebands appear separated by $2\omega_M$ as shown in Fig. 1 for the nitrogen resonance of liquid ammonia.

The real part of the absorption for the nth sideband from equation 6 is given by

$$v_n(0) = a_n(\beta) \frac{|\gamma| H_1 M_0 T_2}{1 + T_2^2 \Delta_n^2 w + \gamma^2 T_1 T_2 (J_n(\beta) H_1)^2} \tag{7}$$

Equation 7 is identical with the corresponding equation in the static magnetic field [5] except for the amplitude factor $a_n(\beta)$ and the reduction of the r-f field from H_1 to $J_n(\beta) H_1$.

The coupling constant for liquid ammonia (10) was determined with a Varian wideline NMR spectrometer operating at 3.076 Mc/s in a field of 10^4 oe. The center band was set manually to zero amplitude by adjusting the reference phase. The amplitude $a_1(\beta) = (2/\beta) J_1^2(\beta)$ was set to a maximum, i.e.

$$\begin{aligned} \beta = \beta_{max} &= 3/2(J_1/J_0) = 1.35 \\ |a_1|_{max} &= .421 \end{aligned} \tag{8}$$

Here β was determined accurately from Fig. 2 by measuring the ratio of the amplitudes of the first and second harmonics which is given by

$$\frac{a_1}{a_2} = \frac{1}{2} \frac{J_1^2(\beta)}{J_2^2(\beta)} = 3.7 \tag{9}$$

when $\beta = 1.35$.

The value obtained for J_{NH} is 40 $\pm$ 1 c/s which is in agreement with the value obtained for the same sample from the proton high resolution spectrum, 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.

The advantages of the sideband technique for studying the resonance absorption of nuclei where T_1, T_2 satisfy conditions (3) are noted by comparing to the derivative method where the maximum voltage deflection is given by [4]

$$(|\gamma| H_M H_1 \frac{d\Delta V}{d\Delta\omega}\Big|_{max} = \frac{3^{3/2}}{8} M_0 |\gamma| H_1 T_2 (|\gamma| H_M T_2) \qquad (10)$$

Here in order to obtain good resultion $|\gamma| H_M T_2 \leqq 0.1$ so that the improvement in signal to noise with the sideband technique is almost an order of magnitude.

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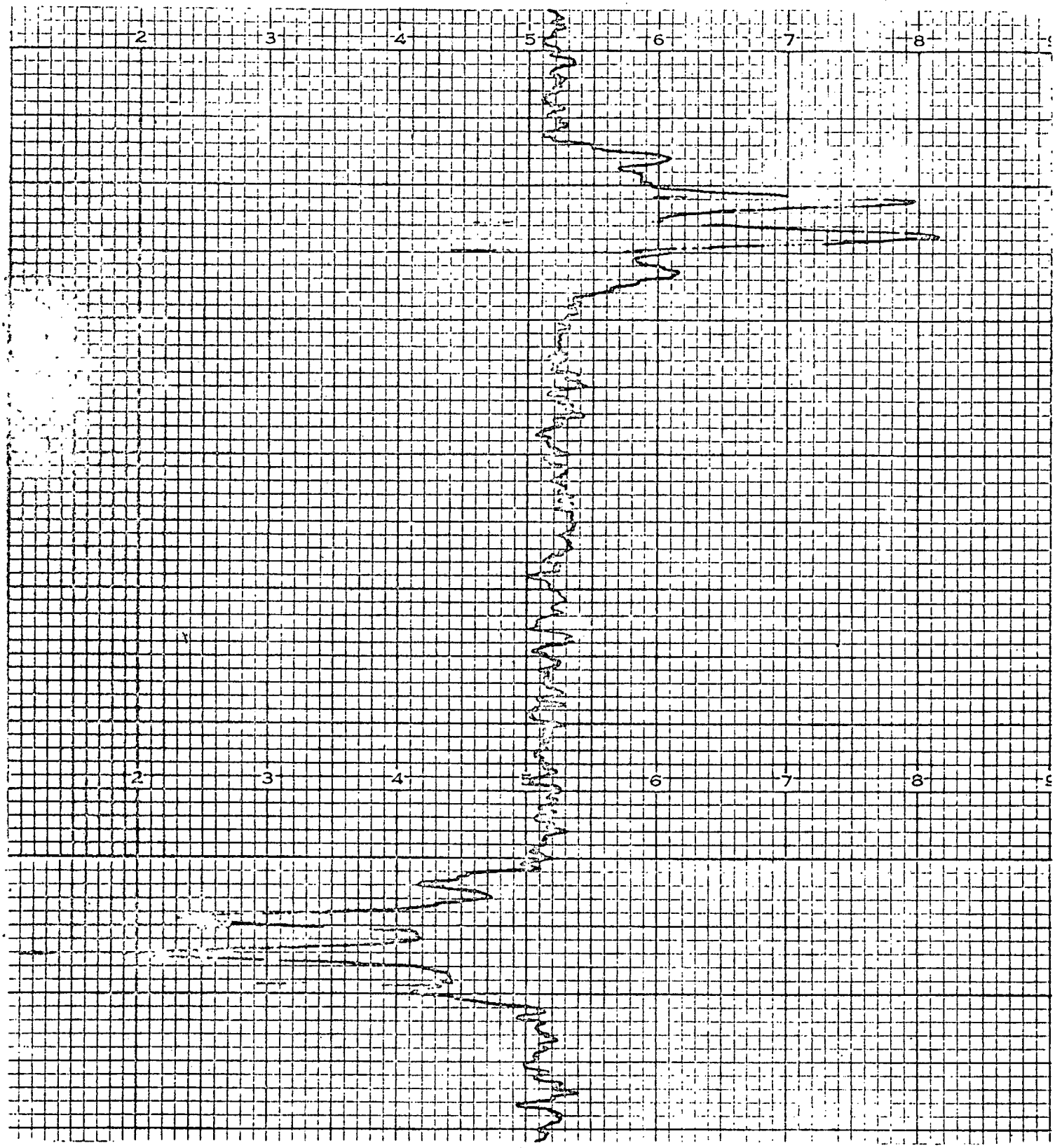

fig 1

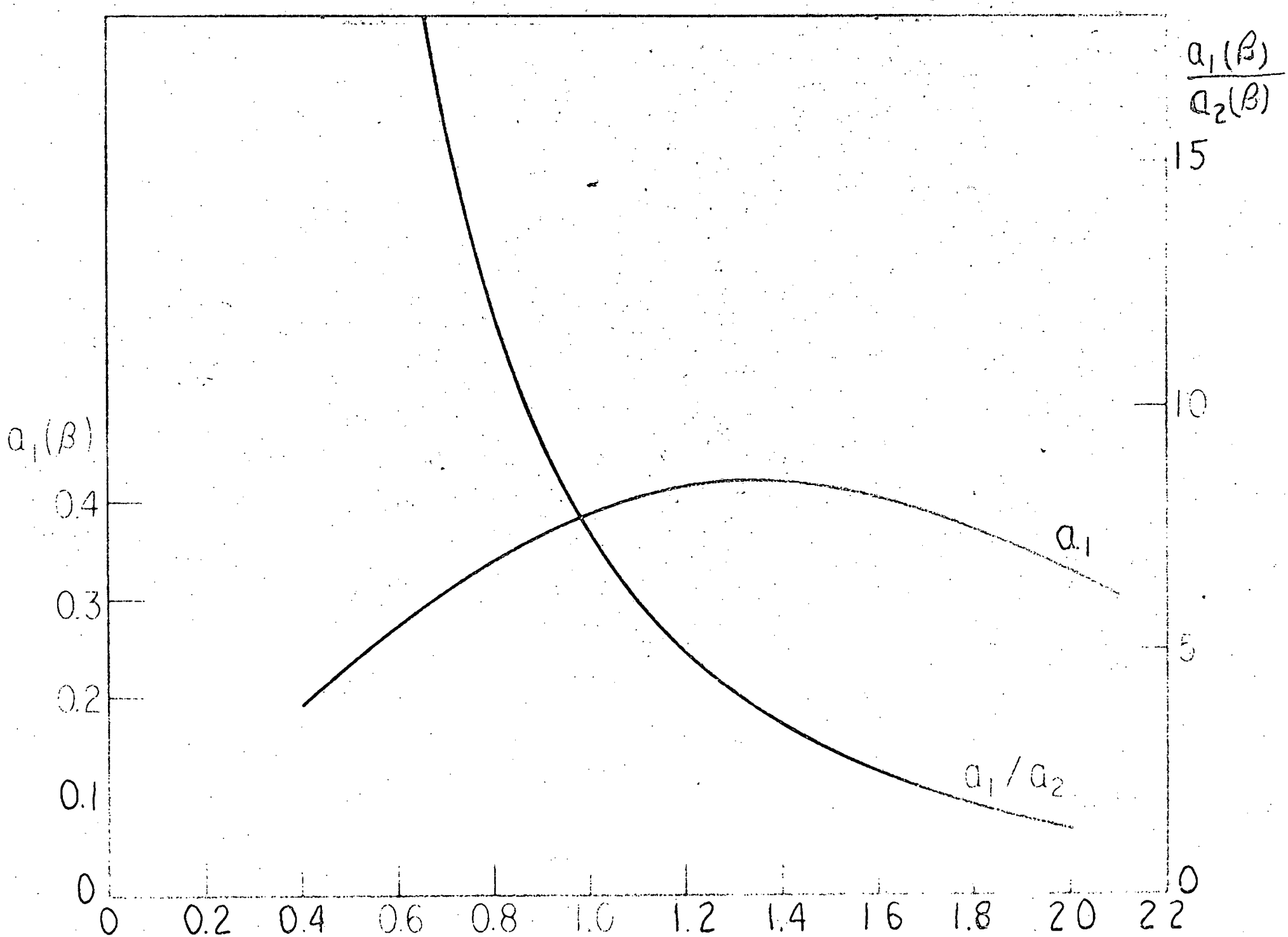
$a_1(\beta)$
$\frac{a_1(\beta)}{a_2(\beta)}$
0.4
0.3
0.2
0.1
0
15
10
5
0
a_1
a_1/a_2
0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1.8
2.0
2.2
$\beta = |\gamma| H_m / \omega_n$

fig 2

Captions for Figures

Fig. 1 Nitrogen NMR resonance (V_1 and V_{-1}) of liquid ammonia at $w = 3.076$ Mc/S, $\omega_M = 392$ c/s, and $\beta = 1.24$.

Fig. 2 Amplitude of the first sideband a_1 and ratio of the amplitudes of the first and second sidebands vs. β.