INCOMMENSURATE SPINNING SIDEBANDS FROM ROTATIONAL FLOW

Marisol Vera and John B. Grutzner*

Department of Chemistry
Purdue University
W. Lafayette, IN 47907 USA

Spinning sidebands are ubiquitous in high resolution nmr. In this paper, incommensurate sidebands arising from coherent but non-uniform rotational flow across a linear field gradient are presented. The experimental spectra can be simulated with the Williams-Gutowsky theory of spinning sidebands (1).

Couette flow(2) is a fluid dynamics paradigm as the flow pattern is described by an analytical solution of the Navier-Stokes equations(3). Physically, this flow occurs when the fluid in the annulus between concentric cylinders is sheared by rotation of the outer cylinder while the inner cylinder is held fixed. Couette flow is also possible when the inner cylinder is rotated and the outer cylinder is fixed, provided the rotation frequency is below the critical Taylor frequency(4). This geometry was chosen for experimental convenience in this work(4,5). The velocity, V(r), across the liquid as a function of radius r is given by(3,6).

$$V(r) = Ar + \frac{B}{r} \qquad (1)$$

where $A = -\omega_i \frac{q^2-u}{1-q^2}$; $u = \frac{\omega_o}{\omega_i}$

$B = \omega_i \, a^2 \frac{1-u}{1-q^2}$; $q = \frac{a}{b}$

and ω_o and ω_i (s^{-1}) are the outer and inner tube rotation frequencies, with radii b and a (cm) respectively. For our experimental configuration of a 5mm tube spinning at F Hz inside a 10mm tube, equation 1 becomes

$$F(r) = -0.4320\ F + 0.08783\ F/r^2 \qquad (2)$$

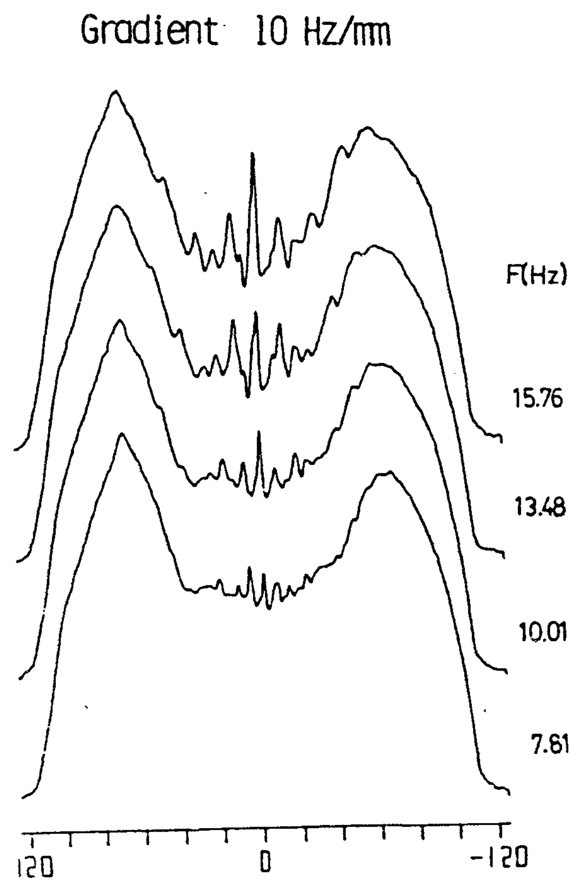

Figure 1. 50 MHz proton decoupled ^{13}C spectrum of ethylene glycol under Couette flow conditions. The glycol was contained in the annulus between a stationary 10mm o.d. tube and a 5mm o.d. tube spinning at the frequencies shown. A linear field gradient of 10 Hz/mm was applied transversely (X shim control).

When a linear transverse field gradient is applied across the sample, Couette flow generated the spinning sideband patterns of Figure 1.

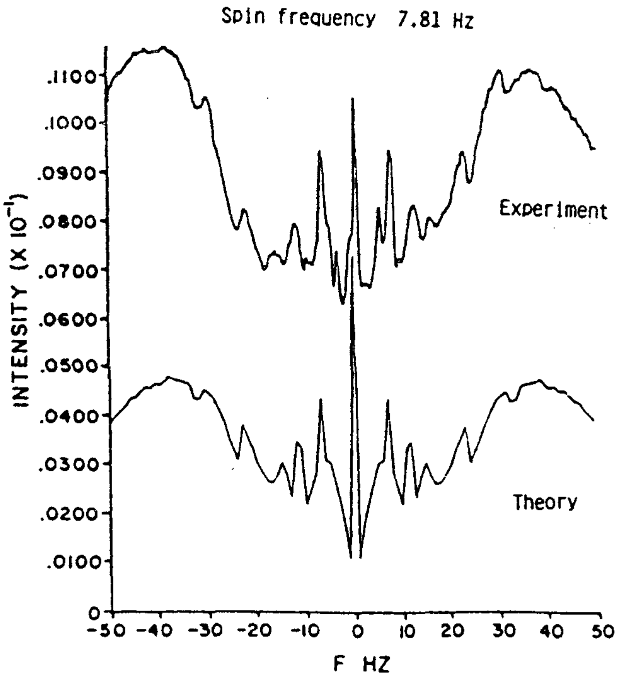

Figure 2. Experimental (Figure 1 for details) and calculated (see text) spectra under Couette flow conditions. Field gradient 5 Hz/mm. Inner tube spinning frequency 7.8 Hz. The calculated spectrum is the sum of components shown in Figure 4.

The observed pattern was dependent on the field gradient strength (compare Fig. 1 and 2 for example). The peak positions were incommensurate with the spinning frequency. No simple relationship could be found relating peak position with either spinning frequency or field gradient. The observed pattern could be simulated convincingly assuming laminar flow and the classical spinning sideband theory of Williams and Gutowsky (1).

A homogeneous sample spinning uniformly with frequency F Hz in a field gradient of G_x Hz/cm produces a centerband and a series of modulation sidebands at integer multiples of F. The intensities of the sidebands are given by the Gutowsky Williams expression(1)

$$I_n = k \int_0^b J_n^2\,(G_x r/F) 2\pi r dr \qquad (3)$$

where $J_n(y)$ is the Bessel function of the first kind of order n; $\pm$ n is the integer sideband number, b is the outer tube radius; k is the instrumental response factor. The sideband pattern is simulated by calculating the spinning sideband pattern for a series annular slices of width Δ (Figure 3) undergoing uniform laminar flow at frequency F(r) and summing over the sample (7). Examples of the sideband components calculated close to the inner wall, at the center of the annulus, and close to the outer wall are shown in Figure 4. The sum over the whole sample is compared with experiment in Figure 2.

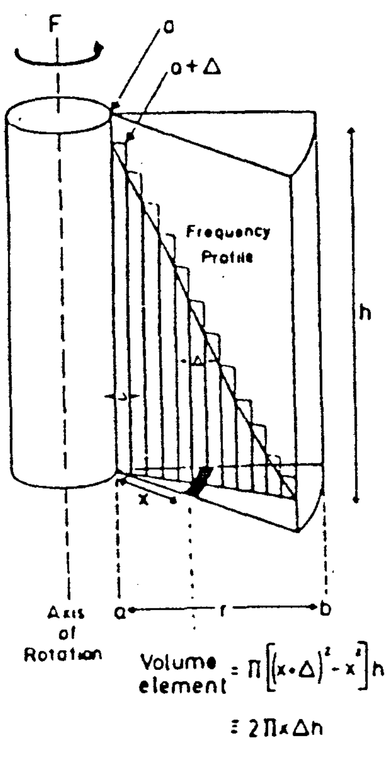

Figure 3. Model for nmr simulation of Couette flow. Inner tube radius a, outer tube b, cylindrical cross-section width Δ = (b−a)/500, spinning frequency F.

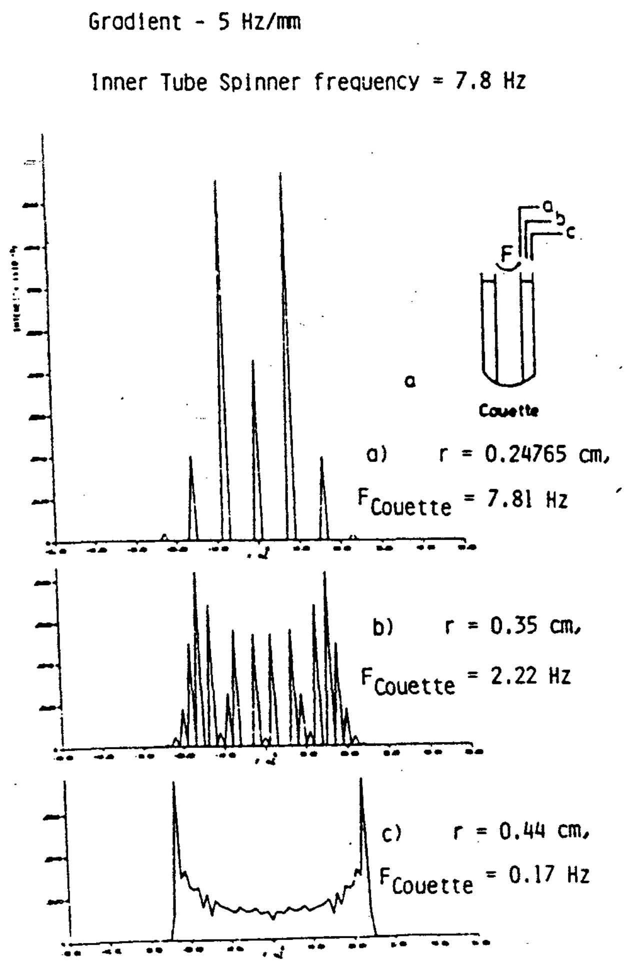

Figure 4. Calculated components of nmr simulated Couette flow shown in Figure 2. (a) top. At inner wall with r=a=0.248 cm, F(r) = 7.81 Hz. (b) At midpoint of annular gap r = (b+a)/2 = 0.35cm, F(r) = 2.22 Hz. (c) close to outer wall with r = (b − Δ) = 0.44 cm, F(r) = 0.17Hz.

Comparison of experimental and calculated spectra at different field gradient strengths and different frequencies (not shown) exhibit comparable agreement. Thus the incommensurate sideband pattern observed experimentally is a consequence of the modulated cross correlation between a linear gradient and monotonically decaying Couette flow across the gradient.

There are a number of implications of these observations.

1. A simple experimental set-up allows nmr studies of molecules in flowing liquids.
2. Coherent (non-uniform) flow across a gradient produces a sideband image. Conversely the nmr image of rotational flow can, in principle, be deconvoluted to give the velocity profile of the flow (8,9).
3. The agreement between simulation and experiment demonstrates that molecules in sheared laminar flow follow streamlines on the nmr time-scale.
4. It should be possible to generate and deconvolute an nmr image arising from laminar pipe flow (8) in a rotating magnetic field gradient (10).
5. It should be possible to extract individual sideband patterns (cf. Figure 4) from the total pattern using a spin-echo pulse sequence and 2D analysis procedures (7,11). Thus nmr parameters for molecules undergoing differential shear flow are measurable.

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(5) The experimental setup is the same as that used for our Taylor vortex-viscosity study. (6) Varian XL-200

spectrometer operating at 50MHz; 5mm o.d. tube rotating inside 10mm o.d. tube; horizontal gradient generated by standard X-gradient shim coils; ethylene glycol sample. The outer spinning tube configuration will be simpler to implement in general.

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