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Toroid Cavities as NMR Detectors in High Pressure Probes

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Abstract

A cylindrical toroid cavity has been developed for application as an NMR detector for high sensitivity and high resolution spectroscopy in metal vessel probes. Those probes are used for *in situ* investigations at high temperature and pressure. Since the transmitted r.f. field is completely confined within the torus, the cavity can be placed inside the pressurized system without magnetic coupling to the metal vessel. Resonance frequencies up to 400 MHz make the toroid cavity detector especially suited for use in ^1H and ^{19}F spectroscopy. Typically achieved static ^1H linewidths, measured on CHCl_3 using cavities in Be-Cu pressure vessels, are 2.0 Hz. On the basis of theoretical considerations that include the radial dependence of the r.f. field within cylindrical or circular toroid detectors, equations were evolved to predict the signal intensity as a function of the pulse width. The equations precisely describe the deviations from the sinusoidal approximation, which is generally used for signal intensities derived from Helmholtz or solenoid coils.

1. Introduction

Nuclear magnetic resonance is known to be a powerful tool for *in situ* investigations of chemical reactions and dynamic processes. The elucidation of mechanisms and kinetics of homogeneously catalyzed reactions is especially important since they often are employed in large scale industrial processes to produce products such as aldehydes and alcohols. However, many catalytic reactions require high temperature and pressure conditions that are unsuitable for standard NMR equipment. Therefore, several methods have been developed to conduct chemical reactions within the spectrometer's magnetic field under elevated pressure over different temperature ranges.^{1,2}

Two basic approaches are pursued for this purpose, where the first takes advantage of the low magnetic permeability and insignificant electric conductivity of glass, quartz, sapphire, or ceramic. Sample containers consisting of these materials show slight interactions with the constant and alternating magnetic fields of the spectrometer, and the NMR detector coil may be placed outside the pressurized system. Using appropriate dimensions, pressures up to 80 bar at temperatures up to 150°C can be applied.³

Higher pressure and temperature limits can only be achieved by using metal pressure vessels or autoclaves (second approach). Because of notable conductivities and permeabilities of metal alloys, significant interactions can occur with both the main magnetic field (B_0) of the spectrometer and the r.f. field (B_1) of the transmitter and detector system.

To minimize interferences with the B_0 field, but also to withstand the elevated pressures, the metal vessel has to be fabricated from a low permeability alloy with a high tensile strength, e.g., titanium or beryllium-copper alloy. To fit inside a probe of a superconducting magnet, the vessel is usually formed as a cylinder. Adequate field corrections and homogeneity adjustments can be accomplished, since standard shim coils have been optimized for cylindrically shaped sample tubes. For the detection of sufficiently sensitive NMR signals, however, any magnetic coupling of the detector's r.f. field (B_1) with the metal vessel must be thoroughly avoided. Therefore, the coil has to be placed inside the pressure vessel, sufficiently remote from the walls of the surrounding vessel.

A special pressure probe has been introduced recently, where a self-supporting toroid coil is affixed inside a cylindrical pressure vessel.⁴ Since the B_1 field is virtually confined inside the torus, interactions with the pressure vessel are substantially reduced, even if the coil is positioned close to the surrounding metal. Furthermore, higher sensitivities and signal-to-noise ratios are achieved when using toroid coils compared with Helmholtz or solenoid coils.⁵

Since, in our experience, a toroid coil requires at least four turns to form a reasonable torus, its inductance is usually too high to be tuned to resonance frequencies much above 100 MHz by standard oscillating circuits. A $\lambda/4$ - or $3\lambda/4$ -transmission line may be used to tune the coil,⁶ although this generally causes a loss of both the transmitted r.f. power and the received signal intensity.

In this study, we report that the inductance is lowered, in analogy to parallel-wired coils,⁷ by replacing the toroid coil with a specially designed toroid cavity. The cavity is readily incorporated into a high pressure NMR probe (Fig. 1) and can easily be tuned to resonance frequencies up to 400 MHz using tapped-parallel-tuned circuits.⁸

Another toroid cavity NMR technique, using a gap reentrant cavity resonator, was suggested earlier by Alderman and Grant.⁹ However, they never published further results.

2. Cylindrical Toroid Cavity

The toroid cavity resonators (Fig. 2) introduced here are made of copper. They consist of an inner, Teflon-coated wire (diameter of 1.4 mm) and a cylindrically shaped, hollow body with an inner diameter of either 9.6 mm or 12.8 mm. The bodies are mounted on mated footings, which include the feedthrough for the inner wire. Four slots in both the body and the footing of the cavity provide homogeneous filling when the vessel is charged with gases, solutions, or supercritical fluids.

A major characteristic of toroid coils or cavities in NMR investigations is their radially dependent B_1 field,¹⁰ which theoretically obeys the equation

$$B_{\text{torus}} = \mu_0 \frac{n I}{2 \pi r} \quad , \quad (1)$$

where μ_0 is the permeability of free space, n the number of turns of the coil, I the current, and r the distance from the center axis of the torus, i.e., the radius.^{11,12} Because of this B_1 -field dependence, no common flip-angle, e.g., a 90° pulse, can be determined therein, and previously reported 90° pulses^{4,5,10} are more accurately defined as pulses that provide the maximum signal intensity. These particular pulses arise from a complex, radially dependent flip-angle distribution and in this article will be termed *maximum intensity pulses*.

Nevertheless, to compare sensitivities and resolutions, we recorded 300 MHz ^1H -NMR spectra of a solution of 1% CHCl_3 in CDCl_3 using toroid cavities in a Beryllco alloy 25 pressure vessel. Typically obtained linewidths are around 2 Hz. However, a linewidth of 1.2 Hz was achieved after we extended shimming over 24 hours using the shim program provided with the spectrometer. At the maximum intensity pulse, signal-to-noise ratios around $S/N = 3350$ of the ^1H -NMR signal of chloroform (1% CHCl_3 in CDCl_3 , linewidth of 1.5 Hz, exponential line broadening of 1.0 Hz) were obtained. A similar spectrum was derived from the same solution in a non-spinning 5-mm sample tube, using the 90° pulse in the standard 5-mm probe of the spectrometer (General Electric GN 300/89). This spectrum indicated a signal-to-noise ratio around $S/N = 4150$ (linewidth of 1.5 Hz, exponential line broadening of 1.0 Hz). Since both probes contained about the same sensitive volume, the circuit using Helmholtz saddle coils in the standard NMR probe is about 1.24 times as sensitive as our home-built toroid circuit. In this

comparison, the higher sensitivity expected on the basis of earlier reports⁵ did not occur owing to losses of inductance in the comparatively long electrical connection of the cavity through the pressure vessel. A quality factor of $Q = 95$ was measured for the entire resonance circuit that includes the toroid cavity.

3. Pulse-Width-Dependent Signal Intensity

a) Theoretical Considerations

Using a sufficiently strong r.f. field B_1 (ideal pulse experiment), a pulse of duration t rotates the equilibrium magnetization about the x-axis of the rotating frame with a pulse rotation angle (flip-angle) $\Theta = -\gamma \cdot B_1 \cdot t$, where γ is the gyromagnetic ratio of the observed nucleus. The NMR signal intensity, I , obtained in both a homogeneous B_0 and a homogeneous B_1 field is given by

$$I = I_0 \sin \Theta . \quad (2)$$

Using solenoid or Helmholtz coils, at which the B_1 field is sufficiently homogeneous throughout the excited sample volume, a 90° pulse and I_0 can easily be determined by a measurement of the intensity I versus the pulse width t . However, since the r.f. field inside a toroid coil or

cavity is inversely proportional to the radius (Eq. 1) and may be written as $B_1 = A/r$, where A is the proportionality constant. Therefore, the flip-angle of the macroscopic magnetization depends upon the radius; $\Theta(r) = -\gamma A t/r$.

Additionally, the induced electromotive forces (e.m.f.) of the rotating spins, which cause the r.f. receiver current in the detector coil, are linearly proportional to the B_1 -field strength of the coil, when it is used as a transmitter. This fact is known as the *principle of reciprocity*.¹³ Accordingly, the maximum intensity of an elementary sample volume inside the torus, e.g., obtained by a local 90° pulse, also depends upon the radius ($= I_0/r$). Transforming Eq. 2 into a function of the radius leads to

$$I_r(r) = \frac{I_0}{r} \sin \left(-\frac{\gamma A t}{r} \right) \quad . \quad (3)$$

Figure 3 (a) shows a plot of Eq. 3, i.e., the intensity $I_r(r)$ that is obtained from elementary sample volumes in a toroid cavity, at two different pulse widths, t_1 and t_2 (solid line and dashed line, respectively), versus the radius r . The left and right margins of the plot represent the inner and outer radius ($r_1 = 0.7$ mm, $r_2 = 6.4$ mm) of one of our toroid cavities, respectively. The solid line illustrates the signal intensity distribution in this cavity at the maximum intensity pulse, the dashed line reflects the distribution at the pulse width that leads to the maximum negative signal intensity. Both were calculated from Eq. 3 for a cavity that is homogeneously filled with a fluid.

The radius r is constant within a cylindrical volume element inside the cavity, and accordingly, the flip-angle is uniform therein. To derive the radially dependent signal intensity $I_v(r)$ of such a cylindrical volume element, $I_r(r)$ has to be multiplied by the surface s of a cylinder; $s = 2\pi rh$, where h is the height of the cylinder. This leads to

$$I_v(r) = 2\pi rh \cdot I_r(r) = 2\pi h I_0 \sin\left(-\frac{\gamma A t}{r}\right) . \quad (4)$$

Figure 3 (b) displays the intensity $I_v(r)$ of a cylindrical volume element as a function of the radius r according to Eq. 4. To compare Fig. 3 (a) and (b), r_1 and r_2 , as well as t_1 and t_2 , used for the calculation of the solid and dashed line, are kept the same in both plots. Since the volume increases with r , the signal intensity, which is contributed from volume elements nearer the outer radius, r_2 , becomes more important in Fig. 3 (b). Nevertheless, the increasing volume is compensated by the weaker B_1 -field, which causes less e.m.f. in the detector coil or cavity.

The total signal intensity I , which is obtained from a homogeneously filled, cylindrical toroid detector by a single-pulse experiment, is determined by the sum of all I_v of the torus, i.e., the integral over I_v from the inner radius r_1 to the outer radius r_2 :

$$I = \int_{r_1}^{r_2} I_v dr = 2\pi h I_0 \cdot \int_{r_1}^{r_2} \sin\left(-\frac{\gamma A t}{r}\right) dr \quad . \quad (5)$$

b) Experimental Confirmation

Several toroid cavities were used to test Eq. 5 in predicting pulse width dependence. Figure 4 shows ¹H-NMR signal intensities (filled circles), that were obtained from two different, homogeneously filled cavity detectors at variable pulse widths in a single-pulse experiment. The cavities had been filled with a solution of 1% CHCl₃ in CDCl₃, and the signals were observed on-resonance. The solid lines in Fig. 4 are theoretical curves calculated from Eq. 5 and computer fitted to the experimental data by refining the parameters I_0 and A . Note that the curves are not simply damped sine waves but show irregularities that depend on the integration boundaries used in the calculation of Eq. 5. However, the agreement of the experimentally derived data with the theory is excellent and confirms that toroid cavity resonators exhibit a mathematically definable r.f. gradient that can be predicted with a high precision. The deviation of the experiment to the theory is less than 2% in the lower plot of Fig. 4, where a *closed* toroid cavity was used, i.e., a cavity with holes in the footing and the top for homogeneous filling but without slots in the cylindrical body.

The 100% marks of the y-axes (intensity axes) in Fig. 4 were calculated to be the hypothetical intensity values that would occur if every elementary sample volume within the torus experienced a 90° pulse, i.e., all spins flipped phase-correlated into the x-y plane of the rotating frame before the acquisition of the free induction decay (FID). Evidently, however, the discussion above shows that achieving 100% intensity is impossible in a single-pulse experiment. The strongest intensity, obtained at the maximum intensity pulse, was 65-72% of the theoretical maximum, depending on the respective toroid detector. Considering that only this amount of the theoretical maximum signal intensity can be achieved in the gradient B_1 field, a toroid detector has to be at least 1.4-1.5 times as sensitive as a conventional Helmholtz or solenoid coil to obtain the same signal-to-noise ratio.

Similar to earlier observations on toroid detectors,⁴ the pulse widths of the first zero intercepts of the signal intensities in Fig. 4 are significantly longer than twice the maximum intensity pulse width. They occur in the present experiments, depending on r_1 and r_2 of the cavity, at values approximately 3.5-4.5 times the maximum intensity pulse width. The agreement of the experiment with the theory (Fig. 4) illustrates this to be a consequence of the complex flip-angle distribution within a toroid detector, represented by Eq. 5.

4. Circular Toroid Detectors

Previous contributions regarding toroid detectors in NMR investigations describe *circular* toroid coils^{5,7,10} that differ from the *cylindrical* geometry documented here. Those coils have been wound on annular ring sample containers having circular rotation symmetry. Since Eq. 5 was developed especially for cylindrical toroid detectors, it has to be modified to predict the signal intensity for a circular torus.

In analogy to a cylindrical torus, the B_1 field inside a circular toroid coil is radially dependent ($B_1 = A/r$); thus Eq. 3 still holds. As pointed out earlier, the radius r , i.e., the distance from the center axis of the torus, is constant within a cylindrical volume element inside the torus, and therefore, the flip-angle is constant therein. However, in contrast with the cylindrical geometry, the height h of such a cylindrical volume element in a circular torus depends upon the radius r . This dependence can be obtained from Fig. 5, which represents a cut through a circular torus:

$$h = 2 \sqrt{R_1^2 - d^2} \quad , \quad (6)$$

where R_1 is the radius of the circle that forms the torus by a rotation with radius R_2 around the center axis, and d is the displacement from the center of this circle. Equation 5 then becomes

$$I_v(r) = 4\pi \sqrt{R_1^2 - d^2} \cdot I_0 \sin\left(-\frac{\gamma A t}{r}\right) . \quad (7)$$

Also obtained from Fig. 5, the radius r obeys $r = R_2 + d$, and

$$R_1 = \left(\frac{r_2 - r_1}{2}\right) , \quad R_2 = \left(\frac{r_2 + r_1}{2}\right) . \quad (8)$$

Therefore, Eq. 7 converts into

$$I_v(r) = 4\pi \sqrt{\left(\frac{r_2 - r_1}{2}\right)^2 - \left(r - \frac{r_2 + r_1}{2}\right)^2} \cdot I_0 \sin\left(-\frac{\gamma A t}{r}\right) , \quad (9)$$

and simplifying yields

$$I_v(r) = 4\pi \sqrt{r(r_2 + r_1) - r_2 r_1 - r^2} \cdot I_0 \sin\left(-\frac{\gamma A t}{r}\right) . \quad (10)$$

Equation 10 describes the intensity $I_v(r)$ that is derived from a cylindrical sample volume inside a circular torus at a certain pulse width t .

The total signal intensity I , which is obtained from a homogeneously filled, circular sample container surrounded by a toroid coil, is calculated according to Eq. 5 by the sum of all I_r inside the torus, i.e., the integral over all I_r from r_1 to r_2 :

$$I = 4\pi I_0 \cdot \int_{r_1}^{r_2} \sqrt{r(r_2 + r_1) - r_2 r_1 - r^2} \cdot \sin\left(-\frac{\gamma A t}{r}\right) dr \quad . \quad (11)$$

Figure 6 shows the predicted signal intensity, derived from a circular toroid detector as a function of the pulse width, according to Eq. 11. The chosen margins $r_1 = 3.5$ mm and $r_2 = 12.0$ mm correspond to a toroid coil (Torus 3) used in investigations described by Glass and Dorn.⁵ Comparison of Fig. 4 and Fig. 6 illustrates that a single-pulse experiment is more efficient when using such a circular detector than one of our cylindrical detectors, since the maximum intensity pulse delivers about 90% of the theoretically possible signal intensity. This observation is also valid if a calculation of a circular torus with the same r_1 and r_2 as used for our cylindrical cavity is performed and compared. Nevertheless, a cylindrical toroid detector uses more of the sample volume inside a cylindrically shaped pressure vessel and, therefore, should be preferred in high pressure investigations. Since in contrast to the cylindrical geometry the volume of a circular torus decreases continuously to zero toward the integration boundaries r_1 to r_2 , the plot in Fig. 6 appears smoother and more similar to a damped sine wave than those in Fig. 4 representing cylindrical toroid detectors.

The first "null" (first zero intercept of the function) in Fig. 6 appears at a pulse width that is slightly longer than twice the maximum intensity pulse width. This also differs from the results of the cylindrical torus geometry but agrees with the experiments of Glass and Dorn,⁵ who reported a residual (in the x-y plane) of about 5% of the equilibrium magnetization after a 180° pulse, i.e., twice the maximum intensity pulse width. A calculation from Eq. 11 gives a residual magnetization of 8% compared to about 50% calculated from Eq. 5 for a cylindrical torus (see Fig. 4).

6. Conclusion

Toroid cavities reveal an appropriate continuation of toroid coils, their advantages^{4,5,10,14} and applications¹⁵ as NMR detectors in high pressure probes for *in situ* investigations. The confidence of machinability and, therefore, reproducibility, combined with the possibility to tune the cavities up to 400 MHz, render them especially attractive for high resolution NMR spectroscopy using nuclei like ¹H or ¹⁹F.

Since a toroid detector confines the B_1 field completely inside the torus, it can be placed inside and close to the walls of a metal pressure vessel without a significant loss of the inductance. As a consequence thereof, a maximum filling factor is accomplished.

The B_1 field of toroid detectors is radially dependent, which is quite a disadvantage for a sensitive signal detection. Only 65-72% of the theoretical signal intensity maximum is achievable using a single-pulse experiment. However, the B_1 field is not merely inhomogeneous but exhibits a very accurate and well-defined gradient, which has now been established by excellent agreement of theoretical considerations with experiment. The high precision to which the gradient can be predicted significantly improves the utility of toroid detector systems. Since the new equations quantify the only known irregularity and, therefore, disadvantage of these detectors, they are also useful for predicting the results of experiments that are more complex than a single-pulse excitation. Standard examples of complex experiments are T_1 relaxation time measurements using the inversion recovery method, or composite pulse sequences to compensate for the strong B_1 gradient.

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Figure Captions

FIG. 1. Schematic diagram of the pressure vessel with a toroid cavity detector.

FIG. 2 Detailed diagram of the toroid cavity detector.

FIG. 3. Radially dependent signal intensity derived from a toroid detector.

The solid lines show the distribution at the maximum intensity pulse, the dashed lines at the most negative signal intensity pulse. Calculations are made for a cylindrical toroid cavity with an inner radius $r_1 = 0.7$ mm and an outer radius $r_2 = 6.4$ mm.

FIG. 4. Signal intensity as a function of pulse width derived from different toroid cavities.

FIG. 5. Diagram of a cut through a circular torus.

FIG. 6. Signal intensity as a function of pulse width derived from a circular toroid detector.

Figure 1

Figure 2

Figure 3

(a) Signal intensity derived from a single volume element

(b) Signal intensity derived from a cylindrical volume element

Figure 4

Figure 5

Figure 6

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