High-Resolution NMR Spectroscopy with a Portable Single-Sided Sensor

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Unlike absorption and fluorescence spectrometers, nuclear magnetic resonance (NMR) instruments are not easily miniaturized for field use. Portable NMR systems have been built, with open single-sided probes for arbitrarily sized samples (1). However, the unavoidable spatial inhomogeneity of the static magnetic field has precluded the use of these devices for high-resolution spectroscopy. These field variations are usually orders of magnitude larger than those created by the microscopic structure of the molecules to be detected, so no chemical shift information can be extracted from the spectra. Thus far, the systems have mainly yielded relaxation times as a crude estimate of material composition, but more detailed information would benefit a broad range of fields, from medical diagnosis to archaeological analysis.

Recently, a solution to this ex situ challenge has been proposed (2). The strategy compensates for the main field inhomogeneity by using parallel variations in the applied radio frequency (rf) field. For spins with the same chemical shift, different Larmor frequencies throughout the sample give rise to progressive dephasing during a free evolution period. At any stage, this loss of coherence can be reversed if a proper position-dependent phase correction is applied. However, when this is done, phase differences accumulated during the evolution and arising from the chemical shift differences must be maintained. Such a position-dependent phase correction can be accomplished by the use of z-rotation pulses (3). In the presence of matched rf and static field profiles, these pulses induce echoes with a phase sensitive only to chemical shift differences. Sampling of the echo maxima occurring after incremental periods of free evolution leads to high-resolution NMR spectra (4). (Discussion of the underlying theory is available as supporting online material.) Unlike other approaches (5–8), this method can be used at low magnetic field strengths and does not rely on any special properties of a given substrate, such as intramolecular interactions.

Here we describe a portable single-sided sensor that functions on the above principle. Two concentric, U-shaped NdFeB magnets inducing opposing magnetic fields were arranged to create a sweet spot 7 mm above the magnet (Fig. 1A). In this region, the magnetic field was parallel to the magnet surface and reached 0.2 T. The dimensions of a rectangular surface
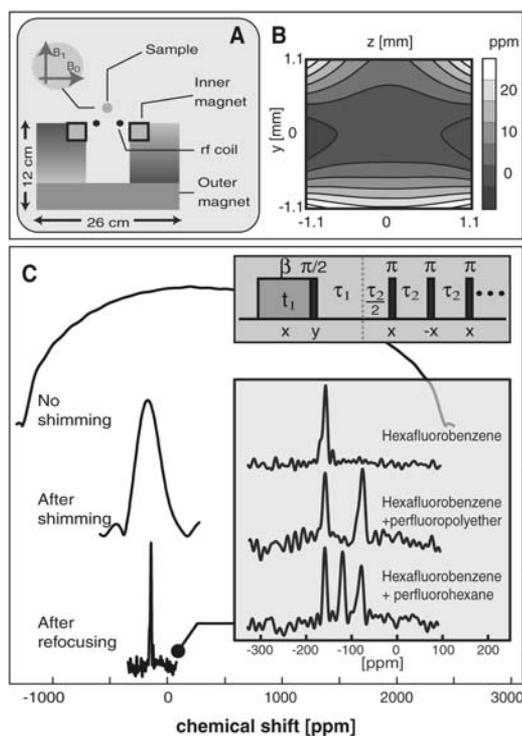

Fig. 1. (A) Schematic. The inner shimming magnet opposes the field of the outer magnet to give a sweet spot 7 mm above the magnet surface. A 3-mm^3 sample tube (inner diameter = 1 mm) placed at this site was oriented parallel to the magnet gap (the x axis). B_0, static magnetic field; B_1, rf field. (B) Field map of the difference (as a fraction of B_0) between the magnitudes of the static and normalized rf fields in the region of the sweet spot, which sets the attainable resolution. The reference frame has the z axis parallel to B_0 and the y axis parallel to B_1. (C) (Upper inset) A spatially inhomogeneous rf z rotation induces an echo after a period of free evolution τ_1. The echo position is incremented by varying the duration t_1 of the pulse β. A train of π pulses with separation τ_2 = 1.5 ms improves the signal to noise ratio. Rf phases are labeled. (Main) Spectra of C_6F_6 before and after we optimized the position of the inner magnet and after we used the refocusing sequence. (Lower inset) Chemical shift–resolved spectra for different samples.

rf coil and the position of the inner magnet were finely adjusted to optimize the correspondence between the static and rf magnetic fields (Fig. 1B). The final configuration did not minimize the static field variations. Rather, a remnant static gradient perpendicular to the magnet surface was retained to better reproduce the natural field inhomogeneity of the rf coil.

We reconstructed a well-resolved spectrum by sequentially incrementing the length of the initial (spatially dependent) pulse β (Fig. 1C). The pulse train after the first echo was used simply to increase detection sensitivity (4). As a proof of principle, we acquired ^{19}F spectra of several fluorinated hydrocarbons. Optimization of the coil and magnet geometry provided a preliminary linewidth of 2500 Hz, which further narrowed to 65 Hz when the pulse sequence was applied (Fig. 1C). This resolution, corresponding to a chemical shift of 8 parts per million (ppm), required only 3 min of acquisition time. These results suggest that proton chemical shift resolution could be achieved in the near future (the ^1H chemical shift range is 12 ppm).

References and Notes

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