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Ramped-Speed Cross Polarization MAS NMR

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The inverse cubic dependency of the acceleration of a rotor on its diameter allows for mechanical dynamics comparable to spin dynamics in coupled spin systems. Rotor acceleration up to 300 kHz/s was measured. This feature can be used to simplify existing experiments and explore entirely new ones in the study of spin topologies and material properties. © 2001 Academic Press

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Cross polarization and magic angle spinning (*1*) are widely used techniques in nuclear magnetic resonance for investigating solid disordered systems.

Originally, the polarization/magnetization transfer was used for detecting the presence of rare spins by studying their influence on the signal of an abundant spin system (*2*), but cross polarization has found its widest application in enhancing the signal of rare spin nuclei directly (*3*). A combination of the cross polarization with the magic angle spinning has proven to be a most valuble asset for studying solid state systems using NMR (*4*). The latest developments exploit cross polarization either to establish connectivity between different nuclear sites or to use this connection to unravel topologies of the spin system. In order to make the magnetization transfer efficient, nuclear magnetic energy levels must match. It is well known (*5*) that in a sample spinning at a frequency ν_r, the energy level matching condition breaks up into four spinning sublevels as a result of the modulation of the dipolar interaction by mechanical motion

$$\nu_{n_1} = \nu_{n_2} \pm (1, 2)\nu_r. \qquad [1]$$

The width of each matching band depends on the residual dipolar coupling among the source and/or target spins and is significantly reduced as compared to the case where the sample is stationary. Thus, it is necessary to carefully adjust the amplifier power to optimize the match condition, and this power must be stable over the course of the experiment. An additional complication is associated with the actual distribution of the RF field in the measurement coil. The field scales along the coil proportionally for different nuclear resonance frequencies, whereas the separation of the matching values remains exactly equal to the sample spinning frequency. At high rotation speeds, this makes it impossible to meet the matching condition over the entire volume of a typical NMR probe solenoid.

A number of ideas have been proposed to alleviate this problem (*6*), some of which require mechanical modification of the probe or inflict loss of the signal. The most efficient, and due to its simplicity also the most widely applied, is a fast ramp where the amplitude of one of the RF fields is increased by a factor of two during the polarization transfer (*7*). For very weakly coupled systems, processes other than through-space rotating frame polarization transfer have been found to be even more efficient (*8*).

We propose yet another approach, this time performing a ramp of the spinning speed ν_r to traverse the matching profile. This technically superceeds ramped RF amplitude technique as it offers full RF bandwidth throughout the CP process. Alternatively, our method can exploit CP conditions for a stationary sample where the most efficient internuclear couplings are present, and it detects at high spinning speeds, thus retaining all high-resolution advantages.

In order for this ramped spinning speed method to work, the dynamic performance, determined by the mechanical rotation design, must provide appropriate acceleration of the rotor. The rotor dynamics are competing with (i) spin–lattice relaxation and, more demandingly, (ii) spin–lock relaxation ($T_{1\rho}$). This Communication demonstrates that not only can condition (i) be met easily, but even (ii) can be achieved with a new generation of reduced diameter rotors.

It is well known that scaling down the diameter of the rotor increases linearly the maximum obtainable spinning frequency. Angular acceleration, however, can be expected to change as an inverse *third* power of the diameter. This dependency can be easily derived from a basic Euler equation

$$\dot{\omega} I = \tau. \qquad [2]$$

Spatial design constraints impose a natural limitation so that the total force, $F = 2\pi d f$, directed to turn the rotor can be assumed to be proportional to the circumference of the rotor.

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Practical manufacturing also dictates that the rotor aspect ratio a (length divided by diameter) remains constant. Inserting the torque, $\tau = Fd/2$, applied to turn the rotor, and the moment of inertia of a homogeneous cylinder, $I = Md^2/8$, one obtains the relationship

$$\dot{\nu}_r = \frac{16f}{\pi \rho a d^3}, \quad [3]$$

where f represents the tangential force per circumference unit and ρ is the average density of the rotor. At first sight surprisingly sharp cubic dependency [3] is a simple consequence of the quadratic scaling of the driving force and the fifth power scaling of the moment of inertia on the diameter.

We designed a spinning system where a ca 2-mm zirconia rotor was driven by four air jets directed tangentially toward grooves at both ends of the rotor. The design followed principally the classic double bearing system (*9*). Maximum spinning rates of 50 kHz were achieved by a continuous application of just one of the two drive channels at a pressure of 5 bar. This spinning system was incorporated into a home-built double resonance probe, and spectra were collected on a Bruker AMX-500 high-resolution spectrometer.

The dynamics of the rotor were measured by the rotational sidebands of the ^1H signal in solid adamantane. Figure 1 shows the dependence of the sideband spacing on the length of the driving air pulse delivered immediately before the start of the data acquisition. Subtracting the experimentally determined latent time of 20 ms for the shock pulse, the rotor was observed to reach 27 kHz in 100 ms. A maximum 300 kHz/s acceleration was observed in the region of 5–15 kHz. These values can be compared to the maximum of ca, 2 kHz/s mentioned in earlier stop-and-go experiments that used an 8-mm rotor (*10*) and 6 kHz/s during adiabatic passage through rotational resonance using a 4-mm rotor (*11*). The acceleration in our experiment is 2–5 times better than would be expected based purely on the smaller rotor size. This can be attributed to an optimized double drive spinning system.

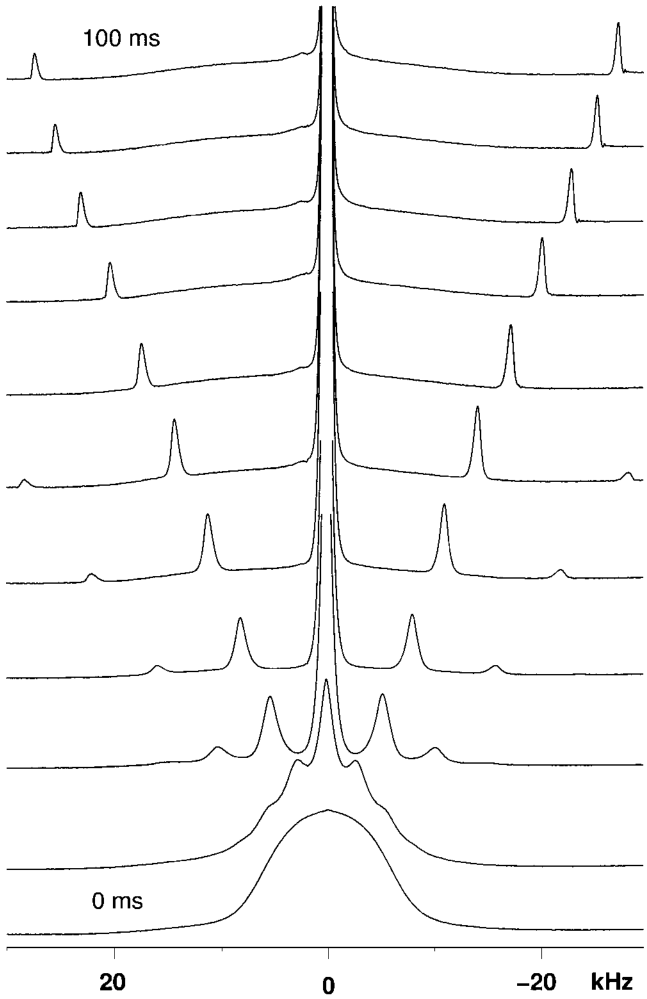

FIG. 1. The dependence of the ^1H signal of adamantane on the rotor drive air pulse duration. (bottom) 0 ms, stationary sample, increased by 10 ms to (top) 100 ms. In the top trace, the spinning sidebands indicate that the rotation speed is 27.2 kHz.

In order to compare the effectiveness of the ramped speed method on the efficiency of cross polarization, we followed the Hartmann–Hahn matching condition during different cross polarization experiments. The intensity of the ^{13}C signal of adamantane, transferred from a bath of abundant hydrogen nuclei, was measured as a function of the resonant carbon RF field amplitude.

At a constant rotation of 10 kHz, matching intensity maxima were located symmetrically at single and at double the rotation frequency, as illustrated in the bottom trace of Fig. 2. A low-intensity area in the middle can probably be assigned to nonmodulated nuclear pairs, where the internuclear vectors are close to the axis of the rotor and/or multispin processes.

A second experiment was performed that gave the matching profile for a stationary sample. Carbon magnetization generated from cross polarization was stored along the Zeeman field for 40 ms until the rotor speed reached 10 kHz, then the magnetization was flipped back to the transverse plane for detection. The profile of the matching condition is essentially determined by the dipolar linewidth of the hydrogen nuclei, as evidenced by the lowest trace in Fig. 1.

The top trace of Fig. 2 shows how the matching profile is broadened by dynamic spinning of the rotor. In this experiment, the nuclei were first polarized during 5 ms while the rotor was stationary, then the spinning speed of the rotor was ramped up to 10 kHz in 40 ms. An approximately 30 kHz wide profile, insensitive to RF conditions, can be observed.

The described experiments, capitalizing on a dynamic motion of the sample, indicate a possibility for the profound modification of the nuclear spin interactions. As one of the utilitary examples, optimization of an interspin cross-polarization process is

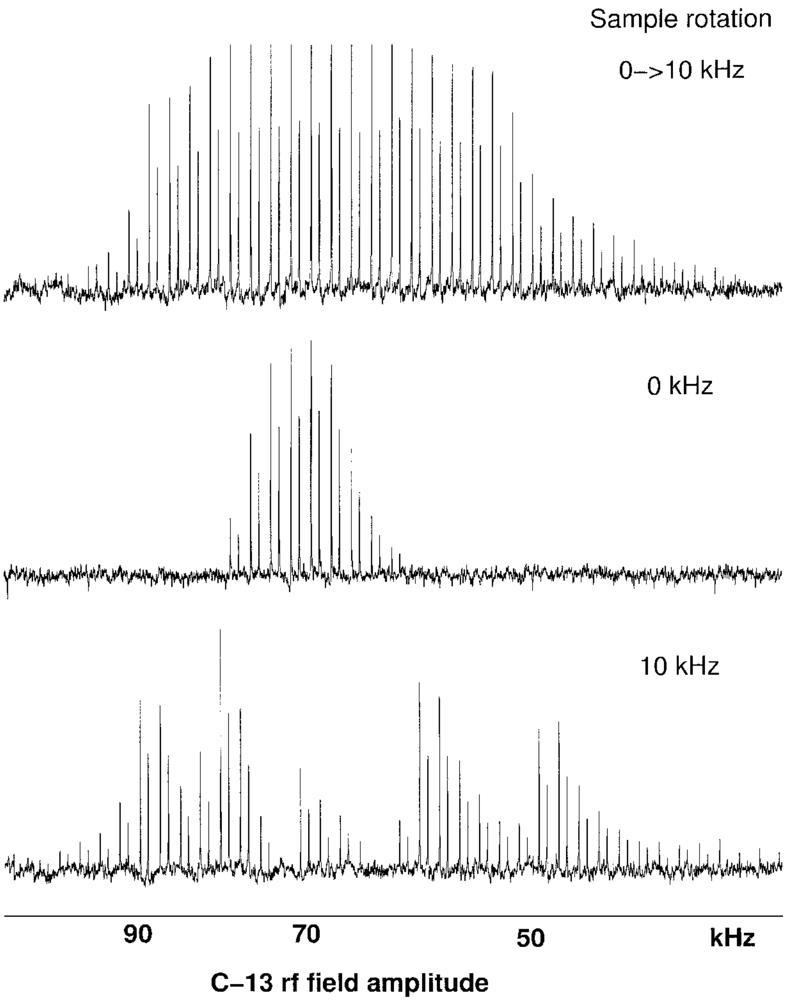

FIG. 2. Cross polarization experiments with sample spinning at (bottom) constant speed, (middle) stationary, and (top) ramped speed. ^{13}C spectra, comprising two lines in a ratio 3 : 2, are stacked from left to right horizontally with a decrement about 0.2 dB in the carbon RF amplitude.

demonstrated. About two orders of magnitude improvement in the rotor acceleration, as compared to earlier experiments, was realized due to the cubic diameter dependency. The enhanced mechanical dynamics extends applications related to anisotropy measurements (*10*) and to selective level crossings (*11*, *12*). During the past 10 years, a major effort has been allocated to the development of various recoupling pulse sequences that reproduce stationary spin environment conditions for a rotating system (*13*, *14*). Mechanical dynamics on a 10 ms timescale, as introduced in this Communication, may also considerably simplify and enhance these recoupling experiments.

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REFERENCES

1. E. R. Andrew, A. Bradbury, and R. G. Eades, *Nature* **182,** 1659 (1958); I. J. Lowe, *Phys. Rev. Lett.* **2,** 285 (1959).

2. S. R. Hartmann and E. L. Hahn, *Phys. Rev*. **128,** 2042 (1962).

3. A. Pines, M. G. Gibby, and J. S. Waugh, *J. Chem. Phys*. **59** (1973) 569.

4. J. Schaefer and E. O. Stejskal, *J. Am. Chem. Soc*. **98,** 1031 (1976), A. N. Garroway, W. B. Monitz, and H. A. Resing, paper presented at the ACS Meeting in San Francisco, Aug. 1976; E. Lippmaa, *Usp. Fiz. Nauk.* **120,** N3 (1976); M. Alla and E. Lippmaa, *Chem. Phys. Lett.* **37,** 260 (1976); E. Lippmaa, M. Alla, and T. Tuherm, *in* "Proceedings of the XIXth Congress Ampere Heidelberg," Sept. 1976, p. 113.

5. E. O. Stejskal, J. Schaefer, and J. S. Waugh, *J. Magn. Reson*. **28,** 105 (1977).

6. M. Sardashti and G. E. Maciel, *J. Magn. Reson*. **72,** 467 (1987), X. Wu and K. W. Zilm, *J. Magn. Reson*. **93,** 265 (1991); T. M. Barbara and E. H. Williams, *J. Magn. Reson*. **99,** 439 (1992); O. B. Peersen, X. Wu, I. Kustanovich, and S. O. Smith, *J. Magn. Reson. A* **104,** 334 (1993); S. Hediger, B. H. Meier, and R. R. Ernst, *Chem. Phys. Lett*. **213,** 627 (1993); R. Pratima and K. V. Ramanthan, *Chem. Phys. Lett*. **221,** 322 (1994); A. C.

Kolbert and S. L. Gann, *Chem. Phys. Lett*. **224,** 86 (1994); A. C. Kolbert and A. Bielecki, *J. Magn. Reson. A* **116,** 29 (1995).

7. G. Metz, X. Wu, and S. O. Smith, *J. Magn. Reson. A* **110,** 219 (1994).
8. D. E. Warschawski and P. F. Devaux, *J. Magn. Reson*. **145,** 367 (2000).
9. E. Lippmaa, M. Alla, A. Salumäe, and T. Tuherm, U.S. Patent 4,254,373, 1981.
10. R. Zeigler, R. Wind, and G. J. Maciel, *J. Magn. Reson*. **79,** 299 (1988).
11. R. Verel, M. Baldus, M. Nijman, J. W. M. Os, and B. H. Meier, *Chem. Phys. Lett*. **280,** 31 (1997).
12. M. Nijman, M. Ernst, A. P. M. Kentgens, and B. H. Meier, *Mol. Phys*. **98,** 101 (2000).
13. A. E. Bennett, R. G. Griffin, and S. Vega, "NMR Basic Principles and Progress," Vol. 33, p. 1 (1994).
14. S. Dusold and A. Seebald, *Ann. Rep. NMR Spectrosc*. **41,** 185 (2000).