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COMMUNICATIONS

A 4-mm Probe for ^{13}C CP/MAS NMR of Solids at 21.15 T

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The design of a broadband 4-mm magic-angle spinning (MAS) X–^{1}H/^{19}F double resonance probe for cross-polarization (CP)/MAS NMR studies at 21.15 T (^{1}H at 900 MHz) is described. The high-frequency ^{1}H/^{19}F channel employs a new and efficient transmission line tuning design. The first ^{13}C CP/MAS NMR spectra recorded at 21.15 T have been obtained with this probe and exhibit the best S/N per milligram sample of hexamethylbenzene achieved so far for a 4-mm rotor. © 2002 Elsevier Science (USA)

In this communication we report the successful construction of an efficient magic-angle spinning (MAS) X–^{1}H/^{19}F double resonance multinuclear NMR probe for use on a high-resolution 900-MHz NMR spectrometer, i.e., at 21.15 T, the highest magnetic field strength commercially available. In addition we report our preliminary results on its performance of the ^{13}C–{^{1}H} cross-polarization (CP) MAS experiment at 900 MHz utilizing a narrow-bore magnet. The probe, which has an outer diameter (o.d.) of 44 mm for the probe shield and a length of about 98 cm, is equipped with a 4-mm MAS module of similar, however, improved design to that reported earlier for the corresponding 5- and 7-mm spinning modules (*1, 2*). A four-turn solenoid coil (flattened gold-plated silver wire), selfstanding on a separate coil support, is mounted into the module. The coil is double tuned with the low-frequency broadband X channel covering the nuclear frequency range from $X = {}^{125}$Te to ^{25}Mg or 284 to 55 MHz and the high-frequency decoupler channel covering the range from ^{1}H to ^{19}F or 910 to 840 MHz. A schematic layout of the electronic circuitry for the double-tuned probe is illustrated in Fig. 1a which shows that the X channel uses standard lumped-circuit tuning elements, while the high-frequency channel employs transmission line tuning (TLT) technology. This new homemade tunable TLT $\lambda/4$ stub renders the standard variable tuning capacitor superfluous and represents the main reason for the high efficiency achieved for the high-frequency channel (*vide infra*). The TLT device is designed and constructed based on a piece of 6.4-mm o.d. (1/4 inch o.d.) semirigid coax cable (length of about 9 cm) for which part of the Teflon insulation has been mechanically removed leaving the inner conductor untouched. A detailed sketch of the lower tunable part of the TLT $\lambda/4$ stub is shown in Fig. 1b along with a description of the individual parts of the device in the figure caption. By appropriate positioning the point for the ground of the inner conductor using the mechanically adjustable sliding contact, the TLT device allows probe tuning over the frequency range from ^{1}H to ^{19}F. This TLT device, which is also used in our probes for lower field magnets, appears very effective in power handling and much less susceptible to arcing at high power. For example, for a 5-mm five-turn coil in a 300-MHz magnet we obtain a ^{1}H PW(90) $= 1.75\ \mu$s (i.e., $\gamma B_2/2\pi = 143$ kHz) for only 85 W of power at the probe.

Employing the new 900-MHz ^{1}H/^{19}F–X double resonance probe we performed, to our knowledge, the first 21.15-T ^{13}C–{^{1}H} CP/MAS NMR experiments using the facilities at the Varian Unity INOVA-900 application laboratory established by Varian Inc. and Oxford Instruments in Eynsham near Oxford, England. This spectrometer employs a Varian 900-MHz high-power CMX amplifier which at this time is capable of delivering a maximum output of about 700 W and with a maximum of about 450 W available at the probe. For the X channel an AMT 1-kW amplifier, capable of giving more than 600 W of RF power at the probe, is available. Following adjustment of the magic angle, optimization of the magnet homogeneity, and calibrations of the RF field strengths for the low- and high-frequency channel of the probe using this spectrometer configuration (some probe data are summarized in Table 1), it was decided to test the ^{13}C CP/MAS probe behavior at 900 MHz before attempting a voltage breakdown of the probe.

The ^{13}C CP/MAS experiment was optimized for a sample of hexamethylbenzene (HMB); i.e., one of the standard samples commonly applied for sensitivity (signal-to-noise, S/N) measurement in ^{13}C CP/MAS NMR. A standard CP pulse sequence with continuous wave (CW) irradiation during CP (without variable amplitude CP or VACP) and with CW ^{1}H decoupling (without the TPPM decoupling scheme) was used

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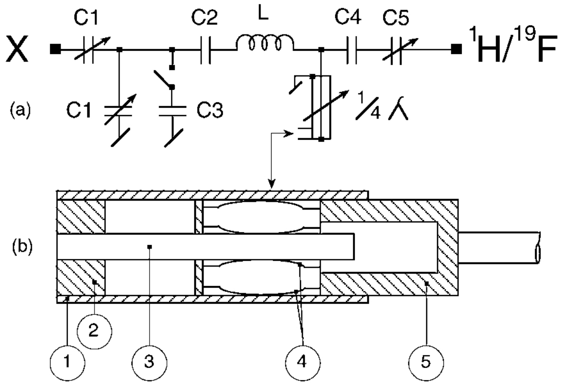

FIG. 1. (a) Schematic layout of the electronic circuitry for the 900-MHz double resonance X–^{1}H/^{19}F CP/MAS probe which employs a homemade tunable (TLT) $\lambda/4$ stub for tuning the high-frequency probe channel. The labeled components have the following typical values and origin. C1: 1–10 pF variable capacitor, Johansson 7585; C2: 65 pF chip capacitor, ATC; C3: 9–70 pF exchangeable chip capacitor wands, ATC; L: 4-turn 4-mm coil; C4: 0.4 pF chip capacitor, ATC; C5: 1–6 pF variable capacitor, Voltronics NMQM6GENL. (b) Expanded view of the lower tunable part of the TLT $\lambda/4$ stub (see also text). (1) Outer copper tube of the 1/4 inch o.d. semirigid coax cable; (2) Teflon insulation from the upper part of the $\lambda/4$ stub; (3) inner conductor of the semirigid coax cable; (4) gold-plated springs of the sliding contact; (5) brass guide soldered onto the springs of the sliding contact and which can slide inside the copper tube by means of a threaded screw device placed at the base of the probe.

throughout. Because a pulse sequence employing VACP was not available in the application laboratory at Oxford during the short time devoted to our experiments we used a slow spinning speed of only 1700 Hz in order to maximize the S/N as measured for the CH_3 groups of HMB. Thereby, the influence of the rotational dynamics of the CH_3 groups on the S/N is partly compensated by the slow spinning speed and by using a long contact time of 5 ms for the CP. Thus, the observed S/N ratios should be considered minimum values compared to the S/N obtainable using VACP. Furthermore, we should note that under these experimental conditions (slow spinning speed at high magnetic field strength), the intensities of the numerous spinning sidebands (a total of approximately 30) arising from the chemical shift anisotropy (CSA) pattern for the nonprotonated aromatic carbon signal appear weak compared to the CH_3 resonance. Finally, we point out that because of the increase in ^{1}H T_1 relaxation time for HMB at high magnetic fields (>9.4 T), the repetition delay between the 4 scans acquired for the S/N measurement must be increased from a standard value of 4 s at low magnetic fields (<9.4 T) to 40 s in the final stages of the optimization for the CP parameters at 21.15 T. Employing the optimized parameters, Fig. 2 shows the ^{13}C CP/MAS NMR spectrum observed with the best S/N (=843 : 1) for 57 mg of HMB in the full sample volume (80 μl) of the 4-mm rotor; i.e., the sample height of 10.5 mm just equals the length of the coil. Similarly Fig. 3 shows an array of 5 such spectra recorded one after the other to illustrate the repeatability and robustness of the probe and to obtain an average S/N for the HMB sample which is seen to be S/N (average) = 760 : 1. The exerimental conditions used to obtain the spectra are given in the caption of Fig. 2. It is noted that the processing of the spectra used "matched filtering," i.e., a linebroadening equal to the natural ^{13}C linewidth for the $^{13}CH_3$ resonance, which is observed to be only 170 Hz or 0.75 ppm at 21.15 T. This linewidth is approximately 10 Hz less than the predicted value of 180 Hz (0.80 ppm) based on the optimum resolution observed for the CH_3 resonance in HMB employing the corresponding type CP/MAS probe at lower magnetic field. Thus, the achieved resolution will give a natural linewidth of <10 Hz for adamantane, and greatly contributes to the high performance observed for the probe. The observed average $S/N = 760 : 1$ is in excellent agreement with or slightly higher than what we would predict from our results

TABLE 1
Some Data for the 4-mm X-^{1}H/^{19}F CP/MAS TLT Probe for a 900-MHz Narrow-Bore Magnet

1. Coil	4-mm four-turn solenoid coil, 10 mm in height, made from flattened gold-plated silver wire.
2. Rotor	4-mm o.d., 3-mm i.d. Si_3N_4 rotor; sample volume is 80 μl, sample height is 10.5 mm.
3. Spinning	Maximum spinning speed is 19–20 kHz for 5 bar (71 psi) drive pressure.
4. X-tuning	284 MHz (^{125}Te) to 55 MHz (^{25}Mg) with ^{1}H decoupling.
5. Decoupler	Transmission line tuning (TLT) with a tuning range from ^{1}H (900 MHz) to ^{19}F (847 MHz).
6. Gamma B_1	PW(90) = 3.9 μs ($\gamma B_1/2\pi$ = 65 kHz) at 226 MHz (^{13}C/^{79}Br) for ~350 watts at the probe. Arcing limit, PW(90) = 3.5–4.0 μs for the probe tuning range.
7. Gamma B_2	PW(90) = 2.9 μs ($\gamma B_2/2\pi$ = 86 kHz) at 900 MHz (^{1}H) for ~70 watts at the probe. Arcing limit, PW(90) < 2.0 μs.
8. Sensitivity	^{13}C CP/MAS of HMB for 4 scans gives $S/N = 760 : 1$ (average of five spectra) for 57 mg (full rotor, 80 μl) of HMB (see also text).

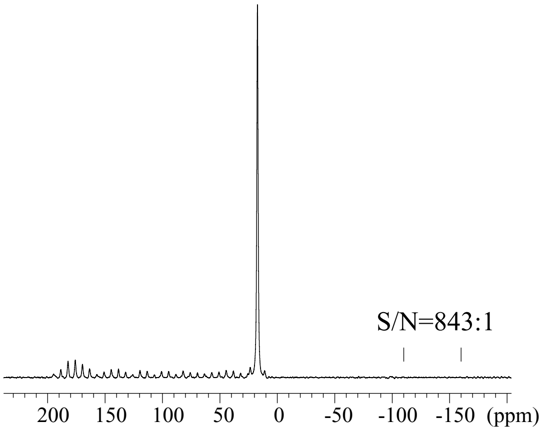

FIG. 2. The 21.15-T ^{13}C CP/MAS NMR spectrum of hexamethylbenzene (HMB) illustrating the best S/N (=843 : 1) achieved for 57 mg of HMB using a 4-mm rotor with a sample volume of 80 μl, 4 scans, a contact time of 5 ms for the Hartman–Hahn match, a relaxation delay of 40 s, and the probe and parameters described in the text.

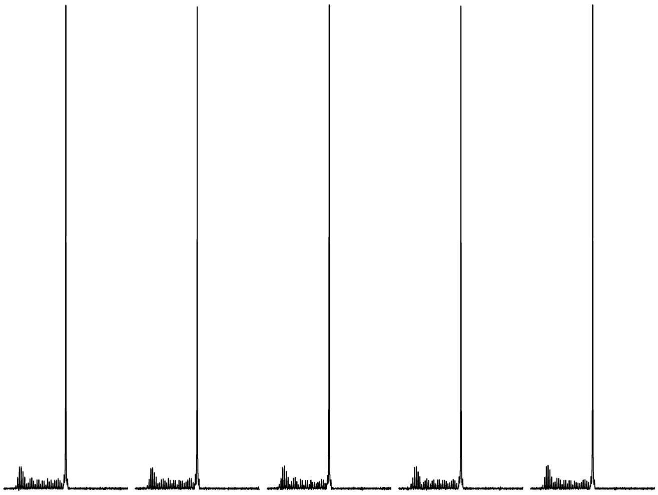

FIG. 3. An array of five ^{13}C CP/MAS NMR spectra for HMB as in Fig. 1, showing an average $S/N = 760:1$ for the five spectra (see also text).

for the same 4-mm rotor HMB sample obtained at lower magnetic fields. For example, from the value of $S/N \approx 200:1$ observed at 9.4 T we predict $S/N \approx (900/400)^{1.5} \times 200 = 675:1$. The observed mean $S/N = 760:1$ for 57 mg of HMB (i.e., the full 80-μl sample volume of the 4-mm rotor) corresponds to a S/N (per mg HMB) $= 13:1$. Furthermore, we should note that by reducing the sample volume by 50%, i.e., to 40 μl at the center of the coil using sample spacers and thereby increasing the RF homogeneity across the sample, we know from experience that the S/N is only reduced by approximately 25%. Thus, for 29 mg of HMB placed in the center of the coil we predict a $S/N = 570:1$. This corresponds to a S/N (per mg HMB) $=$ $20:1$ which should be about the maximum S/N (per mg HMB) for our probe under conditions close to optimum RF homogeneity for the sample. To our knowledge this number represents the best S/N (per mg HMB) achieved so far in ^{13}C CP/MAS NMR using a 4-mm o.d. rotor.

In addition to the excellent S/N observed for the ^{13}C CP/MAS experiment an unexpectedly good performance is also observed for the 900-MHz power handling of the TLT decoupler channel in this narrow-bore probe. For example, the ^{13}C CP/MAS spectra presented in Figs. 2 and 3 were obtained with only 70 W at the probe input (measured using a BIRD RF Power Analyst Model 4391) yielding a decoupler RF field strength $\gamma B_2/2\pi =$ 86 kHz and a PW(90) = 2.9 μs for the ^{1}H 90°-pulse of the CP pulse sequence. Since the 4-mm coil TLT circuitry of our probe will stand more than 200 W of RF power, the arcing limit for this channel will be $\gamma B_2/2\pi > 125$ kHz (or PW(90) < 2.0 μs). Because of the quite broad tuning range for the observe channel (i.e., 283–55 MHz) of the present probe combined with the electronic-circuitry layout for a narrow-bore probe we have observed an arcing limit for this channel of about PW(90) = 3.5–4.0 μs for the frequency range of the probe.

In conclusion, we have demonstrated that using a homebuilt 900-MHz ^{1}H–X double resonance probe, ^{13}C CP/MAS NMR can be carried out in a narrow-bore 21.15-T magnet with a S/N performance equal to or slightly above our predictions based on lower field magnets. The probe has a particularly high efficiency in power handling for the high-frequency ^{1}H/^{19}F channel, which utilizes TLT technology. It is believed that the results, reported here for this prototype broadband probe, will promote further probe developments and CP/MAS NMR studies of solids at ultrahigh magnetic fields. Further, we believe that future solid-state NMR probe development will be easier utilizing the 21.15-T medium-bore magnet.

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