An Efficient Large Sample Volume System for Solid State NMR

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ABSTRACT

An efficient large sample volume system has been developed to carry out MAS solid state NMR experiments. The system components are primarily zirconia and macor and no background ^{13}C is observed. The stator design employs separate air bearing and drive systems and is run using dry air. At a bearing pressure of about 32 psi, the rotor can be spun in a stable manner from less than one hundred Hz (with a driving pressure of 5 psi) to 4.3 KHz (24 psi driving pressure). This low gas pressure feature makes the system easy to operate. The volume of the rotor is 1.8 cm^3 and it can hold 1.1 g of HMB. The S/N ratio obtained is a factor of 4.6 better than the rotor previously designed and used in our laboratory (volume 0.6 cm^3 : 0.28g HMB). This increased sample size allows us to obtain the same S/N ratio in a MAS spectrum with a factor of 21 saving in spectrometer time. The time saving achieved with this rotor system is extremely useful in obtaining data on biological samples and polymers, and is especially useful when experiments on fossil fuels require the use of the Bloch delay technique. Examples of relevant applications will be discussed.

INTRODUCTION

A large MAS spinner system has been designed to achieve spinning speeds from less than a hundred Hz to approximately 4.3 KHz with a relatively large sample volume of about 1.8 cm^3. The reason for employing a large sample volume was to improve the S/N ratio in ^{13}C NMR experiments. This is extremely important for obtaining quantitative ^{13}C Bloch decay (BD) spectra on coal samples with an acceptable amount of spectrometer time, due to their reasonably long T_1 relaxation times.

In order to avoid a ^{13}C background signal the spinner and stator system are constructed from zirconia and macor respectively both of which contain no carbon.[1] Attention has also been focused on increasing the S/N ratio by using a probe electronic circuit which optimizes the sensitivity of the ^{13}C observe channel.[2,3] The result is a system which gives a S/N ratio for a ^{13}C CP/MAS spectrum of 1.10g sample of hexamethylbenzene (HMB) that has a factor of 4.6 improvement over the S/N ratio of a spectrum taken on our traditional spinner system, using 0.28g of HMB and the same spectral parameters.

DESIGN AND CONSTRUCTION OF THE SPINNER

A cross-sectional drawing of the spinner system is shown in Figure 1. There are eighteen flutes in the lip of the rotor. They are driven by a set of eight air jets (with a diameter of 0.025 in.) that are mounted on the stator, along with a set of eight bearing holes of the same diameter located in the middle of the stator. These air holes are spaced at 45° intervals around the circumference of the stator. The clearance between the rotor and stator is approximately 0.002 in. The stator housing is machined from Kel-F which has a stepped surface, as shown in Figure 1, in order to separate the driving and bearing gases. This design leads to ease in assembling the system, and also increases operational safety. The spinning speed of the rotor as a function of the driving gas pressure, with the rotor containing 1.10g of HMB and a bearing gas pressure of 32 psi is shown in Figure 2. Figures 3 through 5 are a series of photographs of this system. Due to the high rotational energy of the spinning system, the probe must either be in the bore of the magnet or behind an explosion screen when in operation.

EXPERIMENTAL RESULTS

Some typical results of data obtained with the large sample spinning system are shown below. Figure 7 shows the CP/MAS ^{13}C spectrum of 1.10g of HMB taken with only 12 scans and with 21 Hz line broadening applied. The S/N ratio of this spectrum is approximately 517. Figure 8 is a comparison of the spectral results using this new large rotor and the standard rotor system previously used in our laboratory. The size of the standard rotor (it holds about 0.28g of HMB) is fairly typical of those commercially available. In Figure 8a, CP/MAS spectrum is shown of 1.10g of HMB consisting of 20 scans with no line broadening. A S/N ratio of 130 is obtained. Figure 8b shows a 20 scan spectrum taken with the smaller standard rotor system which exhibits a S/N ratio of 28, again, with no line broadening. The comparison of Figures 8a and 8b demonstrate that an improvement in the S/N ratio of about 4.6 can be achieved which provides a factor of 21 in terms of spectrometer time. Figure 9 demonstrates that there are no ^{13}C background signals in BD and cross polarization (CP) experiments. This is an important feature in the quantitative application of CP NMR experiments. This rotor/stator system has been used to carefully compare the BD and CP spectra of the eight coals in the Argonne Premium Coal Sample Bank and these data are presented elsewhere.[4]

ACKNOWLEDGMENT

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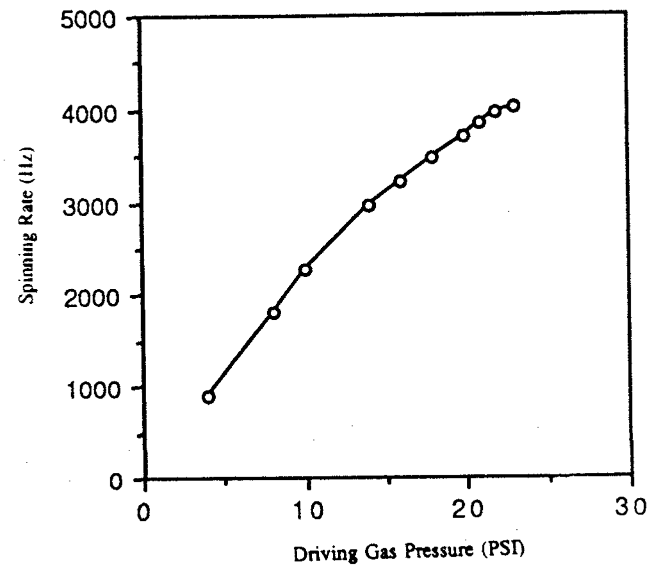

Figure 2: Plot of the spinning speed of the large volume rotor system as a function of the driving pressure used. Bearing pressure was 32 psi.

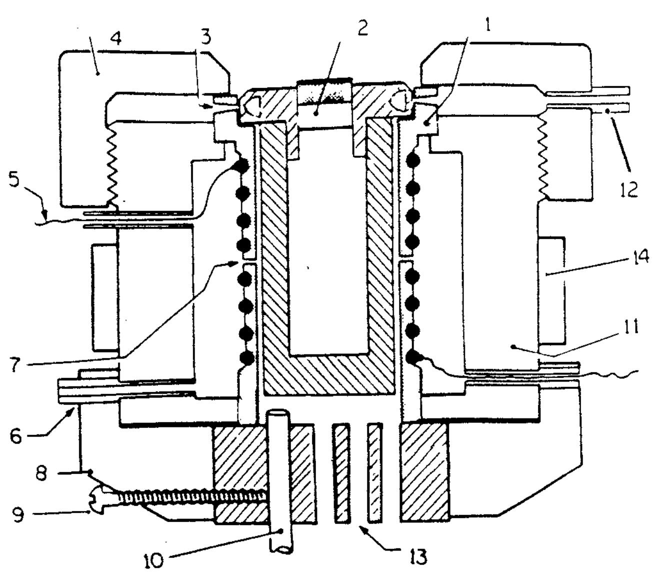

Figure 1: Cross-sectional view of the spinner system: 1. Stator, 2. Rotor, 3. Turbine driving jet, 4. Housing - upper part, 5. NMR coil terminal plug, 6. Bearing gas inlet plug, 7. Bearing gas orifice, 8. Light fiber mount. 9. Screw for fixing light fiber, 10. Light fiber. 11. Housing - lower part, 12. Driving gas inlet plug. 13. Bearing gas exit holes, 14. Mounting ring.

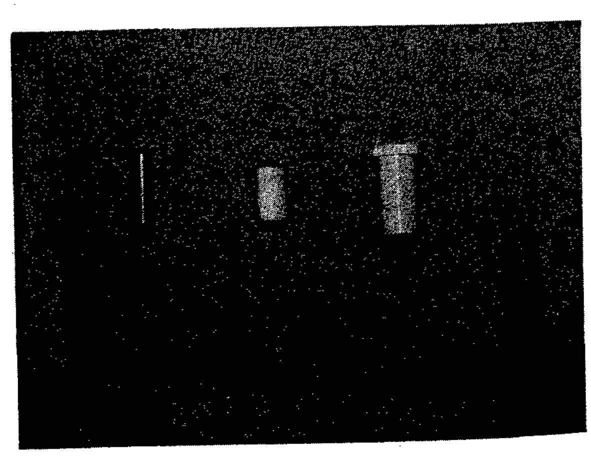

Figure 3: Photograph of the large sample rotor (a) as compared to the typical rotor (b) and the 7mm rotor supplied by Doty Scientific (c).

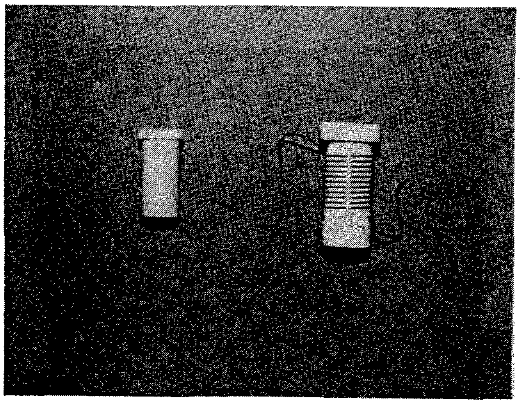

Figure 4: Photograph of the large volume rotor and the stator.

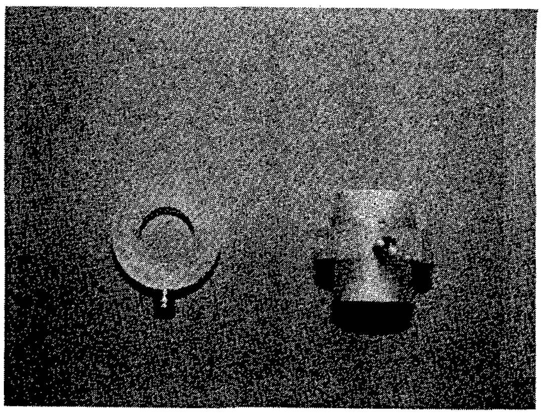

Figure 5: Photograph of the spinner system.

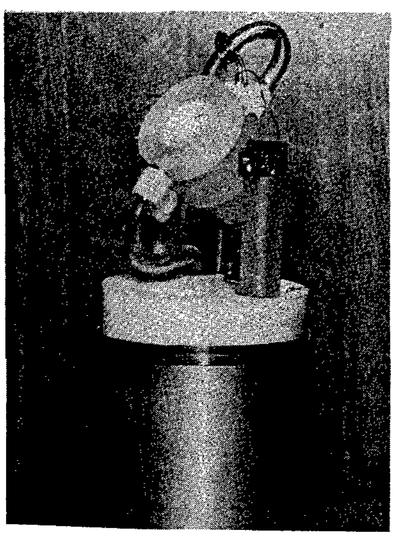

Figure 6: Photograph of the probe containing this spinning system.

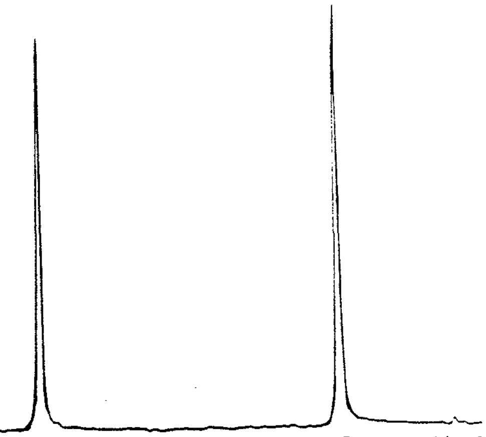

Figure 7: CP/MAS spectrum of 1.10g of HMB, taken with 12 scans, 5ms contact time, 1s delay time, 21 Hz line broadening. Spectrum at 25.12 MHz on a Bruker CXP-100.

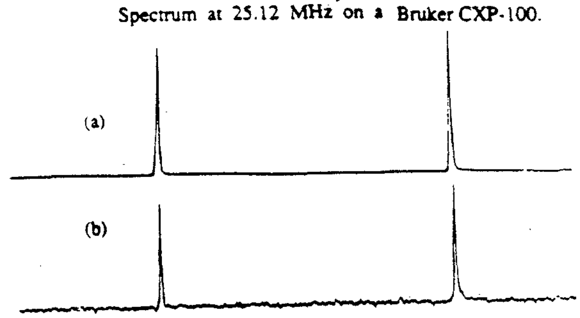

Figure 8: CP/MAS spectra of HMB taken at 25.12 MHz: (a)large volume (1.8 cm^3) system, 1.10g HMB, 20 scans, 3ms contact time, 1s delay, no line broadening, S/N ratio 130; (b) small (0.63 cm^3) rotor system, 0.28g HMB, 20 scans, 3ms contact time, 1s delay, no line broadening, S/N ratio 28.

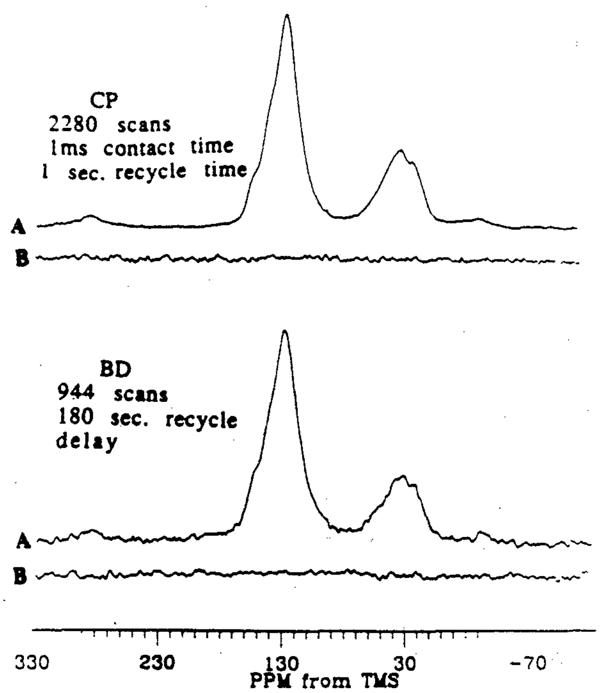

Figure 9: Comparison of the spectral lineshapes obtained for BD and CP experiments on Pittsburgh #8 Argonne Premium Coal. A is the spectrum and B is the background obtained by taking the spectrum with an empty rotor under identical conditions to A.