

A Stratagem for Low-Temperature Magic-Angle Spinning Using Nitrogen Spinning Gas

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Although the lowest temperatures in magic-angle-spinning (MAS) experiments have been reached with helium as the spinning gas (1), it is clear that, between ambient temperature and 77 K, nitrogen gas is preferable in terms of both cost and availability. Since the pressure of the spinning gas must be greater than 1 atm, condensation of gaseous nitrogen inside a liquid-nitrogen-cooled heat exchanger is unavoidable when the liquid nitrogen is kept at atmospheric pressure (2).

This can lead to instabilities of the gas flow and unstable sample spinning. Condensation can, however, be avoided if the liquid-nitrogen bath is operated at an equilibrium pressure greater than that of the spinning gas.

As shown in Fig. 1, this idea can be realized simply by incorporating the heat exchanger (H) into a pressurized liquid-nitrogen Dewar (G). The bath is first allowed to equilibrate at the pressure built up by a liquid-nitrogen fill, and this pressure is determined and maintained by means of a safety valve (E). To prevent ice formation on this valve, and also to conserve liquid nitrogen, a counterflow heat exchanger (F), in which the incoming gas is precooled by the exhaust gas, has been incorporated. A bypass (B) was added for mixing low- and ambient-temperature gas for intermediate temperature work. A conventional control system incorporating a thermocouple and heater was employed for fine temperature control.

This method has worked successfully with a variety of magic-angle spinners (3). The spinning gas temperature which can be achieved may be calculated from the variation of the vapor pressure of liquid nitrogen in the vicinity of 77 K (2), e.g., 84 K at a bath pressure of 2 atm. Depending on heat losses in the gas transfer line and probe, the sample temperature will be somewhat higher. This is especially true if there is not enough space available for adequate thermal insulation. Using a 5 mm double-bearing MAS probe (3b) in a 2.2 cm gap electromagnet, stable operation for several hours at 153 K sample temperature was achieved with spinning rates of 2 kHz. The apparatus can operate at 153 K for 24 h with 100 liter liquid-nitrogen capacity.

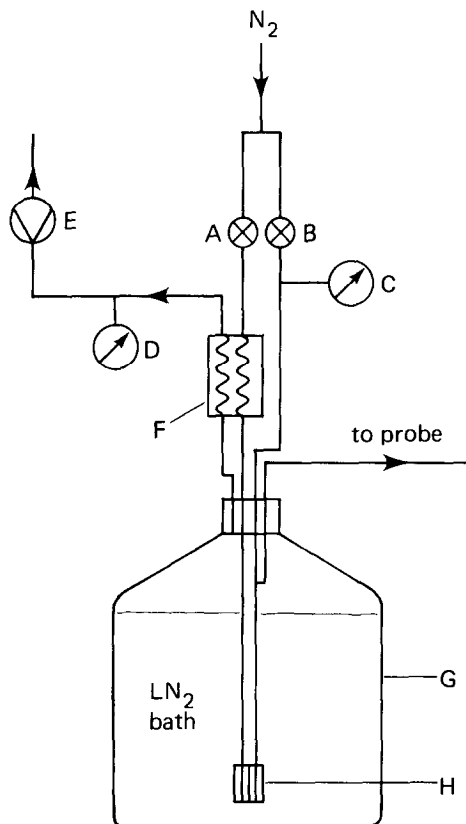
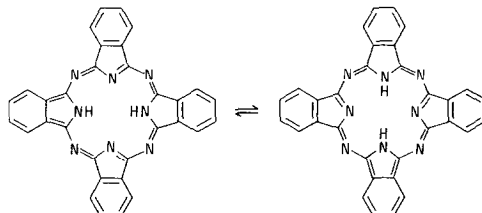


FIG. 1. Apparatus used to produce a smooth condensation-free flow of low-temperature, high-pressure nitrogen. (A and B) Valves for control of low- and ambient-temperature gas flow; (C and D) pressure gauges; (F) counterflow heat exchanger; (G) pressurized liquid-nitrogen Dewar; (H) heat exchanger for spinning gas.

Figure 2 shows ^{15}N CPMAS spectra of solid phthalocyanine at 300 and 153 K using the apparatus shown in Fig. 1 in conjunction with the spinner described in Ref. 3(b). The spectral changes arise from the double proton transfer in a slightly asymmetric double minimum potential as described previously (4) and shown in Scheme 1. The proton transfer is fast on the NMR time scale at 300 K and slow at 153 K.

Scheme 1



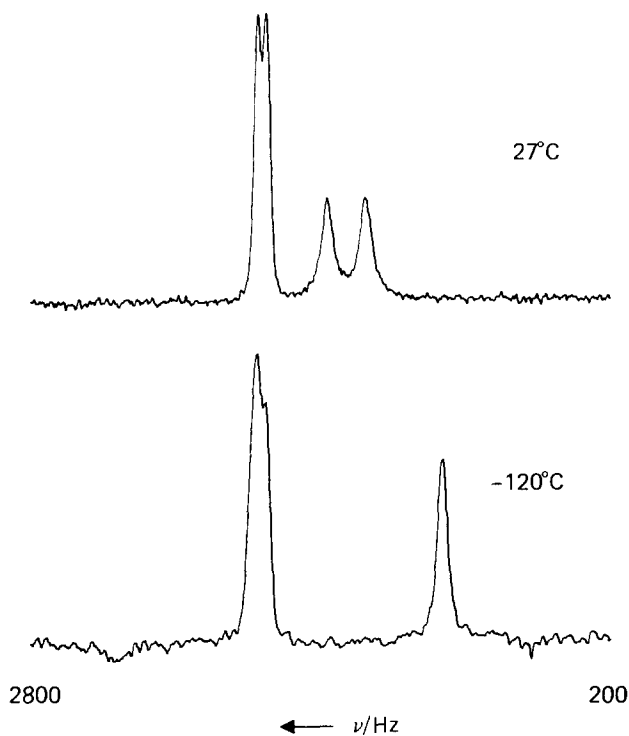


FIG. 2. ^{15}N CPMAS spectra (9.12 MHz) of ^{15}N -enriched phthalocyanine at 300 and 153 K. The spectral change confirms the process shown in Scheme 1. Critical spectral parameters: 300 K: 15 ms CP time, 21,000 scans, 2.1 s repetition time, 2.6 kHz spinning frequency; 153 K: 12 ms CP time, 270 scans, 2.1 s repetition time, 2 kHz spinning frequency. Reference: $^{15}\text{NH}_4\text{Cl}$.

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