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Magic Angle Spinning Nuclear Magnetic Resonance Near Liquid-Helium Temperatures. Variable-Temperature CPMAS Spectra of the 2-Norbornyl Cation to 6 K

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Recently we described a probe for cross-polarization magic angle spinning (CPMAS) NMR experiments at temperatures near that of liquid helium.[1] Reasonable spinning rates are possible since separate gas supplies are used for spinning and cooling. As Figure 1 indicates, liquid-nitrogen-cooled helium drives the rotor, while colder helium gas bathes the sample. This probe was constructed to investigate processes with very low activation barriers as well as tunneling phenomena.

The 2-norbornyl cation was selected for study with this probe since previous spinning (to 77 K) and nonspinning (to 5 K) spectra provide benchmarks,[2] and since an experimental response to alternative interpretations of these spectra seemed warranted.[3] Samples of carbon-13-labeled 2-norbornyl cation were prepared in SbF_5 by codeposition and annealing.[2,4] The codeposit was packed in 5-mm NMR tubes. These tubes were evacuated, sealed, annealed (dry ice, 24 h), inserted in Kel-F rotors at low temperature, and transferred in the cold to the precooled stator. Spinning was initiated after the cold probe was lowered into the cryomagnet.

Spectral results are summarized in Figure 2. Major features are self-evident. Like earlier nonspinning spectra,[2b] the chemical shift of the 125 ppm band assigned to C1 and C2 remains unchanged to 6 K.[5] No lower field bands are found.

Bands in the spectra shown in Figure 2 are broad. There is undoubtedly inhomogeneous broadening attributable to the glassy SbF_5 matrix.[4,6] In addition, the triple-tuned single-coil design used does not allow the ^1H and ^{19}F rf field levels available in previous work.[7] The more limited decoupling fields may also be reflected in the bandwidths. Despite limitations, the spectra represent a distinct improvement over nonspinning spectra.[2b] Kramer and Scouten take published spinning spectra[2a] (from 129 to 77 K) as evidence for slowing of a postulated exchange between enantiomeric norbornyl cations.[3a] The 125 ppm band does broaden some over this temperature range, but as noted previously,[2a] there are a number of factors that can change bandwidths.[8] If the broadening of C1,C2 observed[2a] is due to slowing of a postulated chemical exchange in the 129–77 K region, one must also expect the formation of two bands at temperatures above 40 K.[9] In the CPMAS spectra reported here, the C1,C2 band remains unchanged from 120–6 K, and no new bands are detected at lower field. The ultralow-temperature spinning spectra provide no evidence for selective line broadening that would signal slowing of a dynamic process averaging C1 and C2.

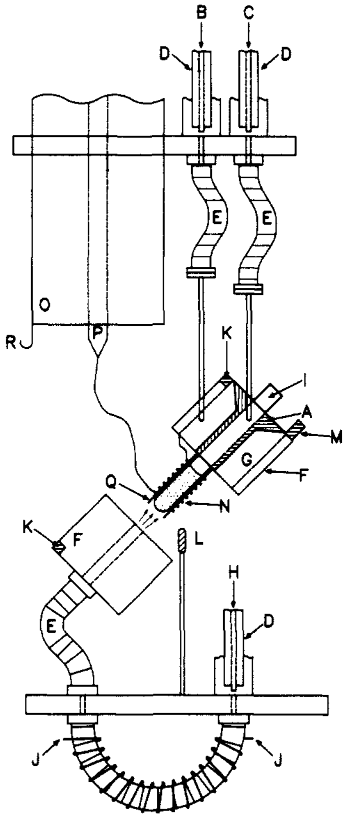

Figure 1. Sketch of the lower portion of the ultralow-temperature MAS probe. Critical components are labeled as follows: A, rotor; liquid nitrogen cooled helium bearing (B) and spinning (C) gas; D, cold gas transfer dewar; E, metal bellows; F, copper cradle to hold stator; G, brass stator; H, liquid helium (or liquid nitrogen); I, glass sample tube; J, chromium wire; K, Cu–constantan thermocouple; L, cryodiode; M, spinning-rate pickup wire; N, rf (sample) coil; O, outer conductor of transmission line; P, inner conductor; Q, rf coil form; R, rf field pickup loop.

Heavy-atom tunneling has been proposed to accommodate both NMR results and a chemically significant activation barrier between postulated enantiomeric norbornyl cations.[3b,10] Saunders and Johnson showed that tunneling could lead to new bands (side bands) in the spectrum with predictable shifts and intensities.[11] These side bands would have splitting equal to or greater than the estimated chemical shift difference between C1 and C2 of the enantiomeric pair (200 ppm = 3 kHz) if the tunneling frequency is ≤ 6 kHz. Sidebands have been observed in systems known to undergo exchange by tunneling.[12a] Further, marked decreases in tunneling frequency with increasing temperature are found.[12,13] The spectra in Figure 2 show no evidence of the tunneling splitting

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[1] Hackman, A.; Seidel, H.; Kendrick, R. D.; Myhre, P. C.; Yannoni, C. S. *J. Magn. Reson.* **1988**, *79*, 148.

[2] (a) Yannoni, C. S.; Macho, V.; Myhre, P. C. *J. Am. Chem. Soc.* **1982**, *104*, 907. (b) Yannoni, C. S.; Macho, V.; Myhre, P. C. *J. Am. Chem. Soc.* **1982**, *104*, 7380.

[3] (a) Kramer, G. M.; Scouten, C. G. *Adv. Carbocation Chem.* **1989**, *1*, 93. (b) Dewar, M. J. S.; Merz, K. M. *J. Am. Chem. Soc.* **1986**, *108*, 5634.

[4] Myhre, P. C.; Yannoni, C. S. *J. Am. Chem. Soc.* **1981**, *103*, 230.

[5] Temperatures reported are those of a cryodiode mounted close to the sample. The cryodiode was calibrated with a Au/Fe–chromel thermocouple during spinning tests with the probe in the cryomagnet.

[6] Bacon, J.; Dean, P. A. W.; Gillespie, R. J. *Can. J. Chem.* **1970**, *48*, 3413.

[7] The maximum rf field achievable with available power amplifiers is about 1.2 mT for ^1H and for ^{19}F; see: Kendrick, R. D.; Yannoni, C. S. *J. Magn. Reson.* **1987**, *75*, 506.

[8] Yannoni, C. S. *Acc. Chem. Res.* **1982**, *15*, 20.

[9] Assume a band broadening due to slowing of chemical exchange of ≥ 10 Hz in the published 77 K spectrum[2a] and a chemical shift difference between C1 and C2 of an equilibrating norbornyl cation ≤ 300 ppm (the chemical shift between C1 and C2 in the static dimethyl norbornyl cation was found to be $\sim$160 ppm; see: Myhre, P. C.; McLaren, K. L.; Yannoni, C. S. *J. Am. Chem. Soc.* **1985**, *107*, 5294). This leads to an estimated exchange rate $\leq 10\ s^{-1}$ at 40 K (see: Sandstrom, J. *Dynamic NMR Spectroscopy*; Academic Press: New York, 1982), well below the minimum required to observe two distinct bands.

[10] Fong, F. K. *J. Am. Chem. Soc.* **1974**, *96*, 7438.

[11] (a) Saunders, M.; Johnson, C. S., Jr. *J. Am. Chem. Soc.* **1987**, *109*, 4401. (b) Johnson, C. S., Jr. *J. Magn. Reson.* **1987**, *73*, 545.

[12] (a) Mottley, C.; Cobb, T. B.; Johnson, C. S., Jr. *J. Chem. Phys.* **1971**, *55*, 8523. (b) Johnson, C. S., Jr.; Mottley, C. *Chem. Phys. Lett.* **1973**, *22*, 430.

[13] Clough, S.; McDonald, P. J.; Saleye, F. O. *J. Phys. C* **1984**, *17*, 4413.

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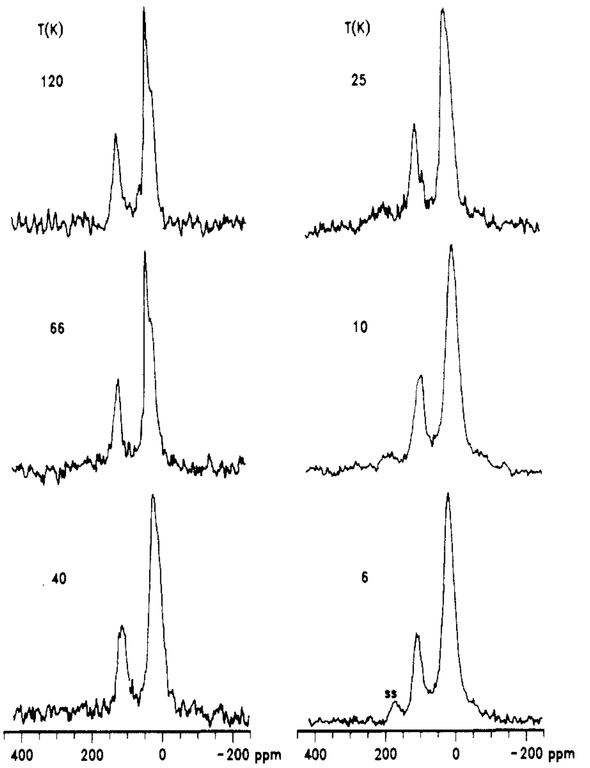

Figure 2. Low-temperature ^{13}C CPMAS spectra of the 2-norbornyl cation. Spinning rates achieved range from 1.7 kHz at 120 K to 1.0 kHz at 6 K. In the 6 K spectrum, SS denotes a spinning sideband of the peak at 125 ppm.

predicted.[14] As Saunders and Johnson have noted, the absence of side bands could be explained by very high frequency tunneling at *all* temperatures.[11a] However, evidence that tunneling rates decrease with increasing temperatures[12,13] makes this explanation less persuasive. One must also recognize that lattice effects which may destroy the symmetry of a hypothetical double-well potential further limit the possibility that tunneling is a valid interpretation. Alternatively, the spectra can be explained by an extremely low barrier or a single minimum potential surface. The absence of a significant barrier *is exactly what the NMR data imply, and all that this kind of NMR experiment can establish.*

The numerous studies of the 2-norbornyl cation have been reviewed and interpreted.[15] Saunders's summation of experimental evidence supporting the bridged structure of the norbornyl cation[11a] and the results of high-level ab initio calculations[16] merit careful consideration. This study demonstrates CPMAS NMR capability at temperatures near that of liquid helium and provides further constraints on structural and dynamic hypotheses raised concerning the 2-norbornyl cation. We anticipate the use of ultralow-temperature MAS NMR in studies of other systems.

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[14] Spinning speeds were 1.7 kHz at 40 K and above. Spinning speed dropped slowly as the temperature was lowered and reached 1 kHz at 6 K. This change is reflected in spinning side bands which are identified in the spectra shown in Figure 2. Their presence should not interfere with identification of sidebands indicative of tunneling.

[15] For accounts of the classical vs nonclassical ion controversy, see: (a) Grob, C. A. *Acc. Chem. Res.* **1983**, *16*, 426. (b) Brown, H. C. *Acc. Chem. Res.* **1983**, *16*, 432. (c) Olah, G. A.; Surya Prakash, G. K.; Saunders, M. *Acc. Chem. Res.* **1983**, *16*, 440. (d) Walling, C. *Acc. Chem. Res.* **1983**, *16*, 448.

[16] (a) Ragavachari, K.; Haddon, R. C.; Schleyer, P. v. R.; Schaefer, H. F. *J. Am. Chem. Soc.* **1983**, *105*, 5915. (b) Yoshimine, M.; McLean, A. D.; Liu, B.; DeFrees, D. J.; Binkley, J. S. *J. Am. Chem. Soc.* **1983**, *105*, 6185. (c) Koch, W.; Liu, B.; DeFrees, D. J. *J. Am. Chem. Soc.* **1989**, *111*, 1527.

Magic Angle Spinning Nuclear Magnetic Resonance Near Liquid-Helium Temperatures. Variable-Temperature CPMAS Studies of $C_4H_7^+$ to 5 K

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After four decades of detailed study, $C_4H_7^+$ remains enigmatic.[1] Recent high-level calculations show *two* isomers with nearly identical energy: the symmetrical bicyclobutonium ion (**1**) and a partially delocalized cyclopropylcarbinyl cation (**2**).[2] Further, these calculations indicate that the energy surface connecting **1** and **2** is quite flat.[2]

A set of interconversions, Figure 1, accounts for the rapid averaging of methylene carbons observed in solution-state NMR studies.[3] If these interconversions could be slowed, **1** could be distinguished from **2** on the basis of chemical shifts of their unique methylene carbons. The pentacoordinate methylene of **1** should have a resonance at high field. The formally charged methylene of **2** should be strongly deshielded. We report here CPMAS spectral studies of $C_4H_7^+$ that provide the first direct spectral evidence for **1** and **2**.

Using the ultralow-temperature magic angle spinning NMR probe,[4] we have obtained CPMAS spectra of methylene carbon labeled $C_4H_7^+$ in amorphous SbF_5 from 170 to 5 K. Spectra are shown in Figure 2. There is correspondence with earlier spectra above 77 K. Below 60 K, four distinct bands are seen at 235, 55, 28, and -15 ppm.[7] The 235 ppm band intensity decreases and the upfield band at -15 ppm increases as the temperature is lowered to 5 K. The two bands at 55 and 28–23 ppm remain with little change. Short- and long-term temperature cycling showed that spectra are reproducible.

The development of distinct bands at 60 K and below requires slowing of a rapid equilibrium. IGLO (individual gauge for localized orbitals) calculations of the chemical shifts of **1** and **2** have been reported by Schindler,[8] and calculated shifts, based on optimized geometries of **1** and **2** at the MP2(FULL)/6-31G* level,[2b] are shown in Table I. Based on Schindler's calculated shifts and an array of supporting experimental data, we assign

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[1] Brittain, W. J.; Squillacote, M. E.; Roberts, J. D. *J. Am. Chem. Soc.* **1984**, *106*, 7280.

[2] (a) Koch, W.; Liu, B.; DeFrees, D. J. *J. Am. Chem. Soc.* **1988**, *110*, 7325. (b) Saunders, M.; Laidig, K. E.; Wiberg, K. B.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1988**, *110*, 7652. (c) McKee, M. L. *J. Chem. Phys.* **1986**, *90*, 4908.

[3] (a) Olah, G. A.; Kelly, D. P.; Juell, C. J.; Porter, R. D. *J. Am. Chem. Soc.* **1970**, *92*, 2544. (b) Olah, G. A.; Juell, C. J.; Kelly, D. P.; Porter, R. D. *J. Am. Chem. Soc.* **1972**, *94*, 7652. (c) Staral, J. S.; Yavari, I.; Roberts, J. D.; Surya Prakash, G. K.; Donavan, D. J.; Olah, G. A. *J. Am. Chem. Soc.* **1978**, *100*, 8018. (d) Staral, J. S.; Roberts, J. D. *J. Am. Chem. Soc.* **1978**, *100*, 8020. (e) Saunders, M.; Siehl, H. U. *J. Am. Chem. Soc.* **1980**, *102*, 6868.

[4] (a) Hackman, A.; Seidel, H.; Kendrick, R. D.; Myhre, P. C.; Yannoni, C. S. *J. Magn. Reson.* **1988**, *79*, 148. (b) Myhre, P. C.; Webb, G. G.; Yannoni, C. S. *J. Am. Chem. Soc.*, preceding paper in this issue.

[5] Discussion of earlier spectral studies at 77 K and above will be included in our full report.

[6] A small peak near 235 ppm persists at higher temperatures. We believe this is due to an allylic ion isomer formed during annealing.

[7] At 60 K, additional bands at 104 ppm and a very sharp band at 40 ppm can also be resolved. The latter is assigned to a fraction of ions undergoing rapid exchange, and the former is assigned to ions undergoing more constrained exchange; see Table I and discussion in the text.

[8] Schindler, M. *J. Am. Chem. Soc.* **1987**, *109*, 1020.

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