

## $^{19}\text{F}$ to $^1\text{H}$ and $^1\text{H}$ to $^{19}\text{F}$ Cross Polarization MAS NMR of Trifluoroethanol Chemisorbed on Magnesium Oxide

David B. Ferguson, Thomas R. Krawietz and James F. Haw\*

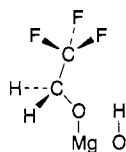
Laboratory for Magnetic Resonance and Molecular Science, Department of Chemistry, Texas A&M University, College Station, TX 77843, USA

$^{19}\text{F}$  magic angle spinning NMR studies of surfaces are greatly facilitated by  $^1\text{H}$  to  $^{19}\text{F}$  cross polarization and  $^1\text{H}$  decoupling.

Fluorine in various chemical forms is involved in many areas of surface chemistry including lubrication,<sup>1</sup> dry etching of semiconductors<sup>2</sup> and finishing textile fibres.<sup>3</sup> Catalyst systems containing fluorine include acidic perfluorosulfonate polymers (Nafion),<sup>4</sup> supported  $\text{SbF}_5$ ,<sup>5</sup> and fluorinated alumina.<sup>5</sup> An extensive catalytic science is also devoted to the production of CFC replacements that contain hydrogen as well as fluorine.<sup>6</sup>

Although  $^{19}\text{F}$  NMR has been successfully applied to a variety of solids including fluoropolymers and minerals,<sup>7</sup> and surface NMR studies employing various nuclei are legion,<sup>8</sup> there have been relatively few high resolution  $^{19}\text{F}$  NMR studies of surfaces or catalysts.<sup>9,10</sup> The reasons for this slow progress are largely technological. Hydrogen occurs along with fluorine in many chemically interesting surface and catalysis contexts, and this introduces appreciable  $^{19}\text{F}$ - $^1\text{H}$  dipolar couplings. Furthermore, fluoropolymers are used extensively in NMR probe construction; although the background signals from these are relatively modest compared with signals from pure compounds and polymers, they nearly preclude  $^{19}\text{F}$  studies of surfaces. Mehring reported non spinning  $^{19}\text{F}$  spectra of solids with  $^1\text{H}$  dipolar decoupling in 1977,<sup>11</sup> but the general application of this technique was, until recently, restricted by the problem of isolating two radio frequencies differing by only 6%. Drawing on improvements in NMR probe technology, Harris and coworkers<sup>12</sup> and Hagaman and coworkers<sup>13</sup> have independently reported studies suggesting that  $^{19}\text{F}$  NMR of solids is coming of age. Harris demonstrated that a combination of magic angle spinning (MAS) and high-power proton decoupling can provide high resolution  $^{19}\text{F}$  spectra of solid fluorinated organic compounds such as steroid derivatives.

In recent months, we have applied  $^{19}\text{F}$  NMR with  $^1\text{H}$  decoupling in preliminary studies of a variety of problems in surface chemistry and catalysis. Here, we report the first description of that effort and emphasize the value of  $^1\text{H}$  to  $^{19}\text{F}$  and  $^{19}\text{F}$  to  $^1\text{H}$  cross polarization processes for surface selectivity. We report results on a single sample, 1,1,1-trifluoroethanol adsorbed on high surface area  $\text{MgO}$ <sup>14</sup> at a coverage,  $1.2 \text{ mmol g}^{-1}$ , slightly greater than one monolayer. The acidic adsorbate readily chemisorbs on the strongly basic surface to give the structure below.



The dynamics of both  $^1\text{H}$  to  $^{19}\text{F}$  and  $^{19}\text{F}$  to  $^1\text{H}$  CP were probed at spinning speeds of 8 kHz and matched spin lock fields of ca. 90 kHz on each channel. Variable contact time studies were fit to determine CP time constants of 0.52 ms for  $^1\text{H}$  to  $^{19}\text{F}$ , and 0.87 ms for  $^{19}\text{F}$  to  $^1\text{H}$ . Direct measurement of  $T_{1\rho}$  values were 15.6 ms for  $^{19}\text{F}$  and 17.1 ms for  $^1\text{H}$ ; these direct values were within 20% of those obtained by fitting the fall-off rates of the variable contact time data. The combination of relatively fast CP and slow  $T_{1\rho}$  relaxation is advantageous for obtaining representative CP spectral intensity, and of the ten or so catalyst-adsorbate systems thus far investigated we have had

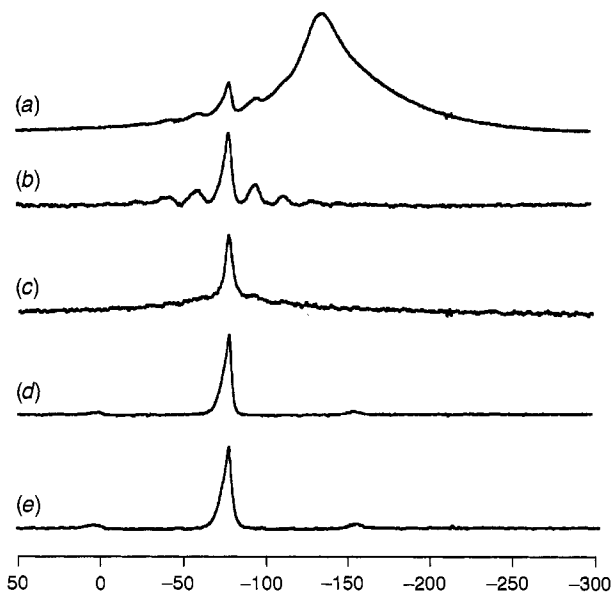


Fig. 1 188.7 MHz  $^{19}\text{F}$  MAS spectra of trifluoroethanol on  $\text{MgO}$ . (a) 3 kHz MAS obtained with single pulse excitation and 90 kHz  $^1\text{H}$  decoupling. (b) 3 kHz CP-MAS ( $^1\text{H}$  to  $^{19}\text{F}$ ) and  $^1\text{H}$  decoupling. (c) 3 kHz CP-MAS obtained without  $^1\text{H}$  decoupling. (d) 14.5 kHz CP-MAS obtained with  $^1\text{H}$  decoupling. (e) 14.5 kHz CP-MAS obtained without  $^1\text{H}$  decoupling. Number of transients: (a) 100, (b-e) 256.  $90^\circ$  pulses were 3  $\mu\text{s}$ , and cross polarization contact times were 2 ms.

difficulty in obtaining  $^1\text{H}$ - $^{19}\text{F}$  CP spectra only for physisorbed species at high temperatures.

Representative  $^{19}\text{F}$  MAS spectra of **1** are shown in Fig. 1. Using single pulse excitation (Bloch decay) the  $^{19}\text{F}$  background signal due to Teflon-containing probe components, including the most commonly used type of tuning capacitors, is sufficient to almost preclude surface NMR [Fig. 1(a)]. In contrast, no background signals were observed with  $^1\text{H}$ - $^{19}\text{F}$  CP, or with the reverse of that prior to  $^1\text{H}$  observation. The  $^{19}\text{F}$  spectrum with  $^1\text{H}$  decoupling and slow speed (3 kHz) MAS, Fig. 1(b), suggests the superposition of signals from a mobile component without sidebands and a less mobile component with spinning sidebands. This interpretation is consistent with an otherwise identical spectrum obtained without  $^1\text{H}$  decoupling during acquisition [Fig. 1(c)].  $^1\text{H}$ - $^{19}\text{F}$  dipolar couplings had no effect on ca. 25% of the total  $^{19}\text{F}$  intensity, but broadened the signal from the remaining spins, including the sideband pattern, to a featureless line 10 to 15 kHz in width. Increasing the spinning speed to 14.5 kHz independently averaged the heteronuclear dipolar couplings, and proton decoupling then had no additional effect on the line shape [Fig. 1(d) and (e)].

We conclude that NMR investigations of fluorine in surface chemistry are now feasible. Support for our *in situ* NMR studies of catalytic reactions and the construction of the spectrometer used in this investigation was provided by the National Science Foundation (CHE-9221406). The  $^{19}\text{F}$  MAS probe was constructed by Otsuka-Chemagnetics and spun 4-mm zirconia sample rotors.

Received, 4th May 1995; Com. 5/02860D

## References

- 1 C. F. McFadden and A. J. Gellman, *Langmuir*, 1995, **11**, 273.
- 2 G. S. Oehrlein, Y. Zhang, D. Vender and M. Haverlag, *J. Vac. Sci. Technol. A*, 1994, **12**, 323.
- 3 N. S. Rao and B. E. Baker, in *Organofluorine Chemistry*, ed. R. E. Banks, B. E. Smart and J. C. Tatlow, Plenum, New York, 1994, ch. 14.
- 4 G. A. Olah, P. S. Iyer and G. K. S. Prakash, *Synthesis*, 1986, 513.
- 5 A. K. Ghosh and R. A. Kydd, *Catal. Rev. Sci. Eng.*, 1985, **27**, 539.
- 6 L. E. Manzer, *Science*, 1990, **249**, 31.
- 7 R. K. Harris and P. Jackson, *Chem. Rev.*, 1991, **91**, 1427.
- 8 *NMR Techniques in Catalysis*, ed. A. T. Bell and A. Pines, Marcel-Dekker, New York, 1994.
- 9 C. V. A. Duke, J. M. Miller, J. H. Clark and A. P. Kybett, *J. Mol. Catal.*, 1990, **62**, 233.
- 10 F. M. Asseid, C. V. A. Duke and J. M. Miller, *Can. J. Chem.*, 1990, **68**, 1420.
- 11 H. Raber and M. Mehring, *Chem. Phys.*, 1977, **26**, 123.
- 12 S. A. Carss, R. K. Harris, P. Holstein, B. J. Say and R. A. Fletton, *J. Chem. Soc., Chem. Commun.*, 1994, 2407.
- 13 S. A. Vierkötter and E. W. Hagaman, presented at the Experimental NMR Conference, Boston, MA, March 1995, poster 378.
- 14 A. A. Kheir and J. F. Haw, *J. Am. Chem. Soc.*, 1994, **116**, 817.