

The Detection of Connectivities of Rare Spin- $\frac{1}{2}$ Nuclei in the Solid State Using Natural Abundance Samples: ^{13}C and ^{29}Si INADEQUATE and COSY Type Experiments

R. Benn,*^a H. Grondey,^a C. Brevard,*^b and A. Pagelot^b

^a Max-Planck-Institut für Kohlenforschung, D-4330 Mülheim a.d. Ruhr, West Germany

^b Laboratoire d'Application Bruker Spektroskopie, F-67160 Wissembourg, France

The cross polarization (c.p.)–magic angle spinning (m.a.s.)–INADEQUATE and c.p.–m.a.s.–COSY techniques for detection of connectivities of rare spin- $\frac{1}{2}$ nuclei in the solid state are introduced and illustrated using the scalar $^1J(^{13}\text{C},^{13}\text{C})$ and $^2J(^{29}\text{Si},^{29}\text{Si})$ coupling of natural abundance samples.

The connectivities of atoms in molecules can be established by a variety of powerful two dimensional n.m.r. techniques.¹ Methods based on double quantum coherences involving the indirect scalar spin–spin coupling are highly effective for the elucidation of the carbon skeleton of dissolved molecules. In the solid state, ^{13}C -enriched samples and dipolar couplings have been employed for similar purposes.^{2,3} Here we present what we believe to be the first two-dimensional solid state n.m.r. spectra from which the connectivities of rare spin- $\frac{1}{2}$ isotopes in organic and inorganic material can be derived using the homonuclear indirect scalar couplings, *e.g.* $J(^{13}\text{C},^{13}\text{C})$ or $J(^{29}\text{Si},^{29}\text{Si})$, of natural abundance samples.

A prerequisite for the determination of connectivities of atoms by n.m.r. techniques is that there is a coupling between magnetically active nuclei. In most organic solids the direct dipolar coupling $D(^{13}\text{C},^{13}\text{C})$ is less than a few kHz⁴ and therefore can be removed by magic angle spinning (m.a.s.). Provided that the line widths of the carbon resonances in the solid state are not too large,⁵ the scalar $^1J(^{13}\text{C},^{13}\text{C})$ coupling (in the range 10–250 Hz in most organic compounds⁶) can be used for the detection of connectivities by an INADEQUATE^{1,7} or COSY^{1,8} type experiment. In the experiments

described here, the initial 90° pulse of the original INADEQUATE or COSY sequences was replaced by a cross polarisation pulsing scheme in order to obtain a better sensitivity for the solid state spectra.[†] Phase sensitive spectra and various variants well known from liquid state pulse experiments¹ such as F_1 -decoupled COSY spectra and double quantum filtered COSY spectra are also feasible.

In Figure 1 the two dimensional 75.5 MHz ^{13}C c.p.–m.a.s.–INADEQUATE spectrum of camphor is presented. The carbonyl carbon was not recorded and consequently the connectivities of C-1 with C-2 and C-6 are missing. All the other one bond relations except that between C-2 and C-3, whose satellite subspectrum is of the AB type, can be obtained unambiguously. The line width of the ^{13}C , ^{13}C satellite lines was greater than 4 Hz thus preventing a detailed comparison of $^1J(^{13}\text{C},^{13}\text{C})$ values in the solid and liquid state.

[†] C.p.–m.a.s.–INADEQUATE: $90^\circ(^1\text{H})$ –Spin Lock(^1H)Spin Contact(^{13}C)– $1/4J(^{13}\text{C},^{13}\text{C})$ – $180^\circ(^{13}\text{C})$ – $1/4J(^{13}\text{C},^{13}\text{C})$ – $90^\circ(^{13}\text{C})$ – t_1 – $135^\circ(^{13}\text{C})$ –FID(t_2). C.p.–m.a.s.–COSY: $90^\circ(^1\text{H})$ –Spin Lock(^1H)Spin Contact(^{29}Si)– t_1 – $90^\circ(^{29}\text{Si})$ –FID(t_2).

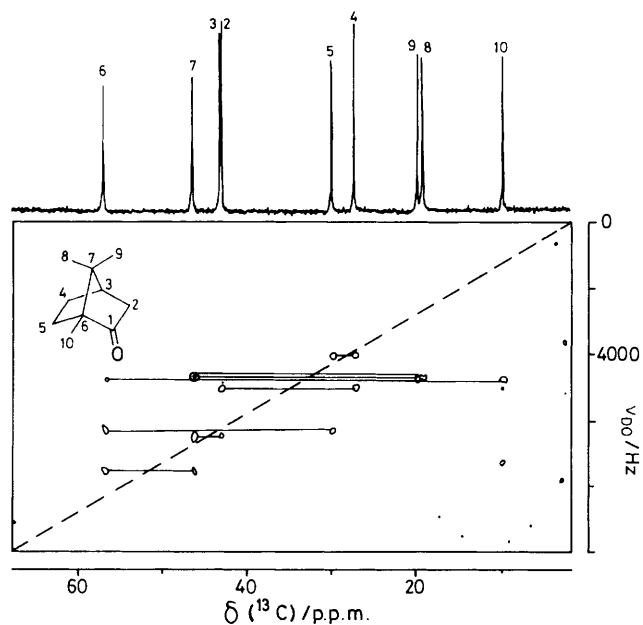


Figure 1. The 75.5 MHz solid state two-dimensional c.p.-m.a.s.-INADEQUATE spectrum of camphor. The spectrum was recorded with a natural ^{13}C isotopic abundance sample packed in a double bearing rotor. Repetition period 4 s, contact time 10 ms, 256 phase cycles, 32 increments in the F_1 -dimension, total acquisition time ca. 10 h.

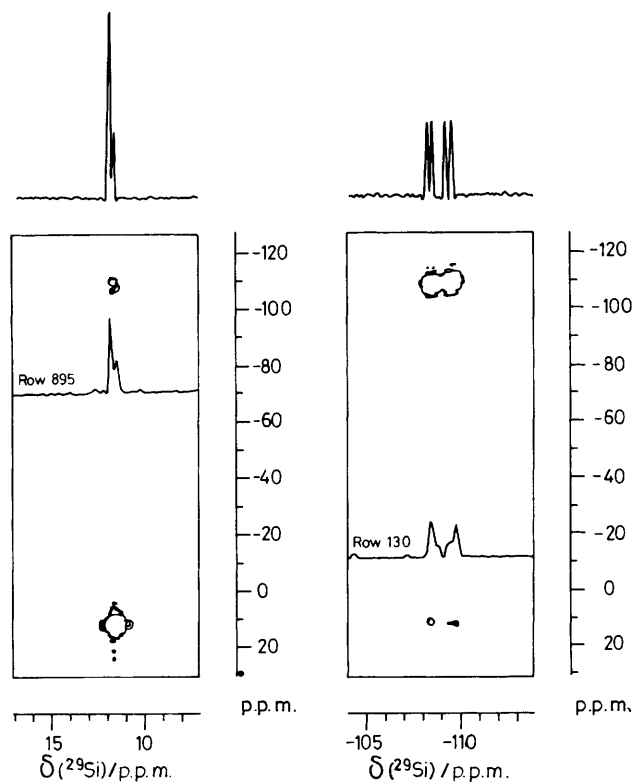


Figure 2. Expansions of the 59.6 MHz solid state two-dimensional c.p.-m.a.s.-COSY spectrum of the silicate Q_8M_8 with ^{29}Si in natural abundance. A delay of 0.05 s was introduced in the evolution period in order to emphasize the long range $J(^{29}\text{Si}-\text{O}-^{29}\text{Si})$ couplings. Repetition time per scan 3.2 s, contact time for the cross polarisation 5 ms. 90 increments in F_1 -dimension, total experimental time 43 h. Individual rows of the cross peaks are illustrated in each of the contour plots. The conventional one dimensional ^{29}Si spectrum of Q_8M_8 is shown at the top.

Connectivities of atoms with rare spin- $\frac{1}{2}$ nuclei can also be detected *via* two-dimensional COSY spectroscopy applied to the satellite subspectra.⁹ A solid state c.p.-m.a.s.-COSY experiment was performed on the silicate Q_8M_8 ¹⁰ similar to the measurements carried out on polytungstates *via* liquid state two-dimensional ^{183}W spectroscopy.⁹ Since $^2J(^{29}\text{Si}-\text{O}-^{29}\text{Si})$ can be assumed to be small (1–4 Hz),¹¹ a long range c.p.-m.a.s.-COSY experiment was performed with a fixed delay of 0.05 s introduced into the evolution period to emphasize cross peaks due to small $^2J(^{29}\text{Si}-\text{O}-^{29}\text{Si})$ couplings.¹² The observed cross peaks (*cf.* Figure 2) provide evidence for the connection of the four high field Q_8 lines with the major and minor [$\delta(^{29}\text{Si})$ 11.77 and 11.55] M_8 lines of the silicate. (Owing to slight distortions of the cubic geometry, the Q_8 silicon atoms give four lines in the solid state spectrum;¹⁰ the splitting of the M_8 lines can be seen at higher fields and under good recording conditions.)

From our findings we conclude that the two dimensional correlation experiments known from solution studies can also be fruitfully applied in the solid state provided that the resonance lines under study are not broad compared to the homonuclear scalar couplings. A wealth of experiments for many areas of inorganic and organic chemistry then can be forseen. Possible applications could include the study of the silicon backbone of zeolites and the identification of the α and β anomers in sugars, or the elucidation of carbon skeletons of natural products, *e.g.* terpenes and steroids.

Received, 13th August 1987; Com. 1191

References

- 1 R. R. Ernst, G. Bodenhausen, and A. Wokaun, 'Principles of Nuclear Magnetic Resonance in One and Two Dimensions,' Clarendon Press, Oxford, 1987.
- 2 E. M. Menger, S. Vega, and R. G. Griffin, *J. Am. Chem. Soc.*, 1986, **108**, 2215; N. Chandrakumar and S. Subramanian, 'Modern Techniques in High Resolution FT-NMR,' Springer, New York, 1987, p. 256.
- 3 W. L. Earl and B. H. Meier, Abstracts 28th ENC, Asilomar, California, 1987, MF 17; for oriented liquid crystal samples, see: M. Gochin, K. V. Schenker, H. Zimmermann, and A. Pines, *J. Am. Chem. Soc.*, 1986, **108**, 6813.
- 4 C. A. Fyfe, 'Solid State NMR For Chemists,' C.F.C. Press, Guelph, Ontario, Canada, 1983, 21.
- 5 For ultra-high resolution m.a.s. n.m.r., see: C. A. Fyfe, J. H. O'Brien, and H. Strobl, *Nature*, 1987, 326, 281.
- 6 P. E. Hansen, *Annu. Rep. NMR Spectrosc.*, 1981, **11A**, 66; V. Wray and P. E. Hansen, *ibid.*, 99.
- 7 A. Bax, R. Freeman, T. A. Frenkiel, and M. H. Levitt, *J. Magn. Reson.*, 1981, **43**, 478; T. H. Mareci and R. Freeman, *ibid.*, 1982, **48**, 158.
- 8 W. P. Aue, E. Bartholdi, and R. R. Ernst, *J. Chem. Phys.*, 1976, **64**, 2229; A. Bax and R. Freeman, *J. Magn. Reson.*, 1981, **42**, 164; K. Nagayama, A. Kumar, K. Wüthrich, and R. R. Ernst, *ibid.*, 1980, **40**, 321.
- 9 (a) C. Brevard, R. Schimpf, G. Tourne, and C. M. Tourne, *J. Am. Chem. Soc.*, 1983, **105**, 7059; (b) For ^{13}C COSY double quantum spectra of natural ^{13}C abundance samples, see: R. Benn, 7th German Magnetic Resonance Discussion Group, Heidelberg, 1985.
- 10 E. Lippmaa, M. Magli, A. Samosan, M. Tarmak, and G. Engelhardt, *J. Am. Chem. Soc.*, 1981, **103**, 4992; E. A. Williams, *Annu. Rep. NMR Spectrosc.*, 1983, **15**, 235f.
- 11 G. Fritz, J. W. Chang, and N. Braunagel, *Z. Anorg. Allg. Chem.*, 1975, **416**, 211; H. Jancke, G. Engelhardt, S. Wagner, W. Dirnens, G. Herzog, E. Thieme, and K. Rühlmann, *J. Organomet. Chem.*, 1977, **134**, 21; H. Marsmann 'NMR Basic Principles and Progress,' Springer, 1981, vol. 17, p. 128.
- 12 A. Bax and R. Freeman, *J. Magn. Reson.*, 1981, **44**, 542.