UK Solid-State NMR Capabilities and Availability

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1. Update on developments in solid-state NMR
2. What is available and how can it be accessed?
3. I have this problem with solid-state NMR…

Solid-state NMR in the (not so) good old days

"Because molecular rotation has almost ceased, spin-lattice relaxation times are very long, **but spin-spin relaxation times are very short**. Hence […] even gathering the murky information may therefore be a lengthy process. Moreover, because the lines are so broad, very high powers of RF radiation may be required, [needing] transmitters rated at several hundreds of watts."

Atkins *Physical Chemistry* (2010)

Traditional picture	**Current status**
Finicky experiments (dodgy MAS, CRAMPS etc.)	Robust hardware and straightforward standard experiments e.g. CP/MAS.
A technique for researchers rather than applications	Understand how / when we can obtain good resolution and useful data.
Spectra of little value beyond fingerprinting	Particularly combined with DFT ("NMR crystallography") full information content of solid-state NMR can be exploited

Trends in solid-state NMR

Solid-state NMR is becoming mainstream:

Year	NMR	Solid-state NMR
1994	12000	1100
2017	18000 (+50%)	2400 (+118%)

Web of Science "Topic" search

Main areas of activity:

Biomolecular solid state (ultra fast MAS; specialised labelling / preparation schemes)

Organic solid state (H-bonding; understanding disorder; "NMR crystallography"; polymers)

Inorganic materials (quadrupolar NMR; paramagnetic / energy materials; MOFs; zeolites)

DNP-MAS for potentially dramatic S/N improvements (e.g. easy INADEQUATE)

Ultra-fast MAS

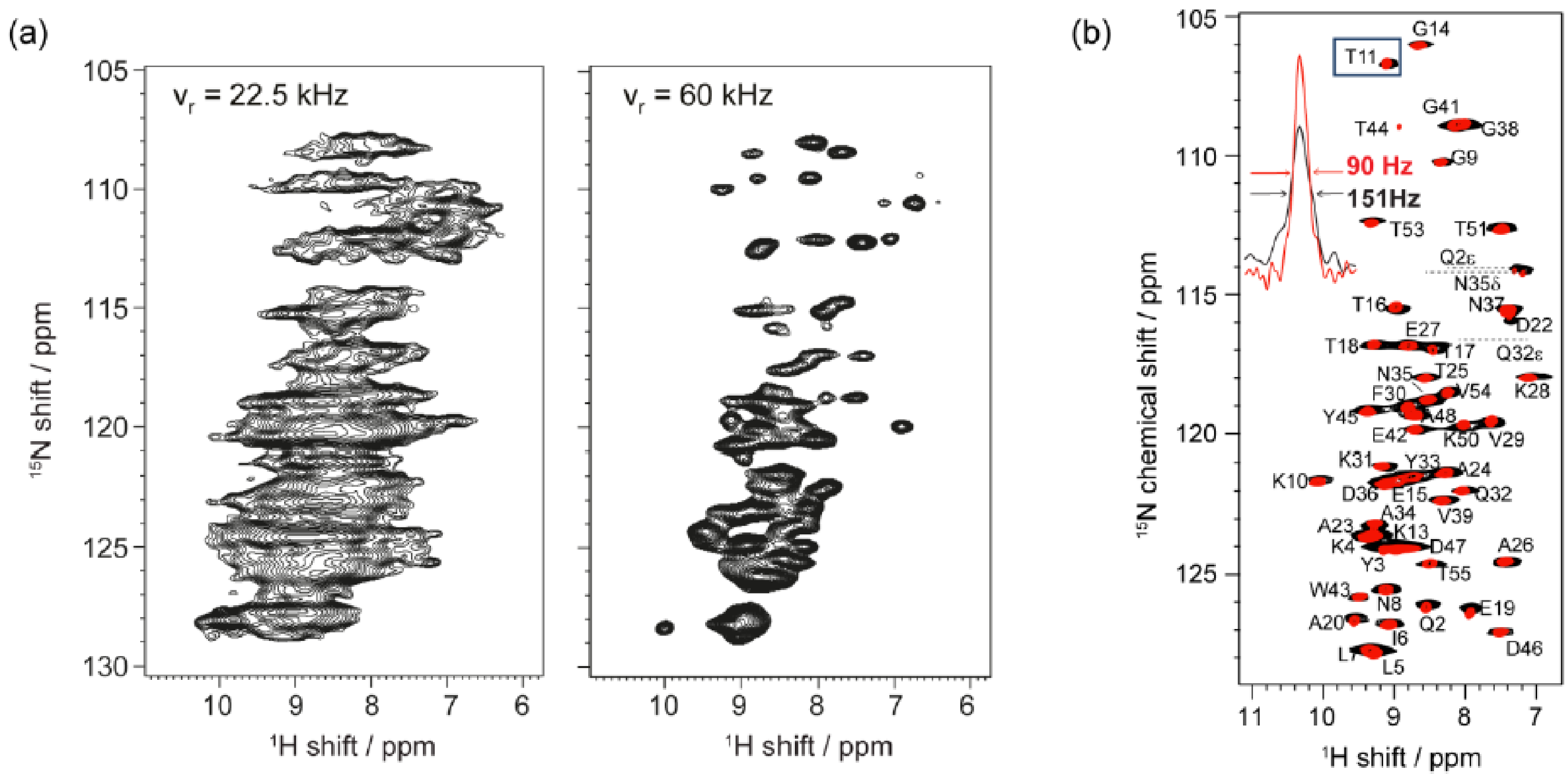


Figure 1. (a) CP-HSQC spectra at 18.8 T (800 MHz ^{1}H NMR frequency) of a fully protonated sample of single-stranded-DNA binding protein at MAS frequencies of (left) 22.5 kHz and (right) 60 kHz respectively. Note the improvement in resolution in the ^{1}H dimension, which closely reflects the ratio of spinning rates. Figure adapted from Ref. [7]. (b) ^{1}H-detected ^{15}N-^{1}H CP-HSQC spectra of a fully protonated microcrystalline sample of the protein GB1 at MAS rates of 60 kHz (black) and 111 kHz MAS (red) at ^{1}H NMR frequency of 1 GHz. Figure adapted with permission from Ref. [8].

Should we all be doing solid-state NMR?

Durham University

For

Dedicated instruments (e.g. wide-bore) rarely needed. Vast majority of experiments can be done with a 4 mm MAS probe on a 400 MHz instrument.

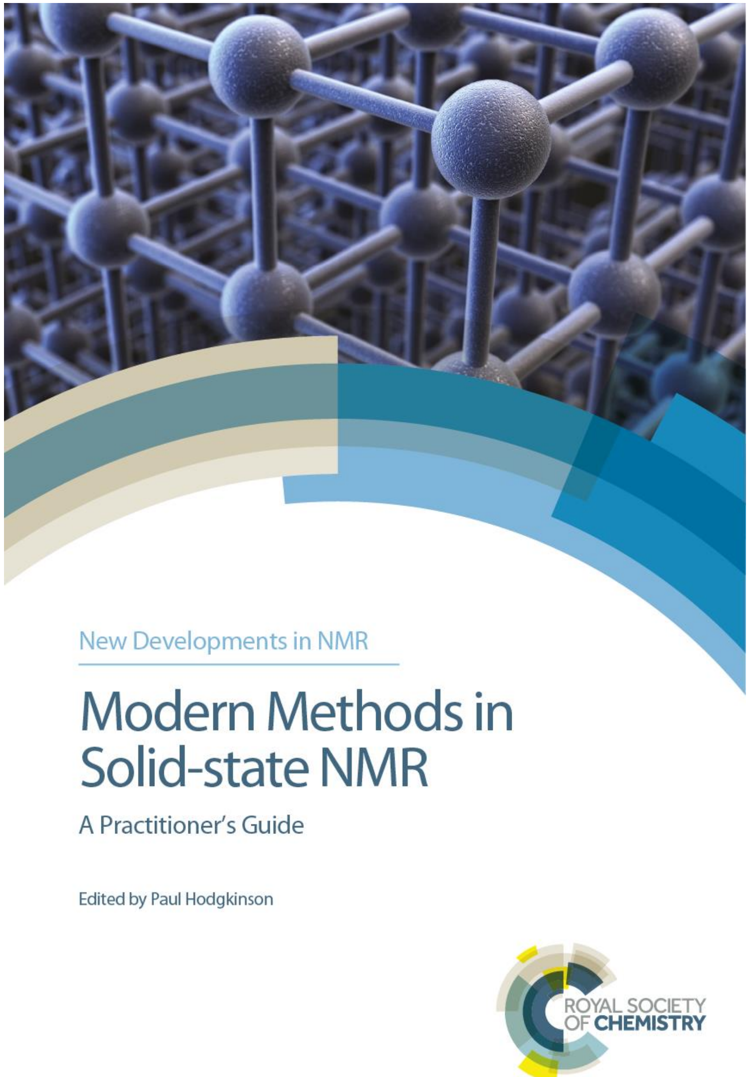
Core experiments are not hard: ^{13}C CP/MAS (number), quantitative ^{29}Si (time)

Against

Understanding the results requires expertise: more going on in NMR + complexities of solid state

Solid-state NMR is extremely diverse (quadrupolar spins e.g. MQMAS; complex materials e.g. glasses; extreme temperatures; ionic dynamics etc.)

Shameless plug 1



1. Heteronuclear correlation spectroscopy with inverse detection
2. High-resolution ^{1}H 2D MAS techniques for organic solids
3. Isotropic vs. anisotropic chemical shift separation
4. 2D methods for half-integer quadrupolar nuclei
5. Nitrogen-14 NMR
6. CODEX-based methods for studying slow dynamics
7. NMR studies of ionic dynamics in solids
8. Low-temperature NMR: techniques and applications
9. NMR at high temperature
10. Isotopically enriched systems
11. NMR studies of electrochemical storage materials
12. Disordered solids
13. Characterisation of liquid crystalline materials by separated local field methods

NB. Excluded biomolecules and DNP

Why is there no longer an EPSRC solid-state NMR service?

For 25+ years there was a simple argument for shared solid-state NMR service: avoiding costly duplication of expensive kit + expertise.

Despite growing demand and flawless reviews, "statement of need" to continue EPSRC mid-field solid-state NMR service was rejected in 2016.

Priority was supporting "flagship" facilities. Faced with two solid-state NMR facilities (850 MHz at Warwick), axing the mid-field service was "rationalising".

EPSRC did not like "free at the point of use". If you're doing worthwhile science, you can fund it through a grant! Equipment must be sustainable…

UK facilities

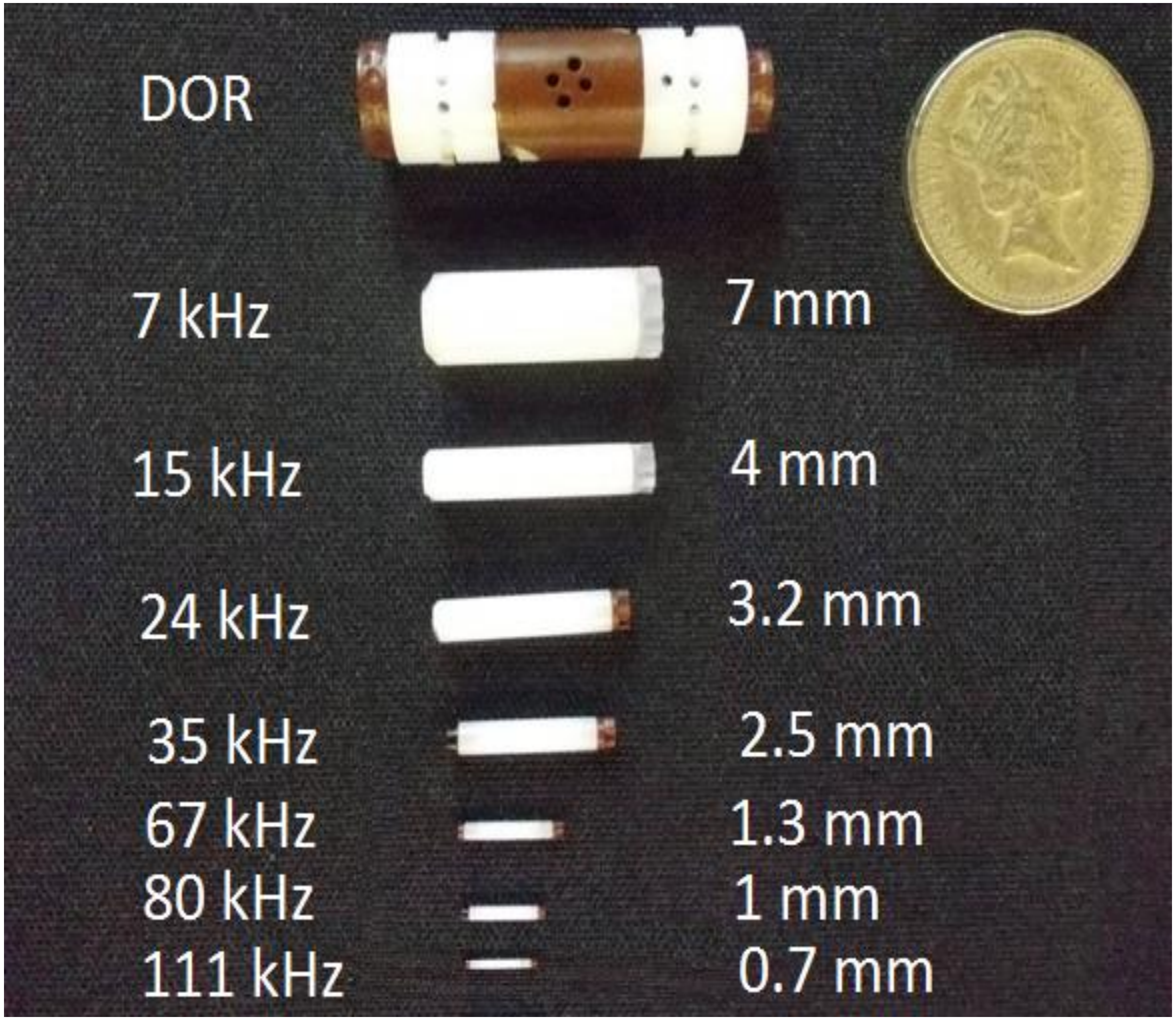
- **850 MHz Solid-State NMR Facility at Warwick**
  - Wide-range of (wide bore) NMR probes
  - Based on expert users visiting facility for allocated days
  - 80% of time allocated based on justification for high field (currently free at point of use)
  - Encouraged to apply for time on grants (£1129 per day)
  - Will host new solids-oriented 1 GHz instrument.

- **600 MHz DNP MAS Facility at Nottingham**
  - Test bed for DNP MAS
  - Low *T* MAS down to 90 K
  - Based on expert users visiting facility for allocated days
  - Some free time available, especially via collaboration
  - Encouraged to apply for time on grants (£1200 per day)

- **Durham Solid-State NMR Service** (2 x 400 MHz)
  - Continues to run on a commercial basis + academic work under contract
  - Based on samples submitted to service and interpreted results

Sample Rotation

Rotors	Volume
DOR	17 μl
7 mm	230 μl
4 mm	99 (50) μl
3.2 mm	32 μl
2.5 mm	14 μl
1.3 mm	1.5 μl
1 mm	0.8 μl
0.7 mm	0.3 μl



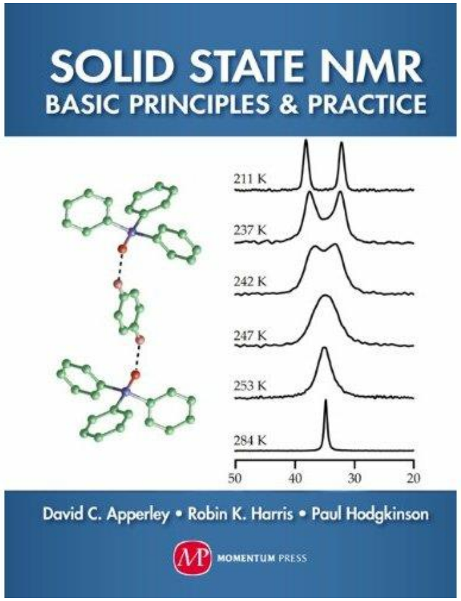
UK researchers

With some highlighted exceptions, expertise and research interests arguably more important than kit

Cambridge	Grey (energy materials; **high T capabilities**) Duer (biomaterials)
Durham	Hodgkinson (molecular organics) Johnston (energy materials)
Lancaster	Smith, Griffin, Wimperis (inorganic materials) Middleton (biomolecular)
Liverpool	Blanc (inorganic materials)
Norwich	Khimyak (molecular organics, gels)
Nottingham	Titman (methodology) Kockenberger (**DNP MAS**)
Oxford	Watts (biomolecular)
Southampton	Carravetta, Levitt (methodology; **low T capabilities?**) Williamson (biomolecular)
St. Andrews	Ashbrook (inorganic materials)
Warwick	Brown (molecular organics), Lewandowski (biomolecular) Hanna (inorganic materials) **High-field solids**

[Apologies for any omissions! There are several more sites with solid-state instrumentation, And also researchers who use solids NMR as opposed to it being their primary research interest.]

I have this problem with solid-state NMR…



Lots of good resources now available on solid-state NMR.

For research investigations, collaborate with the right specialist.

Trickier for "routine" work; encourage academics to be costing solid-state NMR on grants (e.g. Durham), noting dragons of VAT, 80% FEC etc.

What kind of solids NMR can I reasonably do myself?

Can solid-state NMR equipment be "sustainable"? (probably not)

I need to do X. Who can help?

Can anybody provide solids training?