



## Trends

## Recent technique developments and applications of solid state NMR in characterising inorganic materials

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## ABSTRACT

A broad overview is given of some key recent developments in solid state NMR techniques that have driven enhanced applications to inorganic materials science. Reference is made to advances in hardware, pulse sequences and associated computational methods (e.g. first principles calculations, spectral simulation), along with their combination to provide more information about solid phases. The resulting methodology has allowed more nuclei to be observed and more structural information to be extracted. Cross referencing between experimental parameters and their calculation from the structure has given an added dimension to NMR as a characterisation probe of materials. Emphasis is placed on the progress made in the last decade especially from those nuclei that were little studied previously. The general points about technique development and the increased range of nuclei observed are illustrated through some specific exemplars from inorganic materials science.

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**Abbreviations:** 1D, one dimensional; 2D, two dimensional; CASTEP, Cambridge serial total energy package; CP, cross polarisation; CSA, chemical shift anisotropy; CT, central transition; DEISM, direct enhancement of integer spin magnetisation; DFS, double frequency sweeps; DFT, density functional theory; DOR, double angle rotation; DQ, double quantum; DQF, double quantum filter; EFG, electric field gradient; GIPAW, gauge-including projector augmented wave; HETCOR, heteronuclear correlation; HMQC, heteronuclear multiple quantum correlation; HSQC, heteronuclear single quantum correlation; HS, hyperbolic secant; INADEQUATE, incredible natural abundance double quantum transfer experiment; INEPT, insensitive nuclear enhancement by polarisation transfer; MAS, magic angle spinning; MQ, multiple quantum; PT, polarisation transfer; QCPMG, quadrupole Carr Purcell Meiboom Gill; RAPT, rotor assisted population transfer; REAPDOR, rotational echo adiabatic passage double resonance; REDOR, rotational echo double resonance; REINE, refocused INADEQUATE spin-echo; SEDOR, spin-echo double resonance; S/N, signal to noise; ST, satellite transition; STARTMAS, satellite transitions acquired in real time MAS; WURST, wideband uniform rate and smooth truncation; VOCS, variable offset cumulative spectroscopy

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## 1. Introduction

The exact starting point of a specific area of scientific endeavour can often be difficult to pinpoint. The application of high-resolution solid state NMR to inorganic materials is probably no different, but the collaboration in the late 1970s between Engelhardt and the Tallinn Group showing that  $Q^n$  species in solid silicates could be distinguished on the basis of the  $^{29}\text{Si}$  chemical shift under MAS was a pivotal moment [1]. The book by Engelhardt and Michel provides an excellent overview of the development in that period [2]. Since then there has been a rapid expansion in the capability and use of solid state NMR and a comprehensive snapshot of the background and development of the technique in its application to inorganic materials until mid-2001 is provided by Ref. [3]. This Trends article aims to capture some of the new aspects of solid state NMR applied to inorganic materials since that point as the intervening decade has seen some further exciting, major developments in the field. The article is intended to be accessible to the non-expert, who has some background knowledge of, and is a solid state NMR user wanting to increase the use of the technique in his/her research. A number of key aspects of the technique that are to a certain extent taken for granted in 2010 were far from so a decade ago. This article examines some of those key developments, such as in hardware where for example high magnetic fields (i.e. > 14.1 T) and fast MAS (> 35 kHz) have become much more widely available, as have pulse methods built on the high-resolution MQ work of Frydman [4]. Pulsed methods with increasing sophistication to extract structural information have been developed, which exploit the fact that in solids the local J-coupling and dipolar couplings are preserved. The short-range nature of the NMR interactions means that solids, which lack long-range order (e.g. amorphous, atomically disordered crystalline systems), are amenable to investigation. A huge change in the last decade has been the ability to calculate NMR interactions from the structure, via for example DFT, and hence there is a new level of sophistication available to constrain structure from the determination of NMR interactions. To illustrate the progress that has been made the applications part is split into looking at nuclei and some exemplar materials systems that are of much contemporary interest, especially where there is much more activity than a decade ago. To make the scope of the article more manageable a clear focus is placed on examples where the NMR has been applied to simple inorganic solids (as opposed to for example organometallics where there is an increasingly rich literature) or to a key inorganic materials science problem. Where possible, reference is made to recent review articles to provide more details of a specific area.

## 2. Development of techniques applicable to solid state NMR of inorganic materials

### 2.1. Hardware

In any NMR experiment two of the key factors are the magnetic field and the probe chosen. The availability in the

mid-1990s of wide bore (89 mm) 14.1 T instruments made a huge difference to the quality of spectra from a number of key nuclei such as  $^{23}\text{Na}$  and  $^{27}\text{Al}$ , as second-order quadrupolar effects were better suppressed because of their inverse applied magnetic field ( $B_0$ ) dependence [3–6]. Higher magnetic fields also increased sensitivity, such that NMR studies of inorganic materials using insensitive nuclei, such as  $^{17}\text{O}$  became more popular [7\*]. These advantages increased still further as persistent fields of  $\geq 20$  T became more widely available, with currently the state of the art corresponding to wide bore 20 T commercial instruments, with a few higher field facilities for solids equipped with 21.1 and 23.5 T instruments, but with standard bore (57 mm) magnets. The other point about the wider availability of particularly high field magnets and appropriate MAS probes is the variable field approach to determining quadrupolar interaction parameters [3,8] becoming more widely used. The differing field dependencies of the second-order quadrupolar interaction ( $\propto B_0^{-1}$ , in Hz) and chemical shift interaction ( $\propto B_0$ , in Hz) means that measurements at two fields, with three or more preferred, much better constrain the NMR interactions determined. If the CSA, which is averaged by MAS, also needs to be determined then a combination of static and MAS measurements at differing magnetic fields is necessary. Two practical examples are shown in Fig. 1.  $^{25}\text{Mg}$  MAS at three magnetic fields (11.7, 14.1 and 18.8 T) is used to constrain and determine the isotropic chemical shift ( $\delta_{\text{iso}}$ ), the quadrupolar coupling constant ( $\chi_{\text{Q}}$ ) and quadrupolar asymmetry parameter ( $\eta_{\text{Q}}$ , see Refs. [3,5] for definition of these parameters) in  $\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$  [9]. Despite the strong overlap between these two sites the NMR parameters are well constrained by this approach. An example where CSA is also present is the  $^{93}\text{Nb}$  NMR spectra of  $\text{YNbO}_4$  where although there is clearly a large second-order quadrupole interaction, there is also significant CSA. Again data collected at multiple fields (here four) strongly constrains the interactions [10\*]. Work on constraining the NMR interaction parameters has also been pushed forward even for much studied nuclei such as  $^{23}\text{Na}$  and  $^{27}\text{Al}$ . MQ MAS techniques are now well established for resolving overlapping lineshapes from such nuclei. The retention of second-order quadrupolar and isotropic information in the different dimensions of the 2D datasets can also help separate the different NMR interaction parameters. This approach can also be used in combination with multiple field 1D datasets, including iteratively, to constrain a quantitative fit of the 1D MAS lineshape (see Section 2.5.1).

Another key variable in determining the practical limitations that MAS can be applied to is the maximum MAS rate. Increase in the maximum spinning speed has followed a decrease in diameters of the rotors available, with key steps being 5 kHz (7/7.5 mm), 15 kHz (4 mm), 25 kHz (3.2 mm) and 35 kHz (2.5 mm) by the mid-1990s. Increase in rotor speed has meant fewer spinning sidebands (although the anisotropic information conveyed by the sideband intensities can be important) producing cleaner spectra and better S/N for the same amount of sample, as well as larger ranges of interactions, especially dipolar and quadrupolar are able to be averaged to give the best possible resolution. Faster MAS has also meant that paramagnetic systems become more tractable to high-resolution techniques (Section 4.3). The major change in the last decade has been to even smaller

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