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# The complementary use of solid state NMR and XRD to solve zeolite structures

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**Abstract.** Solid state NMR is a powerful technique for the elucidation of structure in crystalline solids. In this paper I will discuss how the complementarity of NMR and X-ray diffraction can be used to improve the models available from X-ray diffraction experiments. In particular I will explain how dipolar recoupling experiments can be used to solve the structures framework materials. In addition I will discuss briefly the prospects for refinement of structural models against both NMR and XRD data at the same time.

## Introduction

Nuclear Magnetic Resonance (NMR) spectroscopy is one of the most widely-used analytical tools in the chemical sciences and one of the most powerful. For solids, the ability of NMR to obtain detailed local (atomic scale) information on structure and dynamics, without relying upon the existence of long-range order, should have resulted in widespread applications to problems in many areas of modern science. However, the anisotropic (orientation-dependent) interactions that affect NMR spectra of solids have hindered such applications, resulting in a wealth of untapped potential. Recent improvements in magnet technology, hardware and methodological development have advanced solid-state NMR to the stage where it can now be employed to provide detailed information on chemically-complex systems of industrial, biological and geological relevance. One of the most attractive features of NMR is its complementarity with diffraction techniques. Single crystal and powder X-ray diffraction of crystalline solids yield information on long range order in the material while NMR is a powerful probe of local structure. Using both techniques together has the potential to provide improved structural models compared to using any one technique in isolation. In this paper I will indicate how solid state NMR has been used to supplement information from powder X-ray diffraction to build better models for zeolite structures in particular. I will concentrate on discussing results from our own work but it should be remembered that there are many examples in the literature where diffraction and NMR have been used to probe the same materials to great effect [1-3]. Zeolites are nanoporous, crystalline solids with many industrial applications in areas as diverse as catalysis, ion exchange and medicine [4,5]. Many of their applications are intimately connected with their structural architecture and so knowledge of the arrangement of atoms in the material is of the utmost importance. Single crystal and powder X-ray diffraction have played a central part in our work, in both porous [6-8] and non-porous materials [9-11]. NMR is, however, playing an increasingly important role in these structural determinations [12-14]. I hope to indicate in the remainder of this publication what sort of information can be gleaned from solid state NMR.

## What information can NMR give?

Solid state NMR is an element specific, non-destructive probe for the study of local structural environment in materials. It has the potential to probe many different interactions that are present in solids to produce both quantitative and qualitative results. These interactions, such as scalar, dipolar and quadrupolar couplings, chemical shielding and chemical shift anisotropies hold information that can be useful in determining the structure of zeolites. The sheer number of interactions contributing to NMR spectra can, however, be a problem and many instrumental and experimental techniques can be used to remove some of these interactions. For example, magic angle spinning, perhaps the most well-known instrumental method in solid state NMR, averages out the dipolar coupling and chemical shift anisotropy to give spectra of much higher resolution, while leaving any scalar and quadrupolar couplings intact. Other techniques can be used to selectively reintroduce other interactions into the experiment, or to select only one interaction. The types of information these experiments can yield are outlined in the following sections.

### General structural and symmetry information

Many researchers during the synthesis of new materials use solid state NMR almost as a routine technique to provide general structural information. For example, for $I=1/2$ nuclei, which in zeolitic materials would most likely be $^{29}$Si or $^{31}$P, it is relatively straightforward to collect a spectrum that gives information on how many crystallographically independent nuclei are present in the sample. This information is often extremely helpful in deciding the actual symmetry of a material, especially since systematic absences from powder X-ray diffraction often do not unambiguously determine the space group on their own. For quadrupolar nuclei, those with $I>1/2$, the situation is often a little more complicated since the peaks in the NMR spectrum tend to be broader due to quadrupolar coupling that is not removed by magic angle spinning [15]. However, modern 2-D experiments such as multiple quantum (MQ) MAS NMR [16] are now relatively standard additions to the armoury of the researcher and result in increased resolution in NMR [17], which means that individual sites can be resolved even when the 1-D spectrum looks hopelessly overlapped (figure 1). In the case of zeolites the most common quadrupolar nucleus present is $^{27}$Al.

### Connectivity and scalar coupling

Another important aspect of NMR is the possibility of selecting signals that are only connected to other atoms through a bond. This makes use of the scalar (or *J*-) coupling. This is the familiar coupling all undergraduates in chemistry learn about when looking at proton spectra in solution. In the solid state, however, the observation of scalar coupling is less common as the interaction frequency is relatively small (often of the order of only a few tens of Hz). One example of where scalar coupling can be observed is in fluoride-containing pure silica zeolites (figure 2). In these materials there are often Si-F bonds present in the structure

[18, 19]. In the $_{29}$Si NMR spectrum shown in figure 2 this manifests itself, for the silicon atom directly bonded to the fluorine, as a doublet with a scalar coupling constant of 165 Hz. By using double resonance experiments where both the $_{29}$Si and $_{19}$F (I =1/2) nuclei are excited, such as INEPT, the only signal seen is that from the silicon directly bound to the fluorine. This is essentially proof of the presence of a bond between the two atoms, and is complementary to diffraction techniques where any bonding is only inferred from the average positions of the atoms (and in cases of disorder this can be misleading).

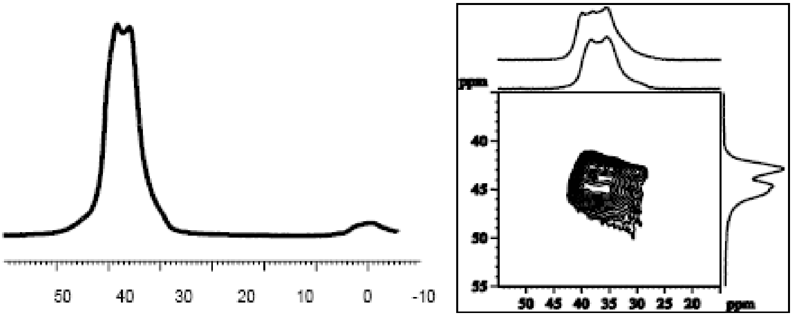

*Figure 1. One dimensional 27Al MAS NMR spectrum (top) and 27Al 2D MQMAS NMR spectrum (bottom) of calcined zeolite SSZ-51. The 1D spectrum looks at first glance to have only two peaks, however, the spectrum along the y-axes is the projection across the 2D plot showing the high resolution spectrum without the broadening from the quadrupolar interaction. This reveals that there are at least three different aluminium sites in the structure. Data from reference 17.*

Another use of the scalar coupling in NMR spectroscopy is to determine the overall connectivity of a material. In pure silica zeolites the framework is built up of $SiO_4$ tetrahedra, connected through the oxygen atoms. Two dimensional experiments such as INADEQUATE use rather complicated pulse sequences to select only signals that occur from pairs of silicon atoms that are connected through a Si-O-Si linkage [20]. The cross peaks in an INADEQUATE spectrum appear in pairs depending on the connectivity and from this spectrum it is possible to determine which silicon atoms in the framework are connected to each other. A large amount of information regarding the structure can be built up in this manner.

## Distance information – Dipolar coupling

As well as through-bond scalar coupling there is another coupling mechanism that takes place in solids which is simply dependent on the distance between two nuclei – dipolar coupling. The dependency of dipolar coupling, D, on distance is given by

$$D = (\mu_0 \gamma_A \gamma_B h)/(16 \pi^3 r^3) \qquad (1)$$

where only r, the distance between two nuclei A and B, is unknown (the other terms are all known constants). Therefore measuring the dipolar coupling between two nuclei is all that is required to measure the distance between them. Unfortunately, dipolar coupling is one of the mechanisms by which solid state NMR spectra are broadened. Magic angle spinning is designed to average dipolar coupling to zero over the course of one rotation of the sample and so removes this broadening. Much of the information on distances is contained in this broadening and much effort has been made by NMR spectroscopists to invent experiments where dipolar coupling is reintroduced but without the broadening of the spectrum.

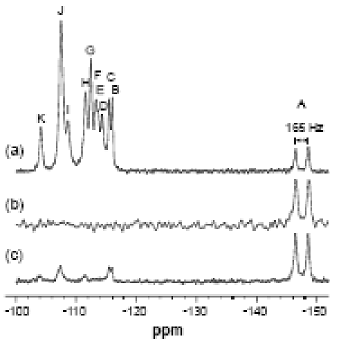

*Figure 2. Fast spinning 29Si NMR spectra of fluoride-containing zeolite STF. (a) High resolution 29Si NMR spectrum showing the doublet caused by scalar coupling to the fluoride (peak A) (b) the spectrum where the signals have been selected so those silicon nuclei only bonded to the fluorine are shown (INEPT experiment) and (c) the spectrum where the signals have been selected so that only those silicon nuclei close (but not necessarily bonded) to fluorine are shown (19F -> 29Si cross polarisation). For more information see reference 18.*

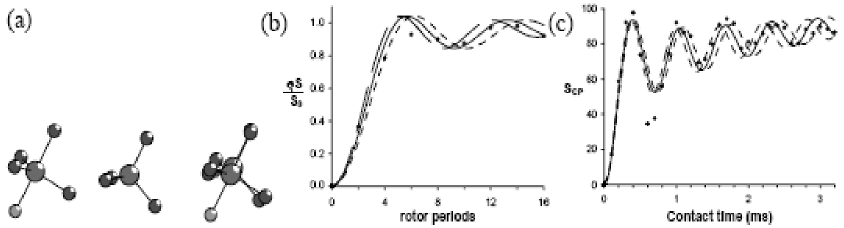

*Figure 3. In zeolite STF the fluoride is 50% occupied, leading to the XRD structure being an average of a tbp SiO4F unit and a tetrahedral SiO4. The measured XRD distance is longer than the real distance as powder XRD cannot resolve the two silicon positions (a). REDOR (b) and 19F-29Si variable contact time CP (c) both probe the local structure of the tbp unit only and the periods of the oscillation of the intensity data (S) give a dipolar coupling of 4.4 ± 0.2 kHz, corresponding to a F−Si internuclear distance of 1.72 ± 0.03 Å. See reference 18 for more details.*

There are several ways in which this can be done. Figure 3 shows two ways in which a distance can be measured in a zeolite. Zeolite-STF is a pure silica compound made in the presence of fluoride [18]. The $_{29}$Si NMR spectrum of zeolite-STF is shown in figure 2. X-ray diffraction studies located the fluoride anion in the structure, but the measured Si-F bond distance was too long at ~1.9 Å. Figure 3 shows why this should be the case. Two NMR experiments, variable contact time cross polarisation (CP) and rotational echo double resonance (REDOR) were used to find the real Si-F distance of around 1.75 Å [18]. In both variable contact time CP and REDOR the intensity of the NMR signal depends on the dipolar coupling between two nuclei. The resultant oscillation in signal intensity is easily modelled to give the dipolar coupling, and hence the distance between the Si and F nuclei in the solid. This experiment is quantitative because the Si and F nuclei constitute an isolated spin pair. If three nuclei are close together at any one time then the theory behind the measurement becomes too complex to obtain quantitative distances at the present time. However, one can still elicit qualitative information, such as for example which nuclei are closest together. REDOR in particular is now a relatively common experiment and can contribute distance information that can either confirm information provided by Rietveld refinement against powder diffraction data, or as in the case of zeolite-STF, add distance information that can be used to improve a structural model.

### Structure solution and refinement

Given the connectivity and distance information that solid state NMR provides, there is clearly the possibility of getting enough information to completely define the arrangement of NMR active nuclei in a material. In structure solution from X-ray diffraction there are three distinct steps; (i) obtaining the unit cell information (indexing), (ii) solving the structure to obtain a starting structural model and (iii) refining the structural model. Clearly NMR, as a short range technique, will not provide any direct evidence for the size of the unit cell. However, we have recently shown that information from solid state NMR can be used very successfully to obtain a good starting model [21]. The technique uses a dipolar recoupling (DQ) experiment to provide both connectivity and distance information at the same time. Two pure silica zeolite samples were used in blind tests. Powder XRD was used to obtain the unit cell and space group, and the Si-O-Si connectivity and Si-Si distances from subsequent DQ NMR experiments were used to constrain a simple grid search. The models that fitted the NMR data best were then used in Rietveld refinement against powder XRD data, and this proceeded smoothly to give the final structural model. The power of the technique is evident in the fact that the diffraction experiment for the second zeolite sample contained severe preferred orientation effects, which causes severe difficulties for structure solution from XRD but doesn't affect the NMR experiments. The distance distribution data recovered from the NMR experiments is very easy to model with a calculated function, and this can be used to complete a least squares refinement against the observed NMR data to obtain the best fit. Clearly, there is scope to obtain improved structural models by refinement against both the XRD and NMR data simultaneously and so contribute to step (iii).

## Prospects for the future

Solid state NMR is developing at a rapid pace, and as new experiments are devised it is clear that it will become a technique that plays a greater and greater part in structural determination. Perhaps its greatest advantage is its complementarity to X-ray diffraction. It is very unlikely that it will replace XRD to any great extent, but the fact that it probes the short range structures rather than long range order make it very attractive in certain situations. Perhaps its main use will still be to provide extra information that will help solve the structures from XRD, particularly in cases where XRD is problematic such as when preferred orientation is significant etc. There are still many issues to solve before NMR becomes a truly routine technique for structure determination. Many of these are, however, currently being tackled around the world. It will certainly grow in importance over the next decades.

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