

NMR: Solid State

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Introduction

Solid state NMR (SSNMR) is still a developing field in which many exciting discoveries are yet to be made. This page will be devoted to the development of Solid State NMR (SSNMR), the theory behind SSNMR, and to the experimental elucidation of structure in the solid state using NMR. While the theory of SSNMR and liquid state NMR is essentially the same, this page will be devoted to aspects of SSNMR not commonly encountered in the liquid state. Scientists primarily use liquid state NMR to understand the structure and dynamics of organic compounds. However, there are many compounds which either cannot be placed into solution or need to be studied in the solid state. Examples of such compounds are glasses, minerals, metals, and battery materials, with new solid state materials being developed daily. Common applications of SSNMR include, but are no means limited to, mechanistic understanding of ion hopping in solid state ionic conductors, short and intermediate range structure of glasses, protein structural dynamics, and quantification of configurational entropy in polymers.

The NMR Hamiltonian

When an atomic nucleus is placed in a magnetic field, the ground state will split into different energy levels proportional to the strength of the magnetic field. This effect is known as Zeeman splitting. While the Zeeman interaction is useful for identifying different types of nuclei placed in magnetic fields, structural and dynamic information may be obtained by considering other magnetic and electronic interactions coupling with the nucleus. These interactions are perturbations to the Zeeman interaction. The full NMR Hamiltonian may therefore be expressed as

$$H^{\wedge}=H^{\wedge}Zeeman+H^{\wedge}J+H^{\wedge}CS+H^{\wedge}DD+H^{\wedge}Q$$

where H_{Zeeman} is the Zeeman interaction, H_J is the J coupling, H_{CS} is the chemical shift coupling, H_{DD} is the dipolar coupling, and H_Q is the quadrupolar coupling. The relative magnitude of these interactions is shown in the table below. The Zeeman interaction is the largest, followed by the quadrupolar interactions which are on the order of MHz. The chemical shift and the dipolar coupling are on the order of kHz while the scalar coupling is the smallest which is only tens of Hz. Clearly, some of these interactions are more pronounced than others.

Interaction	Magnitude (Hz)
Zeeman	10^8
Quadrupolar	10^6
Chemical Shift	10^3
Dipole	10^3
J	10

Table 1. Magnitude of different NMR interactions

In the liquid state, the dipolar and anisotropic contribution to the chemical shift are averaged due to the molecular reorientation occurring in liquids. The averaging of these interactions gives the characteristically narrow isotropic peaks. Additionally, liquid state NMR primarily looks at spin $1/2$ nuclei (^{13}C , ^1H) which eliminates any quadrupole interactions. Only the J coupling and isotropic part of the chemical shift remains. In the solid state, molecular reorientation does not occur and the solids may have a variety of bond lengths and angles of a given chemical site. These factors broaden in the SSNMR spectrum with the broadest peaks over 1MHz wide! Many solid state systems only contain NMR active nuclei which have low natural abundances, which extend experimental time considerably. In the subsequent discussion, it will be shown through expansion of each part of the perturbations of the NMR Hamiltonian how the spectrum is affected by each contribution and what structural details can be learned from analyzing these patterns.

References

Books

1. Duer, M.J., *Solid State NMR Spectroscopy: Principles and Applications*. Blackwell Science Ltd. USA. 2002
2. Fukushima, E., Roeder, S.B.W., *Experimental Pulse NMR A Nuts and Bolts Approach*. Perseus Books Publishing, USA. 1981

Quadrupolar Coupling References

1. Freude, F., *Encyclopedia of Analytical Chemistry*. pp. 12188-12224

Outside Links

1. For useful discussions on CSA: <http://anorganik.uni-tuebingen.de/kl...ns/conventions>
2. For Quadrupol Theory and Pulse Programming: <http://www.pascal-man.com/>
3. For NMR Experiments: <http://www.grandinetti.org/Research/NMR/>
4. A Brief Introduction: http://en.wikipedia.org/wiki/Nuclear...etic_resonance

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