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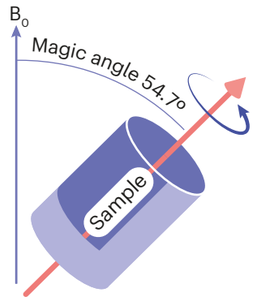
PrimeView
Solid-state NMR spectroscopy

Solid-state nuclear magnetic resonance (NMR) relies on the effect of an external magnetic field on nuclear spin interactions to elucidate atomic level details of solids and semi-solids. For high-resolution spectra that contain site-specific information, samples are physically spun at an angle (54.7°) from the applied magnetic field.

Experimentation

Samples are placed in rotors to enable magic-angle spinning (MAS) at 54.7° at speeds of 5–100 kHz.



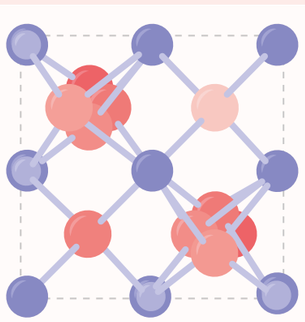
NMR spectra can be acquired for samples at natural isotopic abundance, but isotopic enrichment increases the sensitivity. Pulsed Fourier transformation NMR enables the use of radiofrequency pulses with specific timings, phases and amplitudes. These pulse sequences are used in 1D, 2D and 3D experiments to extract atomic-level structural information. Homonuclear and heteronuclear interatomic distances can be obtained by measuring dipolar couplings. Relaxation rates of magnetized nuclei are measured to determine the rates and geometry of molecular motion. Unpaired electrons can be used to increase spectral sensitivity and probe atomic-level structure by using dynamic nuclear polarization (DNP) and paramagnetic atoms.

Results

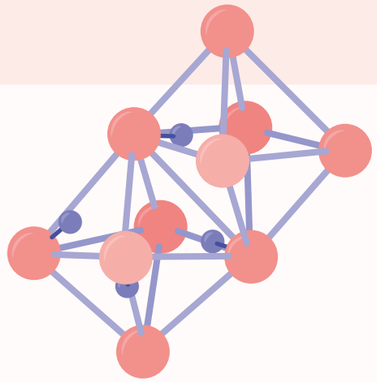
Chemical shift is key to obtaining structural and dynamic information. 1D spectra are often sufficient to characterize small molecules, but multidimensional spectra are required for characterizing complex macromolecules. Inter-atomic distances can be evaluated in qualitative, semi-quantitative or quantitative detail, depending on the pulse sequence parameters. Simulated data can help analyse molecular motion and generate structural models.

Applications

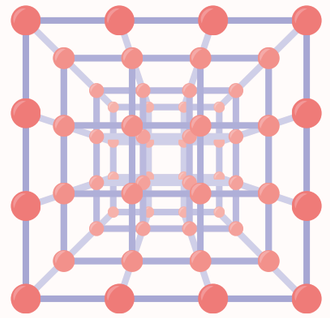
Solid-state NMR can be used to obtain atomic-level information regarding the dynamics and 3D structure of molecules in biology, chemistry and materials sciences.



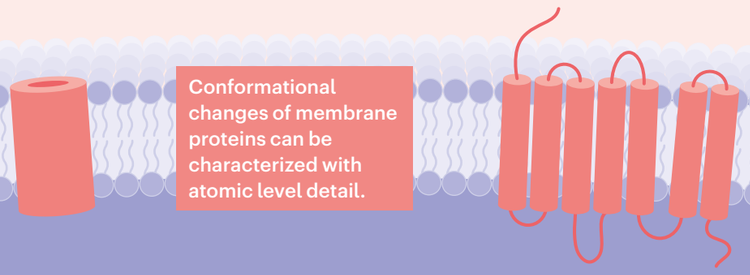
^{1}H-, ^{27}Al- and ^{29}Si-based NMR experiments coupled with simulated data can be used to probe local structure in ceramics.



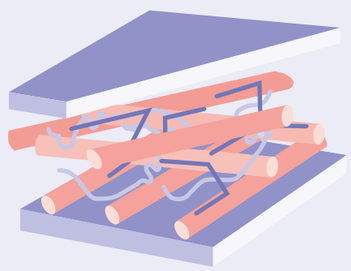
Hydration patterns in deep Earth silicates can be evaluated using random structure searching and ^{1}H, ^{17}O and ^{29}Si NMR.



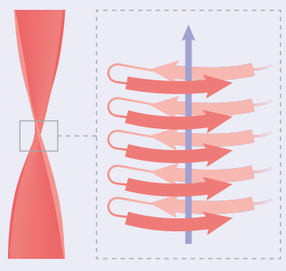
Structures of microporous and mesoporous materials.



Conformational changes of membrane proteins can be characterized with atomic level detail.



Polysaccharides and proteins that make up the complex architecture of plant cell walls can be investigated. Similarly, extracellular matrices can be evaluated.



Amyloid fibrils can result from protein misfolding. Mature fibrils as well as their dynamic intermediates can be studied to understand their role in disease.

Reproducibility and data deposition

As data acquired for a spectrum are averaged over multiple scans, solid-state NMR spectra are largely reproducible. However, differences in sample preparation and probes that influence pulse sequence parameters can affect reproducibility. Therefore, the full sample preparation conditions, as well as the data acquisition and processing parameters, are essential to document in publications. All raw data associated with published results should be deposited for open access. NMR-based structures can be deposited in databases such as the Protein Data Bank (PDB), the Cambridge Structural Database (CSD) and the Inorganic Crystal Structure Database (ICSD).

Limitations and optimizations

Low sensitivity remains a challenge in NMR spectroscopy, but advances in fast MAS and DNP experiments have enabled the acquisition of high-resolution and high-sensitivity spectra. Advances in spectral fitting and methods for interpreting NMR spectra are enabling the refinement of structures with lower computational costs.

Outlook

Higher magnetic field strength and fast MAS will continue to enable advances in solid-state NMR. New experimental methods coupled with machine learning approaches will enable more quantitative analysis of spectra for measuring distances and large-amplitude motions. In situ, in operando and in vivo NMR have become more attractive as the physical and life sciences increasingly move away from pure to complex living or operational systems. Performing experiments at higher temperatures and pressures as well as miniaturizing NMR instruments promise to expand the breadth of solid-state NMR applications across various disciplines.

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