Structural Information from Solid-State NMR

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Abstract. The application of selective averaging techniques combined with multidimensional spectroscopy to solid-state NMR structure determination is discussed. Examples include spin-diffusion and spy-diffusion experiments.

1. Introduction

Nuclear Magnetic Resonance (NMR) of solid materials can reveal detailed information about molecular and crystal structure and about dynamical processes. In the following we will examine some possibilities of characterizing structures with typical length scales in the range from atomic distances up to a few micrometers. Larger length scales can be investigated using NMR imaging methods (not discussed here, see e.g. [1]).

The magnitude of NMR interactions falls off rapidly over a few atomic distances, and the structure is reconstructed from interactions between neighboring atoms. Long-range order is of no consequence for the experiments. NMR is, therefore, a local method for structure determination and grounds heavily on the spectral resolution of signals that originate from isotopically, chemically, or crystallographically distinct sites in the solid material. Diffraction methods, in contrast, are based on the periodic arrangement of unit cells. The more long-range order (good crystals) the better the structure can be determined.

The good success of NMR structure-determination methods in biological macromolecules in the liquid phase [2][3] clearly indicates the power of local methods for the determination of atomic resolution structures even of complicated systems. The very high spectral resolution typically encountered in liquid state spectra (with a typical ratio of linewidth to resonance frequency of $10^{-10}$) is a consequence of the partial dynamic averaging of NMR interactions by the fast (on the NMR time scale) overall tumbling of the molecules in a liquid. In the solid-state, however, a straightforward (one-pulse or continuous wave) NMR experiment leads usually to a single, broad, and featureless resonance line. Starting in the late fifties [4][5], a number of schemes that selectively remove interactions and lead to high-resolution solid-state spectra have been developed [6-11]. These methods, combined with the principles of multidimensional spectroscopy [2][12-15], can be used to construct experiments that elucidate structural and dynamical properties of solid materials. A number of ingenious experiments have already been developed but much work is left to render NMR in the solid state as useful to the chemical community as liquid-state NMR already is.

The application of non-diffraction methods to structure evaluation is most useful, if the standard X-ray and neutron-diffraction techniques fail to fully determine the structure. Diffraction methods are extremely well suited to the investigation of single crystals where, in many cases, the full three-dimensional structure is obtained from a single diffraction experiment. For powdered crystalline samples, where diffraction data are averaged over the crystallographic orientations, a full three-dimensional structure is only obtained in reasonably simple samples. For disordered samples (e.g. glasses, amorphous polymers, polymer blends, ceramics), the real

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Table 1. The Information Contents of Some NMR Interactions

| Interaction         | Information contents                                                                 | Principal values | Euler angles | Relation to structure |
|---------------------|--------------------------------------------------------------------------------------|------------------|-------------|----------------------|
| Dipolar             | Internuclear distances                                                               |                  | 1           | strict               |
| Chemical Shielding  | 'Chemical environment', Coordination, Distinction of different 'sites'              |                  | 3           | approximate          |
| Quadrupolar         | Symmetry properties of environment (electric field gradient) Distinction of different 'sites' |                  | 3           | approximate          |
| J Coupling          | Connectivity through chemical bonds (via electrons), Dihedral angles.                |                  | 0(3)        | strict               |

Space information content of the diffraction data is usually limited to the radial distribution function (RDF) [16-18]. The RDF is a one-dimensional function that describes the pair correlation of the atomic positions or the centers of the electron clouds [19]. From the pair correlation functions, it is, in general, not possible to reconstruct the three-dimensional atomic arrangement.

NMR Spectroscopy provides new information not available in diffraction experiments, because it can distinguish between different 'sites' on grounds of chemical environment, coordination, local symmetry, and orientation with respect to the external magnetic field direction. The magnetic dipole-dipole interaction and the J-coupling interaction allow to establish through-space and through-bond spatial relationships between these resolved sites. This information alone can, in favorable cases, be used to reconstruct the full 3D structure of the object under investigation. In disordered solids, a complete structure determination is not feasible, but valuable information, often complementary to the one obtained by diffraction, can be provided.

Similar techniques can also be employed to obtain information about slow motional processes in solids. An overview over these techniques is found in [20].

2. Information Contents and Symmetry of NMR Interactions in Solids

While the Zeeman interaction with the external magnetic field $B_0$ provides only atom-type and isotope-type resolution, detailed information about the structure and dynamics of the sample is reflected in the weaker internal interactions [7][8], namely the chemical shielding $\sigma$, the $J$ coupling, and the magnetic dipole-dipole interaction, and for nuclei with a spin quantum number larger than $\frac{1}{2}$; the nuclear electric quadrupole interaction. All of these interactions are, in the solid state, anisotropic and depend on the orientation of the molecule-fixed coordinate system with respect to the magnetic field. As a simple illustration, we consider the chemical shielding (CS) tensor. The spin of a given nucleus $k$ in a sample does not experience exactly the externally applied magnetic field $B_0$ but a field $B = B_0 + B_s$ slightly modified in magnitude and direction due to the shielding of the external field by the neighboring electron density (see also Table 1). The additional field $B_s$ is related to the applied field $B_0$ through the chemical shielding tensor $\sigma(k)$: $B_s^k = \sigma(k) B_0$. In matrix notation, we find (for the static field along the $z$ axis):

$$
\begin{bmatrix}
S_x^k \\
S_y^k \\
S_z^k
\end{bmatrix} =
\begin{bmatrix}
\sigma_{xx}(k) & \sigma_{yx}(k) & \sigma_{xz}(k) \\
\sigma_{xy}(k) & \sigma_{yy}(k) & \sigma_{yz}(k) \\
\sigma_{xz}(k) & \sigma_{yz}(k) & \sigma_{zz}(k)
\end{bmatrix}
\begin{bmatrix}
0 \\
0 \\
B_0
\end{bmatrix}
$$

The NMR spectrum is only sensitive to the symmetrical part of the chemical shielding tensor [8] which can be characterized by six parameters (e.g. $\sigma_{xx}^{(k)}$, $\sigma_{yy}^{(k)}$, $\sigma_{zz}^{(k)}$, $\sigma_{xy}^{(k)}$, $\sigma_{xz}^{(k)}$, and $\sigma_{yz}^{(k)}$). $\sigma^{(k)}$ can be diagonalized by a rotation matrix $R$:  

$$
\begin{bmatrix}
S_x^k \\
S_y^k \\
S_z^k
\end{bmatrix} =
R
\begin{bmatrix}
\sigma_{xx}^{(k)} & \sigma_{yx}^{(k)} & \sigma_{xz}^{(k)} \\
\sigma_{xy}^{(k)} & \sigma_{yy}^{(k)} & \sigma_{yz}^{(k)} \\
\sigma_{xz}^{(k)} & \sigma_{yz}^{(k)} & \sigma_{zz}^{(k)}
\end{bmatrix}
R^{-1}
\begin{bmatrix}
0 \\
0 \\
B_0
\end{bmatrix}
$$
where $(\alpha, \beta, \gamma)$ denote Euler angles. It is
often convenient to describe the CS tensor
by the isotropic average $\bar{\sigma}^{(k)}$, the anisotro-
py $\delta^{(k)}$ and the asymmetry $\eta^{(k)}$:

$$\bar{\sigma}^{(k)} = \frac{\sigma_{xx}^{(k)} + \sigma_{yy}^{(k)} + \sigma_{zz}^{(k)}}{3}$$

$$\delta^{(k)} = \sigma_{zz}^{(k)} - \sigma^{(k)}$$

$$\eta^{(k)} = \frac{\sigma_{yy}^{(k)} - \sigma_{xx}^{(k)}}{\delta^{(k)}}$$

and by the three Euler angles $\alpha^{(k)}$, $\beta^{(k)}$, $\gamma^{(k)}$ that
relate the principal axis system (PAS) of the
tensor to the laboratory coordinate
system. The CS tensor can be decomposed
into components according to the behav-
ior under rotations of the coordinate sys-
tem (the rank $k$). The rank 0 component
that transforms like a scalar (is invariant
under any rotation $R$) is called the isotro-
pic chemical shielding, the rank 2 contribu-
tions (that transform like a vector) are irre-
sent as they correspond to the asym-
metrical part of the CS tensor, and the rank
2 contributions are often denoted as the
chemical shielding anisotropy (CSA) ten-
sor, as they express the spatial anisotropy
and asymmetry of the CS tensor. The
components $A_{kk}$ of the rank $k$ tensor $A_k$ in its
principal axis system are easily obtained
from $\sigma^{(k)}$, $\delta^{(k)}$, and $\eta^{(k)}$ by the relations $A_{00} = -\sqrt{3} \bar{\sigma}^{(k)}$, $A_{20} = \sqrt{2} \delta^{(k)}$, and $A_{22} = \delta^{(k)} \eta^{(k)}/2$. No components of rank larger
than two are found for the basic NMR
interactions. If, however, a quadrupole
interaction that is not very much smaller
than the Zeeman interaction is present,
fifth (and higher) rank contributions are
introduced. The NMR spectra depend usu-
ally only on the $A_{00}$ tensor components in
the laboratory frame of reference. For sec-
ded rank interactions,

$$A_{20} = \sqrt{2} \delta^{(k)} [\frac{1}{2}(3 \cos^2 \beta^{(k)} - 1) +$$

$$\frac{1}{2} \sin^2 \beta^{(k)} \cos 2 \alpha^{(k)}]$$

is obtained. The an-
gles $-\alpha$ and $-\beta$ correspond to the polar
angles of the magnetic field vector in the
PAS of the interaction considered and the
orientational dependence of the interaction
can be graphically represented as shown in
Fig. 1, where the size of the interaction for a
given orientation of the magnetic field vector
relative to the PAS is the length of the vector
from the origin of the PAS to the indicated surface. For axi-
ally symmetric tensors ($\eta = 0$) each reso-
nance frequency in the powder pattern
found in the NMR spectrum can be as-
signed unambiguously to a single orienta-
tion of the unique principal axis of the
tensor and the direction of the static mag-
netic field (characterized by the Euler
angle $\beta$). This assignment is illustrated in
Fig. 2. For $\eta \neq 0$, the assignment is, in
general, not unique.

Table I presents an overview of NMR
interactions. Geometrical information is
provided by the two-spin interactions,
mainly the dipolar interaction that yields
the 'through-space' distances and the $J$
coupling that indicates that the coupled
nuclei are connected through one (or sev-
eral) chemical bonds. The one-spin inter-
actions (chemical shielding and quadru-
pole interactions) are primarily useful to

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig1.png}
\caption{Graphical representation of the orienta-
tional dependence of a second-rank NMR inter-
action. Note that the lobe along the $z$-axis and
the lobe in the $xy$-plane have a different sign, leading
to a vanishing isotropic average.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig2.png}
\caption{Correspondence between the Euler angle $\beta$ and the resonance frequency for an axially
symmetric CSA tensor}
\end{figure}
provide the spectral resolution of different sites and to provide a coordinate system for correlation experiments. Through empirical rules (see e.g. [8],[21]) the one-spin interactions can characterize the chemical identity, coordination number, and local symmetry of a site. The symmetry properties of these four interactions under rotations in real space (sample rotations) are indicated in Table 2. Similarly, the behavior of the interactions under rotations in spin space (application of radiofrequency pulses) can be characterized (see Table 3).

3. 2D Correlation Maps and Spin Diffusion

In a one-dimensional NMR experiment of a disordered or polycrystalline sample, the orientational information contained in the Euler angles that relate the PAS of a one-spin interaction and the laboratory coordinate system cannot be exploited, because the measured magnetization is an isotropic average over all possible orientations. In a two-dimensional experiment, it is, however, possible to determine the relative orientation of different sites, provided a mechanism for polarization transfer between the sites exists.

The basic scheme for such an experiment is shown in Fig. 3. During the evolution time \( t_1 \), the initial state of the magnetization is characterized. Each site is labelled by its resonance frequency. During the mixing time, the magnetization is transferred to neighboring sites (see below) whose resonance frequency is determined during the detection time \( t_2 \). As illustrated in Fig. 3, the resulting 2D frequency-domain spectrum provides a pair-correlation map of sites that can exchange their magnetization. The correlation map for a disordered sample where the PAS takes all possible orientations with respect to the external field, is sketched in Fig. 4. For simplicity, it describes the correlation between two sites only. The CS tensors are assumed to be axially symmetric with identical principal values. The principal axis systems, however, differ. The relative tensor orientation (the relative orientation of the two PAS) for this special case is characterized by a single Euler angle \( (\beta) \), that can be evaluated from the pair-correlation map. The correlation of two general second rank tensors allows for the determination of three Euler angles, the correlation of a general with an axially symmetric tensor for two Euler angles and the correlation of two axially symmetric tensors for one Euler angle.

| Interaction            | Spatial symmetry |
|------------------------|------------------|
| Dipolar                |                  |
| Chemical Shielding     |                  |
| Quadrupolar            |                  |
| \( J \) Coupling       | difficult to observe |

Table 2. Symmetry Properties of NMR Interactions under (Spatial) Sample Rotations

| Interaction            | Symmetry under spin rotations |
|------------------------|-------------------------------|
| Dipolar                |                               |
| Chemical Shielding     | yes                           |
| Quadrupolar            | yes                           |
| \( J \) Coupling       | yes                           |

Table 3. Symmetry Properties of NMR Interactions under Spin Rotations

A mechanism for the exchange of magnetization between neighboring sites can be provided by the \( J \) coupling or the dipolar interaction, the latter typically being stronger by two to three orders of magnitude. In a complicated network of many coupled spins, the spatial evolution of the magnetization is approximately described by a diffusion equation.

The 2D CS-tensor correlation spectrum of a powder sample of crystalline benzoic acid, \(^{13}\)C enriched at the carboxylic position, is reproduced in Fig. 5. The spectra have been recorded at long mixing times where spin diffusion has proceeded to completion and represent a pair-correlation map of nuclei that belong to the same microcrystallite. Benzoic acid crystallizes in the space group \( P2_1/c \) with two centrosymmetric dimers per unit cell. As a consequence of the center of symmetry, carbon sites within the same dimer are not distinguishable by NMR (see Table 2 where the symmetry of the interaction is given). Dimers that are related by the two-fold screw axis have CS-tensors with identical principal values but different principal axis directions. From the spectra of Fig. 5, the three Euler angles between the PAS at the two sites can be extracted by a least-squares fit of the experimental lineshape [22]. The best fit is shown in Fig. 5.
It is illuminating to describe the relative tensor orientation as a rotation by an angle $\phi_p$ around an axis specified by the polar coordinates $\theta_p$ and $\phi_p$. These three parameters are listed, as a function of temperature, in Table 4. It is apparent that, within experimental error, the angle $\phi_p$ equals $180^\circ$ for all temperatures as expected from the crystallographic screw axis. The strong temperature dependence of $\phi_p$ is a consequence of the tautomeric dynamic equilibrium depicted in Fig. 6 and can be exploited to determine the asymmetry of the double-minimum potential (Fig. 6) to $418 \pm 128$ J/mol [23].

### 4. Selective Averaging

In the above example, the spectral resolution has been obtained through selective isotopic enrichment. In a non-enriched sample, strong overlap between the seven chemically nonequivalent carbon sites in a dimer prevents a simple analysis of the experimental spectra.

Andrew and coworkers [4] and Waugh and coworkers [5] were the first to realize that the symmetry properties of the NMR interaction under rotations in real space and in spin space can be exploited to selectively average out parts of the interactions while retaining others. The discussion of the symmetry properties of the spin- and spatial tensors provides an elegant illustration of the possibilities of selective averaging [10][11]. Cyclic motions in either space are described by a subgroup of the full rotation group in three dimensions, SO(3). The averaging of terms of rank $k$ according to the symmetry of the motion has been discussed by Pines and coworkers [10][11]. Some results are summarized in Table 5. Averaging in spin space is usually obtained by multiple pulse sequences that, most often, correspond to averaging over a number of discrete orientations in spin space. In real space, however, it is technically most favorable to perform the averaging by a continuous motion of the sample in three-dimensional space. The best known example is magic angle sample spinning where an octahedral symmetry is obtained by a continuous motion around an axis inclined by $54.74^\circ$ with respect to the static magnetic field. Recently, two ingenious continuous schemes to obtain icosahedral symmetry have been developed, double angle spinning [24] and double rotation [25]. It should be pointed out that averaging in spin space and real space is usually not equivalent. The chemical shielding interaction, e.g., is reduced to its isotropic value by appropriate spatial averaging, whereas the chemical shielding interaction is eliminated altogether by spin-space averaging.

### 5. Spin Diffusion

As already mentioned, spin diffusion provides a mechanism to correlate sites in spatial proximity. The so-called flip-flop term of the dipolar Hamiltonian $\hat{H}_{12} = I_1^z I_2^z + I_1^x I_2^x$ exchanges the polarization (magnetization) of two spins with a rate constant $W$, proportional to the square of the dipolar interaction (the inverse sixth power of the internuclear distance $r$) and to the probability that the two spins have the same resonance frequency.
\[ W = \frac{2 \gamma^2 \gamma}{32 \pi r^4} \theta \theta (0) \] (4)

Refers to spin-diffusion spectra of benzoic acid as a function of temperature. Experimental spectra are given on the left (a–c), the best theoretical fit to these spectra to the right (d–f) (adapted from [23]).

\[ \gamma \text{ denotes the gyromagnetic ratio and } g(0) \text{ is a measure for the probability that the two spins have the same resonance frequency [26]. The second contribution is roughly equivalent to the overlap between the resonance lines of the two sites. Spin diffusion is a rather slow process. The highest diffusion constants are found for abundant spins with high gyromagnetic ratio and small chemical shielding differences (e.g. protons) where typical diffusion constants } D = \frac{W r^2}{6} \text{ of the order of magnitude } 10^{-12} \text{ cm}^2/\text{s are found [27]/[28]. In 1 s, the transport of magnetization extends over ca. a hundred inter-atomic distances. Lower isotopic abundance (larger internuclear distances), lower gyromagnetic ratios and better spectral separation.} \]

Table 4. Angles Connecting the PAS of the Carboxyl $^{13}$C CSA Tensors in the Two Magnetically Inequivalent Sites of Benzoic Acid (from [23])

| T/K  | $\theta_\gamma$/deg | $\Phi_\gamma$/deg | $\rho_\gamma$/deg |
|------|----------------------|-------------------|------------------|
| 305  | 133.3±0.5            | -15.6±1.8         | 180.0±2.4       |
| 100  | 132.2±0.6            | -0.5±3.2          | 178.1±4.3       |
| 71   | 130.5±0.8            | 3.8±3.2           | 179.6±4.1       |
| 32   | 129.9±0.8            | 16.4±2.5          | 179.9±3.2       |
| 13   | 130.8±0.8            | 15.4±2.8          | 179.5±3.7       |

Table 5. Averaging of Tensor Interactions of Rank k by Symmetry Operations under Relevant Subgroups of the Full Rotation Group

| Symmetry | Tensor Ranks that Survive Averaging |
|----------|-------------------------------------|
| Tetragonal | $D_4$ | 0 | 2 | 4 |
| Tetrahedral | $T$  | 0 | 4 |
| Octahedral | $O$  | 0 | 4 |
| Icosahedral | $I$  | 0 |
| Spherical | $SO(3)$  | 0 |
Table 6. Averaging Schemes Applied in the Experiment of Fig. 7

| Averaging Scheme       | Evolution                  | Mixing                      | Detection                  |
|------------------------|----------------------------|----------------------------|----------------------------|
| Interactions Averaged  | MAS (spatial)              | RF-Irradiation (spin-space) | MAS (spatial)              |
| Remaining Interactions | Isotropic Chemical Shielding| Dipolar Interaction         | Isotropic Chemical Shielding|

The asymmetry of the potential is a consequence of crystal packing forces [39].

degrade the spin-diffusion rate. Furthermore, in resolved spectra, the diffusion rate is a function of the chemical shielding difference between the involved nuclei and can be too low to be observed in well resolved spectra. To enhance the spin-diffusion rate in the case of resolved spectra and to render it independent of the spectral parameters, a number of driven spin-diffusion schemes have been developed [29-33]. These methods use an external 'heat bath' to provide the necessary energy for a flip-flop transition in a coupled spin pair.

Proton spin diffusion is particularly useful to investigate structures with relatively large mean distances between sites, e.g. the miscibility of polymer blends [28][34], while the observation of driven spin diffusion between rare spins (e.g. $^{13}$C) is useful to establish the relative orientation of neighboring units in disordered systems and for systems where the resolution in the proton spectrum is not sufficient. Fig. 7 shows an rf-driven spin-diffusion spectrum (using a continuous wave spin lock) of a macroscopic and a molecular mixture of adamantane and hexamethylethane. To obtain the desired spectral resolution during evolution and detection and to facilitate spin diffusion during mixing, selective averaging schemes have been applied during the three periods as shown in Table 6. During evolution and detection, MAS is employed to obtain high-resolution spectra. During mixing when spin diffusion takes place, the spatial averaging by MAS is inhibited by an alignment of the spinning axis parallel to the direction of the static magnetic field [33]. From the presence of spin-diffusion cross-peaks between the two components in one of the two samples and from their absence in the other it is obvious that the two components are once mixed on a molecular level and well separated in the other case.

For isolated pairs of spins, the magnetization transfer is oscillatory and the oscillation frequency can be used to determine the internuclear distance. Of particular interest in this context are MAS experiments (rotational resonance) that allow for accurate distance determinations in doubly labelled samples [30][35][36].

6. Spy Diffusion

In the preceding chapter, the 'diffusion' of magnetization between spins that remain at a fixed position (spin diffusion) has been exploited. Spin diffusion is limited to investigations that involve distances smaller than ca. 100 nm. As an alternative to these experiments, it is possible to introduce mobile magnetic 'spy' nuclei and to follow their spatial diffusion. Due to its high polarizability, its chemical inertness and the relatively high gyromagnetic ratio, $^{129}$Xe is a particularly suitable spy nucleus. The chemical shielding of xenon depends on its chemical environment. It is, e.g., easily possible to distinguish Xe dissolved in poly(methyl vinyl ether) and polystyrene. This chemical shielding difference provides the necessary resolution to monitor the diffusion of xenon atoms (carrying their magnetization) between the components of the blend obtained from the polymers mentioned above. Using the exchange scheme of Fig. 3, the diffusion of xenon in a laminar blend of the two polymers has been investigated [37]. The 2D exchange spectrum for different mixing times is shown in Fig. 8. From the buildup of the cross-peak intensity, the exchange rate constant $k$ can be determined which, for a laminar blend, is related to the thickness $d$ of the lamella by the relation
where the effective diffusion constant can be computed from to the diffusion constants of the pure components \( D_a \) and \( D_b \) and their populations \( p_a \) and \( p_b \) by:

\[
D_{\text{eff}} = \frac{2p_a D_a p_b D_b}{p_a D_a + p_b D_b}
\]

Similar experiments have also been performed in 'regular' polymer blends [38].

7. Summary

The combination of selective averaging techniques with multidimensional spectroscopy allows for the development of solid state NMR experiments that provide structural information in the range from atomic distances up to a few micrometers. Promising applications in particular to amorphous and vitreous samples and to partially disordered crystalline materials have already been performed or can be envisioned.

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