

1 Introduction

Background

Solid-state NMR has during the past decade played a key-role in structural investigations of inorganic materials such as zeolites (1, 2), glasses (1), and heterogeneous catalysts (3). High-resolution techniques like magic-angle spinning (MAS) NMR have in particular been used to provide the desired information. More recently and following considerable methodological developments, solid-state NMR is becoming a useful tool for structure elucidation of proteins where dipolar couplings (4) and torsion angles (5) are obtained from MAS NMR of polycrystalline samples or from oriented samples (6).

While spin $I = 1/2$ nuclei (e.g., ^1H , ^{13}C , ^{15}N , ^{29}Si , ^{31}P) are typically used as probes in NMR studies of biological samples, studies of quadrupolar nuclei (spin $I > 1/2$) with half-integer spin (e.g., ^{17}O , ^{23}Na , ^{27}Al , ^{51}V , ^{59}Co , ^{67}Zn , ^{87}Rb , ^{95}Mo , and ^{133}Cs) are often more relevant for structural studies of inorganic solids. Most quadrupolar nuclei are associated with quite strong quadrupole coupling interactions which cause the powder spectra to extend over a large frequency range. For small or intermediate quadrupole couplings (C_Q 's) the spectrum resulting from all single-quantum transitions will normally be observable and with the first-order quadrupolar interaction dominating the satellite transitions. For large C_Q values only the central transition is observed (as this transition is not affected by the first-order quadrupole coupling) and is influenced by the second-order quadrupole coupling interaction. MAS averages all first-order interactions and thus splits the first-order quadrupolar line shape into an envelope of discrete spinning-sidebands (ssb's) (7), thereby increasing the resolution and sensitivity of the spectrum. Contrary, the

second-order quadrupolar line broadening (which is a fourth rank tensorial interaction in contrast to the first-order interactions which are of rank two) is only reduced (but not averaged) by MAS. Thus, even with MAS the resulting second-order quadrupolar broadening will often complicate the spectra to an extent where a spectral interpretation becomes impossible, e.g., in the presence of multiple overlapping sites. Therefore one of the great challenges in solid-state NMR is to achieve high-resolution spectra of half-integer quadrupolar nuclei influenced by the second-order quadrupolar line shape. Some of the approaches are (i) spatial (mechanical) or (ii) spin (pulse) manipulations of the sample, and (iii) increasing the magnetic field strength.

Three major approaches have been developed for elimination of the second-order quadrupolar line shape by spatial manipulations of polycrystalline samples. First, the zero-field (ZF) NMR method (8–16) was developed, in which the magnetization is created in the magnet but evolves outside the magnetic field. This eliminates the spatial encoding and thereby the second-order powder pattern caused by the different crystallite orientations similarly to the NQR technique (17). Second, Llor and Virlet (18) described the dynamic-angle spinning (DAS) technique theoretically while it was realized experimentally by the Pines group (19–22). This technique employs two spinning axes during different periods of the indirect dimension of a 2D NMR experiment and eliminates all anisotropic terms of the second-order quadrupolar Hamiltonian. Third, Samoson, Lippmaa, and Pines (23) developed the double rotation (DOR) NMR technique which employs simultaneous sample spinning about two axes (21–24). In contrast to DAS, the DOR technique allows direct detection of the isotropic signal. It is common for all three methods, however, that they require a quite sophisticated experimental setup.

Tycko presented a pulse sequence that provided ZF NMR spectra solely at high field strength (25–28). Although very appealing, this type of experiments have never been convincingly demonstrated for quadrupolar nuclei. More popular

and generally applicable is the multiple-quantum MAS (MQ-MAS) experiment recently developed by Frydman and Harwood (29) and further improved by numerous groups (30–37). This experiment utilizes MAS along with combined multiple- and single-quantum coherence evolutions to obtain an isotropic spectrum in the indirect dimension of a 2D experiment.

Finally, considering that the second-order quadrupole coupling interaction is inversely proportional to the magnetic field strength (B_0), a spectral simplification may be achieved by increasing the field. Much attention has been paid to the development of super-conducting magnets, mainly because the NMR sensitivity is proportional to $B_0^{3/2}$, and magnets with high magnetic field strengths of $B_0 = 18.8$ T ($\nu_0(^1\text{H}) = 800$ MHz) are now available.

As the CSA interaction is proportional to the magnetic field strength the use of very high magnetic field strengths introduces the CSA interaction in addition to the quadrupole coupling for many quadrupoles. Analysis of powder spectra in terms of the combined effect of quadrupole coupling and CSA was introduced by Baugher and co-workers (38, 39) on the assumption of coincident principal axis systems for the two interactions. Recently this method has been applied to systems where the principal axis systems are non-coincident (40–45). Skibsted *et al.* (46–49) demonstrated that this information may be extracted from the intensities of the ssb's of all transitions, and more recently these parameters have been determined from analysis of the line shape for the central transition in MAS spectra when the second-order quadrupolar line shape is present (50, 51).

Single-Crystal NMR Spectroscopy

In this thesis I shall focus mainly on single-crystal (SC) NMR which is an alternative to NMR of polycrystalline samples as it employs a single-crystalline sample. By acquisition of spectra for different orientations of the crystal it is possible to determine not only the magnitude of the solid-state NMR tensors but also their ori-

entation with respect to the molecular/crystal frame. The latter feature is unique to SC NMR, and has traditionally been the main reason for using SC NMR instead of powder methods (52, 53). However, single-crystal NMR is normally considered elaborate, experimentally sophisticated, and a method that requires large crystals in order to avoid excessively long spectrometer time. Therefore it has been of interest to develop new methods for determining the interaction parameters from polycrystalline samples.

However, SC NMR has an intrinsic high resolution as there is no powder line shapes but only discrete (and quite narrow) resonances in SC NMR spectra. Moreover, this technique is insensitive to intensity distortions caused by imperfect pulse excitation or resulting from a distorted base line as the analysis of SC NMR spectra relies only on the location of the discrete resonances and not on their intensities. This is in contrast to the powder methods from which the interaction parameters are determined from iterative fitting of the powder line shape or ssb intensities.

Most important, SC NMR provides a unique possibility for separation of multiple simultaneous interactions. For example, it has been demonstrated for half-integer quadrupoles with small and intermediate quadrupole coupling constants that the quadrupole coupling parameters may be determined with a high degree of precision from the first-order quadrupolar splitting of the satellite transitions while the central transitions is mainly influenced by the CSA interaction (54–56). Moreover, as discussed in the following chapters these two interactions may also be separated from the central transition alone (57).

I shall demonstrate that we may take full advantage of the unique features of SC NMR described above for determination of very precise and reliable interaction parameters. Moreover, by the use of high-sensitivity SC NMR probes and automation for the rotation of the crystal, SC NMR is a method that is no more time-consuming than the powder methods, neither experimentally nor for the analysis.