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Journal of Magnetic Resonance 188 (2007) 246–259
JMR Journal of Magnetic Resonance
www.elsevier.com/locate/jmr

Determination of NMR interaction parameters from double rotation NMR

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Received 30 May 2007; revised 18 July 2007
Available online 3 August 2007

Abstract

It is shown that the anisotropic NMR parameters for half-integer quadrupolar nuclei can be determined using double rotation (DOR) NMR at a single magnetic field with comparable accuracy to multi-field static and MAS experiments. The ^{17}O nuclei in isotopically enriched L-alanine and OPPh$_3$ are used as illustrations. The anisotropic NMR parameters are obtained from spectral simulation of the DOR spinning sideband intensities using a computer program written with the GAMMA spin-simulation libraries. Contributions due to the quadrupolar interaction, chemical shift anisotropy, dipolar coupling and J coupling are included in the simulations. In L-alanine the oxygen chemical shift span is 455 ± 20 ppm and 350 ± 20 ppm for the O1 and O2 sites, respectively, and the Euler angles are determined to an accuracy of ±5–10°. For cases where effects due to heteronuclear J and dipolar coupling are observed, it is possible to determine the angle between the internuclear vector and the principal axis of the electric field gradient (EFG). Thus, the orientation of the major components of both the EFG and chemical shift tensors (i.e., V_{33} and δ_{33}) in the molecular frame may be obtained from the relative intensity of the split DOR peaks. For OPPh$_3$ the principal axis of the ^{17}O EFG is found to be close to the O–P bond, and the ^{17}O–^{31}P one-bond J coupling ($^1J_{OP} = 161 \pm 2$ Hz) is determined to a much higher accuracy than previously.

Keywords: Solid-state NMR; Double rotation; Quadrupolar interaction; Chemical shift anisotropy; J-coupling; Dipolar coupling; Oxygen-17

1. Introduction

In recent decades, solid-state NMR has developed into an extremely important technique for the characterization of structure and dynamics in condensed matter at an atomic scale. However, the majority of solid-state NMR research has focused on the study of spin $I = 1/2$ nuclei, such as, ^{1}H, ^{13}C, ^{15}N, etc., rather than nuclei of higher magnetic spin $I > 1/2$, although these nuclei constitute ~75% of the NMR-active nuclei in the Periodic Table. Part of the reason for this is the presence of an electric quadrupole moment for nuclei with spin $I > 1/2$ which interacts with any traversing electric field gradient (EFG), giving rise to the quadrupolar interaction (QI). The QI produces broadening which severely worsens the resolution of resonances. Various techniques have been devised in order to regain high-resolution/isotropic NMR spectra for half-integer quadrupolar nuclei ($I = 3/2$, 5/2, 7/2, 9/2) [1], namely, double angle rotation (DOR) [2,3], dynamic angle spinning (DAS) [2,4], multiple quantum magic angle spinning (MQMAS) [5–7] and satellite transition (ST) MAS [8,9]. The former two techniques require dedicated equipment, whereas the latter two can be achieved using standard (commercial) solid-state NMR equipment. Therefore, since their inception MQMAS and STMAS have seen much greater popularity amongst researchers aiming to obtain isotropic NMR spectra of quadrupolar nuclei.

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doi:10.1016/j.jmr.2007.07.009

Among the techniques mentioned above, only DOR is capable of providing isotropic 1D spectra of quadrupolar nuclei in real time. Rather than relying on sophisticated pulse programming, DOR relies on mechanical sophistication in that the polycrystalline sample is spun simultaneously about two axes subtending the angles 54.74° and 30.56°. This process satisfies the conditions necessary to time-average both first- and second-order perturbations to the Zeeman interaction which have the angular dependences $P_2(\cos\beta) = \frac{1}{2}(3\cos^2\beta - 1)$ and $P_4(\cos\beta) = \frac{1}{8}(35\cos^4\beta - 30\cos^2\beta + 3)$, respectively. Recently, another method for, recording high-resolution 1D spectra in real time using standard MAS probes has been reported. This method (dubbed STARTMAS) is only applicable to $I = 3/2$ nuclei and refocuses the second-order quadrupolar broadening which remains under MAS by correlation of satellite and double quantum transitions [10].

Double rotation (DOR) NMR has seen a gradual development since its original implementation in 1988 [2,3]. In particular, spinning sideband (ssb) suppression [11–15] has been actively pursued, since numerous ssbs are often observed in DOR spectra due to the relatively low limits in outer rotor spinning frequency (currently ~2 kHz). The inherently low sensitivity of NMR has also led to the application of satellite transition saturation/inversion signal enhancement techniques under DOR [16,17]. The majority of DOR NMR studies reported have been concerned with the differentiation of sodium, boron, aluminium and oxygen sites in minerals [18–20], materials [21–25] and molecular sieves, including, zeolites [26–29], sodalites [30–32] and aluminophosphates [33–37]. More recently, focus has turned to exploiting DOR for the study of oxygen sites in organic solids [17,38–41].

Almost all of the DOR NMR literature has concentrated on differentiation, rather than characterization, of quadrupolar nuclei largely due to the predominance of 2D techniques such as MQMAS and STMAS, which serve to provide high-resolution spectra for quadrupolar nuclei using widely available MAS equipment. Hence, few reports have explored the possibility of extracting other NMR interaction parameters from analysis of DOR spectra, particularly chemical shift anisotropy (CSA) [37,42]. The present work aims to examine the usefulness of DOR as a technique complementary to acquisition under MAS and static conditions for the extraction of anisotropic NMR interaction parameters. ^{17}O provides an ideal testing ground for this NMR approach because of the ubiquitous nature of oxygen in a whole range of inorganic [43] and organic [44] materials where oxygen sites play a crucial role in determining properties/behavior and because its NMR spectra often exhibit anisotropic quadrupole and chemical shift effects of comparable strength. Furthermore, the fact that oxygen is a light element means that quantum mechanical calculations of the NMR interaction parameters are feasible which will allow full comparison between experiment and computed values. In the present contribution, [35%-^{17}O]L-alanine (zwitterionic form) and [40%-^{17}O]OPPh$_3$ are used as model compounds to demonstrate the viability of using DOR as a routine tool for the extraction of anisotropic NMR interaction parameters.

2. Theory

Thorough theoretical treatments of NMR interactions and the numerical simulation of their effects can be found in the literature [45–49], including the case where samples are spun about two axes simultaneously, such as for DOR [42,50,51]. As such, the following presents only an overview of the key elements, with particular focus on the QI, for which DOR was developed.

DOR NMR spectra are simulated by density matrix calculation of the expectation value of the spin angular momentum lowering operator, $\widehat{I}_-$, yielding a time-domain free induction decay (fid), $s(t)$,

$$s(t) = \left\langle \widehat{I}_- \right\rangle = \mathrm{Tr}\{\widehat{I}_-\hat{\rho}(t)\}, \tag{1}$$

which is given by the trace of the product between $\widehat{I}_-$ and the density matrix as a function of time,

$$\hat{\rho}(t) = \widehat{U}(t)\hat{\rho}(0)\widehat{U}(t)^\dagger. \tag{2}$$

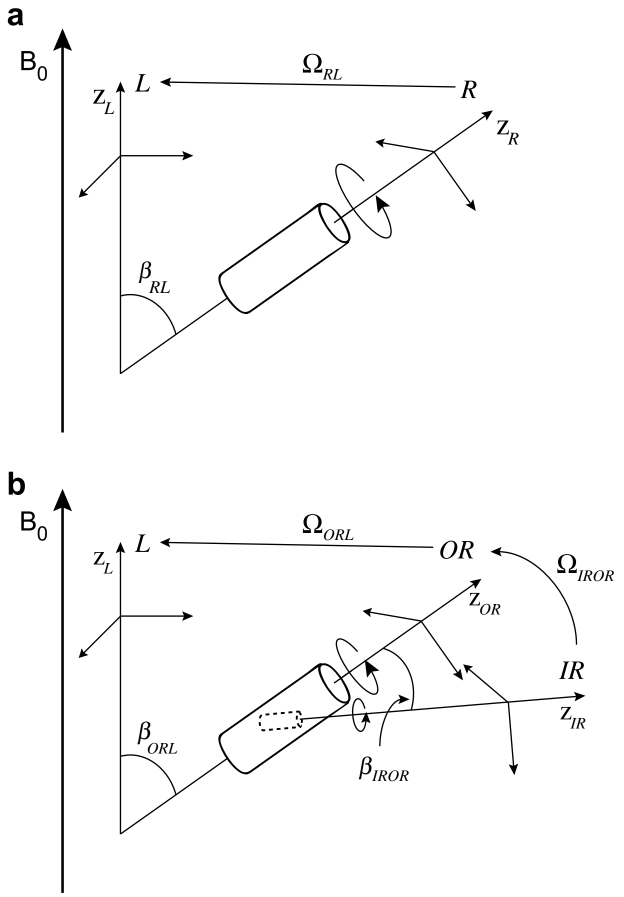

Fig. 1. Schematic depiction of reference frame transformations involved in (a) MAS: rotor (R) → laboratory (L) and (b) DOR: inner rotor (IR) → outer rotor (OR) → laboratory (L).