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Trends

Correlation NMR spectroscopy involving quadrupolar nuclei

J.P. Amoureux [a,*], J. Trébosc [a], L. Delevoye [a], O. Lafon [a], B. Hu [a], Q. Wang [a,b,c]

[a] UCCS, CNRS-8181, Lille-University, Villeneuve d'Ascq, Fr-59652, France
[b] State Key Laboratory of Magnetic Resonance and Atomic and Molecular Physics, Wuhan Center for Magnetic Resonance, Wuhan Institute of Physics and Mathematics, Chinese Academy of Sciences, Wuhan 430071, China
[c] Graduate School of the Chinese Academy of Sciences, Beijing, China

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ABSTRACT

We review the recent developments proposed for integer or half-integer quadrupolar nuclei, focussing on the methods to observe them under high-resolution and to analyze their through-space and through-bond connectivities.

1. Introduction

Quadrupolar nuclei represent c.a. 75% of the table elements, and are thus very important nuclei for nuclear magnetic resonance (NMR). Their observation and usage is relatively recent in solid-state NMR and has really started approximately 15 years ago. The first stage encountered has been to access to high-resolution spectra, and the second stage has been to analyze their through-space and through-bond connectivities and to measure the inter-nuclei distances. As a general comment, it is important to notice that the density matrix of quadrupolar nuclei corresponds to a multi-level system, which means that this matrix is difficult to control with radio-frequency (rf) pulses. This has several consequences: (i) efficient methods are those sending only few rf pulses on the quadrupolar nucleus, (ii) most methods are developed for nuclei submitted to moderate or strong quadrupole interactions, and (iii) in this case only soft pulses, selective for the central transition, are used in addition to the two hard pulses of MQMAS and STMAS. In the case of weak quadrupole interactions (e.g., ^{6}Li or ^{7}Li), methods developed for spin-$\frac{1}{2}$ nuclei can be used most of the time, provided the MAS probe is able to send strong enough rf-fields that cover the frequency ranges.

2. High-resolution of quadrupolar nuclei

The ability of NMR to probe the structure of materials strongly depends upon the possibility to record high resolution spectra, which serve as fingerprints of the physico-chemical surroundings of the studied nuclei. In solids, the nuclear spins experience various anisotropic interactions, which broaden their spectra and render NMR more difficult for structural determinations. For spin-$\frac{1}{2}$ nuclei these interactions include dipole–dipole coupling between spins, chemical shift anisotropy (CSA), indirect spin–spin coupling and interaction with unpaired electrons [1]. As these interactions are weak or moderate with respect to Zeeman interaction, the related broadening can be zeroed, at least in principle, by fast magic-angle spinning (MAS) of the sample at $\theta_m = 54.736^\circ$ with respect to the magnetic field $\mathbf{B}_0$.

Until recently, however, such technique could not overcome the line broadening in NMR spectra of the quadrupolar nuclei, i.e., with spin greater than $\frac{1}{2}$. This broadening arises from the strong coupling of the non-spherical charge distribution of such nuclei with the gradients of the electric field created by the surrounding electrons. The quadrupolar broadening is 'more anisotropic' than the first-order interactions (CSA and dipolar coupling), in the sense that it contains higher-order orientational terms of significant magnitude. Thus, more complex motions of the sample, or of the spin magnetization, are needed in order to achieve the highest possible resolution [2–4].

We first note that the size of the quadrupolar interaction can be described by the quadrupolar frequency ν_Q, which is proportional to the quadrupole moment Q of a nucleus and the electric field gradient (EFG). Depending upon the size of Q and the local electronic environment, the values of ν_Q can range from zero to several hundreds of MHz. In NMR, we generally consider the strong field case, $\nu_0 > \nu_Q$, where ν_0 is the Larmor frequency. In this approximation, the first- and second-order quadrupolar energies can be easily calculated using the perturbation theory.

For *quadrupolar nuclei of half-integer spin, I*, the first-order quadrupolar effect on the satellite transition frequencies ($m-1 \leftrightarrow m$, with m an half-integer number such as $-I \leqslant m \leqslant I$ and

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[*] Corresponding author. Fax: +33 3 20 43 68 14.
E-mail address: Jean-paul.amoureux@univ-lille1.fr (J.P. Amoureux).

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$m\neq\frac{1}{2}$) is of the order of ν_Q. Thus, in a powdered sample, the NMR spectrum is spread over a frequency range that for most quadrupolar nuclei exceeds the range of chemical shifts and the bandwidth of the rf pulses delivered by the current NMR spectrometers. Conversely, the central transition ($-\frac{1}{2}\leftrightarrow\frac{1}{2}$) is not affected by quadrupolar interaction at the first order. In the absence of additional line broadenings from chemical shift and/or dipolar interaction, the width of the powder spectrum for the central transition is determined only by the second-order quadrupolar terms, which are proportional to ${\nu_Q}^2/\nu_0$. Since this contribution is typically 10^2–10^3 times smaller than ν_Q, the central transition yields a narrower and more intense spectrum, which is the subject of most studies on half-integer quadrupolar nuclei. Since second-order broadening and chemical shifts are proportional to $1/\nu_0$ and ν_0, respectively, the spectral resolution scales as ν_0^2.

Even if MAS eliminates the first-order broadening completely, it does not average to zero the second-order terms and the quadrupolar contribution to the central transition line width is only reduced by a factor of approximately 3. Several methods have been proposed to completely cancel the first- and second-order quadrupolar broadenings. In the 1D DOR (double rotation) experiment [2], the sample is spun in a small inner rotor, which is rotating inside an outer rotor. The rotation axis of the outer rotor is set at the magic angle, while the rotation axis of the inner rotor moves continuously on a cone of an aperture of 30.55° or 70.12°. In contrast with DOR, the DAS (dynamic angle spinning) technique uses two discrete rotational orientations (commonly tilted 37.38° and 79.19° away from $\mathbf{B}_0$) and correlates the corresponding resonance frequencies in a 2D experiment [3]. More recently, it has been proposed and demonstrated by Frydman et al. [4] that the line narrowing of the central transition can be obtained without changing the orientation of the spinning axis, as long as the motion of this axis in space is replaced by changing the coherence state of the observed spins. This experiment is referred to as multiple quantum magic-angle spinning (MQMAS). Similar to DAS, MQMAS is a 2D method, except that it allows for observation of a purely isotropic echo by correlating the phase evolutions of the multiple quantum (MQ) and single quantum (1Q) coherences. The change of the coherence state of half-integer quadrupolar spins can be effectively accomplished by strong rf irradiation. The MQMAS method precludes the main shortcomings of DOR (presence of closely spaced spinning sidebands) and DAS (loss of magnetization during the reorientation of the spinner axis) and, being technically straightforward, has found enthusiastic approval in the NMR community. Recently, a new method called STMAS (satellite transition MAS) has been introduced [5,6]. This method is very similar to MQMAS, but more sensitive by a factor of ≈3–7. However, STMAS is technically very demanding as it requires the rotor axis to be adjusted within a few 0.001° from θ_m. This technique is therefore still under development, and we will thus mainly focus on the MQMAS method in the following.

Up to recently, the two most robust versions of MQMAS were the z-filter [7] and the whole echo [8,9] methods (if losses are weak). These two methods use two hard pulses followed by a soft pulse, with a single coherence level, 0Q (z-filter) or +1Q (whole-echo) being selected between the last two pulses. Recently, Gan and Kwak [10] proposed to use the 0Q and $\pm1Q$ coherence levels simultaneously in the SPAM experiment. To avoid any unwanted dephasings of coherences on $\pm1Q$, the hard and soft pulses must be contiguous, forming a composite SPAM conversion sequence [11]. The phase of the hard MQ excitation pulse is cycled to select only the targeted coherence level required for the echo or antiecho pathway (+3Q or $-3Q$ in the case of 3QMAS) [12]. If the optimized pulse durations in the echo (or antiecho) SPAM experiments (denoted SPAM_E and SPAM_AE) are exactly the same as in the z-filter method, the phases of the hard and soft components of the SPAM pulse must be fixed at the same value (e.g., x,x) for $+3Q\rightarrow-1Q$ transfers and at opposite values (e.g., x,–x) for $-3Q\rightarrow-1Q$ transfers. The optimized pulse durations in the echo or antiecho SPAM experiments are exactly the same as in the z-filter method, whereas the resulting intensity is roughly doubled. From the user's standpoint, the only difference between SPAM_E and SPAM_AE experiments lies in the phase cycling, as well as the data acquisition and processing. Indeed, the resulting phase-modulated SPAM_E and SPAM_AE signals must be recorded separately with an inversion of the soft pulse phase, as indicated above. These signals are treated individually and then added to yield a pure-phase $\text{SPAM}_\text{E/AE}$ spectrum with frequency discrimination. Since the antiecho is used solely to eliminate the dispersive contributions from the echo pathway, only its initial part that "overlaps" with the echo has to be acquired [12]. The time performance of the $\text{SPAM}_\text{E/AE}$ experiment is determined by several factors: (a) the twofold increase of echo and antiecho signals due to SPAM, (b) the $\sqrt{2}$ additional noise associated with separate acquisition of the echo and a part of the antiecho, and (c) the fact that it is a phase-modulated experiment that does not require TPPI or hypercomplex acquisition. It has been demonstrated that globally, the truncated $\text{SPAM}_\text{E/AE}$ method has an overall sensitivity three times higher than the z-filter experiment [12].

For *integer quadrupolar spins*, there is no central-transition, and hence previous high-resolution methods cannot be applied. There are two important nuclei with such properties, namely ^{2}H and ^{14}N, both with nuclear spin $I=1$. Quadrupole interactions are weak for ^{2}H nuclei, and thus high-resolution is easily obtained by fast or ultra-fast MAS (up to 70 kHz in 2008). This is not the case for ^{14}N, and until recently, MAS ^{14}N NMR spectra were restricted to nitrogen nuclei featuring weak or moderate quadrupole coupling constants, $C_Q\leqslant1$ MHz [13]. In the last years, a new indirect detection method, using ^{13}C [14,15] or ^{1}H [16] signal acquisition, has been proposed, based on HMQC [14–16] or HSQC sequences [17,18]. Due to t_1 rotor-synchronization, only the second-order broadening is then observed along the ^{14}N dimension, and the 2D resolution is thus proportional to $\mathbf{B}_0^2$.

As a rule, the existence of high resolution NMR methods is a requirement for the measurements of interactions between the observed nuclei and their neighbors. Such measurements provide means for analyzing the intermediate range ordering in complex spin systems. The development of MQMAS offered no exception. There are two types of correlation methods: those based on through-space connectivities and those based on through-bond connectivities.

3. Heteronuclear dipolar correlations between spin-$\frac{1}{2}$ and half-integer quadrupolar nuclei

Several techniques were developed that allow for studies of dipolar interactions between the quadrupolar and spin-$\frac{1}{2}$ nuclei. These include the CP experiment [19], TEDOR (transferred echo double resonance) [20,21], TRAPDOR (transfer of populations double resonance) [22,23], REDOR (rotational echo double resonance) [24], and REAPDOR (rotational echo adiabatic passage double resonance) [25]. In addition, several heteronuclear dipolar recoupling techniques have been introduced in connection with indirect detection (HMQC or HSQC): R^3 (rotary resonance recoupling) [26], SFAM (simultaneous frequency and amplitude modulation) [27,28], and rotor-synchronized symmetry-based sequences [29].