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Piezoelectric signal suppression by a composite-pulse sequence in NMR

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Abstract

Numerous NMR techniques are available for the study of nuclei with spin $I \geq 1$. These nuclei interact with their surrounding electric field gradient, which depends on the symmetry of the crystallographic site. Spurious (or piezoelectric) signals, due to the piezoelectric and ferroelectric properties of a LiNbO_3 crystal and generated by the vibration of the macroscopic electric dipole of the crystal, have been observed with the one-pulse sequence and cancelled using a composite-pulse sequence. The suppression of these piezoelectric signals by this sequence is illustrated by lithium-7 ($I = 3/2$) nuclei. Java applets available in our web site www.pascal-man.com for the determination of quadrupole parameters from one-dimensional nutation method are also presented. **To cite this article:** C. Mignon *et al.*, *C. R. Chimie* 7 (2004).

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Résumé

De nombreuses techniques RMN sont disponibles pour l'étude des noyaux ayant un spin $I \geq 1$. Ces noyaux interagissent avec le gradient de champ électrique de leur environnement, qui dépend de la symétrie du site cristallographique. Les signaux parasites (ou piézoélectriques) dus aux propriétés piézoélectrique et ferroélectrique d'un cristal de LiNbO_3 et générés par la vibration du dipôle électrique macroscopique du cristal ont été observés avec une séquence à une impulsion et éliminés en utilisant une séquence d'impulsion composite. L'annulation des signaux piézoélectriques par cette séquence est illustrée par le lithium 7 ($I = 3/2$). Nous présentons aussi les applets Java de notre site Internet www.pascal-man.com pour la détermination des paramètres quadripolaires à partir des données issues de la méthode de nutation à une dimension. **Pour citer cet article :** C. Mignon *et al.*, *C. R. Chimie* 7 (2004).

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Mots clés : Lithium 7 ; Signal piézoélectrique ; Suppression de signaux parasites ; Spin quadripolaire demi-entier ; Séquence d'impulsion composite ; Spectroscopie RMN

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1. Introduction

In NMR, knowing the quadrupole coupling ω_Q of a nucleus with spin $I \geq 1$ allows us to determine the local symmetry of a crystallographic site in solids. Since the variation of the line intensity with a radio-frequency (RF) pulse duration depends on ω_Q , the one-dimensional (1D) nutation method, which records a series of spectra for increasing RF pulse duration, allows us to extract the value of ω_Q via an iterative fitting of the experimental line intensities to the theoretical curve.

The piezoelectric effect [1,2] from a ferroelectric crystal [3–5] and the ringing effect [6,7] from the NMR probe head tuned for low gyromagnetic ratio nuclei introduce spurious signals when the one-pulse sequence (Fig. 1A) is used to excite the spin system. Experimentally, a suitable modification of the NMR probe head [8] or the application of a two-pulse Hahn echo sequence [9] can cancel these spurious signals. Recently, we have applied a composite-pulse sequence [10], consisting of three pulses (Fig. 1B) with the same duration ($t_1 = t_2 = t_3$), to cancel the ringing effect from

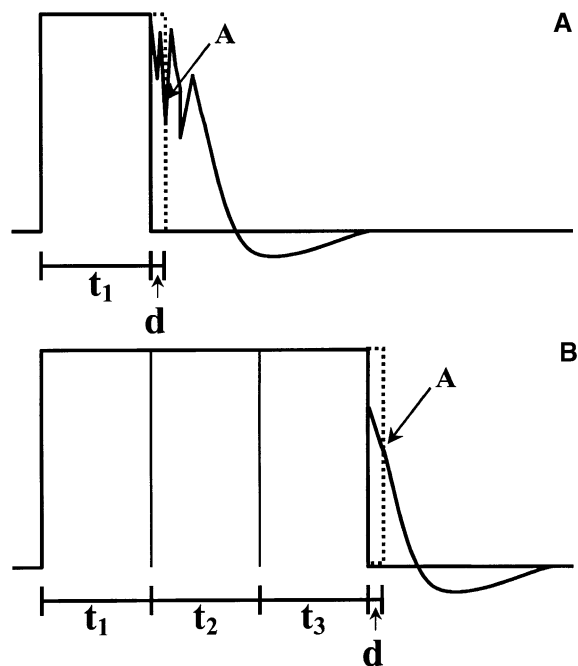


Fig. 1. (A) One-pulse sequence with duration t_1 and (B) composite-pulse sequence consisting of three pulses without any delay between them. We used three pulses of the same duration ($t_1 = t_2 = t_3$). Due to the acquisition delay d , the FID acquisition starts at point A.

the probe head in the spectra of ^{131}Xe ($I = 3/2$) physisorbed on NaY zeolite [11,12]. The main advantages of this sequence over the above two methods are the use of a standard NMR probe head and the simplicity for optimising the line intensity. The Hahn echo sequence requires optimisation of three parameters: the two durations of pulses and that between these two pulses. On the other hand, there is only one parameter to determine for the composite-pulse sequence: the three pulses have the same duration.

The LiNbO_3 crystal is a ferroelectric and piezoelectric oxide with a great variety of applications. It is used, in the undoped form, for acoustic-optic, piezoelectric, linear and non-linear optical applications, and in the doped form, for laser action in bulk samples and in wave-guide structures [13,14]. In fact, the centre of gravity of the positive charges in the LiNbO_3 crystal does not coincide with that of the negative charges, resulting in a macroscopic electric dipole (ferroelectric property). When the one-pulse sequence is applied to ^7Li ($I = 3/2$) in LiNbO_3 crystal, spurious (or piezoelectric) signals are observed [15]. These signals are due to the vibration of the macroscopic electric dipole of the crystal, caused by the electric field associated with the RF magnetic field B_1 during the excitation of the spin system (piezoelectric property).

The present paper proposes the composite-pulse sequence to cancel the piezoelectric signals from a LiNbO_3 single crystal. The 1D nutation method with the one-pulse sequence has already been applied by Shin and co-workers [16] for the study of the electric quadrupole interaction of the ^7Li nucleus in LiNbO_3 crystals. Unfortunately, the spin–lattice relaxation time of ^7Li in the LiNbO_3 crystal is unknown, but certainly more than 100 s. As a result, the line intensities are not quantitative. This fact prevents us from determining ω_Q by fitting the line intensities against the pulse duration of the one-pulse sequence or that of the composite-pulse sequence with the theoretical curve.

2. Java applets

In theoretical NMR studies of half-integer quadrupole spins, usually only the static first-order quadrupole interaction $H_Q^{(1)}$ is taken into account during the RF pulses. This interaction represents the coupling of the nuclear electric quadrupole moment eQ with the

electric-field gradient (EFG) generated by the surroundings of a nucleus. The two terms $H_Q^{(1)}$ and ω_Q are related as:

$$H_Q^{(1)} = \frac{1}{3} \omega_Q [3 I_z^2 - I(I+1)]$$

with:

$$\omega_Q = \frac{3 e^2 q Q}{8 I (2 I - 1) \hbar} (3 \cos^2 \beta - 1 + \eta \sin^2 \beta \cos 2\alpha)$$

where $e^2 q Q / \hbar$ is the quadrupole coupling constant (QCC) and η the asymmetry parameter. These two parameters provide information on the microscopic local structure. The two angles β and α are the polar angles of the static magnetic field \mathbf{B}_0 in the principal-axis system of the EFG tensor.

In the condition of high magnetic field \mathbf{B}_0 , the central line of a half-integer quadrupole spin system in a powder is featureless. As a result, lineshape analysis is not suitable for determining the two quadrupole parameters: QCC and η . The NMR line intensity, which depends on the various interactions involved during the RF pulses, is proportional to the amplitude of the first sampled point of a free-induction decay (FID) or the integrated area of the corresponding spectrum. The 1D nutation method allows the determination of ω_Q for a single crystal or QCC and η for a powder. In other words, the line intensity depends not only on the RF pulse duration, but also on the ratio of ω_Q to the amplitude ω_{RF} of the RF pulse for a single crystal, or the ratio of QCC to ω_{RF} for a powder. However, there is an upper limit to these ratios, above which the line intensity does not change any more for a given RF pulse duration.

Java applets, which calculate 1D nutation line intensities and extract the value of ω_Q in a single crystal or those of QCC and η in a powder, are available in our website www.pascal-man.com. They are software programs that execute via a browser such as Internet Explorer, Netscape, Opera or HotJava, regardless of the computer used (PC, Mac, mainframe...). The four half-integer quadrupole spins ($I = 3/2, 5/2, 7/2, \text{ and } 9/2$) can be excited by various RF pulse sequences (one-pulse, Hahn echo, MQ-MAS, Solomon echo...). First, the Java applet associated with a specific sequence calculates the theoretical nutation line intensities of the central transition with experimental param-

eters (the spin I , the amplitude ω_{RF} , the variable pulse duration and its increment) and estimated values for ω_Q or QCC and η . Then, it extracts the value of ω_Q or that of QCC by fitting your experimental central line intensities with the theoretical curve. One application of these Java applets is the quantification of EFG in the supercage of Y zeolites by means of a ^{131}Xe NMR experiment [17].

3. Experimental

The size of the LiNbO_3 crystal is $5 \times 5 \times 20 \text{ mm}^3$. The ^7Li NMR was performed with a Bruker MSL300 multinuclear high-power spectrometer, where the resonance frequency of ^7Li is 116.6 MHz. The static probe head was equipped with a solenoid coil 10 mm in diameter and 35 mm in length. Two series of experiments were performed with increasing t_1 from 4 to 20 μs by steps of 2 μs : one with the one-pulse sequence and the other with the composite-pulse sequence where $t_1 = t_2 = t_3$. These pulse sequences also include CYCLOPS in their phase cycling. The other acquisition conditions are: a recycle delay of 100 s, an acquisition delay d of 8 μs , and 48 scans. The pulse program of the composite-pulse sequence can be found on our website.

4. Results and discussion

Fig. 2 presents two series of ^7Li FIDs for the LiNbO_3 crystal for increasing t_1 of the one-pulse sequence, observed in the two detection channels u (Fig. 2A) and v (Fig. 2B) of the receiver with quadrature detection. Each curve shows a complex FID superimposed on that of the spin system. This complex FID expresses the piezoelectric effect of the LiNbO_3 crystal and its duration is about 0.6 ms. The latter is comparable to that observed with ^{23}Na ($I = 3/2$) NMR in a NaNO_2 crystal by Pandey and Hughes [18], which is about 0.4 ms. However, it is much longer than that of the complex FID from the ringing effect in the case of ^{131}Xe physisorbed on NaY zeolite, where its duration is about 0.08 ms [11,12,17].

It should be mentioned that when the piezoelectric oxide is in powder form, the centre of gravity of the positive charges from all the crystallites of the powder

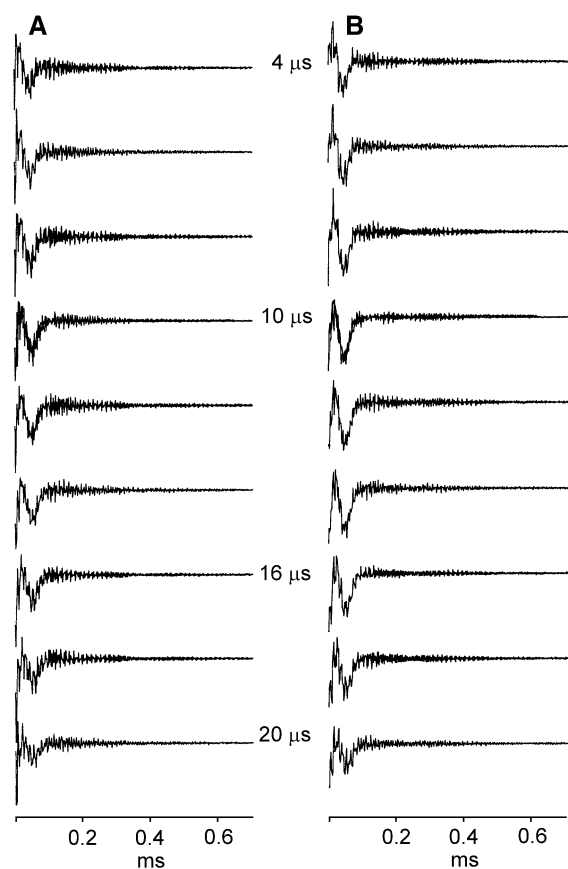


Fig. 2. FIDs of ${}^7\text{Li}$ in a single crystal of LiNbO_3 following the one-pulse sequence for t_1 increasing from 4 to 20 μs in steps of 2 μs and for the two detection channels u (A) and v (B) of the receiver with quadrature detection.

coincides with that of the negative charges. In other words, the macroscopic electric dipole does not exist in a powder. Therefore, the piezoelectric effect is not observed with the one-pulse sequence.

Figs. 3A and 3B show the ${}^7\text{Li}$ FIDs of the LiNbO_3 crystal observed in the two channels u and v of the receiver and for increasing t_1 of the composite-pulse sequence. The complex FIDs (Fig. 2) observed with the one-pulse sequence were cancelled whatever the duration t_1 of the composite-pulse sequence. Only the FID of the spin system remains and its duration is about 0.2 ms, which is shorter than that of the complex FID. In fact, this composite-pulse sequence cancels the ringing and the piezoelectric effects even when the durations of the three pulses are not identical ($t_1 \neq t_2 \neq t_3$); however, the variation of line intensity

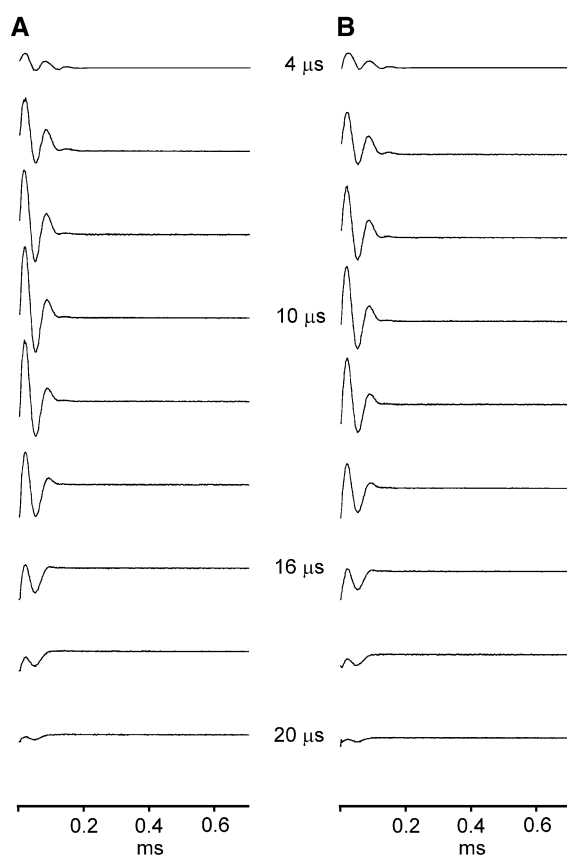


Fig. 3. FIDs of ${}^7\text{Li}$ in a single crystal of LiNbO_3 following the composite-pulse sequence for $t_1 = t_2 = t_3$ increasing from 4 to 20 μs in steps of 2 μs and for the two detection channels u (A) and v (B) of the receiver with quadrature detection.

will be changed. This variation can be predicted with the Java applets.

Fig. 4A shows the Fourier transform of the one-pulse FIDs of Fig. 2. The spectra consist of sharp lines from the piezoelectric effect on both sides of those of ${}^7\text{Li}$ located around 0 ppm. The spectrum of ${}^7\text{Li}$ should consist of a central line and of two equally spaced satellite lines. However, the splitting of these three lines is not sufficient due to the small value of ω_Q , resulting of an overlapping of these lines. Fortunately, the piezoelectric effect on the spectrum is less dramatic than on the FID, since it generates sharp lines outside those of ${}^7\text{Li}$. In comparison, the ringing effect distorts the baseline of the spectrum so efficiently that the NMR line of the nucleus becomes difficult to recognise [17]. Since the spin–lattice relaxation time of ${}^7\text{Li}$ in this crystal is much longer than the recycle delay used,

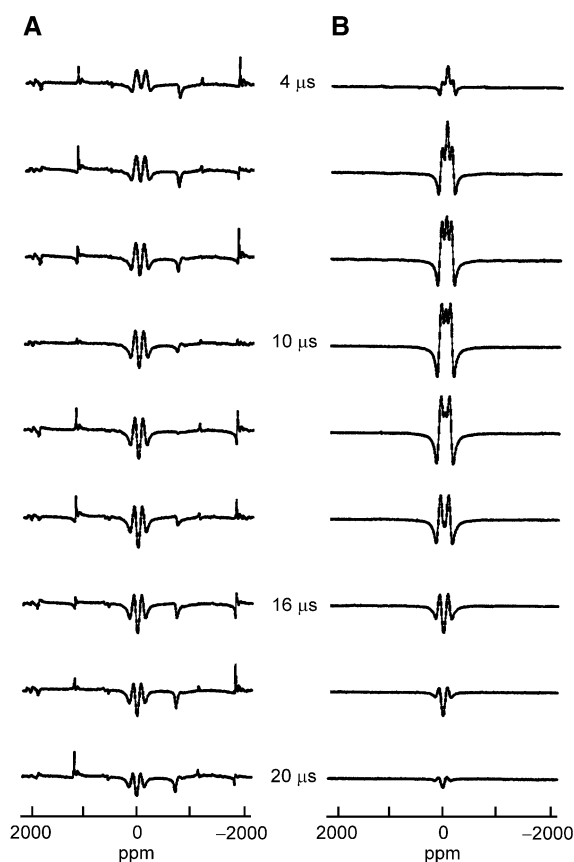


Fig. 4. ${}^7\text{Li}$ (A) one-pulse spectra and (B) composite-pulse spectra of LiNbO_3 crystal corresponding to Figs. 2 and 3, respectively.

we did not attempt to extract the value of ω_Q from our nutation experiments by means of an iterative fitting of the line intensities with our Java applets.

Fig. 4B presents the Fourier transform of the composite-pulse FIDs of Fig. 3. These spectra are those of ${}^7\text{Li}$ without the sharp lines due to the piezoelectric effect, as shown in Fig. 4A. For a pulse duration t_1 shorter than $12\ \mu\text{s}$, the central line and the two equally spaced satellite lines of ${}^7\text{Li}$ are observed. The ${}^7\text{Li}$ spectra in Fig. 4B differ from those of Fig. 4A. This is due to the different spin dynamics involved in the excitation of the spin system by the two sequences. Since the resonance frequency of satellite lines depends on the orientation of the crystal relative to the static magnetic field \mathbf{B}_0 , whereas that of the central line does not [19], it would be necessary to study the crystal with different orientations in the solenoid coil to obtain a better resolution.

5. Conclusion

We have extended our investigation on the cancellation of spurious signals that are not generated by the spin system. The composite-pulse sequence suppresses not only the ringing effect from the NMR probe head tuned for low gyromagnetic ratio nuclei, as shown previously [12], but also the piezoelectric effect due to the vibration of the macroscopic electric dipole in a ferroelectric single crystal. These effects are cancelled whatever the duration of each of the three RF pulses. From a practical point of view, for a featureless central lineshape of a half-integer quadrupole spin system in a powder, the 1D nutation method associated with Java applets should be used to determine QCC and η .

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References

- [1] P.P. Man, *Solid State NMR* 1 (1992) 149.
- [2] D.G. Hughes, L. Pandey, *J. Magn. Reson.* 56 (1984) 428.
- [3] W.G. Cady, *Piezoelectricity: an introduction to the theory and applications of electromechanical phenomena in crystals*, Dover Publications, New York, 1964.
- [4] C.Z. Rosen, B.V. Hiremath, R.E. Newnham, *Key Papers in Physics: Piezoelectricity*, A.I.P., New York, 1992.
- [5] J.F. Nye, *Physical Properties of Crystals: Their Representation by Tensors and Matrices*, Clarendon Press, Oxford, 1995.
- [6] I.P. Gerothanassis, *Prog. Nucl. Magn. Reson. Spectrosc.* 19 (1987) 267.
- [7] M.L. Buess, G.L. Petersen, *Rev. Sci. Instrum.* 49 (1978) 1151.
- [8] P.A. Speight, K.R. Jeffrey, J.A. Courtney, *J. Phys. E* 7 (1974) 801.
- [9] A.C. Kunwar, G.L. Turner, E. Oldfield, *J. Magn. Reson.* 69 (1986) 124.
- [10] S. Zhang, X. Wu, M. Mehring, *Chem. Phys. Lett.* 173 (1990) 481.
- [11] F. Jaque, T.P.S. Han, G. Lifane, *J. Lumin.* 248 (2003) 102–103.
- [12] Y. Millot, P.P. Man, *J. Magn. Reson.* 150 (2001) 10.
- [13] X.H. Zhen, X.J. Zhang, L.C. Zhao, Y.H. Xu, *Solid-State Commun.* 126 (2003) 203.

- [14] F. Jaque, T.P.J. Han, G. Lifane, *J. Lumin.* 102–103 (2003) 248.
- [15] B. Li, Y. Wang, Z. Xu, *J. Phys. C: Solid-State Phys.* 21 (1988) L251.
- [16] H.W. Shin, S.H. Choh, T.H. Yeom, K.S. Hong, D.Y. Han, *J. Korean Phys. Soc.* 32 (1998) S662.
- [17] Y. Millot, P.P. Man, M.-A. Springuel-Huet, J. Fraissard, *C. R. Chimie* 4 (2001) 815.
- [18] L. Pandey, D.G. Hughes, *J. Magn. Reson.* 56 (1984) 443.
- [19] A.R. Lim, J.W. Kim, C.S. Yoon, *Solid-State Commun.* 123 (2002) 505.