

Two-Dimensional NQR Spectroscopy for the Characterization of Crystalline Powders

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Two-dimensional NQR spectroscopy for correlation of homogeneous and inhomogeneous linewidths has been applied to the ^{35}Cl resonance of sodium chlorate powders of different origin. Powder from a ground crystal could be discriminated from technical powder by the ratio of linewidths along the two orthogonal axes in the 2D spectrum. These experiments indicate the applicability of NQR spectroscopy in material science.

Key words: Material science; NQR; Sodium chlorate; 2D spectroscopy; Separation of interactions.

Introduction

Many experiments with multidimensional NMR spectroscopy can be transferred to NQR spectroscopy [1–5]. One of the most simple separates homogeneous and inhomogeneous broadening by use of an echo [6–9]. The lineshape resulting from static disorder and dynamic fluctuations appears in the ω_2 dimension, and the lineshape broadened by dynamic fluctuations appears only in the ω_1 dimension. The inhomogeneous broadening depends on the type and number of lattice defects in a sensitive way. Thus, in crystalline powders the inhomogeneous broadening is characteristic for fabrication of the powder, and methods to quantify the inhomogeneous broadening are of interest. For this purpose two sodium chlorate powder samples of different purity and a single crystal sample were investigated. The observed nucleus was ^{35}Cl , which possesses spin $I = \frac{3}{2}$.

Theory

As shown in [1] the elements of the EFG-tensor $V_{ij}(t)$ of a crystalline compound can be split in a static part $V_{ij}^{(0)}$ and a time-dependent part $\Delta V_{ij}(t)$ [6],

$$V_{ij}(t) = V_{ij}^{(0)} + \Delta V_{ij}(t), \quad (1)$$

thereby leading to a separation of the Hamiltonian $\mathbf{H}_Q(t)$ into a static and a time-dependent part:

$$\mathbf{H}_Q(t) = \mathbf{H}_Q^{(0)} + \Delta \mathbf{H}_Q(t). \quad (2)$$

On the condition that the two parts $\mathbf{H}_Q^{(0)}$ and $\Delta \mathbf{H}_Q(t)$ of the Hamiltonian commute,

$$[\mathbf{H}_Q^{(0)}, \Delta \mathbf{H}_Q(t)] = 0, \quad (3)$$

it is possible to separate them spectroscopically. This can be achieved using the spin echo sequence shown in Figure 1.

For ensembles of spins ($I = \frac{3}{2}$) and non-axial symmetry ($\eta \neq 0$) the evolution of the spin system under the static Hamiltonian $\mathbf{H}_Q^{(0)}$ has been calculated [10, 11]. The maximum echo is achieved for flip angles $\pi/2$ for the first pulse and π for the second pulse. The effects on the frequency of fluctuations which are slow on the t_1 scale, i.e. the time scale of the echo, are refocused by the echo and do not give rise to line broadening in the ω_1 dimension. After 2D Fourier transformation this information can be found in the ω_2 dimension only. Fluctuations which are fast on the t_1 scale are described by $\Delta \mathbf{H}_Q(t)$. Their effect on the

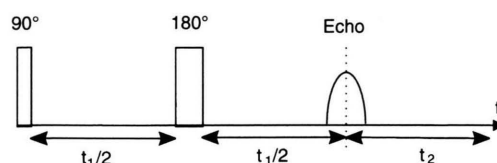


Fig. 1. Echo pulse sequence for 2D NQR spectroscopy.

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frequency cannot be refocussed. Thus the information on these fluctuations is contained in both dimensions, ω_1 and ω_2 , of the 2D spectrum.

The inhomogeneously broadened line $S_b(\omega)$ can be described as a weighted superposition of homogeneously broadened lines $S_n(\omega - \omega')$, which are centered at frequencies ω' . If the distribution of weights is given by $W(\omega')$, then the inhomogeneously broadened line is the convolution of $S_n(\omega - \omega')$ and $W(\omega')$ [1]:

$$S_b(\omega) = \int W(\omega') S_n(\omega - \omega') d\omega'. \quad (4)$$

Denoting the Fourier transforms of corresponding capital-letter terms in (4) by $s_b(t)$, $w(t)$ and $s_n(t)$, the distribution $W(\omega')$ of weights can be evaluated by use of the convolution theorem,

$$w(t) = s_b(t)/s_n(t). \quad (5)$$

Two limiting cases are considered: 1) $W(\omega')$, $S_b(\omega)$ and $S_n(\omega - \omega')$ are Lorentzian and 2) the three functions are Gaussian. For these two cases the linewidth L_w of $W(\omega')$, normalized to the linewidth L_b of $S_b(\omega)$, can be calculated. The following results are obtained:

1) Lorentz:

$$\frac{L_w}{L_b} = 1 - \frac{T_b}{T_n} = 1 - \frac{L_n}{L_b}, \quad (6)$$

where $1/(\pi T)$ is the full width L at half height of a Lorentz line, and the indices b and n refer to the inhomogeneously broadened and the homogeneously broadened lines, respectively.

2) Gauss:

$$\begin{aligned} \frac{L_w}{L_b} &\cong 1 - \frac{1}{2} \left(\frac{\sigma_n}{\sigma_b} \right)^2 - \frac{1}{8} \left(\frac{\sigma_n}{\sigma_b} \right)^4 - \dots \\ &\cong 1 - \frac{1}{2} \left(\frac{L_n}{L_b} \right)^2, \end{aligned} \quad (7)$$

where σ denotes the variance of the Gaussian and thus scales with the linewidth.

An exact result is obtained for the Lorentz case, while the validity of (7) is approximate for the Gaussian case. For the experimental linewidth of the crystal sample (see below), the error made by truncation (7) after the second term is 2%. Thus a measure of the characteristic ratios (6) and (7) is the ratio of linewidths

$$R = \frac{L_n}{L_b} \quad (8)$$

of homogeneously and inhomogeneously broadened lines. It is this ratio which has been determined experimentally for different sodium chlorate powders.

Experimental

NaClO_3 powder was obtained from Bayer AG, Leverkusen, in technical quality. Single crystals with dimensions larger than 3 cm were produced by multiple recrystallization, and polycrystalline samples were produced for comparison with the untreated technical powder by crunching such single crystals.

The experiments were performed on a MARAN® [12] PC-based spectrometer which is suitable for measurements in the frequency range from 0.75 to 64 MHz. The radio frequency (rf) pulses from the MARAN® spectrometer were amplified in an M3426 rf amplifier from American Microwave Technologies applied to the sample using a standard broadband NMR probe from Bruker with the rf coil placed in a dewar at room temperature for shielding from temperature fluctuations. Each sample consisted from 2.2 g powder in sample tubes measuring 1 cm in diameter and 5 cm in length. The single crystal was measured without a sample tube. Its weight was 3.1 g.

The ^{35}Cl resonance frequency in NaClO_3 in zero magnetic field is 29.93 MHz at room temperature. The measurements were performed 20 kHz off resonance for simplicity to avoid quadrature detection. With pulse powers ranging from 0.5 up to 1 kW the pulse length for the $\pi/2$ flip angle was in between 3 and 7 μs . 256 data points were sampled in the t_2 domain, using a dwell time of 10 μs . In the t_1 domain 32 slices were acquired with a time increment Δt_1 of 80 μs . The relaxation delay between subsequent scans was 500 ms.

Identical longitudinal relaxation times T_1 of 35 ms were measured by the inversion recovery technique for all three samples. To reach a temperature equilibrium between sample heating by the rf excitation and heat loss through the dewar by cooling all pulse sequences were started 2 hours before data acquisition. To achieve maximum temperature stability and constant rf energy deposition per time in the sample even when using pulse sequences with variable flip angles and variable time increments, a compensation time just before the relaxation delay was introduced. Thus the total rf power applied was constant over the entire length of the experiment. All experiments leading to the data summarized in Table 2 were measured with a

Table 1. Phase cycles for 2D echo spectroscopy.

PAPS		Full phase cycle											
90°	x -x	y	y	-y	y	y	-y	-y	x	x	-x	x	x
180°	x x	-x	x	y	-y	y	-y	-x	x	-x	x	y	-y
Receiver	x -x	x	x	x	-x	-x	-x	-x	y	y	y	-y	-y

Table 2. Experimental results for sodium chlorate.

Sample	Pulse duration [μs]		Linewidth [Hz]		Ratio <i>R</i> of linewidths
	1. Pulse	2. Pulse	inhom.	hom.	
NaClO ₃	7.0	14.0	1340	760	0.57
Single crystal (3.1 g)	6.5	13.0	1210	690	0.57
	6.0	12.0	1170	700	0.60
	5.5	11.0	1000	600	0.60
	5.0	10.0	990	580	0.59
	4.5	9.0	1000	570	0.57
	4.0	8.0	1070	610	0.57
	3.5	7.0	1420	730	0.51
NaClO ₃	6.0	12.0	1720	640	0.37
Powder (2.2 g)	5.0	10.0	1580	590	0.37
	4.0	8.0	1380	530	0.38
NaClO ₃	6.0	12.0	2070	590	0.29
Techn. powder (2.2 g)	5.0	10.0	1789	560	0.31
	4.0	8.0	1800	530	0.29

pulse power of 0.8 kW. The resulting $\pi/2$ pulse, depending on the thermal-equilibrium sample temperature and the coil volume, was 5 μ s for the powders and 5.5 μ s for the single crystal.

The 2D data sets were evaluated on a SUN Sparc 10 workstation by using software written in PV-Wave™ 6.0 of Visual Numerics [13]. First a one-dimensional Fourier transformation was applied to the data sets in the t_2 domain followed by a zeroth order phase correction. The real parts were subsequently Fourier transformed in the second direction to obtain a purely absorptive spectrum.

A phase cycle was used for successive scans in signal averaging to eliminate experimental imperfections. The well-known CYCLOPS four-phase cycle [14] to cancel DC offset and imperfections of the quadrature detection in a single pulse experiment was extended to a two-pulse experiment leading to the 16-step cycle shown in Table 1. It also eliminates any residual FID from the first pulse after the second pulse, which results from B_1 field inhomogeneities. The improvement of the echo signal of a polycrystalline sodium chlorate sample resulting from use of this phase cycle in com-

parison to using the simple phase alternation pulse sequence (PAPS: Table 1) is illustrated in Figure 2. While the residual FID of the first pulse survives in the echo signal with the PAPS cycle (Fig. 2a) this problem is eliminated by application of the CYCLOPS sequence (Figure 2b).

Results

A typical 2D spectrum is shown in Fig. 3, from which the linewidths in Table 2 were extracted.

Different flip angles were used in the experiments to determine the sensitivity of the results with respect to inaccurate pulse widths. Pulse widths used for excitation, linewidths and linewidth ratios determined from the experimental data are compiled in Table 2. The results of experiments performed with the correct flip angle settings are printed in bold face.

While the individual linewidths vary with the excitation flip angle, this dependence is largely eliminated

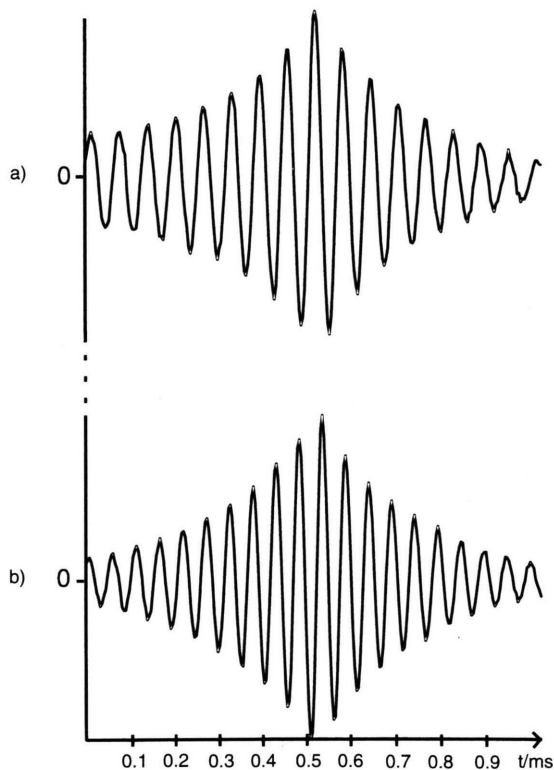


Fig. 2. Echoes of sodium chlorate powder acquired with different phase cycles (cf. Table 1). a) PAPS sequence. b) Extended CYCLOPS sequence.

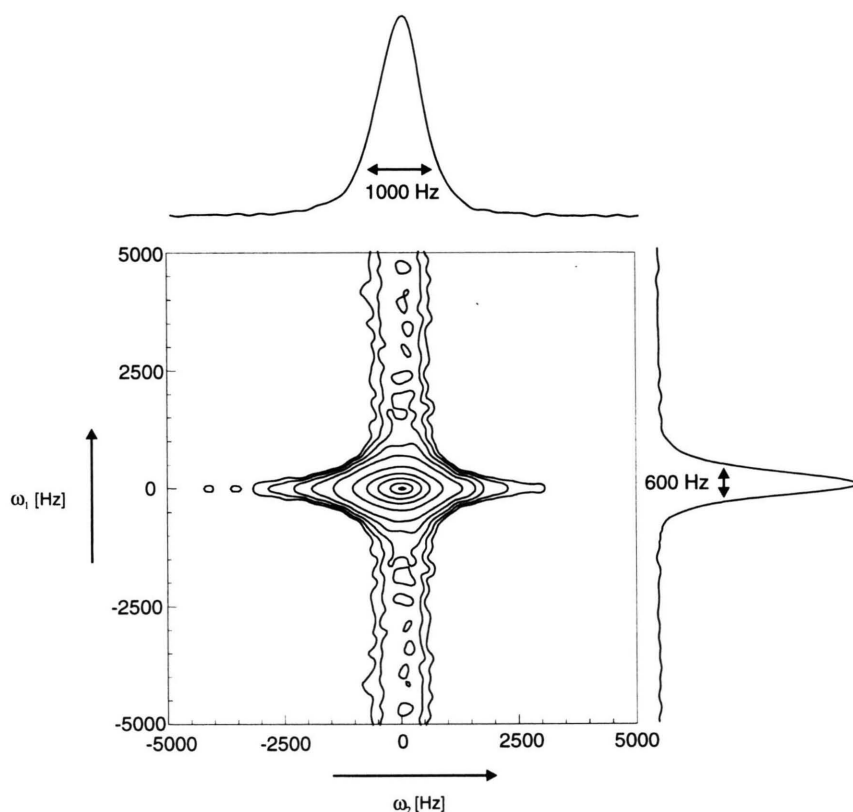


Fig. 3. Two-dimensional NQR spectrum of polycrystalline sodium chlorate powder. Contour lines are drawn at 10, 20, ... 90, 99% of the maximum amplitude.

in the ratio R of linewidths. The single crystal powder exhibits a considerably narrower linewidth than the technical powder. An even smaller ratio is observed for the single crystal. Thus the ratio is indeed indicative of the sample history and follows the expected trend: Small values of R indicate preponderance of static disorder and inhomogeneous broadening. Large values indicate dynamic disorder and homogeneous broadening. Application of this interpretation to the mean values $\langle R \rangle$ of the results summarized in Table 2 shows that the technical powder ($\langle R \rangle \cong 0.30$) exhibits a larger amount of static disorder than the crystalline powder ($\langle R \rangle \cong 0.37$) or the single crystal ($\langle R \rangle \cong 0.57$).

Conclusions

2D echo technique for separation of homogeneous and inhomogeneous interactions has been applied to the measurement of NQR spectra of a single crystal and from polycrystalline powders. In contrast to T_1

measurements, the ratio of linewidths in the two dimensions of the 2D spectra is a characteristic parameter to classify the degree of static versus dynamic disorder of crystalline systems containing various amounts of crystal defects due to variable sample purity. With suitable reference samples the method can be employed to determine the purity of unknown samples. The smaller linewidth ratio of the technical powder compared to that of the grounded crystal can be explained by two contributions: Lattice defects induced by crunching a single crystal and impurities from technical production. Given that static defects lead to a shift of the NQR frequency, the ratio R of linewidths has been shown to characterize the distribution function W of frequency shifts in the limiting cases of Gaussian and Lorentzian lineshapes. While temperature stability is crucial for the success of the experimental outcome, the dependence of the linewidth ratio on variations in the flip angle settings is small. Thus the experiment shows good promise for the characterization of polycrystalline materials.

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