Observation of Order Parameters in Liquid Crystals Via ^{1}H Double-Quantum Methods Under Fast MAS

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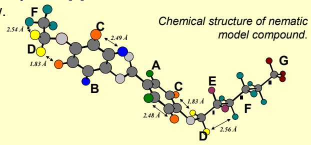
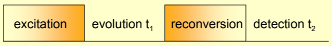
Introduction

Deuteron NMR methods have been used to investigate local order in liquid-crystalline systems. Advanced ^{1}H double-quantum (DQ) NMR techniques under fast magic angle spinning (MAS) can provide equivalent or even more detailed information, without any need for isotopic labeling. This is demonstrated for a nematic model system [1], with the chemical structure shown below.

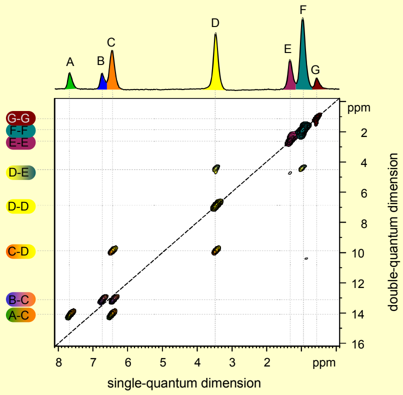


Chemical structure of nematic model compound.



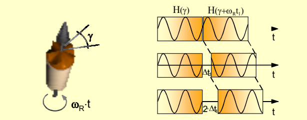
Experimental scheme of a double-quantum experiment.

Combining the basic DQ scheme with fast MAS and appropriate DQ recoupling schemes leads to various experimental features, depending on the synchronization of the t_1-increments to the MAS rotor period.

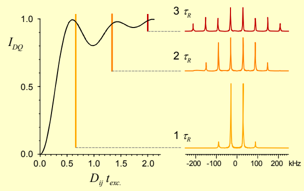


Two dimensional double-quantum spectrum recorded at T = 345 K, 22 kHz MAS and 1 rotor period BABA excitation [2].

- **DQ filtered spectra (t_1=0)** can be used for spectral editing purposes or estimation of DQ intensities, if the 2D DQ spectrum is known.
- **DQ correlation spectra ($\Delta t_1 = n \cdot \tau_R$)** directly probe spatial proximities. Dipolar couplings can be determined by integration of the DQ intensities and analysis of build-up behavior.
- **DQ sideband patterns ($\Delta t_1 << \tau_R$)** are obtained using DQ recoupling schemes without axial-symmetric excitation efficiency, e.g. DRAMA or BABA. Since the patterns depend only on the excitation time and the dipolar coupling, they can be used to measure the dipolar couplings.

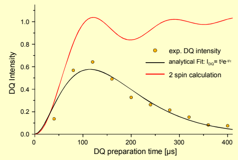


If the t_1-increments of a DQ experiment are not synchronized to the MAS rotor period, the Hamiltonian applied during the DQ reconversion period is modulated with the rotor phase, which leads to sideband pattern in DQ dimension of the spectrum. These sideband patterns can be used to measure dipolar couplings, since they depend only on the DQ excitation time and the dipolar coupling.

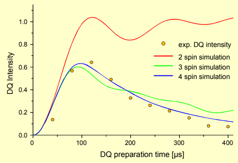


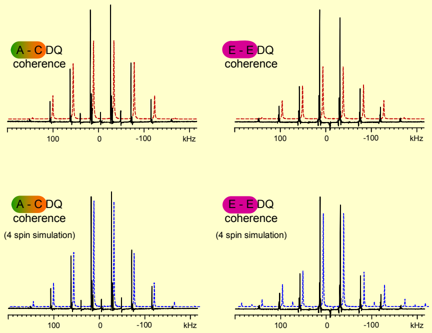
Measurement of Residual Dipolar Couplings and Local Order Parameter

The analysis of the build-up behavior [3] of DQ intensities, extracted from two dimensional DQ correlation spectra by integration, as well as the analysis of DQ spinning sideband patterns [4] have been performed to determine the residual dipolar couplings of the nematic model compound in its liquid-crystalline phase. In both cases, the BABA pulse sequence [2] has been used for the DQ excitation, and the temperature was set to T = 342 K. The obtained experimental results of the two different DQ methods are in good agreement, and the order parameter [3] calculated from the A-C and the B-C dipolar couplings coincide with those obtained from ^{2}H NMR techniques [1].



The data for the build-up analysis of the B - C DQ coherence is obtained by integration of 2D DQ correlation spectra with increasing excitation time. The black lines shows the analytic fit used for the 2 spin evaluation of the DQ build-up behavior. A heuristic exponential decay mimics multi spin effects observed in the DQ build-up behavior of abundant spin systems and known from 3 and 4 spin simulation shown below.



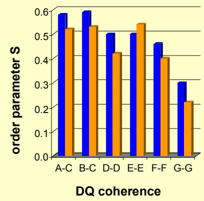


DQ spinning sideband patterns of different coherences extracted from a single two dimensional sideband pattern spectrum, recorded at T = 345 K and 22 kHz MAS spinning frequency with t_{exc}= 270 ms BABA excitation. The spectra shown in red and blue dotted lines are 2 and 4 spin calculations, respectively, performed with the SIMPSON program [5], which include experimental imperfections, e.g. phase switching delays, and finite RF power levels.

DQ coherence		A-C	B-C	D-D	E-E	F-F	G-G
$D_{ij,eff.}$ [kHz]	SBP	4.8	4.9	5.2	5.2	4.8	3.1
	Build-up	4.4	4.3	4.5	5.6	4.3	2.4
S_{ij}	SBP	0.58	0.59	0.50	0.50	0.46	0.30
	Build-up	0.52	0.53	0.42	0.54	0.40	0.22

The graphical representation of the determined order parameters for various ^{1}H - ^{1}H inter-nuclear vectors shown aside exhibits a good agreement between the two different experimental approaches.

The order parameters from the DQ coherences at the phenyl rings match the value 0.6 from ^{2}H line-shape analysis of investigated samples selectively labeled at the phenyl rings [1].

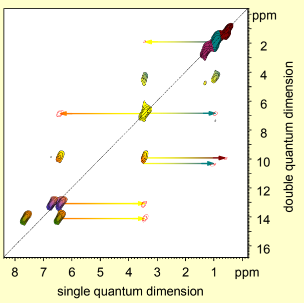


Multi Spin Effects and Higher-Order Multiple-Quantum Coherences

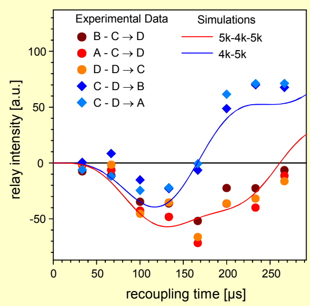
Multi-spin effects such as **relay DQ signals** can be observed for longer DQ recoupling times in abundant spin systems.

DQ polarization transfer during the reconversion process leads to signals of either sign that can not be interpreted within the common DQ scheme and rather resemble exchange peaks.

In most cases, density matrix simulations [5] involving at least four spins are needed to analyze the dynamics of relay intensities, which depend on the topology of the whole spin system.



Two dimensional DQ correlation spectrum (30 kHz MAS, T = 342 K, t_{exc}= 133 µs, BABA). Relay DQ signals with reversed sign indicated by red contour levels are observed.



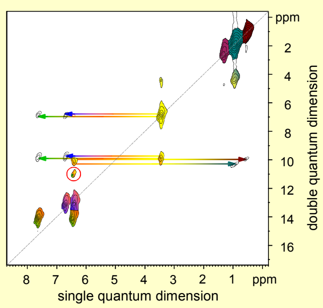
A quantitative analysis of relay DQ intensities is relatively difficult, since they can have both signs and depend on the topology of the whole spin system. However, a significantly different behavior, e.g. of the zero crossing of the relay DQ intensities, is observed, if the initial DQ coherence was excited at a strongly (red line) or weakly (blue line) coupled spin pair.

For longer recoupling times, the recoupled DQ-average Hamiltonian can excite higher order multiple quantum coherences, e.g. 4 spin coherences. Since four quantum coherences are filtered out by the applied 4 step 2 quantum phase cycling, **4 spin DQ coherences** are the only observable 4 spin coherences.

$$H_{4S2Q} = a_{ijkl} I_i^+ I_j^+ I_k^+ I_l^- + a_{ijkl}^* I_i^- I_j^- I_k^- I_l^+$$

In the spectrum shown aside the $(I_A^+ I_C^- I_C^+ I_D^+ + I_A^- I_C^+ I_C^- I_D^-)$ – coherence is observed (see red circle).

Multi spin effects in DQ spectra probe spatial proximities of DQ to additional spins. However, these effects are, in most cases, weak and hard to interpret.



Two dimensional DQ correlation spectrum (30 kHz MAS, T = 342 K, t_{exc}= 266 µs, BABA). Relay DQ signals represent major contributions to the spectrum. Marked in red, a 4 spin 2 quantum coherence is observed.

Conclusions and Outlook

- ^{1}H double-quantum NMR spectroscopy in combination with fast MAS and appropriate recoupling techniques represents a powerfull tool for the investigation of dipolar coupled networks in abundant spin systems.
- DQ methods can be used to determine local order parameters of mobile systems, e.g. liquid crystals, and both strategies, analysis of the DQ build-up behavior and of DQ spinning sideband patterns, give comparable results.
- Relay DQ signals with alternating sign, depending on the recoupling time, can be observed and analyzed.
- Two spin evaluation of DQ spinning sideband pattern restricted to higher order sidebands give reasonable results, even though multi spin effects such as relay signal are already observed for the analyzed recoupling time.

References

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