

Multispin moments edited by multiple-quantum NMR: application to elastomers

M.A. Voda, D.E. Demco, J. Perlo, R.A. Orza, B. Blümich*

*Institut für Technische Chemie und Makromolekulare Chemie, Rheinisch-Westfälische Technische Hochschule,
Worringerweg 1, D-52056 Aachen, Germany*

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Abstract

The spin system response to the five-pulse sequence used for measurements of double-quantum and triple-quantum buildup curves is evaluated in the initial excitation/reconversion regime. The multispin dipolar network that is present also in many soft solids like elastomers was considered. It is proved rigorously that the relevant quantity for analysis of double-quantum build-up curves in the initial regime is the second van Vleck moment. The higher-order moments edited by double-quantum as well as higher-order coherences in the multiple-quantum build-up experiments are different from van Vleck moments. These results can be applied to compare ^1H residual moments edited by double-quantum and triple-quantum experiments with those measured by other NMR methods. The sensitivity of multiple-quantum coherences to the changes in the values of residual dipolar couplings for cross-linked natural rubber under uniaxial elongation is also discussed. Under such conditions ^1H second van Vleck moments were measured for different elongation ratios of a cross-linked natural rubber. Moreover, ^1H triple-quantum edited moments were also measured for the same sample under uniaxial compression. The dependence of the second van Vleck moment and the time of the maximum of the double-quantum buildup curve on the cross-link density of natural rubber measured at low magnetic field was also investigated.

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1. Introduction

Proton residual dipolar interactions measured by NMR provide information about the structure and molecular dynamics in soft solids like elastomers and biological tissues [1–3]. Structure-function relationships can be investigated for the broad class of elastomer materials [1,2] (and references therein) via changes induced in the residual dipolar couplings by cross-link density, the presence of fillers, the action of mechanical deformation forces, and the adsorption of small pen-

trant molecules. The difficulties related to these measurements are due to the small values of the residual spin couplings, the many-body character of the dipolar couplings and the presence of molecular motions, which, in some cases produce a supplementary encoding of the spin system response.

In the last years ^1H residual dipolar couplings were measured by different one-dimensional and two-dimensional NMR techniques [1,2] (and references therein). On approach to *model-free* access to the residual dipolar couplings and dynamic order parameters uses multiple-quantum (MQ) buildup [4–9] and decay [10] curves recorded in the initial regime of the excitation/reconversion periods. These measurements can be performed in low magnetic fields [9–11] and even in the presence of

* Corresponding author. Fax: +49 241 80 22 185/88 88 185.
E-mail address: bluemich@mc.rwth-aachen.de (B. Blümich).

strongly inhomogeneous static and radio-frequency magnetic fields [10,11].

One-dimensional NMR methods based on the transverse magnetization relaxation [1], the dipolar correlation effect in combination with Hahn and solid echoes [12,13], the stimulated echo [14] (and references therein), and the magic echo [15] provide access only to the second van Vleck moment via a model which takes into account the solid-like and liquid-like contributions to the spin system response. Magnetization-exchange experiments [16,17] performed in the limit of short mixing times give residual van Vleck moments based on a specific spin model. Recently, a new method, the accordion magic sandwich (AIMS), was introduced [18], to measure ^1H residual van Vleck moments. A magic sandwich of variable duration leads to a Hahn echo which samples the shape of the magic echo. In this way residual dipolar couplings can be determined *model free* without contributions of inhomogeneous spin interactions and relaxation of transverse magnetization.

Time-resolved solid-state MQ NMR has been applied previously to characterize the distribution of spin-1/2 nuclei in a variety of quasi-rigid materials, typically on a 1–2 nm length scale [19,20]. In these materials the ^1H or ^{19}F dipolar couplings are relatively strong and the effect of molecular motions is only limited. Information on the spin distribution is obtained from the number of nuclei correlated through their dipole couplings as a function of spin preparation time τ [19–21]. The main objective of these studies were to measure the effective number of correlated spins $N(\tau)$, inside a cluster, that is determined from the variance of the Gaussian fit to the distribution of MQ coherence intensities.

The aim of this paper is to discuss how edited moments measured from MQ buildup curves are related to the van Vleck moments having in mind an application to elastomers. This is important when the edited residual moments are compared with those measured by other independent NMR methods. To this purpose the multi-spin system response to a radio-frequency pulse sequence with five pulses are considered. Our result allows us to investigate the sensitivity of MQ coherences of higher order to the changes in ^1H residual dipolar coupling of cross-linked natural rubber under uniaxial elongation. Proton residual van Vleck moments were measured from DQ buildup curves for a cross-link series of natural rubber using a low-field NMR spectrometer. Moreover, the possibility to use the time to the maximum of the MQ buildup curve to characterize the properties of elastomer networks is discussed. The effect of uniaxial deformation of a natural rubber band was investigated by measurements of second van Vleck moments and fourth moments edited by DQ, and TQ coherences, respectively.

2. Theory

2.1. Multispin second van Vleck moment from the DQ NMR build-up curve

In the following, we will evaluate the spin system response to the pulse sequence shown in Fig. 1. The general case of a multispin dipolar coupled system is considered. The pulse sequence of Fig. 1 creates even-order MQ coherences if applied to a spin system initially polarized in the static magnetic field [22,23]. In the short excitation/reconversion time regime, mainly DQ coherences are detected.

The quantum-mechanical propagators which describe the action of 90_x^0 and 90_y^0 radio-frequency pulses are given by

$$P_x = \exp \left\{ i \frac{\pi}{2} I_x \right\}. \quad (1a)$$

and

$$P_y = \exp \left\{ i \frac{\pi}{2} I_y \right\}, \quad (1b)$$

respectively. The total spin operator \vec{I} has the components (I_x, I_y, I_z) . The propagator corresponding to the free evolution periods of excitation and reconversion is

$$E = \exp \{ -i H_d^{(0)} \tau \}, \quad (2)$$

where $H_d^{(0)}$ is the secular multispin dipolar Hamiltonian [22]. For a polymer network system like elastomers, this is the residual dipolar Hamiltonian [1,15]. For short excitation/reconversion times τ compared to the transverse relaxation time the dipolar Hamiltonian modulated by molecular motions can be neglected in a good approximation.

At the end of excitation/reconversion for short evolution time $t_1 \rightarrow 0$ (cf. Fig. 1) the density operator of the spin system can be written as

$$\rho(2\tau) = \hat{P}_y^{-1} \hat{E} \hat{P}_y \hat{P}_x^{-1} \hat{E} \hat{P}_x \rho(0), \quad (3)$$

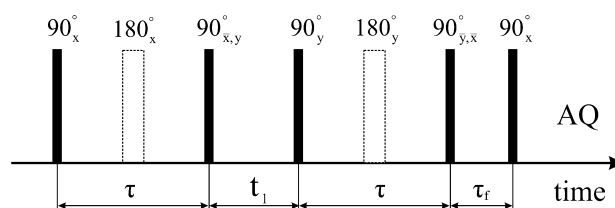


Fig. 1. Five-pulse sequence used for excitation of even-order and odd-order MQ coherences. In the former case, the phases of the excitation pulses differ by 180° , and in the latter case by 90° . The reconversion period contains a sequence of radio-frequency pulses with the phases orthogonal to the excitation pulses to generate a time-reversed dipolar DQ Hamiltonian. In some of the experiments a 180° refocusing pulse (dashed lines) is introduced in the middle of excitation and refocusing periods. For measurements of MQ buildup curves, the evolution of MQ coherences during the period t_1 is kept very short.

where the density operator at the initial moment of time is $\rho(0)$. The Liouville operator is denoted by $\exp\{i\hat{O}\}$, i.e., $\exp\{i\hat{O}\}\rho \equiv \exp\{iO\}\rho \exp\{-iO\}$, and $\hat{O}\rho \equiv [O, \rho]$.

To evaluate Eq. (3) it is easy to show that the effective propagator of the excitation period is given by

$$\begin{aligned} P_x^{-1}EP_x &= \exp\{-iP_x^{-1}H_d^{(0)}P_x\tau\} \\ &= \exp\left\{-i\left(-\frac{1}{2}H_d^{(0)} - H_{\text{DQ}}\right)\tau\right\}, \end{aligned} \quad (4a)$$

and for the reconversion period by

$$\begin{aligned} P_y^{-1}EP_y &= \exp\{-iP_y^{-1}H_d^{(0)}P_y\tau\} \\ &= \exp\left\{-i\left(-\frac{1}{2}H_d^{(0)} + H_{\text{DQ}}\right)\tau\right\}. \end{aligned} \quad (4b)$$

The secular multispin dipolar Hamiltonian [22] is

$$H_d^{(0)} = \sum_{i \neq j} d_{ij}(3I_{iz}I_{jz} - \vec{I}_i \cdot \vec{I}_j), \quad (5)$$

and the pure double-quantum dipolar Hamiltonian is given by

$$H_{\text{DQ}} = \frac{3}{4} \sum_{i \neq j} d_{ij}(I_{i+}I_{j+} + I_{i-}I_{j-}), \quad (6)$$

where d_{ij} is the dipolar coupling constant of spins i and j . Residual secular and DQ dipolar Hamiltonians can be obtained from Eqs. (5) and (6) by substituting $d_{ij} \rightarrow K(R, \beta)S^{ij}d_{ij}$, where the coefficient K depends on the end-to-end vector \vec{R} and the local orientation of \vec{R} relative to the direction of the static magnetic field specified by the angle β [1,15]. Site selective dynamic order parameter is denoted by S^{ij} .

In the limit of short excitation time, i.e., $\|H_d^{(0)}\|\tau \ll 1$, where $\|H_d^{(0)}\|$ is the strength of the dipolar interactions, using Eqs. (3) and (4a) the density operator at the end of the excitation period can be written as

$$\begin{aligned} \rho_{\text{exc}}(\tau) &\approx \left\{ \hat{1} - i \left[-\frac{1}{2}\hat{H}_d^{(0)} - \hat{H}_{\text{DQ}} \right] \tau \right. \\ &\quad \left. - \frac{1}{2} \left[-\frac{1}{2}\hat{H}_d^{(0)} - \hat{H}_{\text{DQ}} \right]^2 \tau^2 + \dots \right\} \rho(0), \end{aligned} \quad (7)$$

where $\hat{1}$ is the unity operator. The DQ coherences present at the end of the excitation period can be obtained from the total density operator $\rho_{\text{exc}}(\tau)$ taking into account that $\rho_{\text{DQ}}(0) \propto I_z$. Finally, we obtain

$$\rho_{\text{DQ}}(\tau) \propto \left\{ i\hat{H}_{\text{DQ}}\tau - \frac{1}{2} \left[\hat{H}_{\text{DQ}}^2 + \frac{1}{2}\hat{H}_d^{(0)}\hat{H}_{\text{DQ}} \right] \tau^2 + \dots \right\} I_z. \quad (8)$$

At the end of the reconversion period the final density operator encoded by the DQ coherences excited in the first period of the experiment is described by

$$\begin{aligned} \rho_{\text{DQ}}(2\tau) &\propto \left\{ \hat{1} - i \left[-\frac{1}{2}\hat{H}_d^{(0)} + \hat{H}_{\text{DQ}} \right] \tau \right. \\ &\quad \left. - \frac{1}{2} \left[-\frac{1}{2}\hat{H}_d^{(0)} + \hat{H}_{\text{DQ}} \right]^2 \tau^2 + \dots \right\} \\ &\quad \times x \left\{ i\hat{H}_{\text{DQ}}\tau - \frac{1}{2} \left[\hat{H}_{\text{DQ}}^2 + \frac{1}{2}\hat{H}_d^{(0)}\hat{H}_{\text{DQ}} \right] \tau^2 + \dots \right\} I_z. \end{aligned} \quad (9)$$

At the end of the pulses sequence shown in Fig. 1 the double-quantum filtered signal can be evaluated from Eq. (9) taking into account that $\hat{H}_d^{(0)}I_z = 0$ and $\exp\{-i\frac{\pi}{2}I_z\}H_{\text{DQ}} = -H_{\text{DQ}}$. For short values of excitation/reconversion times τ the normalized DQ signal is given by

$$S_{\text{DQ}}(2\tau) \approx -\frac{1}{2} \frac{\text{Tr}\{\{\hat{H}_{\text{DQ}}I_z\}^2\}}{\text{Tr}\{I_z^2\}} \tau^2 - \dots \quad (10)$$

For the general case of a multispin dipolar system the DQ buildup curve can be approximated at short τ values by a term proportional to τ^2 of the form

$$S_{\text{DQ}}(2\tau) \approx \frac{1}{2} M_2^{\text{DQ}} \tau^2 - \dots, \quad (11)$$

where the double-quantum edited moment of the buildup curve is given by

$$M_2^{\text{DQ}} = -\frac{\text{Tr}\{\{\hat{H}_{\text{DQ}}I_z\}^2\}}{\text{Tr}\{I_z^2\}}. \quad (12)$$

This result generalizes the cases of isolated spin-1/2 pairs and of a methyl group discussed in [4].

The spin pair nature of the dipolar coupling Hamiltonian and the editing of these pairs by DQ filtering leads to the fact that M_2^{DQ} equals the van Vleck moment M_2 [24,25], i.e., $M_2^{\text{DQ}} = M_2$ (see Appendix A). Therefore, the dipolar coefficient of τ^2 measured in static DQ filtered experiments on elastomers [4] and reported as the residual dipolar coupling is equal to half of the residual second van Vleck moment $\langle M_2 \rangle$. For longer excitation times DQ coherences involve high-order spin correlations [21]. Moreover, high-order MQ coherences are created [21]. Hence, the dipolar coefficients of high-order terms in τ^2 edited by DQ filtered signal are expected to be different from higher-order van Vleck moments.

It is not possible to obtain an exact analytical expression for the DQ buildup curve of a multispin system at all excitation/reconversion times. Therefore, the DQ filtered signal is described in a heuristic manner by

$$S_{\text{DQ}}(2\tau) \propto \left\{ 1 - \exp \left[-\frac{M_2}{2} \tau^2 \right] \right\} \exp \left[-\frac{2\tau}{T_2^*} \right], \quad (13)$$

where the transverse relaxation during the free evolution windows (cf. Fig. 1) is accounted for by the effective transverse relaxation time T_2^* . For $\tau \ll T_2^*$ and $(M_2)^{1/2}\tau \ll 1$ the DQ filtered signal given by Eq. (13) is in agreement with

that given by Eq. (11). The double-quantum filtered signal of Eq. (13) is normalized to the integral intensity of the single quantum signal. Eq. (13) generalizes the Gaussian ansatz proposed in [8] and provides a physical significance to the exponent in τ^2 .

We should note that in soft solids like elastomers the ratio $\langle M_4 \rangle / (\langle M_2 \rangle)^2$ that characterizes the solid-like contribution to the transverse relaxation of single-quantum (SQ) coherences is of the order of 10^2 [18], i.e., the Gaussian line-shape is a poor approximation [25]. This is expected to be also valid for Eq. (13) especially for longer τ values, i.e., for $(\langle M_2 \rangle)^{1/2} \tau \geq 1$. Moreover, as the excitation/reconversion time increases DQ multispin correlations are present as well as high-order MQ coherences of even order. The change in the size of the dipolar network produced by these effects has to be taken into account by DQ edited moments of higher order. Therefore, a more justified expression for the DQ build-up signal of an elastomer is a polynomial function in τ^2

$$S_{\text{DQ}}(2\tau) \propto \left\{ \frac{\overline{M}_2}{2} \tau^2 - \frac{\overline{M}_4^{\text{DQ}}}{4!} \tau^4 + \dots \right\} \exp \left[-\frac{2\tau}{T_2^*} \right], \quad (14)$$

where T_2^* is the effective transverse relaxation time which can be replaced by T_2 when refocusing 180° pulses are used in the middle of excitation/reconversion periods. The residual higher-order DQ moments $\langle M_{2n}^{\text{DQ}} \rangle$, ($n > 1$) in Eq. (14) are different from the residual van Vleck moments $\langle M_{2n} \rangle$, ($n > 1$). In principle, double-quantum edited moments $\langle M_{2n}^{\text{DQ}} \rangle$, ($n > 1$) can be evaluated using Eq. (9).

2.2. Multispin moments edited by the TQ build-up curve

Odd-order MQ coherences can be created using the pulse sequence of Fig. 1 that acts on the spin system with z polarization [22,23]. The density operator at the end of the excitation period of the five pulse sequence is given by

$$\begin{aligned} \rho_{\text{exc}}(\tau) &\propto \exp \left\{ i \frac{\pi}{2} \hat{I}_y \right\} \exp \left\{ -i \hat{H}_d^{(0)} \tau \right\} \exp \left\{ i \frac{\pi}{2} \hat{I}_x \hat{I}_z \right\} \\ &= \left(\exp \left\{ i \frac{\pi}{2} \hat{I}_y \right\} \exp \left\{ -i \hat{H}_d^{(0)} \tau \right\} \exp \left\{ -i \frac{\pi}{2} \hat{I}_y \right\} \right) I_y \\ &= \exp \left\{ -i \left[-\frac{1}{2} \hat{H}_d^{(0)} + \hat{H}_{\text{DQ}} \right] \tau \right\} I_y. \end{aligned} \quad (15)$$

It can easily be shown that the term in Eq. (15) of lowest order in τ^2 which creates triple-quantum (TQ) has the form

$$\rho_{\text{TQ}}(\tau) \propto -\frac{1}{2} \left[\hat{H}_{\text{DQ}}^2 - \frac{1}{2} \hat{H}_{\text{DQ}} \hat{H}_d^{(0)} \right] \tau^2 I_y. \quad (16)$$

The signal encoded by TQ coherences obtained by z -filtering at the end of the reconversion part of the pulse sequence (Fig. 1) can be evaluated in the manner similar to that of the DQ signal. Finally, for the normalized signal we can write

$$\begin{aligned} S_{\text{TQ}}(2\tau) &\approx \frac{1}{4 \text{Tr}\{I_y^2\}} \text{Tr} \left\{ \left[\left(-\frac{1}{2} \hat{H}_d^{(0)} + \hat{H}_{\text{DQ}} \right)^2 I_y \right] \right. \\ &\quad \left. \times \left[\left(\hat{H}_{\text{DQ}}^2 - \frac{1}{2} \hat{H}_{\text{DQ}} \hat{H}_d^{(0)} \right) I_y \right] \right\} \tau^4 - \dots \end{aligned} \quad (17)$$

The equation above reveals that TQ buildup curve is described in the lowest order of τ by a term proportional to τ^4 . This generalizes the results obtained for an isolated methyl group [4]. The dipolar coefficient of this term can be defined as the fourth moment (M_4^{TQ}) edited by the TQ buildup curve. Finally one can write

$$S_{\text{TQ}}(2\tau) \approx \frac{M_4^{\text{TQ}}}{4!} \tau^4 - \dots \quad (18)$$

The explicit general expression for the edited fourth moment which characterizes the TQ buildup curve can be obtained from Eqs. (17) and (18), i.e.

$$\begin{aligned} M_4^{\text{TQ}} &= \frac{6}{\text{Tr}\{I_y^2\}} \text{Tr} \left\{ \left[\left(-\frac{1}{2} \hat{H}_d^{(0)} + \hat{H}_{\text{DQ}} \right)^2 I_y \right] \right. \\ &\quad \left. \times \left[\left(\hat{H}_{\text{DQ}}^2 - \frac{1}{2} \hat{H}_{\text{DQ}} \hat{H}_d^{(0)} \right) I_y \right] \right\}. \end{aligned} \quad (19)$$

In Appendix B, it is shown that M_4^{TQ} is different from the fourth van Vleck moment M_4 . This is expected based on the fact that M_4^{TQ} edits only the dipolar sums of the form $\sum_{i \neq j \neq k}$. Besides these dipolar sums M_4 contain also sums of the form $\sum_{i \neq j}$.

Similar to the DQ buildup curve the normalized TQ filtered signal can be approximated by the rapidly convergent function

$$S_{\text{TQ}}(2\tau) \propto \left\{ 1 - \exp \left[-\frac{M_4^{\text{TQ}}}{4!} \tau^4 \right] \right\} \exp \left[-\frac{2\tau}{T_2^*} \right]. \quad (20)$$

This ad hoc function allows us to measure M_4^{TQ} which provides information about three-spin correlations. A function with slower convergence but better justified from first principles, especially in the case of soft solids is given by the polynomial expansion (see also Eq. (14))

$$S_{\text{TQ}}(2\tau) \propto \left\{ \frac{M_4^{\text{TQ}}}{4!} \tau^4 - \frac{M_6^{\text{TQ}}}{6!} \tau^6 + \dots \right\} \exp \left[-\frac{2\tau}{T_2^*} \right]. \quad (21)$$

For soft solids like elastomers the edited moments of the MQ buildup curves can be correlated with the dynamic order parameters. For instance, $\langle M_4^{\text{TQ}} \rangle = S^4 M_{4,\text{rigid}}^{\text{TQ}}$.

The above considerations show that no assumptions related to the configuration of the dipolar network or the mechanism of average induced by the molecular motions are needed to derive the shapes of the MQ buildup curves in the initial time regime. Therefore, the measurement of the corresponding moments is performed *model free*.

2.3. Evaluation of τ_{\max}

The multiple-quantum build-up curves of many elastomers are characterized by a well-defined maximum. This is rigorously valid for a polymer network without a distribution of residual dipolar couplings [6]. The existence of the maximum in the MQ filtered signal is due to the creation process of the MQ coherences and the dephasing of the SQ coherences by the transverse relaxation during the excitation/reconversion periods. Approximate relationships describing this behaviour of the MQ build-up curves are given by Eqs. (13), (14), (20), and (21).

The excitation/reconversion time τ_{\max} for the position of the maximum in the DQ build-up curve can easily be obtained from the analytical expression of the normalized DQ filtered signal that can be approximated by $S_{\text{DQ}}(\tau) \approx F_D(\tau)R_2(\tau)$, where $F_D(\tau)$ describes the dipolar encoded DQ build-up curve and $R_2(\tau)$ is the transverse relaxation function. In the approximation of exponential transverse magnetization relaxation, we can write $R_2(\tau) \cong \exp\{-2\tau/T_2^*\}$. The transverse magnetization relaxation is approximated only by a single exponential and in the presence of 180° refocusing pulses (Fig. 1) T_2^* has to be replaced by T_2 . For a Gaussian dipolar encoding function of

$$F_D(\tau) \propto \left\{ 1 - \exp \left[-\frac{\langle M_2 \rangle}{2} \tau^2 \right] \right\},$$

we finally get

$$\frac{\langle M_2 \rangle T_2 \tau_{\max}}{\exp \left\{ \frac{1}{2} \langle M_2 \rangle \tau_{\max}^2 \right\} - 1} \approx 2. \quad (22)$$

In the following, the ratio in Eq. (22) will be defined by a function R . A similar equation can be written for the maxima of the TQ build-up curves with $\langle M_2 \rangle$ replaced by $\langle M_4^{\text{TQ}} \rangle$. We note that τ_{\max} is independent of the normalization of MQ filtered signals. Nevertheless, an equation like Eq. (22) implies approximations that cannot be fully justified.

2.4. Sensitivity to the residual dipolar couplings

The residual moments (for instance, $\langle M_2 \rangle$ and $\langle M_4^{\text{TQ}} \rangle$) of elastomers change due to physical and chemical agents acting on the polymer network. Therefore, it is important to compare different NMR methods from the point of view of sensitivity to the changes in the residual dipolar couplings.

The sensitivity of DQ and TQ edited signals to such changes can be estimated from the relative sensitivity defined by $\frac{\Delta S_{\text{DQ}}(2\tau)}{S_{\text{DQ}}(2\tau)}$ and $\frac{\Delta S_{\text{TQ}}(2\tau)}{S_{\text{TQ}}(2\tau)}$, respectively. In the limit of short excitation/reconversion times these quantities can be evaluated from Eqs. (11) and (18)

$$\frac{\Delta S_{\text{DQ}}(2\tau)}{S_{\text{DQ}}(2\tau)} \approx \frac{\Delta \langle M_2 \rangle}{\langle M_2 \rangle}, \quad (23)$$

and

$$\frac{\Delta S_{\text{TQ}}(2\tau)}{S_{\text{TQ}}(2\tau)} \approx \frac{\Delta \langle M_4^{\text{TQ}} \rangle}{\langle M_4^{\text{TQ}} \rangle}. \quad (24)$$

It is evident that the sensitivity is proportional to the changes of the residual moments, i.e., $\Delta \langle M_2 \rangle$ and $\Delta \langle M_4^{\text{TQ}} \rangle$. This result generalizes the one obtained for isolated methylene and methyl protons [26]. Furthermore, as TQ experiments edit an extended dipolar network, it is expected that these experiments are more sensitive than DQ experiments. This was shown previously for a cross-link series of natural rubber [26] and a supplementary proof is given below for a stretched, cross-linked natural rubber band.

For longer excitation/reconversion times the sensitivities can be evaluated from Eqs. (14) and (21). These equations provide the basis for describing the loss in sensitivity to residual dipolar couplings when τ increases (see below).

3. Experimental

3.1. Samples

The investigated type of elastomer is based on commercially available natural rubber (NR) SMR10 (Malaysia). As additives, the samples of the cross-linked NR series contain 3 parts-per-hundred-rubber (phr) ZnO and 2 phr stearic acid. Seven differently cross-linked samples were investigated. The sulfur and accelerator contents are shown in Table 1. The accelerator is of the standard sulfenamide type (TBBS, benzothiazyl-2-tert-butyl-sulfenamide). After mixing the compounds in a laboratory mixer at 50°C , the vulcanisation was performed at 160°C in a Monsanto MDR-2000-E vulcameter. The degree of cross-linking was measured by the low frequency shear modulus (G) at a temperature of 160°C in the vulcameter directly after the vulcanisation. The measurements were performed with an oscillation amplitude of $\pm 0.5^\circ$ and a frequency of 1.67 Hz. The values of G are shown in Table 1 for the cross-linked NR series. For the same samples swelling measurements

Table 1
Properties of the series of cross-linked NR samples

Sample	Sulfur–accelerator content (phr)	Shear modulus ^a G (dNm)	Increase in mass ^a c_s (%)
NR1	1–1	5.2	499.1
NR2	2–2	8.5	400.4
NR3	3–3	11.2	347.8
NR4	4–4	13.2	324.4
NR5	5–5	14.5	310.7
NR6	6–6	15.4	304.0
NR7	7–7	16.2	287.2

^a The uncertainties are less than 10%.

were performed. The samples were kept in toluene/ethanol (85/15) for 24 h at room temperature. The increases in sample mass are listed in Table 1.

3.2. NMR experiments

The NMR experiments were performed at a ^1H frequency of 299.87 MHz on a Bruker DMX-300 spectrometer and at 40 MHz on a Bruker Minispec MQ 40. Even and odd order multiple-quantum build-up curves were measured using the five-pulse sequence (Fig. 1) [22,23]. The phase cycling scheme used for detection of the MQ coherences of the order $\pm p$ is described in [22,23]. The maximum MQ coherences detected in the sample series was $p = \pm 4$. The length of the 90° radio-frequency pulse was about $9 \mu\text{s}$, and a 1 s recycle delay was used. The pulse sequence implemented on the Bruker Minispec had 180° refocusing pulses in the middle of excitation and reconversion periods. The MQ evolution time and the z -filter delay were fixed to $t_1 = 20 \mu\text{s}$ and $\tau_f = 20 \mu\text{s}$, respectively. The transverse relaxation time was measured with Bruker Minispec using the Carr–Purcell–Meiboom–Gill pulse sequence [14] (and references therein) with an echo time of $80 \mu\text{s}$. Simple homemade devices for measurements of the natural rubber bands under elongation and compression were used.

4. Results and discussion

4.1. Sensitivity to the changes of ^1H residual dipolar couplings in natural rubber under uniaxial elongation

Proton MQ buildup curves measured at 300 MHz in NR1 under uniaxial elongation and in the relaxed state (i.e., for $\lambda = 1$) are shown in Fig. 2. Systematic changes are observed in the initial slopes and positions of the maxima with increasing elongation λ .

The relative sensitivity $(S_\lambda(\tau) - S_{\lambda=1}(\tau))/S_{\lambda=1}(\tau)$ to the changes of residual dipolar couplings is plotted in Fig. 3 versus the excitation/reconversion time τ for different λ values. The uniaxial elongation leads to an increase of the residual dipolar couplings due to the higher chain orientation and interchain interactions [27] (and reference therein). Therefore, as predicted by Eqs. (23) and (24), the relative sensitivity increases with increasing elongation ratio. This is fully supported by the data shown in Fig. 3. Based on Eqs. (14) and (21), we can predict a decrease of the relative sensitivity when τ is increased. The data presented in Fig. 3 for the DQ, TQ, and FQ filtered signals support this prediction.

The relative sensitivities to the changes in ^1H residual dipolar couplings detected by DQ, TQ, and FQ filtered signals are compared in Fig. 4 for the same values of the elongation ratio. It is obvious that the relative sensitivity

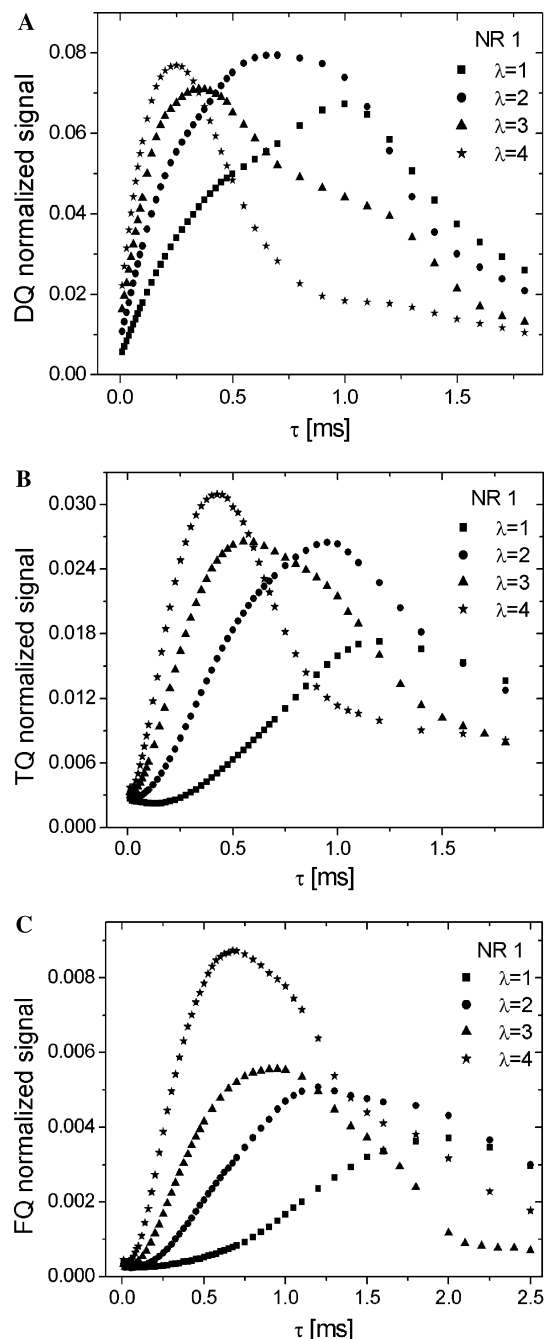


Fig. 2. Normalized ^1H double-quantum (DQ) (A), triple-quantum (TQ) (B), and four quantum (FQ) (C), buildup curves for the sample NR1 of different values of the elongation ratio λ .

increases with the order of the MQ coherences. Four-quantum coherences show an increase of almost one order of magnitude in the sensitivity with respect to the DQ coherences. The same effect was detected for differently cross-linked natural rubber samples and reported recently in [26]. The present result represents another independent experimental confirmation of the enhancement in sensitivity by the use of higher-order of MQ coherences.

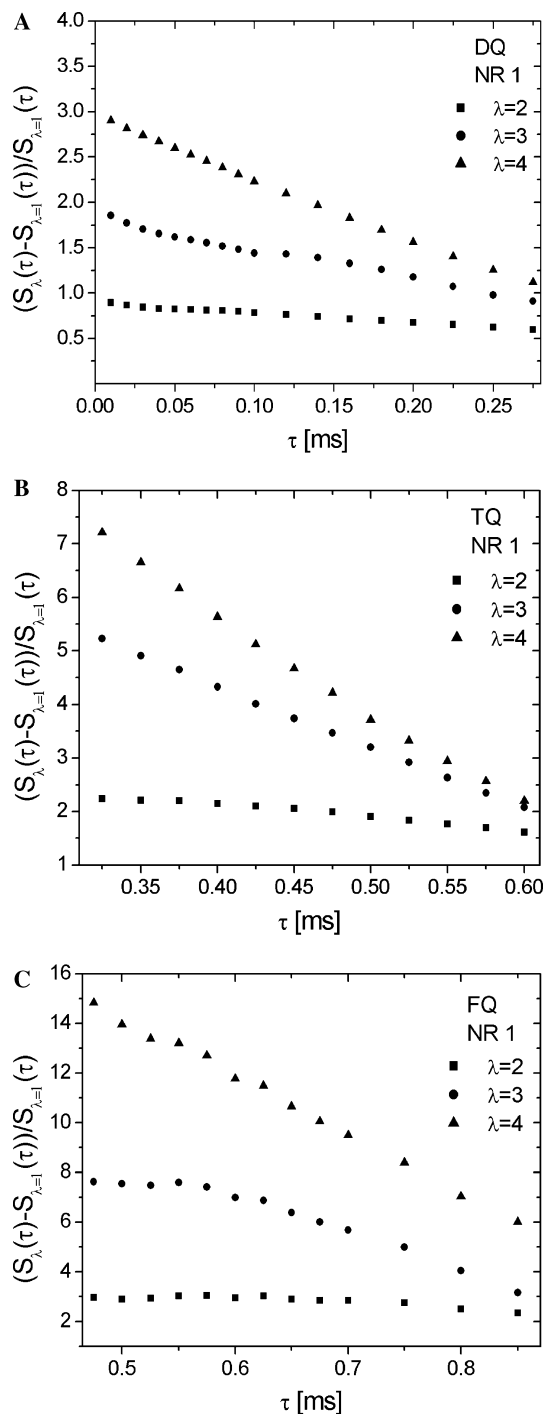


Fig. 3. The relative sensitivity $(S_\lambda(\tau) - S_{\lambda=1}(\tau)) / S_{\lambda=1}(\tau)$ to the residual dipolar couplings as a function of the excitation/reconversion time τ . (A) DQ, (B) TQ, and (C) FQ sensitivity ratios for the sample NR1 at different λ values.

4.2. Residual second van Vleck moments for a cross-linked natural rubber series

Proton DQ buildup curves were measured at a resonance frequency of about 40 MHz on a Bruker Minispec at a temperature of 40 °C for the natural rubber samples

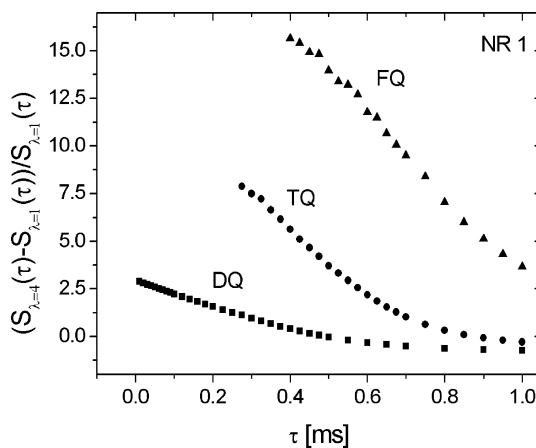


Fig. 4. The relative sensitivity ratios for DQ, TQ, and FQ coherences are compared for the sample NR1 and the MQ filtered ^1H signals of Fig. 3 with $\lambda = 1$ and $\lambda = 4$.

of Table 1. The DQ buildup curves of the samples NR1 and NR7 with the extreme values of the cross-link density are shown in Fig. 5. For the sample NR1 the DQ buildup curves measured at 300 MHz (see Fig. 2A) are different from the curves measured at 40 MHz (Fig. 5). This is due to the differences in the sample temperature and the inaccuracy in the normalization value. These buildup curves were fitted with the polynomial function of Eq. (14), and the ^1H residual second van Vleck moments are shown in Fig. 6. In agreement with previous findings [15,18] the dependence of $\langle M_2 \rangle$ on cross-link density (phr) and shear modulus G is not linear. The dependences are clearly different showing that the characterization of the cross-link network can better be approximated by c_s or G quantities. This is due to the fact that at higher sulfur–accelerator concentration the vulcanisation reaction is not completely terminated.

The values of the ^1H residual second van Vleck moment measured as short times of the MQ buildup curves

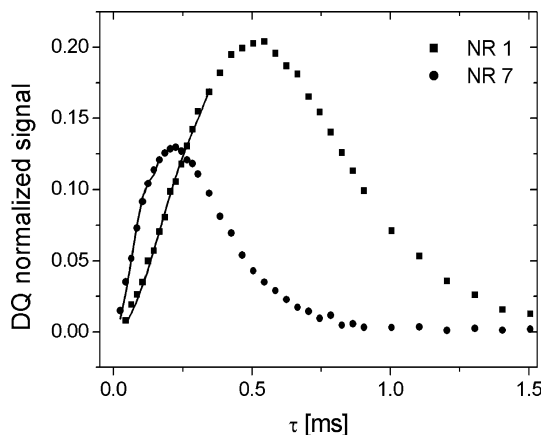


Fig. 5. Proton DQ buildup curves for samples NR1 and NR7 (see Table 1) measured with the pulse sequence of Fig. 1. The solid lines represent the polynomial fits given by Eq. (14).

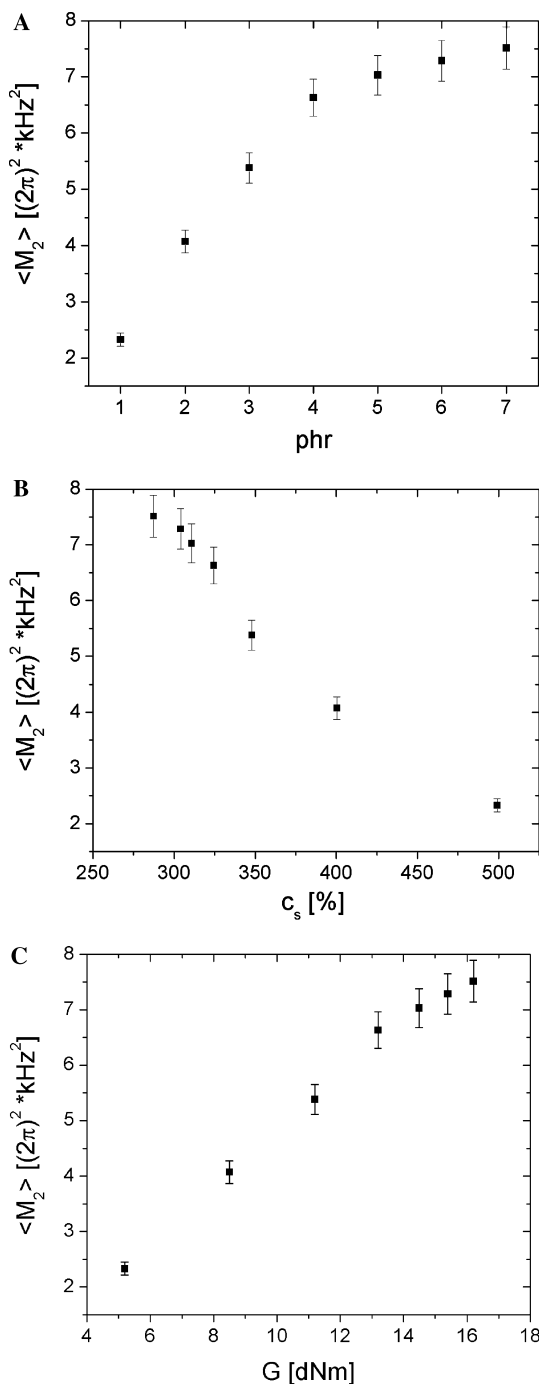


Fig. 6. Proton residual second van Vleck moments measured for the series of cross-linked natural rubber samples as a function of cross-link density (A), concentration of toluene/ethanol absorbed at saturation c_s (B), and shear modulus G (C) (see Table 1).

correspond to a NMR observation time of the order of 10 μs . Other NMR methods like AIMS [18] have NMR observation time of the order of 100 μs . Therefore, the motional averaging of dipolar couplings is more efficient in the latter case and $\langle M_2 \rangle$ has a smaller value. This is confirmed by comparing the data reported in [18] with the values of $\langle M_2 \rangle$ from Fig. 6.

4.3. Maxima of DQ buildup curves for a cross-link natural rubber series

The position (τ_{max}) of the maximum of the DQ buildup curves are plotted in Fig. 7 for the different values of the cross-link density measured in pHR (see Table 1), the concentration c_s of toluene/ethanol absorbed at saturation, and the shear modulus G . The sensitivity of these parameters to the changes in cross-link density is smaller

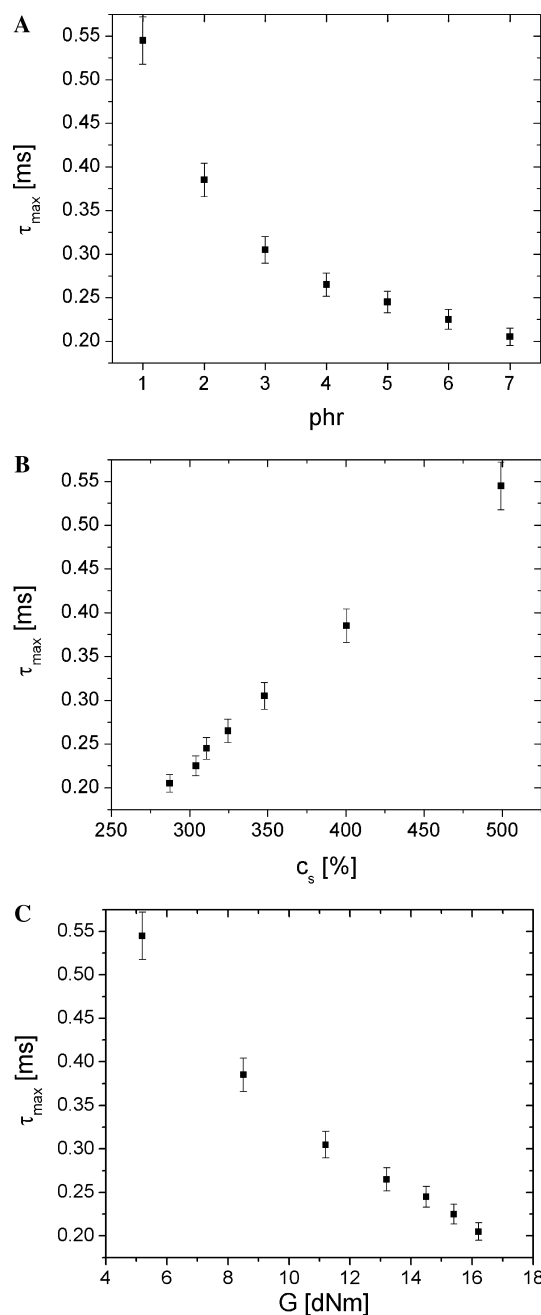


Fig. 7. The duration τ_{max} to reach the maximum of DQ buildup curves from Fig. 5 as a function of the cross-link density (A), concentration of toluene/ethanol absorbed at saturation c_s (B), and shear modulus G (C) for the series of cross-linked NR samples (Table 1).

than that due to changes in $\langle M_2 \rangle$ (compare Figs. 6 and 7). Transverse relaxation rates are shown in Fig. 8.

The quantity R given by Eq. (22) is shown in Fig. 9 as a function of cross-link density for samples of natural rubber (Table 1). For small values of the cross-link density $R \cong 2$ but starts to deviate when the values of the cross-linking densities increase. This shows that assump-

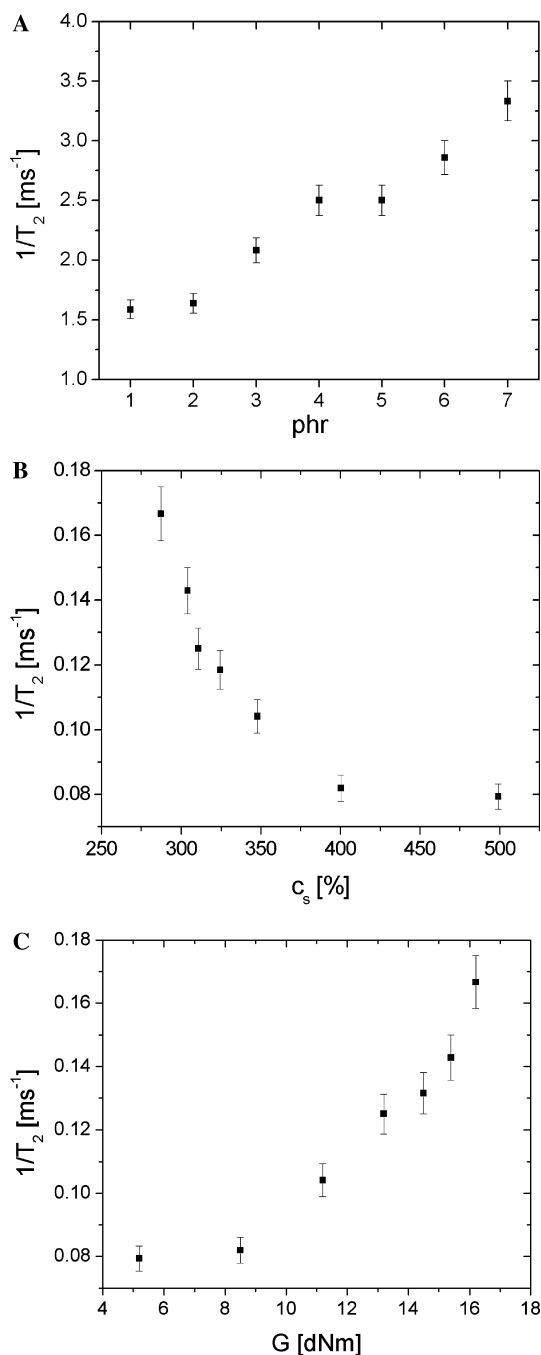


Fig. 8. Proton transverse relaxation rates $1/T_2$ as a function of cross-link density (A), concentration of toluene/ethanol absorbed at saturation c_s (B), and shear modulus G (C) measured for the series of cross-linked NR samples (Table 1).

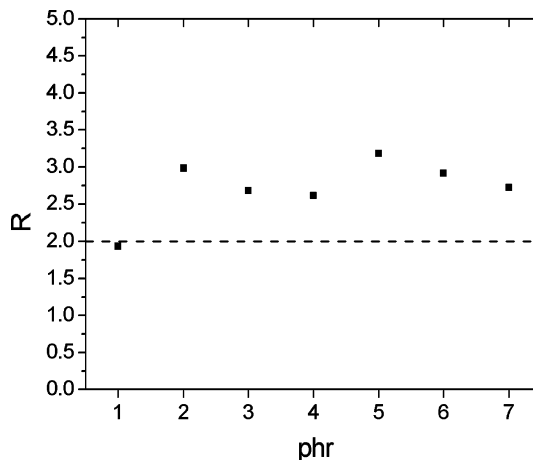


Fig. 9. The quantity R defined by Eq. (22) as a function of cross-link density for the series of cross-linked NR samples. The value of two for R predicted by the Eq. (22) is shown by the dashed line.

tion of exponential transverse relaxation and the Gaussian approximation (see Eq. (13)) involved in the derivation of Eq. (22) are no longer valid.

The quantity τ_{\max} can be measured without any normalization of the MQ buildup curves. Nevertheless, the interpretation of this parameter is, in general, more complex than that of $\langle M_2 \rangle$, and details of the spin dynamics as well as the segmental dynamics have to be taken into account.

4.4. Residual dipolar moments edited by TQ buildup curves for natural rubber under uniaxial elongation and compression

The proton double-quantum buildup curves of Fig. 2A were evaluated for the second van Vleck moments $\langle M_2 \rangle$ of sample NR1 as a function of the elongation ratio. The DQ buildup curves were fitted using Eq. (14), and the values of $\langle M_2 \rangle$ are shown in Fig. 10. These data cannot be compared quantitatively with $\langle M_2 \rangle$ measured

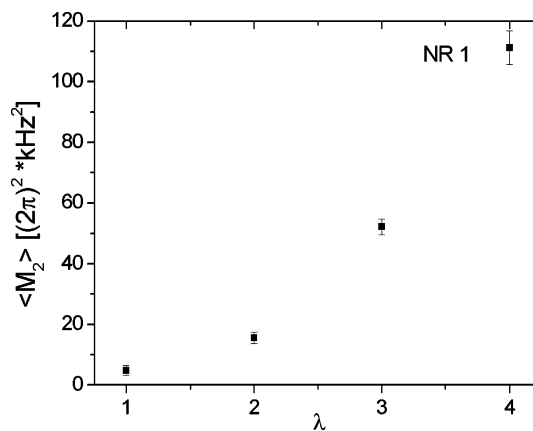


Fig. 10. Proton $\langle M_2 \rangle$ versus the elongation ratio λ from DQ buildup curves for sample NR1.

by the dipolar correlation function [13] in a stretched natural rubber band because the samples have different values of cross-link densities. Nevertheless, we detect an increase of $\langle M_2 \rangle$ by about one order of magnitude which is closer to the expected λ^4 dependence [13].

Proton TQ buildup curves were shown above to be more sensitive to the changes in the values of the residual dipolar couplings compared to the DQ buildup curves. The TQ buildup curves were measured for the NR1 sample under elongation (Fig. 2b) and compression

(Fig. 11A). From these data the residual moments $\langle M_4^{\text{TQ}} \rangle$ were evaluated using Eq. (21). These moments are shown in Figs. 11B and C as a function of the elongation and compression ratios λ , respectively. As expected the changes in the M_4^{TQ} edited moment of the NR1 sample under elongation is larger than that under compression due to the wider range of λ ratios used. Moreover, the ratio $M_4^{\text{TQ}}(\lambda = 4)/M_4^{\text{TQ}}(\lambda = 1) \approx 300$ is larger compared to $M_2(\lambda = 4)/M_2(\lambda = 1) \approx 20$ estimated from the data of Fig. 10. The dependences on λ shown in Figs. 10 and 11 can be used to test the models of the deformed polymer network [28,29], but this is beyond the scope of this work.

5. Conclusions

The measurements of residual moments edited by MQ buildup curves has some advantages compared to the measurements of other NMR quantities like the popular transverse magnetization relaxation. In the case of transverse relaxation, the residual dipolar couplings as well as the thermal modulation of dipolar interactions simultaneously contribute to the signal decay. The correlation of these moments with, for instance, cross-link density can be accomplished more easily than with transverse magnetization relaxation. In the last case, the second van Vleck moment as well as the distribution of correlation times has to taken into account via some model.

Soft solids like elastomers, gels and ordered tissues benefit from NMR measurements under static conditions. Sample deformations due to centrifugal forces at fast MAS can be avoided. The study of network deformation under MAS cannot be performed with the convenience of the static measurements. Moreover, site selective measurements of residual dipolar couplings of elastomers can be performed from ^1H - ^{13}C heteronuclear DQ buildup curves even under static conditions by using the ^{13}C resolved spectrum [30].

The significance of the residual dipolar coefficients which can be measured from DQ and TQ buildup curves was demonstrated. In the initial time regime of the excitation/reconversion periods only DQ buildup curves give a residual dipolar quantity that is equal to second van Vleck moment. This enables one to compare these moments with the van Vleck moments measured by other NMR techniques. It was shown that higher-order MQ buildup curves edit moments different from the van Vleck moments. These higher-order edited moments are more sensitive to the changes in the polymer network properties than the residual second van Vleck moment.

Based on the above results ^1H residual second van Vleck moment obtained from DQ buildup curves measured in low magnetic fields were correlated with the degree of cross-linking for a series of samples from natural rubber. This confirms the value of using low-field NMR

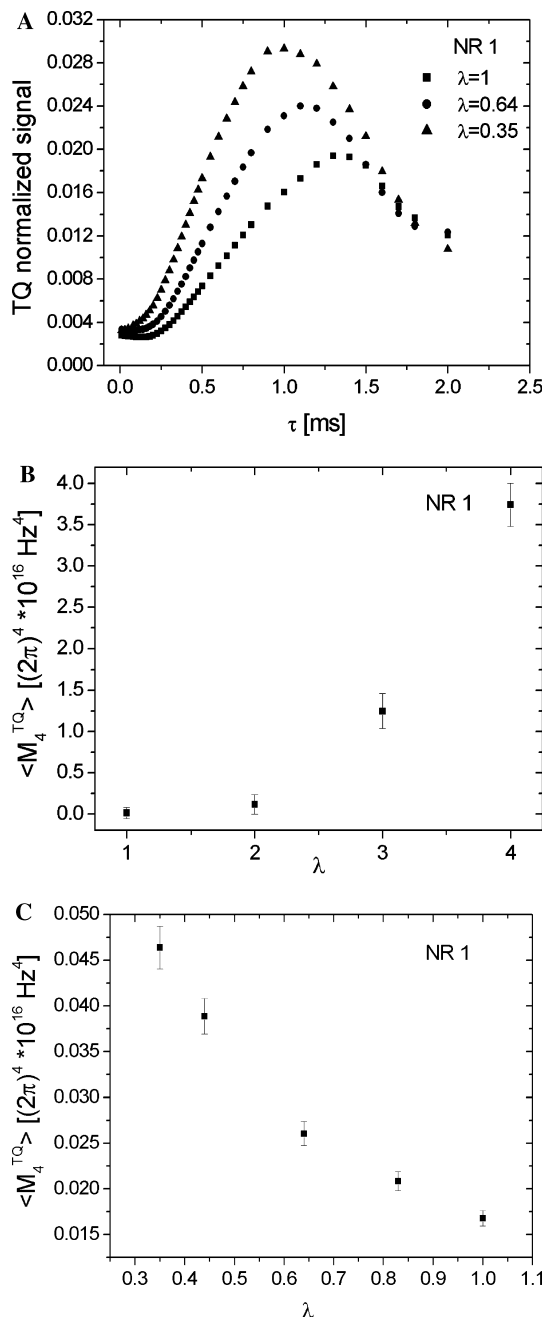


Fig. 11. (A) Proton TQ buildup curves as a function of compression ratios for NR1 (Table 1). Residual four moment M_4^{TQ} measured from TQ buildup curves for the cross-linked sample NR1 as a function of the elongation (B) and compression (C) ratio λ .

spectrometers to characterize viscoelastic materials [10,11,9].

The possibility to use the maximum in the MQ build-up curves as a measure of cross-link density was also discussed. This quantity is independent of a normalization of MQ signals, but more complex models are necessary in order to correlate it quantitatively with the properties of the polymer network.

The increased sensitivity of higher-order MQ coherences to changes in the ^1H residual dipolar couplings induced by uniaxial forces in cross-linked natural rubber was demonstrated and explained. As an application, ^1H TQ build-up curves of cross-linked natural rubber were measured under uniaxial elongation and compression. The edited residual fourth moment obtained from these curves as a function of the deformation ratio λ can be used to test the models of viscoelasticity.

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Appendix A

Second van Vleck moment for a multispin system described by the secular dipolar Hamiltonian $H_d^{(0)}$ is given by [24,25]

$$M_2 = -\frac{\text{Tr}\left\{\left[\hat{H}_d^{(0)} I_x\right]^2\right\}}{\text{Tr}\left\{I_x^2\right\}}. \quad (\text{A.1})$$

Taking into account the invariance of the trace under unitary operations, we can rewrite Eq. (A.1) as

$$M_2 = -\frac{\text{Tr}\left\{\left[\exp\left\{-i\frac{\pi}{2}\hat{I}_y\right\}\left[\hat{H}_d^{(0)} I_x\right]\right]^2\right\}}{\text{Tr}\left\{I_x^2\right\}}. \quad (\text{A.2})$$

The above equation can be rewritten using the transformations

$$\exp\left\{-i\frac{\pi}{2}\hat{I}_y\right\}I_x = -I_z. \quad (\text{A.3})$$

and

$$\exp\left\{-i\frac{\pi}{2}\hat{I}_y\right\}H_d^{(0)} = -\frac{1}{2}H_d^{(0)} + H_{\text{DQ}}. \quad (\text{A.4})$$

Because $\hat{H}_d^{(0)} I_z = 0$, we finally get

$$M_2 = -\frac{\text{Tr}\left\{\left[\hat{H}_{\text{DQ}} I_z\right]^2\right\}}{\text{Tr}\left\{I_z^2\right\}}. \quad (\text{A.5})$$

If Eq. (A.5) is compared to Eq. (12) it is obvious that van Vleck second moment is equal to the second moment edited by the DQ buildup curve, i.e., $M_2 = M_2^{\text{DQ}}$.

Appendix B

Fourth van Vleck moment for a multispin system is given by [24,25]

$$M_4 = \frac{\text{Tr}\left\{\left[\hat{H}_d^{(0)} \hat{H}_d^{(0)} I_x\right]^2\right\}}{\text{Tr}\left\{I_x^2\right\}}. \quad (\text{B.1})$$

An equivalent form can be obtained when using the unitary transformation $\exp\left\{-i\frac{\pi}{2}\hat{I}_z\right\}I_x = I_y$, so that from Eq. (B.1) one finally obtains

$$M_4 = \frac{\text{Tr}\left\{\left[\hat{H}_d^{(0)} \hat{H}_d^{(0)} I_y\right]^2\right\}}{\text{Tr}\left\{I_y^2\right\}}. \quad (\text{B.2})$$

Using the unitary transformation given by Eq. (A.4) in Eq. (B.2) we can write

$$M_4 = \frac{\text{Tr}\left\{\left[\left(-\frac{1}{2}\hat{H}_d^{(0)} + \hat{H}_{\text{DQ}}\right)\left(-\frac{1}{2}\hat{H}_d^{(0)} + \hat{H}_{\text{DQ}}\right)I_y\right]^2\right\}}{\text{Tr}\left\{I_y^2\right\}}. \quad (\text{B.3})$$

A relationship between M_4 and M_4^{TQ} can be established using Eqs. (B.3) and (18). Finally, we get

$$M_4 = \frac{8}{45}M_4^{\text{TQ}} + \delta M_4, \quad (\text{B.4})$$

where δM_4 contains the trace over mixed terms like $\hat{H}_{\text{DQ}}\hat{H}_d^{(0)} I_y$ and $\hat{H}_d^{(0)} \hat{H}_{\text{DQ}} I_y$.

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