A model for the ^2H nuclear magnetic resonance lineshape of crosslinked elastic polymers

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The theory of the ^2H nuclear magnetic resonance (n.m.r.) lineshape of elastic polymer networks is developed on the basis of existing concepts of quadrupole effects in n.m.r. Averaging of the quadrupole interaction Hamiltonian is carried out with the help of the freely jointed chain model. The ends of the model chain are assumed to be fixed in space. It is found that a broad doublet should be expected for a regular network. The doublet splitting is proportional to the degree of crosslinking. The peculiar lineshape is shown to be expected for an irregular network. Irregularities such as distribution of chain lengths through the sample and presence of macromolecular loose ends are considered. The results of theoretical evaluations with the irregularity of the network taken into account are consistent with the experimental data.

(Keywords: nuclear magnetic resonance; crosslinked polymers; crosslinking; network)

INTRODUCTION

It was shown earlier by Deloche *et al.*[1] that the ^2H n.m.r. lineshape of crosslinked deuteron-labelled rubbers is rather unusual. It has wide wings (much more intense than the wings of the corresponding Lorentzian) and a relatively narrow central peak. No explanation of the unusual lineshape is given. In order to discover the origin of the unusual lineshape and to understand the relations between molecular and spectral parameters of polymer networks, the simplest model of a chain incorporated into a network is considered in the present study. The theory of magnetic resonance of deuterons linked to a model chain is developed on the basis of existing concepts of n.m.r. of quadrupole nuclei.

It is well known for more than 10 years that one of the most striking features of polymer network magnetic resonance is the inability of polymer segment motion to average out to zero the tensorial interactions governing the n.m.r. spectrum[2-4]. For example, the appearance of the high-temperature plateau region in the spin–spin relaxation time–temperature dependence of swollen polymer networks had given evidence[2] that crosslinks produce constant restrictions on polymer segment motion, and the related internuclear vector cannot proceed through the whole space angle unless the crosslinks are broken. The anisotropy of motion generates a solid-like (non-averaging) contribution to the n.m.r. signal. If motion is fast on the n.m.r. timescale then time averaging of the tensorial interactions does not depend on details of the motion and therefore can be substituted by space averaging[5]. This is just the case in swollen thermoplastic and rubber networks[2,6,7]. The freely jointed chain model[8] with both ends fixed in space is convenient for calculation of non-averaged residual tensorial interactions in elastic polymer networks. This model was used earlier for calculation of residual proton magnetic dipole interactions in ref. 6 and then in ref. 9. The adequacy of the model was supported by experimental work on swollen networks of polystyrene (PS), poly(methyl methacrylate) (PMMA), poly(ethylene oxide) (PEO)[6] and some other polymers[7], and on entangled polymer melts of linear poly(dimethylsiloxane) (PDMS) and polybutadiene (PB)[10].

In the present study the same model is used to derive the expression for residual quadrupole interactions partially averaged by fast anisotropic segmental motion. First the equation for a regular, or ideal, network is obtained. A regular network is assumed to have the following properties. All ends of macromolecules are incorporated in a network, no pendant chains being present. The chain length or the number of statistical segments Z in a chain connecting two neighbouring knots is the same throughout the sample (Z = constant). Only neighbouring pairs of links are connected by chains, and every pair of neighbours is connected by only one chain (*Figure 1*). Then the possible consequences of irregularity of the network are taken into account. An irregular network is assumed to have a distribution of Z. The presence of pendant chains is allowed. In the case of an irregular network, the theoretical results are consistent with the experimental curves obtained in ref. 1. That supports the assertion that the peculiar ^2H n.m.r. lineshape of polymer networks is due to irregularity of network structure.

GENERAL EQUATIONS

Since anisotropic motion of a polymer network segment possesses axial symmetry (the symmetry axis is parallel to the vector connecting chain ends that coincide with corresponding crosslinks), the spherical basis is of most use in calculations.

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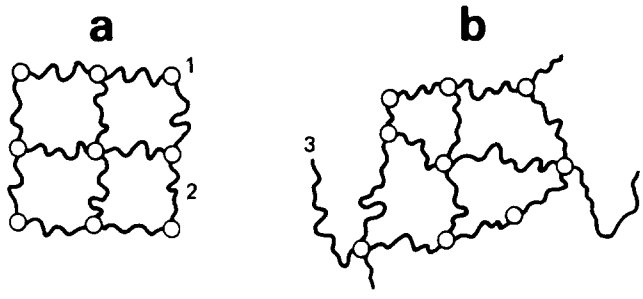

Figure 1 Schematic simplified representation of the basic difference between a regular (a) and an irregular (b) network: 1, knots; 2, chains connecting nearest-neighbour knots; 3, pendant chains

It is well known that the quadrupole moment of a deuteron causes each line of the ^2H n.m.r. spectrum to be split into a doublet[5,6]. The splitting $\nu_Q = \nu_+ - \nu_-$ is given by:

$$\nu_\pm = \pm\tfrac{3}{4}\frac{eQ}{h}V_B^{(2,0)} \tag{1}$$

where e is the elementary charge, Q the deuteron quadrupole moment, $V_B^{(2,0)}$ the irreducible component of the electric field gradient spherical tensor in the laboratory-fixed coordinate system; the z axis of this frame coincides with the fixed magnetic field B_0 direction. The tensor elements in principal frame $V_P^{(2,m)}$ are given in terms of their cartesian components V_{ik} as[11,12]:

$$\begin{aligned} V_P^{(2,0)} &= V_{zz} = eq \\ V_P^{(2,\pm1)} &= \pm\sqrt{\tfrac{2}{3}}(V_{xz} \pm iV_{yz}) = 0 \\ V_P^{(2,\pm2)} &= \sqrt{\tfrac{1}{6}}(V_{xx} - V_{yy} \pm 2iV_{xy}) = \sqrt{\tfrac{1}{6}}\eta eq \end{aligned} \tag{2}$$

with $\eta = (V_{xx} - V_{yy})/V_{zz}$ (asymmetry parameter) and q the electrostatic field gradient parameter.

Since gradient tensor components are usually known in the principal frame, it is necessary in order to find out the doublet spacing value to define $V_B^{(2,0)}$ in terms of $V_P^{(2,m)}$ components. This transformation is accomplished with the help of Wigner rotation matrices[13] $D_{kn}^{(2)}(\alpha\beta\gamma)$:

$$V_B^{(2,n)} = \sum_{k=0,\pm1,\pm2} D_{kn}(\alpha\beta\gamma)V_P^{(2,k)} \tag{3}$$

where α, β, γ are Euler angles defining the subsequent rotations transforming the principal coordinate system to the laboratory frame.

LINESHAPE FOR REGULAR NETWORK

In order to analyse the influence of segmental motion and fast intramolecular rotation about the axis fixed with respect to a segment, let us examine the set of subsequent transformations of the coordinate system. The first transformation rotates principal system x,y,z to a new one x_0,y_0,z_0. The z_0 axis is parallel to the axis of intramolecular rotation (*Figure 2*). Let the Euler angles through which this rotation is accomplished by $\alpha_1,\beta_1,\gamma_1$. The next rotation transforms the x_0,y_0,z_0 frame through Euler angles $\alpha_2,\beta_2,\gamma_2$ to a new one x_1,y_1,z_1 where z_1 coincides with the segment axis. The next transformation given by angles α',β',γ' rotates the segment coordinate system to x_2,y_2,z_2, where z_2 coincides with the chain end-to-end vector. The last rotation through angles $\alpha'',\beta'',\gamma''$ implements the transformation from x_2,y_2,z_2 to the laboratory frame. Now the expression can be written for $V_B^{(2,n)}$ in terms of $V_P^{(2,s)}$:

$$\begin{aligned} V_B^{(2,n)} = &\sum_{m=0,\pm1,\pm2} D_{mn}^{(2)}(\alpha''\beta''\gamma'') \sum_{l=0,\pm1,\pm2} D_{lm}^{(2)}(\alpha'\beta'\gamma') \\ &\times \sum_{q=0,\pm1,\pm2} D_{ql}^{(2)}(\alpha_2\beta_2\gamma_2) \sum_{s=0,\pm1,\pm2} D_{sq}^{(2)}(\alpha_1\beta_1\gamma_1)V_P^{(2,s)} \end{aligned} \tag{4}$$

Since fast anisotropic motions of a segment and intramolecular rotations of deuteron-labelled groups usually take place, averaging of tensorial interactions occurs. So the next step is to carry out averaging in equation (4). Some details of this averaging procedure have been given earlier[14]. The main features of this procedure are the following. The model of a freely jointed chain with the ends fixed in space is used. The end-to-end distance is supposed to be equal to its mean-square value. The last proposal is consistent with the well known concept of near-equality of macromolecular dimensions in condensed state to the unperturbed dimensions[15]. The averaging yields:

$$\begin{aligned} \nu_\pm = \pm\frac{9}{160Z}\frac{e^2qQ}{h}&(3\cos^2\beta_2 - 1)(3\cos^2\beta'' - 1) \\ &\times (3\cos^2\beta_1 - 1 + \eta\sin^2\beta_1\cos^2\alpha_1) \end{aligned} \tag{5}$$

The most important result that immediately comes out is the inverse proportional dependence of doublet spacing on the length Z of the chain connecting two neighbouring knots of a network.

The probable contribution of the space-limited random motion of knots can be taken into account using certain simplifications. In order to substitute motional averaging by space averaging, it is necessary to be sure that the correlation time of knot motion τ is much shorter than ν_Q^{-1}. If the motion of the knots is considered to be equivalent to random swaying of the knot-to-knot axis

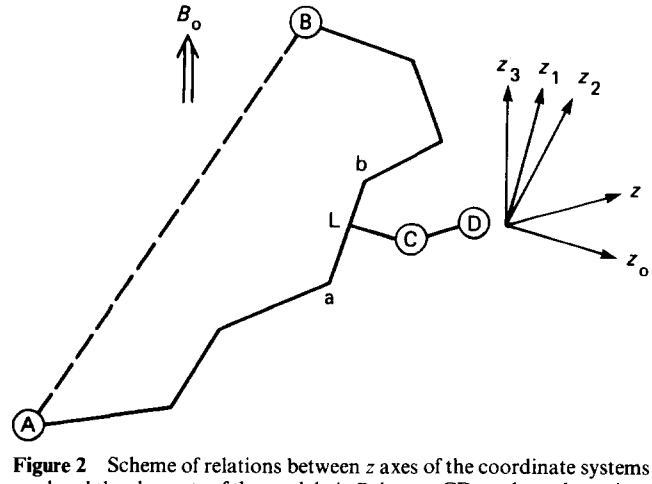

Figure 2 Scheme of relations between z axes of the coordinate systems used and the elements of the model: A, B, knots; CD, carbon–deuterium bond; LC, about this bond rotation is supposed to occur; ab, segment of the freely jointed chain; B_0, external constant magnetic field. The z direction is parallel to CD, z_0 to LC, z_1 to ab, z_2 to AB, z_3 to B_0

(end-to-end vector) inside the limited conic angle, then the contribution of this motion to the averaging process can be easily determined. The only term in equation (5) which depends on this motion is $\cos^2\beta''$. The application of the addition of the spherical functions theorem and subsequent averaging yields:

$$3\cos^2\beta'' - 1 = (3\cos^2\theta_0 - 1)\frac{\cos\sigma + \cos^2\sigma}{2} \qquad (6)$$

where θ_0 is the angle between field B_0 and the axis of the cone of knot-to-knot vector swaying, and σ is the angle of maximum deviation of this vector relative to its average position. Thus the lineshape depends on the distribution of θ_0 angles or β'' angles in the case of immobile knots ($\tau \gg \nu_Q^{-1}$). A random network has equal probability over all sphere directions of knot-to-knot vector. Therefore the lineshape $g(\nu)$ is rendered by the following equation[16]:

$$g(\nu) = -\tfrac{1}{2}\frac{\mathrm{d}\cos\theta_0}{\mathrm{d}\nu}$$

Bearing in mind that every individual line for each θ_0 is broadened due to magnetic interactions with neighbouring nuclei, and the broadening quite often can be approximated[16] by a Gaussian, one gets the lineshape function (unnormalized):

$$g(\nu) = \int_0^{\pi/2} \exp\left(-\frac{[\nu \pm \nu(\theta_0)]^2}{2\langle\Delta\nu\rangle^2}\right)\sin\theta_0 \mathrm{d}\theta_0 \qquad (7)$$

In the absence of other magnetic nuclei, deuteron magnetic dipole interactions determine the $\langle\Delta\nu\rangle^2$ value. Using equations obtained earlier[6] for description of ^1H n.m.r. of polymer networks, the value $\langle\Delta\nu\rangle^2$ for deuterons can be written as

$$\langle\Delta\nu\rangle^2 = \langle\Delta\nu\rangle_0^2(3/5Z)^2 \qquad (8)$$

where $\langle\Delta\nu\rangle_0^2$ is the contribution of deuteron dipole interactions to the second moment of the rigid lattice. Here this condition means the absence of segmental motion. Let us denote

$$S = \tfrac{3}{40}(3\cos^2\beta_2 - 1)(3\cos^2\beta_1 - 1 + \eta\sin^2\beta_1\cos 2\alpha_1) \times (\cos\sigma + \cos^2\sigma) \qquad (9)$$

Then

$$g(\nu) = \int_0^{\pi/2} \exp\left(-\frac{[\nu \pm (3/8Z)(e^2qQ/h)S(3\cos^2\theta_0 - 1)]^2}{(18/25)Z^{-2}\langle\Delta\nu\rangle_0^2}\right)\mathrm{d}\cos\theta_0 \qquad (10)$$

It is noteworthy that a network lineshape does not depend on η, contrary to polycrystallites. The asymmetry parameter affects only a spacing value. Independence of η is the consequence of axial symmetry of fast segmental motion.

It is known that equations of type (7) and (10) imply[16,12] either a doublet or, if $\langle\Delta\nu\rangle^2$ is sufficiently large, a cupola-shaped broad line with a flat top. In order to compare the obtained equation (10) with the experimental data of ref. 1 in more detail, the spacing ν_Q is estimated. The following values of the parameters involved are used[11]; $e^2qQ/h = 170$ kHz, $\eta = 0$, β_1 = tetrahedral angle, $\beta_2 = \pi/2$. Bearing in mind that a statistical segment of PDMS is approximately five monomeric units[17], one easily obtains the Z value of macromolecules investigated in ref. 1 to be near 60. The data discussed earlier[2,6] strongly support the notion that correlation times of knot motion are either longer than 10^{-1} s, or the amplitude of this motion is heavily restricted to give a significant contribution to averaging of tensorial interactions. Thus $\sigma = 0$ can be proposed. The value $\langle\Delta\nu\rangle_0^2$ is easy to get by multiplying the known protonic rigid lattice second moment for PDMS by the factor $\gamma_D^4 I_D(I_D+1)/\gamma_H^4 I_H(I_H+1)$. Here γ is the magnetogyric ratio, I the spin number, subscript H denotes proton, D deuteron. Fast rotation of methyl groups is taken into account by multiplication of the final result[16] by the factor 1/4 before substitution in equation (10). These parameter values yield $\nu_Q \simeq 300$ Hz, $\sqrt{\langle\Delta\nu\rangle^2} \simeq 10$ Hz and $K = \sqrt{\langle\Delta\nu\rangle^2}/\nu_Q \simeq 0.03$. The lineshape corresponding to this K is known to be[12] a well resolved doublet consisting of two sharp peaks with spacing equal to ν_Q. The experimental line has only one sharp peak in the centre of the spectrum and broad wings, the width at the half height being about 30 Hz. Thus the experimental line does not correspond to equation (10) derived for a regular network.

LINESHAPE FOR IRREGULAR NETWORK

It was shown earlier[6,7,10,18,19] that analysis of the proton spectra of an elastomeric network requires the irregularity of the network to be taken into consideration. The simplest type of irregularity, such as presence of pendant chains and distribution of chain lengths, was under study. The description of the proton spectra was accomplished on the basis of either a broad continuous distribution of chain lengths or a bimodal distribution. In the latter case the spectrum was thought to be a superposition of two signals. The first signal is generated by chains of equal length with both ends incorporated in a network (regular network); the other one arises from pendant chains. But both descriptions of irregularity are based on the concept that segments of loose ends or rarely crosslinked areas can take all directions in space and tensorial interactions can be averaged out to zero in principle. The same consideration is applied here to interpretation of ^2H n.m.r. data. The bimodal distribution which proved to be adequate for proton spectra of PDMS crosslinked in different ways[19] results in the following lineshape $G(\nu)$:

$$G(\nu) = (1-\phi)g(\nu) + \phi f(\nu) \qquad (11)$$

where ϕ is the fraction of free end deuterons, $g(\nu)$ the normalized function of equation (10), and $f(\nu)$ the loose end deuteron lineshape. No information on loose end lineshape and linewidth is available in the literature. A Lorentzian may be supposed since the motion of free ends of sufficient length should be isotropic and liquid-like:

$$f(\nu) = \frac{1}{\pi\delta\nu}\frac{1}{1 + [(\nu - \nu_0)/\delta\nu]^2} \qquad (12)$$

The width parameter $\delta\nu$ should not be more than the linewidth for chains belonging to a network with both ends and less than that of a free molecule in the same medium. It should be mentioned that the substitution of the Lorentzian by a Gaussian of approximately the same width does not change the conclusions below. Since for the crosslinked PDMS the linewidth at half height is about several tens of hertz[1], it is reasonable to suppose that $\delta\nu$ for macromolecular loose ends in these systems should not exceed the order of 10 Hz. If such values of $\delta\nu$ are expected and ϕ is about 0.5 (as found for poly(dimethylsiloxane) networks[19]), then signal superposition including a regular network doublet and the loose end singlet $f(\nu)$ located in the centre of the doublet should resemble a triplet. Thus equation (11), with ϕ and $(1-\phi)$ being of the same order of magnitude, is unlikely to correspond to the experimental curves of ref. 1. It should be emphasized that if $\delta\nu$ and ϕ are sufficiently large, then the contribution of the doublet to the total line diminishes and the 'triplet' structure of the signal smoothes out.

At last, a broad continuous distribution of chain lengths through the sample can be tried in the same way as for proton resonance curves of PS swollen to equilibrium[18]. The quantity Z can be expressed by the equation ($Z \gg 1$):

$$Z = 1/nm \tag{13}$$

where m is the number of monomers in a segment and n is the mole fraction of crosslinking agent in a chain, which is considered to begin with the first monomeric unit after a knot and to end with the molecule of the second knot. For the PS networks studied in ref. 18, the normal distribution $\Phi(n)$ was fitted:

$$\Phi(n) = \exp[-(n-n_0)^2/(\Delta n)^2] \tag{14}$$

where n_0 is the centre of the distribution, $(\Delta n)^2$ the dispersion. The value $n=0$ corresponds either to a chain of infinite length or to a loose end. In both cases quadrupole and dipole interactions can be averaged out to zero in principle. This possibility is reflected in equations (5) and (8). For $n=0 (Z \to \infty)$ these equations give quadrupole splitting and dipole linewidth equal to zero. However it was shown[2,6,7] for rarely crosslinked networks ($n < 1$ mol%) that conditions of typical experiments are insufficient for averaging out to zero even the interactions which in principle can be averaged out to zero by fast segmental motion. For complete averaging, other conditions (higher temperature, lower viscosity of solvent, etc.) are required. In order to deal with this type of incomplete averaging, equation (10) should be transformed in the following way[18]:

$$F(\nu) = \int_0^1 (n+\beta)^{-1} \exp\left[-\left(\frac{n-n_0}{\Delta n}\right)^2\right] dn \times \int_0^{\pi/2} \exp\Psi(\nu, n, \cos\theta_0) \, d\cos\theta_0 \tag{15}$$

where $F(\nu)$ is the unnormalized lineshape function, and

$$\Psi(\nu, n, \cos\theta_0) = -\frac{25[\nu \pm \frac{3}{8} nme^2 qQh^{-1} S(3\cos^2\theta_0 - 1)]^2}{18 (n+\beta)^2 m^2 \langle \Delta\nu \rangle_0^2}$$

$$\beta = (5/3m)[\Delta\nu / (\langle \Delta\nu \rangle_0^2)^{1/2}] \tag{16}$$

where $\Delta\nu$ is a dipole linewidth, which can be averaged in principle but is not averaged under the conditions of the experiment. It was shown earlier that an expression of type (15) can imply a symmetrical line with narrow peak and broad intense wings exceeding those of a Lorentzian. Though the direct comparison of equation (15) with the experiment of ref. 1 is impeded by the lack of information on several parameters, such an attempt was undertaken and is reflected in *Figure 3*. All parameters used in the equation (15) are estimated above except for Δn and $\Delta\nu$. The value of Δn is taken to be equal to n_0, since this was appropriate for crosslinked PS[18]. The value of several hertz for $\Delta\nu$ seems to be reasonable; here $\Delta\nu$ is taken to be 1 Hz. *Figure 3* shows that equation (15) agrees in general with the experimental data. More detailed comparison of equation (15) with the experiment and the choice between the bimodal and the broad distributions are hampered by lack of reliable information on the nature of the distribution of chain lengths, on $\delta\nu$ values and for some other reasons discussed in the Conclusion.

It should be mentioned that a doublet structure of the ^2H n.m.r. spectrum of crosslinked rubbers was observed[1] only on elongation (uniaxial) of a sample. Doublet structure here arises probably due to restrictions imposed by the stretched network on the motion of pendant chains. This proposal corresponds closely to the previously described experiment[20] on deuteron-substituted solvents in crosslinked rubber matrices. Even small molecules of a solvent expose anisotropic motional behaviour, i.e. spectral doublet structure. For linear pendant chains with one of the ends included in the network structure, the anisotropy should be much more pronounced, and thus more distinct splitting than for small unbound molecules should occur. A broad background signal (a pedestal) revealed[1] in this case should be expected according to the developed theory if the network deviates from the ideal form.

CONCLUSION

Comparison of deuteron and proton magnetic resonance capabilities in determining details of polymer network structure leads to the following conclusions. A value of

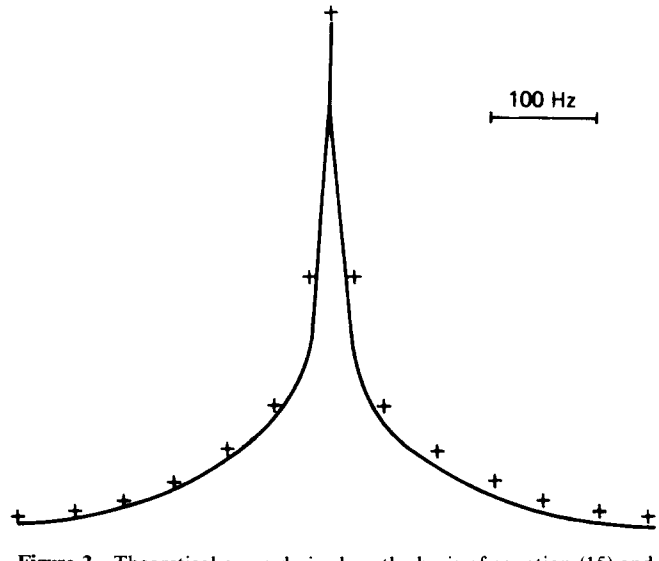

Figure 3 Theoretical curve derived on the basis of equation (15) and experimental points (+) obtained from the data of ref. 1

quadrupole splitting as shown above and a value of dipole splitting as shown earlier[18] enables one to judge upon a degree of crosslinking for a regular network. But the approximation of isolated spin pairs is valid only as an exception. Since a polymer molecule is generally a multispin system, the dipole splitting of the two nearest neighbours is masked and smoothed away in a spectrum by other interactions. A deuterium resonance splitting of the CD bond on the contrary is not influenced significantly by neighbouring deuterons. Therefore a plain doublet should be expected in a regular network in the ^2H n.m.r. spectrum. The doublet spacing should be proportional to the degree of crosslinking. It should be emphasized that the quadrupole splitting for the CD bond is an order of magnitude larger than the proton dipole splitting for the CH_2 group. Thus ^2H n.m.r. seems to be suitable for polymer network investigations. But for solving the problem of determination of network structure details, the further development of the theory is necessary. The theory should take into account non-equivalence of deuterons located on a macromolecule loose end at different distances from the knot (the place of attachment). The theory should consider the more complicated types of irregularity that the network may have[21]. Experimental data on the loose end lineshape and its width are necessary. These are the main reasons preventing the choice between a bimodal and broad distribution or a combination of both. Nevertheless in spite of certain obstacles in obtaining information on details of network structure from ^2H n.m.r. spectra, comparison of the derived equations with the experimental results leads to the following notion. Irregularity or deviation from ideal network structure should result in a peculiar lineshape with broad wings and relatively narrow central peak.

It deserves to be mentioned that alternative lineshape explanations, based on a distribution of correlation times, are possible. In order to judge more definitely on the adequacy of the theory proposed in this paper, specially set experiments on networks of *a priori* known structure are desirable.

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