Frequency Dependence of Proton Spin Relaxation in Liquid Crystalline PAA

W. Wölfel, F. Noack and M. Stohrer

Physikalisches Institut der Universität Stuttgart

(Z. Naturforsch. **30 a**, 437—441 [1975]; received February 11, 1975)

We report on measurements of the Larmor frequency dependence of the proton spin relaxation time T_1 in the nematic and isotropic phase of p-azoxyanisole (frequency range: 3.8 kHz $\leqq \omega_L/2\pi \leqq$ 75 MHz). In both cases our results clearly support the Pincus-Cabane mechanism of spin relaxation by order fluctuations ("$\omega_L^{-1/2}$-law") and exclude the alternative translational diffusion model ("$\omega_L^{+1/2}$-law"). For the isotropic phase it was possible to evaluate the correlation time τ of the liquid crystalline order fluctuations from the observed T_1 dispersion. As a function of the deviation $\Delta\vartheta = \vartheta - \vartheta_c$ from the critical nematic-isotropic transition temperature, $\vartheta_c = (136 \pm 0.5)$ °C, we found $\tau = 2.71 \cdot 10^{-7} \cdot \Delta\vartheta^{-0.25}$ s.

1. Theory

In recent years there has been a lot of discussion on the Larmor frequency dependence of the nuclear spin relaxation in nematic liquid crystals [1–4], since this property is expected to reveal decisive aspects of the long-range and short-range order fluctuations (OF) in such mesophases, as first recognized by Pincus [2a]. According to refinements of the theory by various authors [2b-2j], particularly by Lubensky [2c] and by Sung [2f], the dispersion of the longitudinal relaxation rate $1/T_1$ of nuclear spins due to these order fluctuations in the *nematic phase of a liquid crystal* should follow the relation

$$1/T_{1(\mathrm{OF})} = A(\vartheta) + B(\vartheta) \cdot \omega_L^{-1/2}, \qquad (1)$$

where $\omega_L \equiv 2\pi\nu$ represents the Larmor frequency of the considered spin species. A and B are parameters dependent upon the temperature ϑ and on the specific structural and dynamical data of the liquid crystal, such as the elastic deformation constant, the viscosity, the self-diffusion coefficient, the nematic order, the short-range order correlation time, the long-range order cutoff frequency and the local dipolar magnetic field. The unusual "$\omega_L^{-1/2}$-law" implied in Eq. (1) has been confirmed during the last years, more or less quantitatively, for several nematogens [3, 4], particularly for the benzene-ring protons in p-azoxyanisole (PAA), the most thoroughly investigated liquid crystal [3]; but until now only within the rather restricted frequency ranges of conventional NMR spectrometers, i. e. 1.5 MHz $\leqq \omega_L/2\pi \leqq$ 60 MHz at most. Therefore it was emphasized first by Vilfan, Blinc and Doane [3k] and later by others [1, 3] that, presently, the predictions of Eq. (1) could not be critically distinguished from features of the classical relaxation models based on translational molecular diffusion (Diff), which in the low-frequency limit can be written in a form very similar to Eq. (1), namely [5]

$$1/T_{1(\mathrm{Diff})} \cong C(\vartheta) - D(\vartheta) \cdot \omega_L^{+1/2}. \qquad (2)$$

Here C and D denote parameters characteristic of the underlying diffusion mechanism, i. e. temperature dependent functions of completely different origin than A or B. In fact, from the order of magnitude of the self-diffusion coefficient in nematics [1d] it follows that a clear decision in favour of one of the alternative theories, Eq. (1) or Eq. (2), is only possible by evaluating a more extended range of Larmor precession frequencies than available up to the present. Unfortunately, the straightforward application of the $T_{1\varrho}$-technique [6], convenient for indirect relaxation experiments in the kilohertz region and thus, in principle, capable of extending standard measurements to lower values of ω_L, was not as helpful as expected. Most $T_{1\varrho}$-results published in the literature [3, 4] are not in agreement with the frequency dependences predicted by appropriate $T_{1\varrho}$-modifications of either Eq. (1) or Eq. (2) and were interpreted in terms of additional, anomalous relaxation mechanisms. However, one could argue that the problem lies in the experimental technique, not in the basic equations.

Similar difficulties arise in trying to differentiate the frequency dependent relaxation rates due to orientational order fluctuations or molecular dif-

Reprint requests to Doz. Dr. F. Noack, Physikalisches Institut der Universität Stuttgart, *D-7000 Stuttgart*, Pfaffenwaldring 57, BRD.

fusion in the *isotropic phase of a nematic liquid crystal,* i. e. somewhat above the nematic-isotropic phase transition temperature ϑ_c, where the theory predicts relaxation by orientational modes because near ϑ_c short-range order in the molecular orientation persists. In this case Cabane's extension [2i] of the Pincus theory, generalized by means of Lubensky's arguments [2c] by a frequency independent term (A') similar to that (A) of Eq. (1), results [7] in the replacement of Eq. (1) with the relation

$$1/T_{1(\mathrm{OF})} = A'(\vartheta) + B'(\vartheta)\,[1 + (1 + \omega_L^2\,\tau^2)^{1/2}]^{-1/2}\,, \qquad (3)$$

where A' and B' are model parameters and τ is the correlation time of the relevant order fluctuation. It should be emphasized that the form of the frequency dependent contribution is an approximation also involved in the derivation of $B\,\omega_L^{-1/2}$, implying that the wave number of the order fluctuations, q, extends from zero to $q_{\max} = \infty$. As is easily seen, Eq. (3) reduces to the familiar "$\omega_L^{-1/2}$-law" of Eq. (1) for large values of the dispersion product $\omega_L \cdot \tau$, whereas the opposite regime ($\omega_L \cdot \tau \ll 1$) gives a liquid-like relaxation rate independent of the frequency. Since this latter behavior is identical with the behavior of the diffusion model Eq. (2), which does not distinguish between the isotropic and nematic phase of a nematogen, the separation of the alternative concepts is still more complicated in the isotropic state of a liquid crystal than in the proper nematic range. Therefore one should realize that Eq. (2) is only valid for small values of ω_L and without this approximation has to be replaced, e. g. in the most simple case of three-dimensional isotropic diffusion of spin $I = 1/2$ nuclei, by the Abragam-Pfeifer relaxation formula [5b, 5c]

$$1/T_{1(\mathrm{Diff})} = \tfrac{9}{8}\,\gamma^4\,\hbar^2\,[J(\omega_L) + 4\,J(2\,\omega_L)] \qquad (4\,\mathrm{a})$$

with

$$J(\omega_L) = \frac{16\,\pi\,N}{15\,d^3} \int\limits_0^\infty \frac{[B_{3/2}(\varrho\,d)]^2}{\varrho} \cdot \frac{3\,\tau_D/(\varrho\,d)^2}{1 + 9\,\omega_L^2\,\tau_D^2/(\varrho\,d)^4}\,\mathrm{d}\varrho \qquad (4\,\mathrm{b})$$

and

$$\tau_D = D_S/(6\,d^2)\,; \qquad (4\,\mathrm{c})$$

or more generally by Torrey's random walk relaxation formalism [5a] (γ, N, d, ω_L, τ_D and D_S: magnetogyric ratio, density, distance of closest approach, Larmor frequency, correlation time and self-diffusion coefficient of the considered spins, respectively; $\hbar$: Planck's constant divided by $2\,\pi$; $B_{3/2}$: Bessel function of order 3/2). The exact relations permit a considerable simplification of the problem. The decisive point is that from Eq. (4) it follows that $T_{1(\mathrm{Diff})}\,(\omega_L\,\tau_D \ll 1) \sim \omega_L^0$ and that $T_{1(\mathrm{Diff})}\,(\omega_L\,\tau_D \gg 1) \sim \omega_L^{3/2}$, which contrasts to the low- and high-frequency regimes of Eq. (1) and to the high-frequency regime of Equation (3). In the Torrey theory, including subsequent refinements introduced by Harmon and Muller [5e, 5g], one obtains similar limits, namely $T_{1(\mathrm{Diff})}\,(\omega_L\,\tau_D \ll 1) \sim \omega_L^0$ and $T_{1(\mathrm{Diff})}\,(\omega_L\,\tau_D \gg 1) \sim \omega_L^2$. Accordingly, by means of a sufficiently large frequency variation the different exponents of ω_L offer a both convenient and exact criterion to distinguish the relaxation mechanisms in question.

2. Experimental Results and Discussion

2.1. Experimental Results

We have measured the proton spin relaxation time T_1 in both the nematic and the isotropic phase of the liquid crystal PAA in the Larmor frequency range from $\nu \equiv \omega_L/2\,\pi = 3.8$ kHz up to $\nu \equiv \omega_L/2\,\pi = 75$ MHz, extending data given previously in the literature [3] by nearly three decades! This extension was essentially realized by means of NMR field-cycling techniques described elsewhere [8-10]. Above the nematic-isotropic transition temperature ϑ_c, the measurements were performed with a pulse spectrometer originally designed [8] for the investigation of liquids, where the NMR free induction decay is slow and hence easy to be detected. Below the critical temperature we used a newly developed, more powerful instrument [9, 10], allowing experiments in the nematic phase, where the induction decay proved to be too fast for our older apparatus. The nematogen PAA was obtained from Merck (Darmstadt), the clearing point of the material was found to be $\vartheta_c = (136 \pm 0.5)$ °C by means of the melting point capillary method. The chemicals were carefully degassed and sealed in evacuated glass vials of appropriate diameters, normally without any purification. Within experimental error, zone refining had no influence on the relaxation rate and therefore was omitted except for some controls.

Our results are presented in Figs. 1, 2, 3 and 4 in the form of $\log T_1$ versus $\log \nu$ plots. Addition-

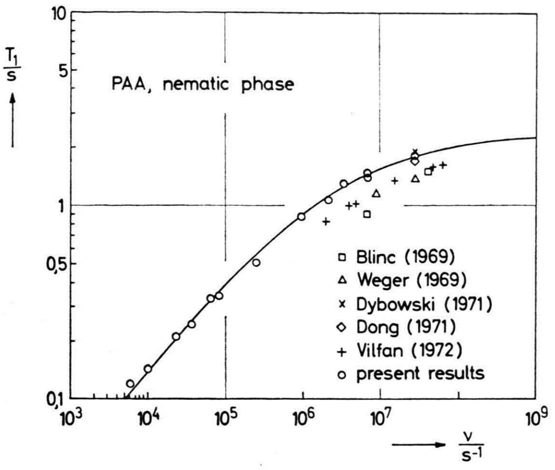

Fig. 1. Larmor frequency dependence of the longitudinal proton spin relaxation time T_1 in the nematic phase of PAA at a temperature $\vartheta = 123.5$ °C. Points: Experimental results from this work (○); from Ref. 3 a (□); from Ref. 3 b (△); from Ref. 3 g (×); from Ref. 3 i (◇); from Ref. 3 k (+). Full curve: Computer fit of the Pincus model, Eq. (1), to (○); $A = 0.431\ \mathrm{s}^{-1}$, $B = 673.7\ \mathrm{s}^{-3/2}$.

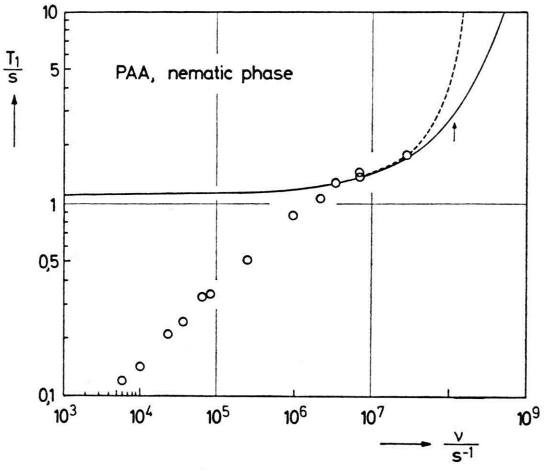

Fig. 2. Experimental results from Fig. 1 compared with the prediction of the diffusion models, Eq. (2) and Eq. (4). Dashed curve: Eq. (2) with $C = 0.90\ \mathrm{s}^{-1}$ and $D = 2.6 \cdot 10^{-5}\ \mathrm{s}^{-1/2}$. Full curve: Eq. (4) with $1/T_1\ (\omega = 0) = 0.90\ \mathrm{s}^{-1}$ and $\tau_D = 5.03 \cdot 10^{-10}$ s. The arrow marks $\nu = 1/(6\,\pi\,\tau_D)$.

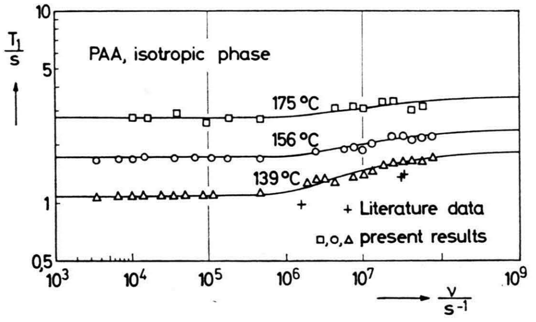

Fig. 3. Larmor frequency dependence of the longitudinal proton spin relaxation time T_1 in the isotropic phase of PAA at three temperatures. Points: Experimental results from this work for $\vartheta = 139$ °C, 156 °C and 175 °C (△, ○, □); literature data for $\vartheta = 139$ °C (interpolated) from Ref. 3 a, 3 b and 3 i (+). Full curves: Computer fit of the Cabane model, Eq. (3), to (△, ○, □); the fitted parameters are summarized in Table 1.

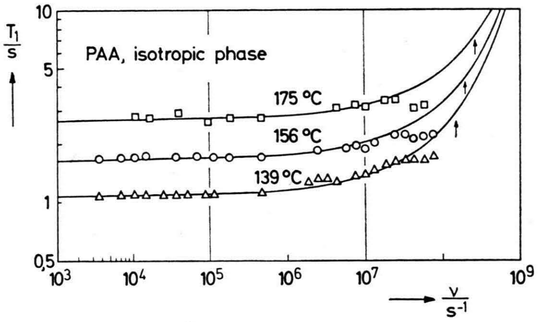

Fig. 4. Experimental results from Fig. 3 compared with the prediction of the diffusion model, Eq. (4). Upper curve: $1/T_1(\omega = 0) = 0.38\ \mathrm{s}^{-1}$, $\tau_D = 1.22 \cdot 10^{-10}$ s. Intermediate curve: $1/T_1(\omega = 0) = 0.61\ \mathrm{s}^{-1}$, $\tau_D == 1.89 \cdot 10^{-10}$ s. Lower curve: $1/T_1(\omega = 0) = 0.93\ \mathrm{s}^{-1}$, $\tau_D = 2.79 \cdot 10^{-10}$ s. The arrows mark the frequencies $\nu = 1/(6\,\pi\,\tau_D)$.

ally, T_1 points reported earlier by other workers [3] in the upper Larmor frequency range are included in the diagrams for comparison. Since we estimate the accuracy of our T_1's, derived from the experimental scatter of repeated measurements, as better than $\pm 5\%$ for large values of ν ($\nu \geqq 7$ MHz) and approximately $\pm 8\%$ for the smaller values, there exists a notable discrepancy between our high-frequency results and most of the literature data. The origin of these deviations ($\approx +25\%$) is not clear to us, particularly because of their positive sign which excludes an explanation by potential impurities of Merck's PAA. Furthermore, a $T_1(\nu)$ decrease in the high-frequency regime discussed by Martins [3f] in the isotropic phase could not be reproduced.

2.2. *Discussion*

As illustrated in Fig. 1, in the nematic state of PAA the experimental $T_1(\nu)$ behavior is in excellent agreement with the prediction of Equation (1). This was a surprise; for it should be noted that the prediction cannot extend to arbitrary low frequencies, where the Pincus model gives an infinitely high relaxation rate. From a cumputer fit[10, 11] of the adjustable parameters to the experimental relaxation times we obtained $A = 0.431\ \mathrm{s}^{-1}$ and $B = 673.7\ \mathrm{s}^{-3/2}$, i. e. constants slightly different from evaluations based on more restricted frequency ranges[3]. Due to the considerable T_1 decrease in the kilohertz regime and the related extensive validity of the "$\omega_L{}^{-1/2}$-law", the diffusion model can be excluded definitively as shown in Figure 2. This is one essential consequence of our investigation in the nematic phase. Another interesting aspect arises from the fact that the low-frequency anomaly believed to be reflected by $T_{1\varrho}$ experiments, as mentioned above[3h, 3i], has completely disappeared. Discrepancies between T_1 and $T_{1\varrho}$ relaxation rates are well-known[12] and seem to originate from erroneous $T_{1\varrho}$-techniques in the case of long time constants and large rotating field strengths.

Similar conclusions on the dominant relaxation mechanism as in the nematic phase can be drawn from the measurements in the isotropic phase of PAA, where Cabane's order fluctuation theory allows a satisfactory description of the observed $T_1(\nu)$ data (see Figure 3). As expected, the simpler Pincus theory fails because it cannot reproduce the experimental low-frequency behavior, and the diffusion model predicts a too rapid increase in T_1 in the high-frequency range (see Figure 4). Values of A', B' and τ found by computer optimization[11] for the three considered temperatures are summarized in Table 1; the various sets of fitted parameters imply a divergent temperature dependence of the correlation time, namely

$$\tau = 2.71 \cdot 10^{-7}\ (\vartheta - \vartheta_c)^{-0.25}\ \mathrm{s}\,. \qquad (5)$$

Table 1. Parameters of the Pincus theory [Eq. (1)] and of the Cabane theory [Eq. (3)] evaluated from $T_1(\nu)$ measurements in PAA by computer optimization.

Temperature	Pincus theory		Cabane theory		τ s
ϑ °C	$A\ \mathrm{s}^{-1}$	$B\ \mathrm{s}^{-3/2}$	$A'\ \mathrm{s}^{-1}$	$B'\ \mathrm{s}^{-1}$	
123.5	0.431	$6.74 \cdot 10^2$			
139			0.529	$1.24 \cdot 10^3$	$2.06 \cdot 10^{-7}$
156			0.413	$6.65 \cdot 10^2$	$1.28 \cdot 10^{-7}$
175			0.281	$3.51 \cdot 10^2$	$1.08 \cdot 10^{-7}$

Both the absolute value of the correlation time and the critical exponent differ substantially from comparable data derived in the literature[3d, 3j, 4k] by means of more indirect NMR techniques. This is a problem to be solved. Using our results, in combination with the relationship between τ and the coherence length ξ of the nematic order[2i], i. e.

$$\xi = \xi_0\,[\vartheta_c/(\vartheta - \vartheta_c)]^{1/2} = [\tau \cdot L/\eta]^{1/2} \qquad (6)$$

(L: local elastic constant; η: shear viscosity), one obtains that L/η should be proportional to $(\vartheta - \vartheta_c)^{-0.75}$. However, both exponents are not very accurate due to the experimental error of $T_1(\nu)$, which did not allow a more precise computer fitting. For the same reason it was not possible to distinguish the two types of critical temperature $(\vartheta_c, \vartheta^*)$ discussed in the literature[2i]. Therefore further investigations in the vicinity of ϑ_c are necessary to clarify whether above the transition point the experimental T_1 is totally due to order fluctuations, or if in addition to the relaxation caused by fluctuational modes one must consider also the influence of diffusionally controlled interactions.

Acknowledgements

The authors gratefully acknowledge the assistance of Dr. G. Held and Dr. G. Preißing throughout the progress of this work. Thanks are also due to Dr. G. Krüger (Ispra) for many stimulating discussions and to Dr. J. Vitek for correcting the English translation. Further the authors are greatly indebted to Prof. M. Pilkuhn for his continuous support. The work was sponsored by the Deutsche Forschungsgemeinschaft.

---

[1] *Reviews:* (a) N. Boden, NMR Specialist Periodical Reports **1**, 144 [1972]. (b) N. Boden, NMR Specialist Periodical Reports **2**, 144 [1973]. (c) D. Tomlinson, NMR Specialist Periodical Reports **3**, 136 [1974]. (d) P. de Gennes, The Physics of Liquid Crystals, Clarendon Press, Oxford 1974, p. 198.

[2] *Theoretical Papers:* (a) P. Pincus, Solid State Commun. **7**, 415 [1969]. (b) R. Blinc, D. Hogenboom, D. O'Reilly, and E. Peterson, Phys. Rev. Lett. **23**, 969 [1969]. (c) T. Lubensky, Phys. Rev. **A 2**, 2497 [1970]. (d) J. Doane and D. Johnson, Chem. Phys. Lett. **6**, 291 [1970]. (e) J. Visintainer, J. Doane, and D. Fishel, Mol. Cryst. Liqu. Cryst. **13**, 69 [1971]. (f) C. Sung, Chem. Phys. Lett. **10**, 35 [1971]. (g) E. Samulski, C. Dybowski, and C. Wade, Chem. Phys. Lett. **11**, 113 [1971]. (h) J. Doane and D. Moroi, Chem. Phys. Lett. **11**, 339 [1971]. (i) B. Cabane, Advan. Mol. Relaxation Processes **3**, 341 [1972]. (j) J. Doane, C. Tarr, and M. Nickerson, Phys. Rev. Lett. **33**, 620 [1974].

[3] *Experimental Papers on PAA:* (a) see (2 b). (b) M. Weger and B. Cabane, J. de Phys. **30**, C 4–72 [1969]. (c) J. Doane and J. Visintainer, Phys. Rev. Lett. **23**, 1421 [1969]. (d) B. Cabane and W. Clark, Phys. Rev. Lett. **25**, 91 [1970]. (e) C. Watkins and C. Johnson, J.

Phys. Chem. **75**, 2452 [1971]. (f) A. Martins, Mol. Cryst. Liqu. Cryst. **14**, 85 [1971]. (g) C. Dybowski, B. Smith, and C. Wade, J. Phys. Chem. **75**, 3834 [1971]. (h) R. Dong, W. Forbes, and M. Pintar, Solid State Commun. **9**, 151 [1971]; R. Dong, W. Borbes, and M. Pintar, J. Chem. Phys. **55**, 145 [1971]. (i) see (2 i). (j) A. Martins, Phys. Rev. Lett. **28**, 289 [1972]. (k) M. Vilfan, R. Blinc, and J. Doane, Solid State Commun. **11**, 1073 [1972]. (l) E. Samulski, C. Dybowski, and C. Wade, Phys. Rev. Lett. **29**, 340 [1972]; **29**, 1050 [1972]. (m) E. Samulski, C. Dybowski, and C. Wade, Mol. Cryst. Liqu. Cryst. **22**, 309 [1973]. — (n) A. Sharp, W. Forbes, and M. Pintar, J. Chem. Phys. **59**, 460 [1973]. (o) M. Schwartz, P. Fagerness, C. Wang, and D. Grant, J. Chem. Phys. **60**, 5066 [1974]. (p) R. Dong, M. Wiszniewska, E. Tomchuk, and E. Bock, Mol. Cryst. Liqu. Cryst. **27**, 259 [1974]. — (q) R. Thompson, D. Kydon, and M. Pintar, J. Chem. Phys. **61**, 4646 [1974]. (r) R. McElroy, R. Thompson, and M. Pintar, Phys. Rev. **A 10**, 403 [1974].

[4] *Experimental Papers on Other Nematogens:* (a) C. Tarr, M. Nickerson, and C. Smith, Appl. Phys. Lett. **17**, 318 [1970]. (b) R. Dong and C. Schwerdtfeger, Solid State Commun. **8**, 707 [1970]. (c) R. Dong, M. Marusic, and C. Schwerdtfeger, Solid State Commun. **8**, 1577 [1970]. (d) C. Tarr, A. Fuller, and M. Nickerson, Appl. Phys. Lett. **19**, 179 [1971]. (e) see (2 e). (f) R. Dong, Chem. Phys. Lett. **9**, 600 [1971]. (g) see (3 g). (h) R. Dong, M. Pintar, and W. Forbes, J. Chem. Phys. **55**, 2449 [1971]. (i) R. Dong, W. Forbes, and M. Pintar, Mol. Cryst. Liqu. Cryst. **16**, 213 [1972]. (j) R. Dong, J. Magn. Resonance **7**, 60 [1972]. (k) S. Ghosh, E. Tettamanti, and P. Indovina, Phys. Rev. Lett. **29**, 638 [1972]. (l) B. Deloche and B. Cabane, Mol. Cryst. Liqu. Cryst. **19**, 25 [1972]. (m) R. Hayward and K. Packer, Mol. Phys. **26**, 1533 [1973]. (n) R. Dong, M. Wiszniewska, E. Tomchuk, and E. Bock, J. Chem. Phys. **59**, 6266 [1973]. (o) K. Easwaran, J. Magn. Resonance **9**, 190 [1973]. (p) A. Fuller and C. Tarr, Mol. Cryst. Liqu. Cryst. **25**, 5 [1974]. (q) see (2 j). (r) S. Goren, C. Korn, S. Marks, and R. Potashnik, Chem. Phys. Lett. **24**, 249 [1974]. (r) see (3 p). (s) R. Dong, M. Wiszniewska, E. Tomchuk, and E. Bock, Can. J. Phys. **52**, 766 [1974]. (t) R. Dong, M. Wiszniewska, E. Tomchuk, and E. Bock, Can. J. Phys. **52**, 1331 [1974]. (u) R. Dong, M. Wiszniewska, E. Tomchuk, and E. Bock, Chem. Phys. Lett. **25**, 299 [1974]. (v) see (3 r). (w) A. Pines and J. Chang, Phys. Rev. **A 10**, 946 [1974].

[5] (a) H. Torrey, Phys. Rev. **92**, 962 [1953]. (b) A. Abragam, The Principles of Nuclear Magnetism, Clarendon Press, Oxford 1961. (c) H. Pfeifer, Ann. Phys. **8**, 1 [1961]. (d) G. Krüger, Z. Naturforsch. **24 a**, 560 [1969]. (e) J. Harmon and B. Muller, Phys. Rev. **182**, 400 [1969]. (f) F. Noack, NMR-Basic Principles and Progress **3**, 83 [1971]. (g) G. Held and F. Noack, Proc. 18th Ampere Congress, Nottingham 1974.

[6] T. Farrar and E. Becker, Pulse and Fourier Transform NMR, Academic Press, New York 1971.

[7] I. Gradshteyn and I. Ryzhik, Table of Integrals, Series and Products, Academic Press, London 1973.

[8] R. Kimmich and F. Noack, Z. angew. Phys. **29**, 248 [1970].

[9] M. Stohrer and F. Noack, Proc. 18th Ampere Congress, Nottingham 1974.

[10] M. Stohrer, Dissertation, Universität Stuttgart 1975.

[11] G. Held, Dissertation, Universität Stuttgart 1974.

[12] F. Noack and M. Weithase, to be published.