

so ergibt sich mit Hilfe einer Fourier-Cosinus-Transformation⁵:

$$\int_0^\infty \exp\{-\sqrt{k^2 + \alpha^2} |z|\} J_0(k \varrho) dk = \frac{1}{\pi} \alpha |z| \int_0^\pi \frac{K_1(\alpha \sqrt{z^2 + \varrho^2 \sin^2 \vartheta})}{\sqrt{z^2 + \varrho^2 \sin^2 \vartheta}} d\vartheta. \quad (\text{A } 4)$$

Der Integrand auf der rechten Seite dieser Gleichung läßt sich auf Grund der Additionstheoreme für die

Zylinderfunktionen in folgende Reihe entwickeln⁶:

$$\frac{K_1(\alpha \sqrt{z^2 + \varrho^2 \sin^2 \vartheta})}{\sqrt{z^2 + \varrho^2 \sin^2 \vartheta}} = \sum_{n=0}^{\infty} \frac{(-\frac{1}{2} \alpha \varrho^2 \sin^2 \vartheta)^n}{n! |z|^{n+1}} K_{n+1}(\alpha |z|). \quad (\text{A } 5)$$

Damit ist das Integral in Gl. (A 4) auf das Integral

$$\int_0^\pi \sin^{2n} \vartheta d\vartheta = \pi \frac{\Gamma(n + \frac{1}{2})}{n! \Gamma(\frac{1}{2})} \quad (\text{A } 6)$$

zurückgeführt.

⁵ F. OBERHETTINGER, Tabellen zur Fourier-Transformation, Springer-Verlag, Berlin-Göttingen-Heidelberg 1957.

⁶ V. MANGULIS, Handbook of Series for Scientists and Engineers, Academic Press, New York und London 1965.

Dynamic Nuclear Polarization Experiments on ¹⁹F in Solutions and their Interpretation by the "Pulse Model" of Molecular Collisions

W. MÜLLER-WARMUTH, R. VAN STEENWINKEL

EURATOM CCR ISPRA (ITALY)

and F. NOACK

I. Physikalisches Institut der Technischen Hochschule Stuttgart (Germany)

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The dynamic fluorine polarization by the Overhauser effect has been studied at four different magnetic field values and at various temperatures in several fluorocarbon solutions. The importance of intermolecular contact couplings is very sensitively dependent on the chemical environment of the fluorine nuclei. The experimental data are interpreted in terms of the stochastic "pulse model" of molecular collisions derived in a preceding paper. The parameters of the model, such as the relative contribution of scalar couplings, the shape and the time scale of collision pulses and the correlation times of the molecular motion are given explicitly for six fluorocarbon solutions of free radicals.

Fluorine-electron double resonance experiments in liquids have shown that, in contrast to hydrogen, intermolecular scalar contact couplings, as well as dipole-dipole interactions between ¹⁹F and electron spins are important¹⁻⁵. The dynamic polarization of fluorine spins by the Overhauser effect has proved to be either positive or negative depending on the magnetic field (i.e. on the resonance frequencies), on the temperature and on the particular system of interacting molecules. Whilst the existence of scalar

intermolecular interaction itself is now well established by experiments in both weak^{1, 5-7} and strong magnetic fields^{2, 5, 8}, the time-dependence of the interaction has so far been explained only qualitatively^{1, 5}. Neither the model used by us¹, nor that of HUBBARD⁹, which was even less good, provided a completely satisfactory quantitative interpretation of the experimental data available^{5, 8}.

In a preceding paper¹⁰ statistical models used until then for the description of relaxation and

¹ W. MÜLLER-WARMUTH, Z. Naturforsch. **21 a**, 153 [1966].

² R. A. DWEK, J. G. KENWORTHY, D. F. S. NATUSCH, R. E. RICHARDS, and D. J. SHIELDS, Proc. Roy. Soc. London A **291**, 487 [1966].

³ E. H. POINDEXTER, J. R. STEWART, and D. D. THOMPSON, Bull. Am. Phys. Soc. **11**, 201 [1966].

⁴ G. BERTHET and J. P. IMBAUD, Proc. XIVth Colloque Ampère, Ljubljana 1966; J. P. IMBAUD, Thesis, Université de Clermont 1966.

⁵ G. J. KRÜGER, W. MÜLLER-WARMUTH, and R. VAN STEENWINKEL, Proc. XIVth Colloque Ampère, Ljubljana 1966, North-Holland Publish. Comp., Amsterdam, p. 99.

⁶ E. H. POINDEXTER, J. R. STEWART, and P. J. CAPLAN, J. Chem. Phys., in press.

⁷ J. R. STEWART, E. H. POINDEXTER, and J. A. POTENZA, in press.

⁸ R. A. DWEK, J. G. KENWORTHY, J. A. LADD, and R. E. RICHARDS, Mol. Phys. **11**, 287 [1966].

⁹ P. S. HUBBARD, Proc. Roy. Soc. London A **291**, 537 [1966].

¹⁰ F. NOACK, G. J. KRÜGER, W. MÜLLER-WARMUTH, and R. VAN STEENWINKEL, Z. Naturforsch. **22 a**, 2102 [1967].



dynamic polarization in spin systems were extended to more general stochastic processes. It was one of the main purposes of that work to find a model that could explain the dynamic mechanism of the scalar coupling in the aforementioned systems. This model was called the "pulse model" and will be used here to interpret a great number of dynamic polarization experiments. In order to test the proposed model, detailed experimental measurements on several solutions of different free radicals in fluorocarbons have been necessary. In particular, information has been obtained by studying the dynamic polarization of fluorine nuclei over a magnetic field range of several orders of magnitude and over the whole temperature range of the liquid state of the solutions.

Furthermore, a quantitative description of the dynamic polarization of fluorine nuclei in solutions of free radicals permits determination of the average amplitude of the coupling and the average time of interaction. It will thus be possible to obtain detailed information on the chemical environment of certain nuclei in particular systems by dynamic polarization experiments.

1. Experimental Details and Results

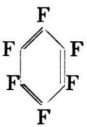

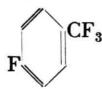

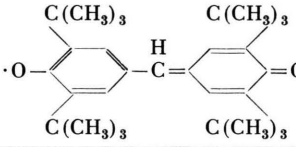
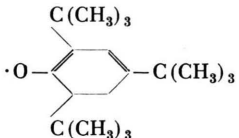
Dynamic polarization measurements were made at various temperatures and in magnetic fields of 15, 175, 3430 and 12 230 gauss. The corresponding resonance frequencies of the ^{19}F nuclei (and of the electrons) are 65 kHz (45 MHz), 706 kHz (493 MHz), 14 MHz (9.8 GHz) and 53 MHz (37 GHz). The electron spin resonance lines of two different free radical molecules dissolved in four fluorocarbon solvents were saturated as completely as possible, and the changes in the nuclear magnetic resonance spectrum of the solvent detected as usual. Details of the apparatus and of the procedure are given elsewhere¹¹.

The enhancement of the NMR signal is related to the gyromagnetic ratios of the electron (γ_s) and the nucleus (γ_I). In the steady state it is given by the equation

$$\frac{P}{P_0} = 1 - \rho f s \frac{\gamma_s}{\gamma_I}, \quad (1)$$

with P being the nuclear polarization and P_0 its thermal equilibrium value. The leakage factor f was derived from measurements of the relaxation times T_1 of the solution, and T_{10} of the pure solvent in the usual way. By extrapolation to infinite microwave power the saturation factor s may be put equal to one. Thus, from the measurement of the signal enhancements the nuclear-electron coupling parameters ρ were derived. For the majority of experiments radical concentrations could be chosen that yielded f values between 0.90 and 0.99 together with a fairly good saturation of the electronic lines. Values for ρ were thus obtained without important errors arising from the extrapolation. With the exception of the very low field data, which are distinguished by a poorer measurement of the unenhanced signal, the errors in ρ should be less than $\pm 10\%$.

The materials, both free radical molecules and fluorocarbon solvents, which have been chosen for this study, are listed in Tab. 1. In Figs. 1, 2 and 3 the results of the measurements in three magnetic fields are presented as a function of the inverse of the temperature. The lines correspond to the interpretation of the data that will be given in the next

	C_6F_6 = Hexafluorobenzene
	$\text{C}_6\text{H}_5\text{CF}_3$ = Benzotrifluoride
	$\text{FC}_6\text{H}_4\text{CF}_3$ = p-Fluorobenzotrifluoride
	CF_3COCH_3 = 1,1,1-Trifluoroacetone
	GV = Galvinoxyl
	TBP = Tertiary butyl phenoxyl

Tab. 1. Fluorocarbon compounds and free radicals as used in the dynamic nuclear polarization studies.

¹¹ 15 G: W. MÜLLER-WARMUTH, Z. Naturforsch. **15a**, 927 [1960]; 175 G: H. GRÜTZDIEK, K. D. KRAMER, and W. MÜLLER-WARMUTH, Rev. Sci. Instrum. **36**, 1418 [1965]; 3000 G: K. D. KRAMER, W. MÜLLER-WARMUTH, and J. SCHINDLER, J. Chem. Phys. **43**, 31 [1965]; 13 000 G: G. J. KRÜGER, W. MÜLLER-WARMUTH, and R. VAN STEENWINKEL, Z. Naturforsch. **21a**, 1224 [1966].

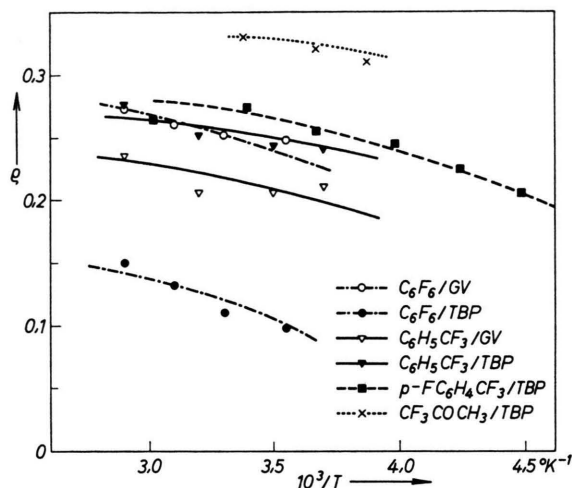


Fig. 1. Nuclear-electron coupling parameter as a function of the inverse of the temperature, measured by dynamic fluorine polarization in a magnetic field of 175 gauss. The abbreviations for the particular solutions correspond to the solvent and free radical molecules of Table 1.

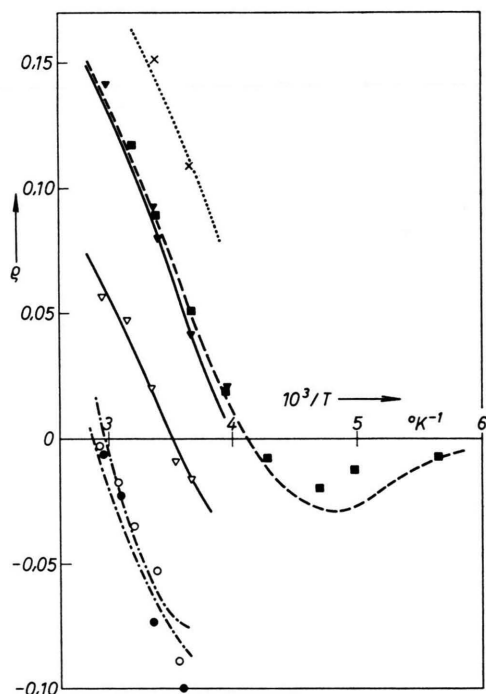


Fig. 2. Same as Fig. 1, but measurements at 3430 gauss.

paragraphs. In cases where comparisons with data of other workers are possible — DWEK et al.^{2, 8} studied several systems at 3300 and 12 500 gauss, POINDEXTER et al.^{6, 7} at 74 gauss — there is good agreement of the experimental results within the limits of accuracy.

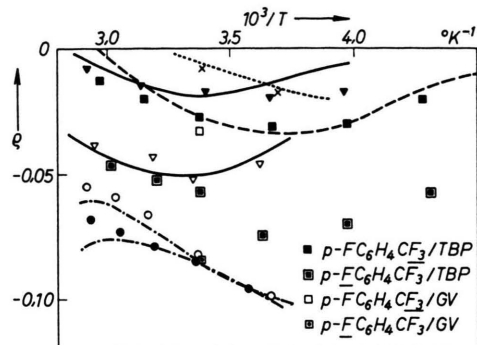


Fig. 3. Same as Fig. 1, but measurements at 13230 gauss. Data which were only obtained at this field value, are not theoretically interpreted.

2. Calculation of the Nuclear-Electron Coupling Parameter

The parameter ρ depends on the nature of the nuclear-electron interaction and on the details of the processes of molecular motion in the solution. It can be expressed in terms of the dipolar and scalar spectral intensity functions $J_1^D(\omega)$ and $J^{\text{SK}}(\omega)$ of the spin-lattice fluctuations^{10, 12}, as

$$\rho = \frac{5 J_1^D(\omega_S) - \frac{2}{3} J^{\text{SK}}(\omega_S)}{7 J_1^D(\omega_S) + 3 J_1^D(\omega_I) + \frac{2}{3} J^{\text{SK}}(\omega_S)}, \quad (2)$$

where ω_S and ω_I are the electron and nuclear resonance frequencies, resp. Furthermore we made the realistic assumption that $J(\omega_S \pm \omega_I) \approx J(\omega_S)$ and that the motion is isotropic.

Relaxation and dynamic polarization studies on protons in solutions of free radicals had suggested that the dipolar couplings between solvent nuclei and radical electrons are mainly modulated by translational diffusion of the molecules in question¹²⁻¹⁴. These results were confirmed in further experiments on many different systems and are in agreement with those of other authors^{2, 15}. We therefore suppose for the dipolar part of the fluorine-electron interaction that the random motion of the molecules is also

¹² K. D. KRAMER and W. MÜLLER-WARMUTH, Proc. XIIth Colloque Ampère, Bordeaux 1963, North-Holland Publish. Comp., Amsterdam, p. 315; K. D. KRAMER and W. MÜLLER-WARMUTH, Z. Naturforsch. **19a**, 375 [1964].

¹³ J. HAUPT, K. D. KRAMER, and W. MÜLLER-WARMUTH, Proc. XIth Colloque Ampère, Eindhoven 1962, p. 709.

¹⁴ R. HAUSSE and F. NOACK, Z. Phys. **182**, 93 [1964]; K. H. HAUSSE, G. J. KRÜGER, and F. NOACK, Z. Naturforsch. **20a**, 91 [1965].

¹⁵ K. H. HAUSSE, Z. Phys. **183**, 265 [1965].

governed by translational diffusion. This assumption is supported by dynamic proton polarization measurements of the same solvents as used in this study⁵. We have, therefore,

$$J_1^D(\omega) = J_1^D(0) f_t(\omega \tau_t) = \frac{32\pi N_S \tau_t}{75 d^3} f_t(\omega \tau_t), \quad (3)$$

with the translational correlation time¹⁶ τ_t , the distance of closest approach of diffusing molecules d , and the electron spin concentration N_S . The explicit form of the normalized spectral function f_t is given elsewhere^{17, 12}.

With $f_{SK}(\omega \tau_{SK})$ being the normalized spectral function of the fluctuations of the scalar couplings,

$$J^{SK}(\omega) = J^{SK}(0) f_{SK}(\omega \tau_{SK}), \quad (4)$$

we may bring Eq. (2) into the form

$$\varrho = \frac{[f_t(\omega_S \tau_t) - K f_{SK}(\omega_S \tau_{SK})] 0,5}{0,7 f_t(\omega_S \tau_t) + 0,3 f_t(\omega_I \tau_t) + 0,5 K f_{SK}(\omega_S \tau_{SK})} \quad (5)$$

where K expresses the relative importance of the scalar and the dipolar coupling

$$K = \frac{2}{15} \frac{J^{SK}(0)}{J_1^D(0)}; \quad (6)$$

and τ_{SK} is connected with the average time of contact interaction. For a quantitative derivation of J^{SK} in terms of molecular parameters the nature and the time dependence of the contact interaction between fluorine and electron spins must be considered.

3. The "Pulse Model" of Molecular Collision and its Application to the Contact Coupling

In order to explain the experimental results, we shall use the "pulse model" introduced in the preceding paper¹⁰. From the aforementioned interpretation of a great number of proton relaxation and dynamic polarization studies it was obvious that the mutual nuclear-electron interactions are mainly governed by an independent random motion of individual molecules. As a consequence the scalar coupling $A(r)$ is a random function of the separation r of interacting spins. $A(r)$ is large during a collision of solvent and solute molecules, it

will more or less rapidly decrease, as the distance r increases. Since the explicit dependence of $A(r)$ on the position is unknown and since the mathematical procedure of evaluating ensemble averages is cumbersome, the position dependence is replaced by the corresponding fluctuation in time, $A[r(t)] = A(t)$, which is the only interesting quantity for relaxation studies. In the time scale, the collision is characterized by a maximum height of a pulse shaped function $A(t)$. The time of interaction is then connected with the width of the pulse τ_w , and the range of interaction with the decay time of the pulse.

The occurrence of pulses is closely connected with the diffusion of molecules in the liquid. The validity of the ordinary diffusion equation corresponds to a Poisson process of fluctuations in time, with an average jumping rate τ_p^{-1} which is related to the mean square of a displacement Δr

$$\tau_p \sim \frac{\langle \Delta r^2 \rangle}{D_p}, \quad (7)$$

where D_p is the diffusion constant. In our two-spin model of the scalar interaction, τ_p is the mean difference in time between the occurrence of pulses of interaction, whilst Δr might be identified with the average distance travelled by a nucleus between consecutive collisions with electrons.

In order to calculate the frequency- and temperature-dependence of the function of interest J^{SK} , statistical averages

$$\langle A(0) A^*(t) \rangle_T$$

must be formed. Using the pulse model¹⁰,

$$A(t) = \gamma_I \gamma_S \hbar^2 \sum_{n=1}^{\infty} a_n v(t - t_n),$$

where $A(t)$ obeys a Poisson process with amplitudes a_n and pulse shape $v_n(t)$, an intensity function

$$J^{SK}(\omega) = \frac{\sigma^2}{\tau_p} |V(\omega)|^2 = \frac{4 \sigma^2 \tau_w}{\tau_p} f_{SK}(\omega \tau_w) \quad (8)$$

is obtained. The pulse spectrum $V(\omega)$ in Eq. (8) is given by

$$V(\omega) = \int_{-\infty}^{+\infty} v(t) e^{-i\omega t} dt. \quad (9)$$

leads to $\tau_t = d^2/5 D$ (D = diffusion coefficient of the related molecules), which would in fact be more correct than the relation $\tau_t = d^2/6 D$ used by us.

¹⁷ H. PFEIFER, Ann. Phys. Leipzig **8**, 1 [1961].

¹⁶ For the correlation time of the "translational two spin model" three different values are used in the literature. It has been shown by one of us (F. N.) that Kubo's general definition of correlation times in magnetic spin systems

$\sigma^2 = \langle a_n^2 \rangle$ is the mean square of the pulse amplitudes. With Eqs. (8) and (3), Eq. (6) finally yields

$$K = \frac{5 \sigma^2 d^3 \tau_w^2}{4 \pi N_S \tau_p \tau_t} \quad (10)$$

A rigorous procedure for testing this model would be to derive a scalar intensity function from the measured frequency-dependence of ρ , and to compute the pulse shape from Eqs. (8) and (9). Because of experimental reasons, however, ρ could only be measured for a limited number of frequencies, whilst the range of the intensity function in between has been covered by a variation of the temperature. This means that the relation between the correlation times and the temperature enters into the description. A second reason for choosing a less rigorous procedure is to avoid the numerical Fourier transformation, which introduces complications without any gain in the understanding of the physical mechanism.

We have selected, therefore, a limited number of pulse shapes $v(t)$, see Tab. 2, whose Fourier transforms $V(\omega)$ are explicitly known. The corresponding spectral functions f^{SK} have then been used in Eq. (5) to find a best fit of the experimental data. Furthermore, the same temperature-dependence of τ_t , τ_p and τ_w has been assumed, which seems reasonable from the molecular physical point of view. The dependence is given by an Arrhenius law with the activation energy E_t . The parameters of the model (K , $\alpha = \tau_w/\tau_t$, τ_t , E_t), which have been evaluated in this way, and the best-fitting spectral functions (number I to VIII from Tab. 2) are listed in Tab. 3.

System	Pulse	K	α	$\tau_t(25^\circ)$ in 10^{-11} sec	E_t in kcal/Mole
C_6F_6/GV	VI	0,24	0,32	4,7	3,4
C_6F_6/TBP	VII	0,51	0,95	2,4	3,4
$C_6H_5CF_3/GV$	III	0,36	0,35	1,3	2,5
$C_6H_5CF_3/TBP$	II	0,30	0,30	0,72	2,5
$FC_6H_4CF_3/TBP$	IV	0,28	0,33	1,1	2,6
CF_3COCH_3/TBP	II	0,19	0,20	0,87	2,0

Tab. 3. List of spectral functions and parameters of the pulse model, which have been used for the best-fitting interpretation of the experimental data of Figs. 1, 2 and 3.

It was possible to describe the experimental results of most of the solutions fairly well with one simple spectral function II, III or IV. The experimental

results of both solutions in C_6F_6 indicate, however, that the corresponding pulse consists of a sharp peak with a more or less flat tail. This has been realized analytically by a combination of the functions I and III, respectively, with a δ -like function, leading to VI and VII (Tab. 2). The exact form of the sharp peak itself could not be determined, because even at the highest frequency and lowest temperature no upturn of the negative ρ values towards zero could be observed (Fig. 3). A change in the pulse shape for $t > 0.1 \tau_w$, on the other hand acts very sensitively on the resulting spectral dependence of ρ . Within the limits of the model, the pulse shapes of Fig. 4 are therefore quite accurately determined by the experiments. By introducing very slight changes in

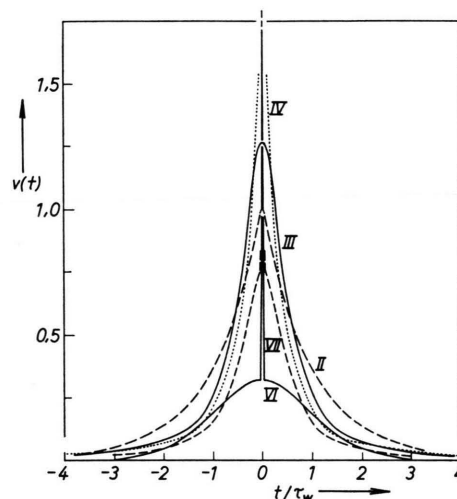


Fig. 4. Pulse shapes as used in the interpretation (Tab. 3) of the time-dependence of the intermolecular fluorine-electron scalar couplings. The analytical expressions and the corresponding Fourier transforms are given in Tab. 2.

some details of the pulses, it would easily be possible to improve the best fits, which are drawn in Figs. 1, 2 and 3. This would however be inconsistent with our intention to utilize only simple functions.

As examples of best fitting ρ -functions, resulting from the described procedure, Fig. 5 shows a comparison of the theoretical curve with experimental data. ρ is plotted against $\omega_S \tau_t$ using Eq. (5), the wellknown translational intensity function f_t , and the parameters of Tables 2 and 3. The abscissa of the experimental points already involve the connection between τ_t and the temperature.

Pulse	$v(t)$	$V(\omega)$	$f_{\text{SK}}(ax)$
I	$\sqrt{2/\pi} \exp\{-t^2/2\tau_w^2\}$	$2\tau_w \exp\{-\frac{1}{2}\omega^2\tau_w^2\}$	$\exp\{-(ax)^2\}$
II	$\exp\{- t /\tau_w\}$	$\frac{2\tau_w}{1+\omega^2\tau_w^2}$	$\left(\frac{1}{1+a^2x^2}\right)$
III	$\frac{4}{\pi} \frac{(\tau_w/2)^2}{(\tau_w/2)^2+t^2}$	$2\tau_w \exp\{-\frac{1}{2}\omega\tau_w\}$	e^{-ax}
IV	$\frac{1}{\pi} \ln \frac{\tau_w^2+t^2}{t^2}$	$2\tau_w \left(\frac{1-\exp\{-\omega\tau_w\}}{\omega\tau_w}\right)$	$\left(\frac{1-e^{-ax}}{ax}\right)^2$
V	$2\tau_w \delta(t)$	$2\tau_w$	1
VI	$0,48 v_{\text{I}} + 0,52 v_{\text{V}}$	$0,48 V_{\text{I}} + 0,52 V_{\text{V}}$	$[0,48 e^{-\frac{1}{2}a^2x^2} + 0,52]^2$
VII	$0,60 v_{\text{III}} + 0,40 v_{\text{V}}$	$0,60 V_{\text{III}} + 0,40 V_{\text{V}}$	$[0,60 e^{-\frac{1}{2}ax} + 0,40]^2$

Tab. 2. Pulse shapes $v(t)$, pulse spectra $V(\omega)$ and normalized spectral functions $f_{\text{SK}}(ax)$, $x = \omega\tau_t$, as used in the interpretation of the experimental results. The total area of the pulses is by definition $2\tau_w$.

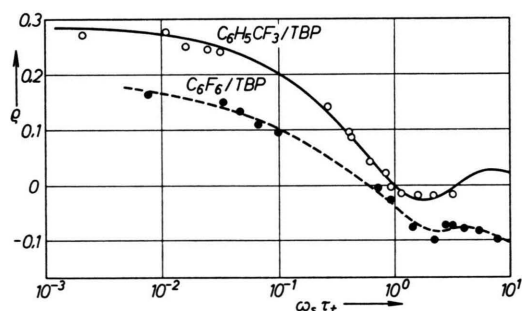


Fig. 5. Theoretically derived best-fitting ρ -functions for TBP solutions in C_6F_6 and $\text{C}_6\text{H}_5\text{CF}_3$.

$$\frac{1}{T_1'} = K_t \tau_t [7 f_t(\omega_S \tau_t) + 3 f_t(\omega_I \tau_t) + 5 K f_{\text{SK}}(\omega_S \tau_w)],$$

$$\frac{1}{T_2'} = K_t \tau_t \left\{ \frac{1}{2} f_t(\omega_S \tau_t) + \frac{3}{2} f_t(\omega_I \tau_t) + 2 + \frac{5}{2} K [1 + f_{\text{SK}}(\omega_S \tau_w)] \right\} \quad (11)$$

with

$$K_t = \frac{16\pi}{75} \gamma_I^2 \gamma_S^2 \hbar^2 S(S+1) \frac{N_S}{d^3}.$$

In Fig. 6 both $\frac{1}{T_1'}/K_t \tau_t$ and $\frac{1}{T_2'}/K_t \tau_t$ are plotted against $\omega_S \tau_t$. In case a) the scalar coupling is zero, e. g. $K=0$ in Eq. (11). For case b) the data of $\text{C}_6\text{F}_6/\text{TBP}$ (see Tab. 3) have been taken for K and f_{SK} in Eq. (11).

Inspection of Fig. 6 shows immediately that the differences in the spectral dependence are not as pronounced as in the case of the Overhauser effect.

4. Relaxation via the Nuclear-Electron Coupling

One of the main difficulties encountered in earlier attempts to explain the scalar coupling was the lack of agreement with measurements of the frequency- and temperature-dependence of the relaxation time in hexafluorobenzene solutions¹⁸. These data could be fairly well interpreted in terms of dipolar interactions only. The agreement was less good, if a scalar contribution with a Debye spectrum was included in the theoretical description.

Using the pulse model and Eqs. (3), (4) and (6), the well known relations for the nuclear relaxation rates due to the coupling with the electrons may be written as follows,

The experimental data of T_1' for $\text{C}_6\text{F}_6/\text{TBP}$ of ref.¹⁸ might now equally well be explained with curve b), leading to a distance of closest approach $d=4,2 \text{ \AA}$ instead of $3,9 \text{ \AA}$. It remains difficult, however, to distinguish between a) and b), if only a limited number of experimental data over five decades of frequency is available. For the other solutions listed in Tab. 3, this would be still more difficult, because the scalar contributions are less.

A certain, and perhaps the best, test for the presence of scalar couplings with relaxation measure-

¹⁸ W. MÜLLER-WARMUTH and V. PRINTZ, Z. Naturforsch. **21a**, 1849 [1966].

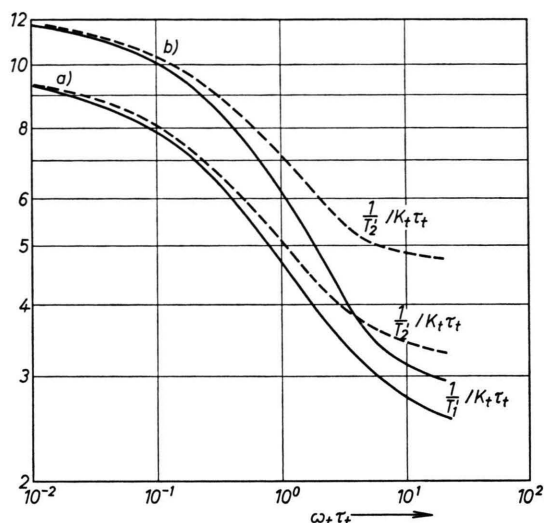


Fig. 6. Spectral dependence of the nuclear relaxation rates $1/T_1'$ and $1/T_2'$. a) Only dipole-dipole interactions modulated by translational diffusion; b) dipolar and contact coupling with $K=0.51$ and intensity function VII of Tab. 2.

ments would be an investigation of the ratio T_1'/T_2' . With dipolar interactions only this ratio increases from 1 at low frequencies to 1.28 at $\omega_S \tau_t = 20$. In case b) of Fig. 6, on the other hand, T_1'/T_2' increases to 1.60. This is in agreement with experimental data of GUTOWSKY and TAI, reinterpreted by RICHARDS et al.¹⁹, who measured in a number of different solutions at 20 MHz and 21 °C, T_1'/T_2' -ratios between 1.12 and 1.19 for protons, but ratios between 1.40 and 1.74 for fluorine nuclei.

5. Discussion

The pulse model of molecular collisions has provided an explanation of the time-dependence of intermolecular nuclear electron contact interactions. In combination with the modulation of the dipolar part of the coupling by translational diffusion, it may describe a great number of experimental dynamic polarization studies over several orders of magnitude of frequency and at various temperatures. Relaxation data may also be understood. The particular advantage of this model is the uniform picture of the diffusional motion of individual molecules which modulates both dipolar and scalar couplings. It should be pointed out, on the other hand, that

this model is not the only molecular physical concept that could describe a certain spectral dependence. If the latter is of the Debye type, for instance, as assumed in a first attempt to interpret the frequency-dependence of the Overhauser effect¹, this could be explained by all, sticking-, flipping-, rotational- and pulse models¹⁰. Only the pulse model, however, yields different intensity functions from the same physical concept.

Since the same process of molecular diffusion governs the fluctuations of both couplings, the three correlation times τ_t , τ_p and τ_w should be related. The assumption of equal temperature-dependence seems therefore not only justified, but it explains also the independence of K from the temperature, required for the interpretation of the data. The values of τ_t , τ_w and τ_p are different, however. Whilst τ_t characterizes the average time scale of a single diffusion step, τ_p is the time between two collisions. τ_t is related to the distance of closest approach of molecules¹⁶, whereas τ_p [Eq. (7)] should depend on the concentration of electron spins. The time of a molecular collision τ_w , defined by the normalization of the pulse function, also depends on the diffusion in the liquid. Moreover it is related to the properties of the particular system that interacts. From these arguments one gets the condition

$$\tau_p > \tau_t \geq \tau_w.$$

From dynamic polarization experiments on protons it is known that the nuclear-electron coupling parameter does not depend on the electron spin concentration. In fluorocarbon solutions, however, the scalar contribution increased a little with increasing concentration. Since there are no systematic experimental investigations on this dependence so far, we shall not discuss this effect, which merely renders a quantitative evaluation of Eq. (10) more difficult. In our experimental studies free radical concentrations of little less than 10^{-2} M. have been used.

The experiments have shown that slightly different intensity functions must be used for the fluctuations of the contact coupling. This leads to the different collision pulses of Fig. 4. It is remarkable that the results for aromatic fluorine nuclei can only be explained by a strong interaction of very short duration combined with a smaller long range coupling, whilst the CF_3 fluorine nuclei have a much more regular time scale for their interaction with electron spins. Within the frame of the pulse model,

¹⁹ H. S. GUTOWSKY and J. C. TAI, J. Chem. Phys. **39**, 208 [1963]; J. G. KENWORTHY, J. A. LADD, and R. E. RICHARDS, Mol. Phys. **10**, 469 [1966].

the dependence of the scalar contributions on the chemical environment is mainly explained by different collision times and different ranges of the interaction, and not by much different coupling constants. This is particularly noticeable with TBP solutions in hexafluorobenzene, where the scalar contribution is relatively strong, but only because of the larger τ_w value. From Eqs. (10) and (7) a root mean square value $\sqrt{\langle A^2/\hbar^2 \rangle}$ for the coupling constants of the order of 1 MHz or a little less is estimated for all the systems of table 3.

Concerning the nature of the interaction, POINDEXTER et al. have suggested two possible mechanisms that may affect the contact coupling between a radical electron and a magnetic nucleus attached to another molecule⁷. According to these authors, spin information can either be transmitted to the nucleus indirectly by exchange polarization of the fluorocarbon molecular orbitals during collision, or by charge transfer from radical to solvent by the formation of complexes. The study of the frequency- and temperature-dependence of this work and its interpretation with the pulse model favours the first concept, though preferential orientation during collision seems to be responsible for some of the pulse shapes of Fig. 4. If complex formation occurs, the pulse shape would be not so steep, and τ_w should no longer be governed by diffusion.

Another argument against the formation of complexes is that dynamic proton polarization gives, in low fields, enhancements very close to the theoretical value of -330 for dipolar type of interaction. However the possibility of very slow time modulation of a scalar type hamiltonian (formation and dissociation of long lived complexes) cannot be discarded due to this low field measurement alone. If the scalar hamiltonian modulation is slow enough, it will not effect the relaxation or the Overhauser effect of the nuclei. The main point against this complex formation lies in the frequency dependence of ρ , which in the great majority of cases can be explained with the aid of translational spectral den-

sities whilst random rotation should play the essential role in the relaxation of nuclei participating in a complex molecule.

From the chemical point of view it is interesting to note the changes in the scalar contribution K to the intermolecular fluorine-electron spin interactions with the particular solvent and radical. The parameter K (which is by the way not particularly dependent on the choice of the best intensity function) is very sensitive to the detailed chemical environment of the fluorine nuclei. An inspection of Tab. 3, and of the data of Fig. 3, which were not included in the theoretical interpretation, suggests that K depends on both the functional group to which the fluorine belongs, and on the radical. Qualitatively the scalar contribution increases in the following sequence: aromatic fluorine nuclei — TBP, methyl fluorines attached to aromatic rings — GV, methyl fluorines attached to aromatic rings — TBP, aromatic fluorines — GV, aliphatic methyl fluorines — TBP. This sequence was especially well demonstrated on the solvent molecule $p\text{-FC}_6\text{H}_4\text{CF}_3$, in which the enhancements could be measured separately by high resolution techniques. It is also supported by measurements of POINDEXTER et al., who studied the dynamic polarization of ^{19}F nuclei for a selection of different fluorocarbons⁷ and many different free radicals⁶ in a magnetic field of 74 gauss.

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