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High Pressure NMR Study of the Molecular Dynamics of Liquid Methylfluoride and Deutero-Methylfluoride

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Diffusion / High Pressure / Liquids / Spectroscopy, Nuclear Magnetic Resonance / Transport Properties

The ^{2}D-, ^{1}H- and ^{19}F-spin-lattice relaxation rates R_1 have been investigated in fluid methylfluoride in the temperature range 150 K $\leq T \leq$ 450 K and at pressures up to p = 200 MPa. In addition, the self-diffusion coefficient D has been obtained with NMR techniques in the same p, T-interval. — The latter are interpreted within the rough hard sphere model yielding a temperature independent RHS diameter d and a strongly temperature dependent rotation-translation coupling parameter A. The total ^{2}D-, ^{1}H- and ^{19}F-relaxation rates in CD_3F and CH_3F are decomposed into their respective quadrupolar, dipolar and spin-rotation contributions. Furthermore orientational and spin-rotational correlation times are estimated. It is shown that they are in good agreement with the predictions of the extended M-diffusion model (EDM). Inertial effects influence the molecular dynamics in the whole p, T-range investigated. The self-diffusion coefficients and orientational correlation times are in excellent agreement with MD-simulation data.

Introduction

An increasing number of experimental techniques [1—4] like IR and Raman bandshape contours, light scattering, dielectric relaxation and absorption, neutron scattering and NMR relaxation have been applied in recent years to the investigation of molecular dynamics in low molecular weight liquids. From high-frequency methods orientational correlation functions $C_1(t)$ may be deduced over a limited time range thus revealing the short time dynamics of orientational fluctuations mainly. Nuclear magnetic relaxation studies have limitations in probing details of the microdynamics since in low viscosity liquids only the area of the relevant correlation function is normally determined, and not its shape. Dynamic parameters obtained from NMR methods include the self-diffusion coefficient D, the molecular orientation correlation time $\tau_{\theta,l=2}$ and the correlation time τ_ω of the molecular angular velocity. The importance of simultaneous measurement of $\tau_{\theta,2}$ and τ_ω lies in the model-dependent relationship between these microscopic parameters. Thus together they may provide insight into the state of molecular motion.

The present investigation is a study, by NMR methods, of the small polar symmetric-top molecule CH_3F and its deuterated analogue in the neat liquid phase over the temperature range 150 K to 450 K and a pressure range 0.1 to 200 MPa. The self-diffusion coefficient D is the only dynamic parameter that can be obtained directly from the experiment. The various correlation times ($\tau_{\theta,2}$, τ_ω) may be extracted according to motional models from the measured spin-lattice relaxation rates caused by magnetic dipole-dipole-, electric quadrupole- and spin-rotation interactions of the nuclear spin with motional degrees of freedom of the molecules.

Experimental

Spin-lattice relaxation times were measured by the inversion-recovery method with alternating phase [5] on a Bruker MSL-300 multi-purpose solid-liquid NMR spectrometer operating at 300 MHz for ^{1}H, 282 MHz for ^{19}F and 46 MHz for ^{2}D and on a Varian XL-100 high resolution spectrometer operating at 100.1 MHz for ^{1}H, 94.07 MHz for ^{19}F and 15.35 MHz for ^{2}D. Self-diffusion coefficients D were determined by the spin-echo technique on a Varian XL-100 using a home-built quadrupole coil to apply a steady field gradient. The experimental procedure and high pressure set-up have been described elsewhere [6]. The pressure was measured with a Heise-bourdon gauge (Heise, Connecticut, U.S.A.) with a precision of ± 0.5 MPa. The temperature was altered by blowing precooled gaseous N_2 around the sample using the modified variable temperature units of the two spectrometers. The temperatures were measured with a 0.5 mm Chromel-Alumel thermocouple (Philips, Kassel, F.R.G.) and are considered reliable to ± 1 K. The self-diffusion coefficients and spin-lattice relaxation times are judged reliable to ± 10%.

Substances

CH_3F (99%) was purchased from J. T. Baker (Groß-Gerau, F.R.G.), CD_3F (99% deuterated) was obtained from I. C. Chemikalien (München, F.R.G.). The substances were stored in glass flasks. Residual moisture was removed over molecular sieve 3 Å. In addition the gaseous compounds were kept for approximately one day in contact with potassiumhydroxide resp. phosphorpentoxide in order to remove reactive impurities. After these treatments the ^{1}H-, ^{2}H- and ^{19}F-NMR spectra showed no sign of any impurity.

Results and Discussion

The Self-Diffusion Coefficient of Methylfluoride

Structure and dynamics of simple liquids are determined mainly by short-range, repulsive interactions [7]. An idealized simple liquid is composed of smooth hard spheres. It's self-diffusion coefficient may be expressed as [8]

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$$D_{\mathrm{SHS}}=\frac{3}{8}\left(\frac{kT}{m\cdot\pi}\right)^{1/2}\cdot d\cdot P(\varrho d^{3}) \tag{1}$$

with d the hard sphere diameter and ϱ the number density. The coefficients of an empirical polynomial $P(\varrho d^3)$ in the packing fraction of the molecules have been obtained by various authors [8] via fitting Eq. (1) to the MD-simulation results of Alder et al. [9].

Table 1
Molecular Constants in CH_3F and CD_3F

1) distances and angles (CH_3F) [31, 32]	
$r_{CH} = (1.106 \pm 0.001) \cdot 10^{-10}$ (m)	(HCH) = $109^\circ\ 59' \pm 3'$
$r_{CF} = (1.3852 \pm 0.00005) \cdot 10^{-10}$ (m)	(HCF) = $108,95^\circ$
$r_{HH} = 1.812 \cdot 10^{-10}$ (m)	
$r_{HF} = 2.034 \cdot 10^{-10}$ (m)	
2) dipole moment (CH_3F) [24]	
$\mu = 1.8585$ (Dy)	
3) principal moments of inertia	
CH_3F [33]	CD_3F
$I_\perp = 34.82 \cdot 10^{-47}$ (kg · m²)	$45.96 \cdot 10^{-47}$ (kg · m²)
$I_\parallel = 5.47 \cdot 10^{-47}$ (kg · m²)	$10.94 \cdot 10^{-47}$ (kg · m²)
$\langle I\rangle = \left(\frac{1}{3}\sum_{i=x,y,z}\frac{1}{I_i}\right)^{-1}$	
$= 12.5 \cdot 10^{-47}$ (kg · m²)	$22.2 \cdot 10^{-47}$ (kg · m²)
4) principal spin-rotation tensor components [24]	
CH_3F	CD_3F
^{19}F: $C_\perp = 4.0 \pm 1.9$ (kHz)	3.03 (kHz)
$C_\parallel = -51.1 \pm 1.3$ (kHz)	−25.55 (kHz)
^1H: $C_\perp = \frac{1}{2}(C_x + C_y) = 0.8$ (kHz)	
$C_\parallel = 14.66$ (kHz)	

Rough hard spheres provide the simplest model liquid representing real, non-spherical molecules or spherical molecules with anisotropic intermolecular interactions. In these liquids a coupling of rotational and translational fluctuations may occur leading to a decrease of D_{SHS}. This R-T-coupling may be accounted for simply by introducing a R-T-coupling parameter A such that [10]

$$D_{\mathrm{exp}} \simeq D_{\mathrm{RHS}} = A \cdot D_{\mathrm{SHS}}\,. \tag{2}$$

Table 2 collects the experimental self-diffusion coefficients D together with the mass-density ϱ. The latter have been measured between 300 K and 600 K and at pressures up to 300 MPa by Bozdag and Franck [11]. These data have been extrapolated linearly to lower temperatures in accord with known densities at s.v.p. [12].

Fig. 1 shows the isothermal density dependence of the self-diffusion coefficient. The lines drawn through the data are calculated with Eqs. (1) and (2). The rough hard sphere diameter may be obtained from the isothermal density dependence of the self-diffusion coefficient D from a non-linear least-squares fit (NAG E04FCF) with Eqs. (1) and (2). A temperature independent hard sphere diameter d = (0.357 ± 0.004) nm results for the fluid phase of CH_3F. The R-T-coupling parameter A is also obtained from the fit. It is temperature dependent and increases from A = 0.37 at low temperatures to A = 1 at the highest temperatures (see Table 3). Hence the coupling of rotational and translational de-

Table 2
Self-Diffusion Coefficient D and Mass-Density ϱ of CH_3F (T [K], p [MPa], D [10^{-9} m²/s], ϱ [kg/m³])

T^p	s.v.p.	20	50	100	150	200	
153	2.10	1.90	1.65				D
	965	998	1027				ϱ
178	3.70	3.20	2.75	2.30	1.95	1.75	
	917	950	990	1035	1060	1087	
204	5.70	5.10	4.40	3.60	3.05	2.60	
	860	905	952	1005	1033	1065	
230	8.50	7.30	6.20	5.00	4.30	3.80	
	800	855	910	970	1005	1040	
256	12.30	10.50	8.30	6.70	5.80	5.10	
	720	805	870	940	980	1015	
284		14.50	11.00	8.60	7.30	6.20	
		755	833	905	950	990	
314		20.00	15.00	11.20	9.00	7.40	
		675	785	867	920	960	
345		28.00	19.00	13.50	10.80	9.20	
		570	730	830	885	930	
375		41.00	25.00	16.00	13.00	11.00	
		490	677	792	857	905	
405		52.00	30.00	20.50	15.50	12.50	
		390	630	755	832	880	
440		74.00	37.00	23.50	17.50	14.50	
		295	570	715	797	850	

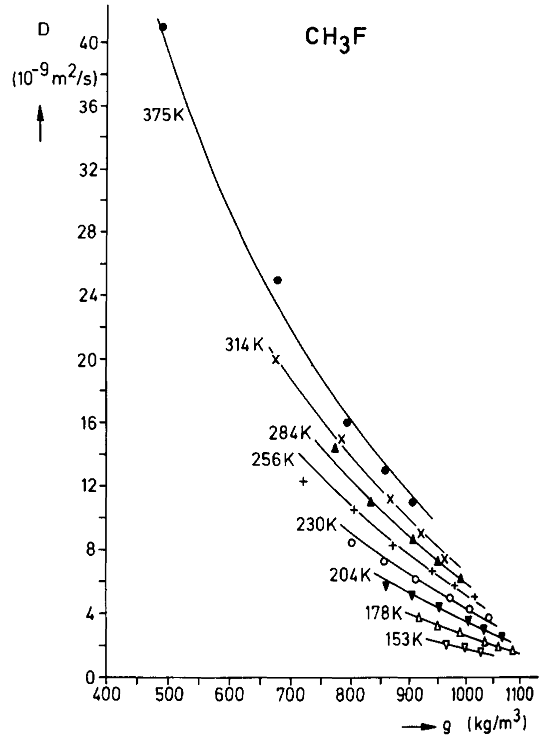

Fig. 1
Isothermal density dependence of the self-diffusion coefficient D

grees of freedom decreases with increasing temperature. Recently Böhm et al. [13] developed a new interaction potential for methylfluoride molecules in the liquid phase and performed molecular dynamics calculations to deduce various structural and dynamic properties of the liquid. Their self-diffusion coefficients are in good agreement with the results obtained in this study (see Table 5). The present data offer the possibility for further testing their potential function over a wide range of temperatures and pressures.

Table 3
Temperature dependence of the Rotation-Translation Coupling Parameter A

T [K]	153	178	204	230	256	284	314	345	375	405	440
A	0.37	0.50	0.62	0.71	0.80	0.87	0.93	0.94	0.99	1.00	0.98

^{2}D Spin-Lattice Relaxation Rates in CD_3F

Deuterium nuclei possess a spin I = 1 and interact predominantly via intramolecular electric quadrupole interactions. Presuming rigid molecules of spherical shape spin-lattice relaxation rates in the fast motion regime are given in a laboratory-fixed frame (L) as [14]

$$(R_1)_Q = \frac{3\pi^2}{10}\left(\frac{e^2 q_{zz} Q}{h}\right)^2 \left(1+\frac{\eta^2}{3}\right) \cdot \left(\frac{2I+3}{I^2(2I-1)}\right) \cdot j(\omega_0 \simeq 0) \tag{3}$$

where I is the spin of the quadrupole nucleus. $\left(\frac{e^2 q_{zz} Q}{h}\right)$ is the quadrupole coupling constant in Hertz with eQ the electric quadrupole moment of the nucleus and eq_{zz} the largest component of the electric field gradient (efg) tensor along the C-D bond. The efg asymmetry parameter $\eta = (q_{xx}\text{-}q_{yy})/q_{zz}$ is generally small and will be neglected.

The spectral density $j(\omega)$ for the motion in the lattice is the Fourier-Laplace transform of the relevant correlation function for orientational fluctuations of the molecular main axis system (M) of the efg-tensor

$$j(\omega) = \int_0^\infty g(t)\, e^{-i\omega t}\, dt = \int_0^\infty \sum_m \langle D^{(2)}_{0m}(\Omega_{LM})\, D^{(2)}_{0m}(\Omega_{LM}\, t)\rangle\, e^{-i\omega t}\, dt. \tag{4}$$

In the fast motion regime the spectral density is independent of the observing frequency ω and an orientational correlation time $\tau_{\theta,2}$ may be defined through the relation

$$\tau_{\theta,2} = \int_0^\infty \frac{g(t)}{g(0)}\, dt = \int_0^\infty \sum_m \frac{\langle D^{(2)}_{0m}(0)\, D^{(2)}_{0m}(t)\rangle}{\langle |D^{(2)}_{0m}|^2\rangle}\, dt \tag{5}$$

giving finally (I = 1)

$$(R_1)_Q = \frac{3\pi^2}{2}\left(\frac{e^2 q_{zz} Q}{h}\right)^2 \cdot \tau_{\theta,2}\,. \tag{6}$$

If independent information from solid state NMR or molecular beam studies is available on the magnitude of the deuterium quadrupole coupling constant, the integral orientational correlation time $\tau_{\theta,2}$ may be obtained directly from the measured deuterium relaxation rates. The only source of information available is an FT-NMR study of the spectrum of CD_3F in the nematic phase of a liquid crystalline solvent [15]. The deuterium quadrupole coupling constant (referred to the C-D bond) has been obtained to 133 ± 7 kHz with an asymmetry parameter $\eta = 0.03 \pm 0.03$. Bhattacharyya and Daily [15] quote a private communication by Griffith saying that a comparison of Raman and NMR data suggests a deuterium quadrupole coupling constant of 143 kHz. An ab initio calculation [16] of the efg yielded a coupling constant of 212 kHz, however. Also a comparison with known quadrupole coupling constants of similar compounds (see Table 4) suggests that the rather low value of 133 kHz obtained in a liquid crystalline solvent may not be appropriate to the neat liquid phase [37]. As will be explained later, a value of 143 kHz will be used. It should be noted that the integral correlation time $\tau_{\theta,2}$ must be considered as an effective correlation time. This is because of the asymmetric mass distribution in the symmetric top, although its shape is almost spherical ($a = 4.5$ Å, $b = 4.0$ Å), with concomitant different moments of inertia parallel and perpendicular to the symmetry axis of the molecule. Hence two different correlation times could arise for orientational fluctuations around the symmetry axis and an axis perpendicular to it. Within a diffusional model this would lead to [14]

$$\tau_{\theta,2} = \frac{1/2\cdot(3\cos^2\theta - 1)^2}{6D_\perp} + \frac{3\sin^2\theta\cos^2\theta}{5D_\perp + D_\parallel} + \frac{3/4\sin^4\theta}{2D_\perp + 4D_\parallel} \tag{7}$$

in terms of the components of the rotational diffusion tensor and the angle θ between the symmetry axis and the C-D bond axis. However, even within this motional model, two

Table 4
Deuterium quadrupole coupling constants in various halomethanes

Compound	e^2qQ/h (kHz)	
CD_3F	133 ± 7	[15]
	143	[15]
	212	[16]
CD_3Br	173 ± 4	[37]
	177 ± 1	[34]
	178 ± 3	[35]
CD_3I	181.7 ± 0.4	[36]
	182 ± 5	[37]
CD_2Cl_2	171.7 ± 0.8	[44]
CD_2Br_2	180 ± 1	[43]
CD_2I_2	175 ± 2	[45]
CDF_3	159 ± 5	[40]
	170.8 ± 2	[41]
$CDCl_3$	180 ± 3	[39]
	167 ± 1	[36]
	166.9 ± 0.1	[38]
$CDBr_3$	171.2 ± 0.8	[42]
	184 ± 1	[34]

quadrupole nuclei in different positions would be neccessary to extract $D_\perp$ and $D_\parallel$, which are not available in CD_3F. Intramolecular dipole-dipole interactions provide equivalent information about orientational fluctuations, if it is possible to separate the intra-rate from the various contributions to the total rate measured for ^1H and ^{19}F nuclei. However, in either case is the intra-rate negligible and cannot be obtained with any reasonable degree of accuracy. Thus it is not possible to extract detailed information about the anticipated [46, 47] fast spinning motion around the C_3 axis and the tumbling motion of this axis. Eq. (7) has been used frequently to deduce the diffusional anisotropy $\varrho = D_\parallel/D_\perp$ in various halomethanes, methylcyanide and its halogenated derivatives although the small step diffusion model is certainly not appropriate for the fast axial spinning motion. In these investigations the largest motional anisotropy has been observed for molecules with large dipole moments and highly anisotropic molecular shape. As a rule, a large inertial anisotropy $I_\perp/I_\parallel$ corresponds to a substantial diffusional anisotropy $D_\parallel/D_\perp$. Thus within the series of halomethanes, CH_3F is expected to exhibit the smallest motional anisotropy. Despite the above mentioned inconsistency, one can, at least at low temperatures, estimate the anisotropy ϱ from Eq. (7) because in the rotational diffusion model the relation

$$D_\perp = (2\,\tau_{\text{diel}})^{-1}$$

holds and τ_{diel} have been measured in the temperature range T_c-T_{tripl} at saturation vapor pressure [17]. At the two lowest temperatures $T = 153$ K: $\varrho = 1.84$ and $T = 170$ K: $\varrho = 2.1$ is obtained indicating a modest diffusional anisotropy only. Hence in the following we will only discuss effective integral correlation times. These integral correlation times as well as the self-diffusion coefficients are in good agreement with the molecular dynamics results corroborating the usefulness of the potential functions developed by Böhm et al. [13].

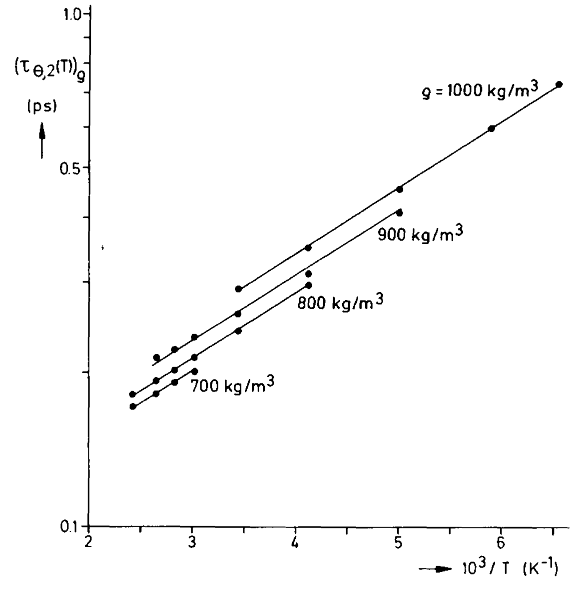

Fig. 2
Isochoric temperature dependence of the orientational correlation time $\tau_{\theta,2}$

Fig. 2 shows the isochoric temperature dependence of the correlation times $\tau_{\theta,2}$. At constant density the temperature dependence reflects the sole influence of the kinetic energy of the molecules upon the orientational fluctuations. Because "collisions" occur more frequent, i.e. intermolecular torques fluctuate more rapidly, at higher temperature, orientational correlations decay on a shorter time scale leading to decreasing correlation times. The latter are seen to be shorter than 1 ps in the p, T-range investigated. Furthermore, the isochoric temperature dependence reveals an Arrhenius-dependence with a density independent "activation energy" $E_\varrho^\ddagger = 2.48$ (kJ/mol) corresponding to kT at room temperature roughly. A correspondingly low apparent activation energy of 3.77 kJ/mol has been obtained from dielectric measurements along the saturation vapour pressure curve.

Fig. 3 shows the isothermal density dependence of the correlation times $\tau_{\theta,2}$. At constant temperature the correla-

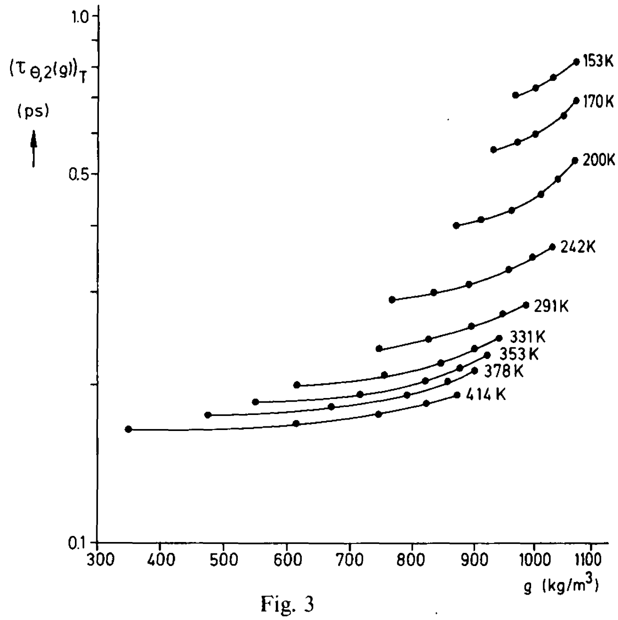

Fig. 3
Isothermal density dependence of the orientational correlation time $\tau_{\theta,2}$

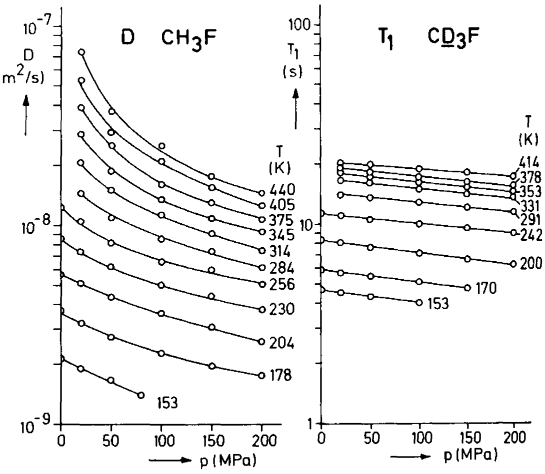

Fig. 4
Comparison of the p,T-dependence of the deuterium spin-lattice relaxation time $T_1(^2H)$ and the self-diffusion coefficient D

tion times increase in a nonlinear fashion with density reflecting the retarding influence of molecular torques upon the reorientation process at higher packing fractions. The increase is the more pronounced the lower the temperature. A comparison of the pressure and temperature dependence of the self-diffusion coefficient D and the ^2H spin-lattice relaxation time T_1 (Fig. 4) reveals that orientational fluctuations are much less hindered by compression or removal of thermal energy than are positional fluctuations. Together with the fairly short correlation times $\tau_{\theta,2} \leq 1$ ps and the low barrier to rotation $E_\varrho^\neq = 2.48$ kJ/mol this weak dependence on p, T indicates that the reorientational processes must proceed rather freely. This raises the question whether inertial effects may be important. An indication of the importance of inertial effects upon orientational fluctuations may be obtained by comparing the orientational correlation times $\tau_{\theta,2}$ with the free rotor correlation time $\tau_f = \frac{3}{5}\sqrt{\frac{\langle I \rangle}{kT}}$.

If the ratio $\tau_{\theta,2}/\tau_f \gg 1$, reorientational processes are diffusive and inertial effects may be neglected. If $\tau_{\theta,2}/\tau_f \simeq 1$ inertial effects severely influence orientational time correlation functions. In CD_3F at low temperatures the ratio $\tau_{\theta,2}/\tau_f$ yields values ~ 2 whereas at high temperatures values ~ 1 are found. Hence it must be concluded that the molecular dynamics of methylfluoride do not correspond to a diffusive process over most of the p, T range investigated.

^1H and ^{19}F Spin-Lattice Relaxation Rates in CD_3F, CH_3F

Protons and fluorine nuclei possess a spin $I = 1/2$, their spin-lattice relaxation proceeds mainly via magnetic dipole-dipole interactions and spin-rotation interactions. The dipole-dipole interactions have to be decomposed into intramolecular and intermolecular interactions. In the fast motion regime the various dipolar relaxation rates are given, again presuming rigid molecules of spherical shape, as [12]

a) dipole-dipole, intra, like spins $I = 1/2$

$$R_{1,\mathrm{dd}}^{\mathrm{intra}} = \frac{3}{2}\gamma_I^4\left(\frac{\mu_0}{4\pi}\right)^2 \cdot \hbar^2 \cdot \sum_{I' \neq I} r_{I,I'}^{-6} \cdot \tau_{\theta,2} \tag{9}$$

b) dipole-dipole, intra, unlike spins $I = 1/2$, $S = 1/2$

$$R_{1,\mathrm{dd}}^{\mathrm{intra}} = \gamma_I^2\gamma_S^2\left(\frac{\mu_0}{4\pi}\right)^2 \cdot \hbar^2 \sum_S r_{IS}^{-6} \cdot \tau_{\theta,2} \tag{10}$$

c) dipole-dipole, inter, like spins $I = 1/2$

$$R_{1,\mathrm{dd}}^{\mathrm{inter}} = \frac{8\pi}{9}\left(\gamma_I^2 \cdot \frac{\mu_0}{4\pi}\right)^2 \cdot \hbar^2 \cdot \frac{n_I}{D} \cdot \sum_{I' \neq I} a_{I,I'}^{-1} \tag{11}$$

d) dipole-dipole, inter, unlike spins $I = 1/2$, $S = 1/2$

$$R_{1,\mathrm{dd}}^{\mathrm{inter}} = \frac{16\pi}{27}\left(\gamma_I\gamma_S \frac{\mu_0}{4\pi}\right)^2 \cdot \hbar^2 \cdot \frac{n_S}{D}\sum_S a_{IS}^{-1}. \tag{12}$$

The expressions for the intermolecular dipolar relaxation rate may be obtained with a diffusion equation with reflecting boundary conditions [18, 19]. Any off-center effects have been neglected as they contribute less than 10% to the leading term [20]. The relative diffusion coefficient has been replaced by twice the measured self-diffusion coefficient. The distance of closest approach a has been taken from radial pair distribution functions as obtained by molecular dynamics simulations of Böhm et al. [13]. Otherwise a uniform distribution of the molecules has been assumed.

The spin-rotation relaxation rate is given for a spherical top by [21]

$$R_1^{\mathrm{SR}} = \frac{2k_BT}{\hbar^2} \cdot \langle I \rangle [C_0^2 \cdot \tau_\omega + 2(\Delta C)^2 \cdot \tau_{\mathrm{SR}}] \tag{13}$$

with $\langle I \rangle = \left(\frac{1}{3}\Sigma I_i^{-1}\right)^{-1}$ the mean moment of inertia of the molecule. $C_0 = \frac{1}{3}(C_\parallel + 2C_\perp)$ and $\Delta C = \frac{1}{3}(C_\parallel - C_\perp)$ give the isotropic and the anisotropic part of the spin-rotation interaction tensor in terms of the parallel and perpendicular component of the tensor in its main axis system.

τ_ω is the correlation time for fluctuations of the molecular angular velocity and τ_{SR} is the correlation time for the angular velocity-orientational product correlation function which characterizes the anisotropic spin-rotational interactions. Eq. (13) is equivalent to an expression given by Hubbard [22, 23]

$$R_1^{\mathrm{SR}} = \frac{2k_BT}{\hbar^2}\langle I \rangle \cdot \frac{1}{3}(2C_\perp^2 + C_\parallel^2) \cdot \tau_{\mathrm{SR}} \tag{14}$$

if due account is taken of the different definitions of τ_{SR}. Eq. (14) has been used to calculate the correlation times τ_{SR}. The necessary molecular constants are compiled in Table 1.

Separation of the ^{19}F-Relaxation Rates in CD_3F

The ^{19}F spin-lattice relaxation rate is a sum of different contributions according to

$$\begin{aligned} R_1(^{19}F) = {} & R_{1,\mathrm{SR}}(^{19}F) + R_{1,\mathrm{dd}}^{\mathrm{inter}}(^{19}F\text{-}^{19}F) \\ & + R_{1,\mathrm{dd}}^{\mathrm{intra}}(^{19}F\text{-}^{2}D) + R_{1,\mathrm{dd}}^{\mathrm{inter}}(^{19}F\text{-}^{2}D). \end{aligned} \tag{15}$$

Because of the small gyromagnetic ratio of the deuterium nucleus, the last two terms contribute but little to the measured relaxation rate and will be neglected.

Inspection of Fig. 5 reveals that the spin-rotation relaxation rate dominates the observed rate over almost the entire p, T-range investigated. It may be obtained by subtracting from the total rate the intermolecular dipolar rate $R_{1,\mathrm{dd}}^{\mathrm{inter}}(^{19}F\text{-}^{19}F)$ as calculated with the help of Eq. (11). Here the measured self-diffusion coefficient has been used together with a distance of closest approach $a = 0.30$ nm as taken from the MD simulations [13]. At high temperatures the spin-rotation rate is practically identical with the observed rate. To calculate correlation times τ_{SR} independent information about the components of the spin-rotation tensor is neccessary. These have been determined in the case of CH_3F from molecular-beam electric resonance spectra (see Table 1)

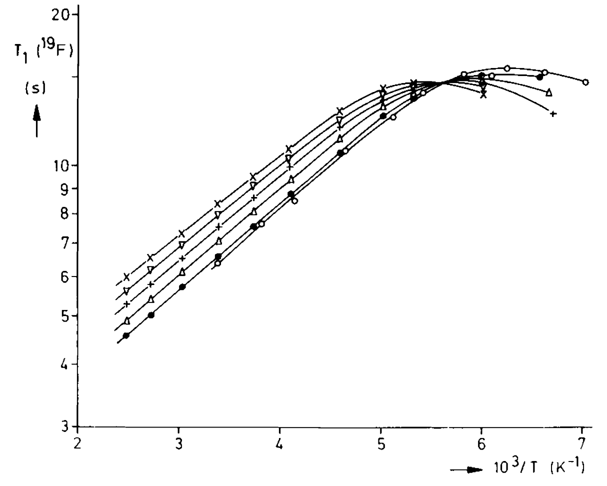

Fig. 5
Isobaric temperature dependence of the fluor-19 spin-lattice relaxation times in CD_3F. (○ s.v.p., ● 20 MPa, △ 50 MPa, + 100 MPa, ▽ 150 MPa, × 200 MPa)

[27]. The corresponding components of the tensor in CD_3F may be obtained from the relation [25]

$$C_\alpha = g_{^{19}F} \cdot \lambda_\alpha \cdot \hbar/(2 \cdot I_\alpha) \tag{16}$$

where $g_{^{19}F}$ is the nuclear g-factor, I_α the α-th component of the moment of inertia tensor (see Table 1) and λ_α a dimensionless quantity independent of the isotopomere.

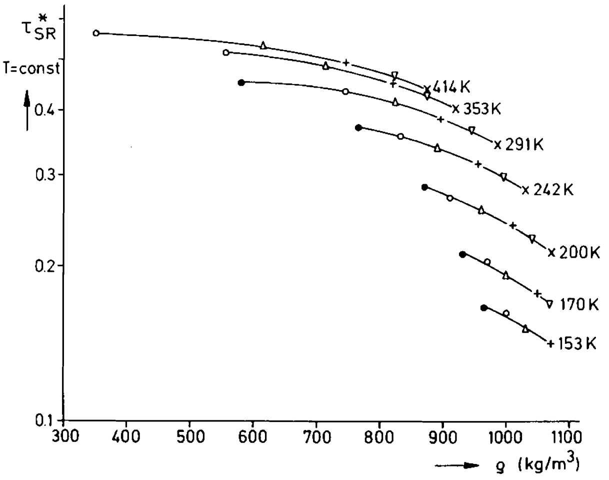

Fig. 6
Isothermal density dependence of the reduced spin-rotational correlation time τ^*_{SR}

Fig. 6 shows the isothermal density dependence and Fig. 7 gives the isochoric temperature dependence of the reduced correlation times $\tau^*_{SR} = \tau_{SR}(kT/\langle I \rangle)^{1/2}$. With increasing density τ^*_{SR} decreases due to the stronger perturbing influence of molecular torques at higher packing fractions. Also the decrease is the more pronounced the lower the temperature. However, even at the lowest temperatures τ^*_{SR} does not fall below 0.1 which corresponds roughly to the upper limit of validity of the rotational diffusion model. Furthermore the product $\tau^*_{\theta,2} \cdot \tau^*_{SR} > 6^{-1}$, even for $\tau^*_{SR} \ll \tau^*_{\theta,2}$, indicating that the Hubbard relation $\tau^*_\theta \cdot \tau^*_{SR} = 6^{-1}$ is not obeyed. The isochoric temperature dependence of τ^*_{SR} deviates from an Arrhenius-dependence with a weaker dependence on temperature at lower densities.

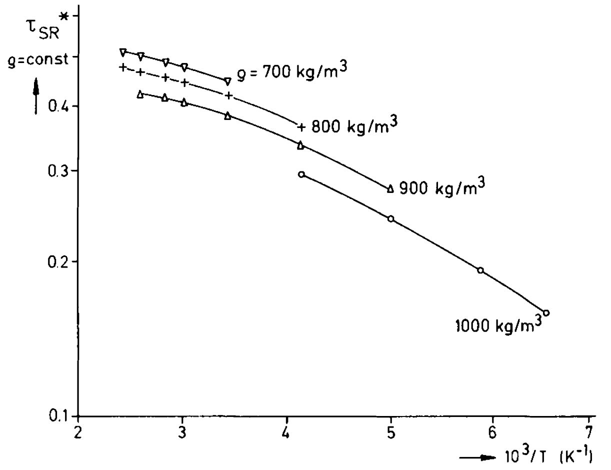

Fig. 7
Isochoric temperature dependence of the reduced spin-rotational correlation time τ^*_{SR}

Table 5
Comparison of MD-results and experimental results for the self-diffusion coefficient D and the integral orientational correlation time $\tau_{2,i}$ of methylfluoride

	MD		Expt.	
T [K]	192	132	192	132
D [10^{-9} m^2 s^{-1}]	4.7	1.2	4.8	1.15[a]
$\tau_{2,i}$ [ps]	0.45	1.2	0.44	1.1[a]

[a] Obtained by slight extrapolation.

Separation of the Relaxation Rates in CH_3F

The total ^{19}F spin-lattice relaxation rate in methylfluoride is composed of

$$\begin{aligned} R_1(^{19}F) = {} & R_{1,SR}(^{19}F) + R^{\text{intra}}_{1,dd}(^{19}F\text{-}^1H) \\ & + R^{\text{inter}}_{1,dd}(^{19}F\text{-}^1H) + R^{\text{inter}}_{1,dd}(^{19}F\text{-}^{19}F). \end{aligned} \tag{17}$$

Isobars of the total rate are shown in Fig. 8. Again the spin-rotation relaxation dominates over most of the p, T-range investigated, especially at low pressures. Fig. 9 gives the temperature dependence of the various contributions to the total ^{19}F relaxation rates at three pressures. The intermolecular dipolar relaxation rates were calculated using a distance of closest approach a(F-F) = 0.3 nm and a(F-H) = 0.22 nm as explained in the case of deuteromethylfluoride. At the lowest temperatures measured the intermolecular dipolar rates provide the main contribution to the total rate measured. Subtracting these contributions one is left with the conclusion that the intramolecular dipolar rate contributes but little to the total rate at all temperatures and pressures. This entails a large uncertainty in the estimate of the intramolecular dipolar rate and in the concomitant effective correlation time $\tau_{0,2}^{dd}$ which could not be estimated with any reasonable degree of accuracy. Hence at high temperatures the total rate is to good approximation equal to the spin-rotation relaxation rate. With the components of the spin-rotation interaction tensor [24] the correlation times τ_{SR}^{H} may be calculated. A comparison with the correlation times τ_{SR}^{D} as obtained in CD_3F allows an estimation of the isotope effect on the correlation times τ_{SR}. They scale with the square root of the mean moment of inertia. This is to be expected with motions influenced by inertial effects. It is to be noted that the experimental ratio $[R_1(CH_3F)/R_1(CD_3F)]_{^{19}F} \simeq 1.6$, which is practically equal to $[R_1^{SR}(CH_3F)/R_1^{SR}(CD_3F)]_{^{19}F}$ at high temperatures, may only be obtained if the mean moment of inertia in Eq. (14) is calculated as given in Table 1 [26] and τ_{SR}^{*} independent of the isotopomere.

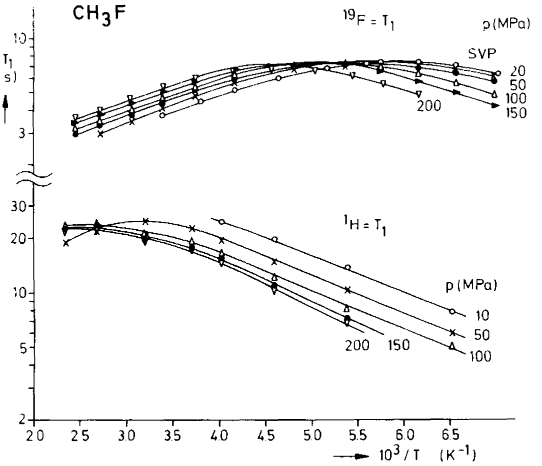

Fig. 8

Isobaric temperature dependence of the fluor-19 and proton (^1H) spin-lattice relaxation times T_1 in CH_3F

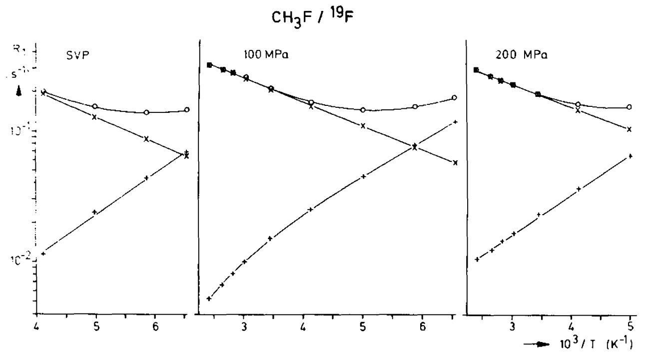

Fig. 9

Temperature dependence of the various relaxation rates contributing to the total fluor-19 spin-lattice relaxation rate $R_1(^{19}F)$ in CH_3F. (+ $R_{1,dd}^{inter}$, × R_1^{SR}, ○ ($R_{1,dd}^{inter} + R_1^{SR}$))

The total ^1H spin-lattice relaxation rate in methylfluoride is composed of

$$R_1(^1H) = R_{1,SR}(^1H) + R_{1,dd}^{intra}(^1H\text{-}^1H) + R_{1,dd}^{intra}(^1H\text{-}^{19}F) + R_{1,dd}^{inter}(^1H\text{-}^1H) + R_{1,dd}^{inter}(^1H\text{-}^{19}F). \tag{18}$$

The intermolecular dipolar relaxation rates may again be estimated with the known self-diffusion coefficients and the distance of closest approach a(H-F) = 0.22 nm and a(H-H) = 0.22 nm as obtained from MD simulations. At low temperatures they provide the main contribution to the total rate measured (Fig. 10). At the highest temperatures the latter reaches a maximum (see Fig. 8) indicating the importance of spin-rotation relaxation at these temperatures. As the components of the spin-rotation tensor for the protons have been determined also by Wofsy et al. [24], $R_{1,SR}(^1H)$ may be calculated using the correlation times τ_{SR} derived from the ^{19}F relaxation. Again intramolecular dipolar relaxation rates are small and may not be obtained with any reasonable degree of accuracy. If one scales the orientational correlation times $\tau_{0,2}$ as obtained from the deuterium relaxation rates in CD_3F, with the square root of the mean moment of inertia, intramolecular relaxation rates of the right order of magnitude and correct temperature dependence may be derived. This, again, is an indication of the importance of inertial effects on the orientational fluctuations of methylfluoride.

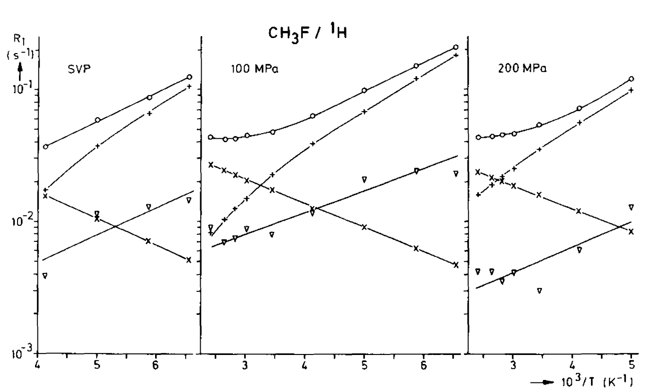

Fig. 10

Temperature dependence of the various relaxation rates R_1 contributing to the total proton spin-lattice relaxation rate $R_1(^1H)$ in CH_3F. (+ $R_{1,dd}^{inter}$, × R_1^{SR}, ∇ ($R_1^{exp} - (R_{1,dd}^{inter} + R_1^{SR})$), ○ ($R_{1,dd}^{inter} + R_{1,dd}^{intra} + R_1^{SR}$))

Orientational (τ_2)- and Spin-Rotational (τ_{SR}) Correlation Times in CD_3F and CH_3F

In this study only integral orientational correlation times could be determined. The orientational correlation functions, however, as obtainable by high-frequency methods over limited time spans show characteristic features of orientational fluctuations. At very short times purely kinetic (inertial) effects dominate as a simple consequence of the time reversal symmetry of classical autocorrelation functions [4]. At intermediate times and lower temperatures librational oscillations show up characteristic for motions in a cage [2]. The long-time tail of orientational correlation functions is almost always found to be exponential. This Markovian behaviour is a simple consequence of the long-range isotropy of the liquid [1]. All these charactersitic features are included in the orientational correlation times being the time integral of the corresponding orientational autocorrelation function in an unspecific way. Therefore it is difficult to draw detailed conclusions about the nature of a reorientation process because integral correlation times always accentuate the Markovian nature of the orientational fluctuations. Spin-rotation relaxation relates to fluctuations of the angular velocity and of the orientation of the molecules. Again only integral spin-rotational correlation times τ_{SR} of the angular velocity-orientational product correlation function can be determined from an NMR experiment. Also it is only within certain motional models that these bivariate correlation functions have been obtained. Because orientational correlation functions may also be obtained within the realm of these models, a comparison of both τ_2 and τ_{SR} may prove useful in providing insight into the state of molecular motion. The two most often used motional models for this purpose are the extended diffusion model (EDJ and EDM) [27] and the Fokker-Planck-Langevin model (FPL) [21, 23, 29]. In the two models applied to spherical tops a single parameter, τ_ω, is changed to produce the limits of free rotation and rotational diffusion. Both models assume successive uncorrelated instantaneous collisions, but differ in the strength of these collisions. In the FPL-model the angular impulse of each collision is so small that the angular momentum changes infinitesimally. In the EDJ-model collisions are strong with large angular impulses which randomize the angular momentum at each step whereas in the EDM-model only the direction of the angular momentum is randomized. However, random uncorrelated collisions cannot cause a reversal of the angular momentum as is observed in most molecular liquids and indeed has been observed in methylfluoride also [28]. Hence τ_ω must be considered a lower limit to the "lifetime" of the angular velocity correlation function. Because of these shortcomings of both models when applied to high-torque liquids their usefulness has been questioned recently [30].

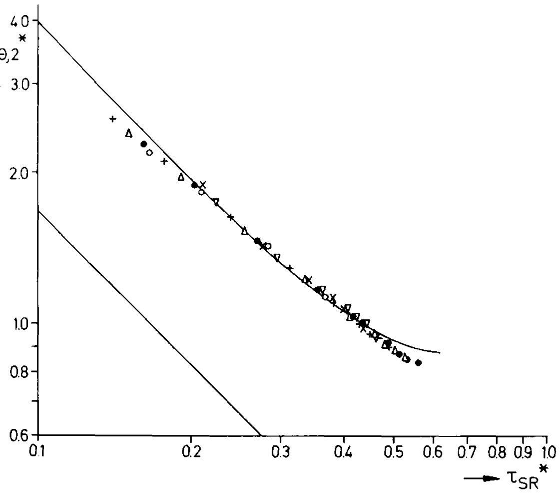

Fig. 11
Reduced orientational correlation times τ_2^* versus reduced spin-rotational correlation times τ_{SR}^*. Full curve gives $\tau_2^*(\tau_{SR}^*)$ according to the EDM-model. Straight line represents the Hubbard relation $\tau_2^* \cdot \tau_{SR}^* = 6^{-1}$. (○ s.v.p., ● 20 MPa, △ 50 MPa, + 100 MPa, ▽ 150 MPa, × 200 MPa)

Fig. 11 shows a plot of $\tau_2^* = \tau_2 \cdot \sqrt{\frac{kT}{\langle I \rangle}}$ versus $\tau_{SR}^* = \tau_{SR} \cdot \sqrt{\frac{kT}{\langle I \rangle}}$. The full curve gives the dependence of τ_2^* (τ_{SR}^*) according to the EDM-model [27]. Furthermore the Hubbard-relation $\tau_2^* \cdot \tau_{SR}^* = 6^{-1}$ is shown corresponding to the Debye rotational diffusion model. The latter is contained in the EDJ-model and the FPL-model in the limit $\tau_{SR}^* \ll \tau_2^*$.

However, the experimental data clearly show that the Hubbard relation is not obeyed in the limit $\tau_\omega^* \ll \tau_2^*$. Only the EDM-model allows for a deviation from the Hubbard relation in this limit. Originally the orientational correlation times τ_2^* had been calculated with a deuterium quadrupole coupling constant of 133 kHz with the result that the data fell above the theoretical curve for the EDM-model. Changing the coupling constant to 143 kHz as suggested by a comparison of Raman and NMR data [15] brings the experimental data in coincidence with the theoretical curve predicted by the EDM-model. For the Hubbard relation to be fullfilled at least approximately in the limes $\tau_{SR}^* \ll \tau_2^*$, one would have to change the coupling constant to 188 kHz. This seems to be too large if compared with coupling constants of similar compounds (see Table 4) although the theoretical estimate (212 kHz) is even larger. For comparison Fig. 12 gives the graph τ_2^* versus τ_{SR}^* with τ_2^* calculated with a coupling constant of 188 kHz. Also the prediction of the FPL-model [23, 29] and the Debye rotation diffusion model are shown. The agreement with the FPL-model is less convincing, hence the EDM-model offers the most satisfactory description, within the realm of these models, of the molecular dynamics of methylfluoride.

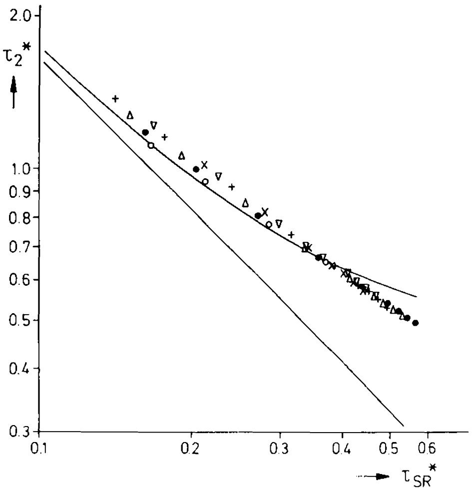

Fig. 12
Reduced orientational correlation times τ_2^* versus reduced spin-rotational correlation times τ_{SR}^*. Full curve represents the prediction according to the Fokker-Planck-Langevin model. τ_2^* has been calculated with (e^2qQ/h) (^2H) = 188 (kHz). Symbols as in Fig. 11. The straight line gives the Hubbard relation $\tau_2^* \cdot \tau_{SR}^* = 6^{-1}$

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High Pressure NMR Study of the Molecular Dynamics of Liquid Fluoroform and Deutero-Fluoroform

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Diffusion / High Pressure / Liquids / Spectroscopy, Nuclear Magnetic Resonance / Transport Properties

The ^{2}D-, ^{1}H- and ^{19}F-spin-lattice relaxation rates R_1 have been investigated in fluid fluoroform in the temperature range 150 K $\leq T \leq$ 450 K and at pressures up to p = 200 MPa. Previous measurements of the self-diffusion coefficient D have been supplemented to cover the same p, T-interval. Within the rough hard sphere (RHS) approximation a temperature independent RHS diameter d and a strongly temperature dependent rotation-translation coupling A_{RT} are obtained. Both parameters are also compared with those obtained in a series of related halomethanes. The total ^{2}D-, ^{1}H- and ^{19}F-relaxation rates in CDF_3 and CHF_3 are decomposed into their respective quadrupole, dipolar and spin-rotation contributions and orientational and spin-rotational correlation times are extracted from these rates. It is shown that they are in good agreement with the predictions of the Fokker-Planck-Langevin model. Inertial effects influence the molecular dynamics at high temperatures and low densities. The agreement of self-diffusion coefficients and orientational correlation times with MD-simulation data is very satisfactory.

Introduction

The molecular dynamics of liquid fluoroform have been studied in recent years by a variety of experimental techniques such as NMR, dielectric relaxation and absorption, Raman scattering, and IR-spectroscopy [1–10]. From the high frequency methods orientational correlation functions may be obtained over a limited time range and details of the short time dynamics of orientational fluctuations unravelled. NMR studies cannot yield such detailed information since in the short correlation time limit only the area of the relevant correlation function is determined and not its shape. However, if spin-rotation interactions dominate,

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