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# DENSITY DEPENDENCE OF THE MOLECULAR DYNAMICS OF FLUID $CH_3F$ AND $CF_3H$ STUDIED BY NMR

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The dynamic behaviour of compressed $CH_3F$ and $CF_3H$ has been studied between 150 and 400 K and to pressures of 200 MPa by measuring the spin–lattice relaxation times ($T_1$) of the proton and fluor nuclei. Also the deuteron $T_1$ of $CD_3F$ and $CF_3D$ were obtained in the whole $p$, $T$ range. Both substances reveal a significant non-Arrhenian behaviour when the whole temperature range is studied.

In addition the self-diffusion coefficients of these compounds and of their analogues $CH_3Cl$, $CH_2Cl_2$ and $CHCl_3$ have been investigated. The data obtained can be described best by the rough hard sphere model. It is found, that the rough hard sphere diameter ($d_{RHS}$) of all compounds is almost independent of temperature ($CF_3H$ $d_{RHS} = 0.39$ nm, $CH_3F$ $d_{RHS} = 0.35$ nm, $CH_3Cl$: 0.40 nm, $CH_2Cl_2$: 0.44 nm, $CHCl_3$; 0.48 nm).

## 1. Introduction

Methane derivatives in which some of the hydrogens have been substituted by fluorine or chlorine atoms are used as model compounds in experimental and theoretical studies of the dynamic properties of simple liquids. Due to their low boiling points the experimental study of the liquid state of fluorinated compounds is rather complicated and can only be performed under elevated pressures. Recent developments in the computer simulation of the liquid state of the methane derivatives [1] have made it desirable to obtain dynamic experimental data for some of the compounds over a wide range of temperatures and densities, in order to have a reliable control for the MD simulations. In the following we therefore present spin–lattice relaxation times of the protons, deuterons, and fluorine atoms of $CH_3F$ and $CF_3H$ as well as self-diffusion data for the two compounds and for $CH_3Cl$, $CH_2Cl_2$ and $CHCl_3$.

## 2. Experimental

Details of the experimental procedures have already been published [2, 3]. The data were obtained at a field of 2.34 T in a modified version of the strengthened glass cell design [4]. $CH_3F$, $CF_3H$ and $CH_3Cl$ were obtained from J.F. Baker Chemikalien (Groß-Gerau, FRG), $CH_2Cl_2$ (UVASOL) and $CHCl_3$ (UVASOL) from E. Merck (Darmstadt, FRG). The gases were dried over a 3 Å molecular sieve prior to use in 5 l glass-flasks [5]. Deuterated $CD_3F$ and $CF_3D$ were obtained from IC Chemikalien (München, FRG).

## 3. Theory

In the fast motion regime presuming rigid molecules of spherical shape, spin–lattice relaxation rates are generally given for various couplings by [6]

$$1/T_1 = K\tau ,$$

$K$ measures the strength of the various interactions coupling the spin and the "lattice". The correlation time $\tau$ contains information about molecular motions within the "lattice".

Explicit expressions for the different interactions are listed below:

(1) magnetic dipole–dipole interaction

(a) $K = (4/3)\hbar^2\gamma_I^2\gamma_S^2 S(S+1) r_{IS}^{-6}$
intramolecular

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(b) $$K = 18\gamma^4\hbar^2 f_n \rho/\langle r^2\rangle \int_0^\infty \mathrm{d}k \times \left(\int_0^\infty \mathrm{d}r g_{\mathrm{HH}}(r)\,\frac{J_z(kr)}{r}\right)^2$$
intermolecular .

(2) magnetic spin–rotation interaction

$$K = (2/3)kT/\hbar^2 \sum_{i,j=x,y,z} \theta_j C_{ij}^2 .$$

(3) electric quadrupole interaction

$$K = (3/40)(e^2Qq_{zz}/\hbar)^2(1+\eta^2/3) \times (2I+3)/[I^2(2I-1)] .$$

Magnetic dipole interactions monitor single particle orientational fluctuations (intramolecular) as well as positional fluctuations (intermolecular), whereas electric quadrupole interactions are, in most cases, sensitive to reorientational motions only. The correlation time of the spin–rotation interaction measures the decay of angular momentum correlations, hence supplies information not obtainable with other techniques.

## 4. Results and discussion

Fig. 1 gives us a representative example from the spin–lattice relaxation times of $^1H$ and $^{19}F$ of $CF_3H$. From the temperature and pressure dependence of the proton-$T_1$ one sees immediately, that the dipole–dipole interaction dominates the relaxation of this nucleus. $T_1$ becomes longer with rising temperatures and falls with increasing pressure. The same behaviour is observed for the $^{19}F$-$T_1$ only at the lowest end of the temperature range studied. At higher temperatures all $T_1$-isobars pass through a maximum. At the highest temperatures the pressure dependence of the experimental $T_1$ is reversed. This indicates, that the spin rotation mechanism provides the largest contribution to $^{19}F$-relaxation at $T > 200$ K. From the temperature dependence of the $^1H$-$T_1$ isobars an activation energy of ~4 kJ mol$^{-1}$ is calculated.

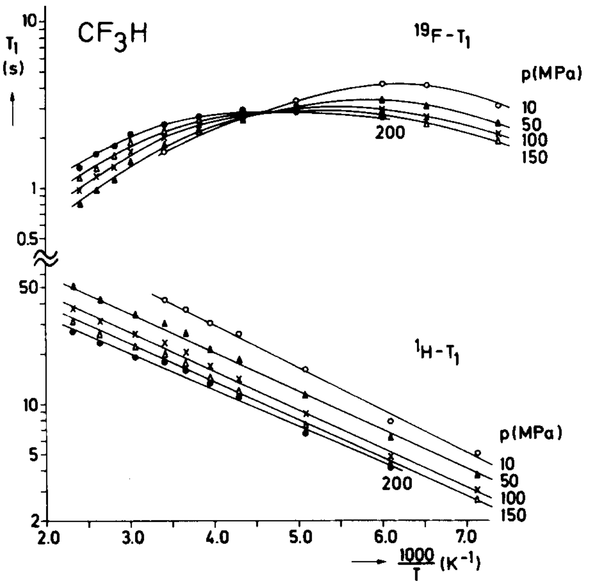

Fig. 1. Isobars of the spin–lattice relaxation times $T_1$ of the $^{19}F$ and $^1H$ atoms in $CH_3F$.

The complete analysis of the data will be presented elsewhere.

In fig. 2 the self-diffusion coefficient $D$ of $CH_3F$ is given together with the $^2H$-$T_1$ of $CD_3F$. The $^2H$-$T_1$ monitor the rotational motion of the C–D bond of the molecules. It is obvious, that this motion is much less influenced by changes in $p$ and $T$ than the translational motion of the whole molecule as monitored by the self-diffusion coefficient.

The limited space available prohibits a detailed analysis of the various spin–lattice relaxation times. We will therefore, in the following, restrict our discussion to an analysis of the self-diffusion coefficients. Fig. 2 shows clearly, that all isotherms reveal a pronounced curvature, also the representation of the data in an Arrhenius plot (cf. fig. 3) shows, that all isobars are curved. It appears thus meaningless to describe the data by activation parameters like the activation volume $\Delta V^*$ or $E_a$ the activation energy. In the description of the dynamic properties of simple liquids the rough hard sphere model has been applied with considerable success [7–9]. It combines results for the $\rho$, $T$-dependence of the dynamic properties of the hard sphere liquid as obtained from computer simulations [10], with older gas kinetic theories. In this model the experimental self-diffusion coefficient $D_{exp}$ is given by

$$D_{exp} \approx D_{RHS} = A D_{SHS} , \qquad (1)$$

$$D_{SHS} = \tfrac{3}{8}(kT/\pi M)^{1/2} d P(\rho d^3) , \qquad (2)$$

with $D_{SHS}$ the self-diffusion coefficient of the smooth hard sphere liquid as defined by eq. (2) $d$ is the hard sphere diameter and $P(\rho d^3)$ an empirical polynomial in the packing fraction as obtained from the MD simulations by Alder et al. [10]. The parameter $A$ characterizes for real

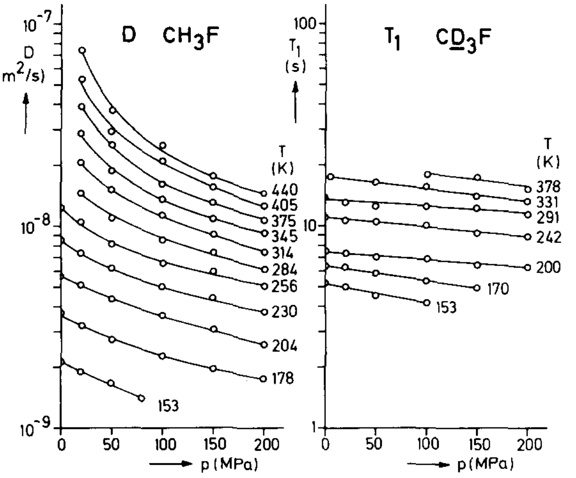

Fig. 2. Isotherms of the self diffusion coefficient $D$ and the deuteron spin–lattice relaxation times $T_1$ in methylfluoride.

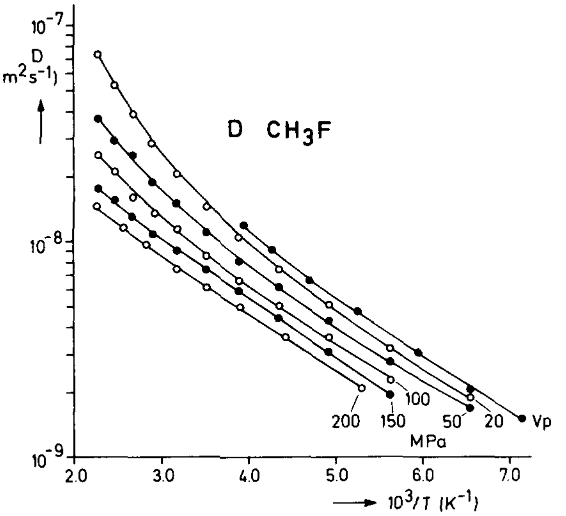

Fig. 3. Isobaric Arrhenius-plot of the self diffusion coefficient of $CH_3F$.

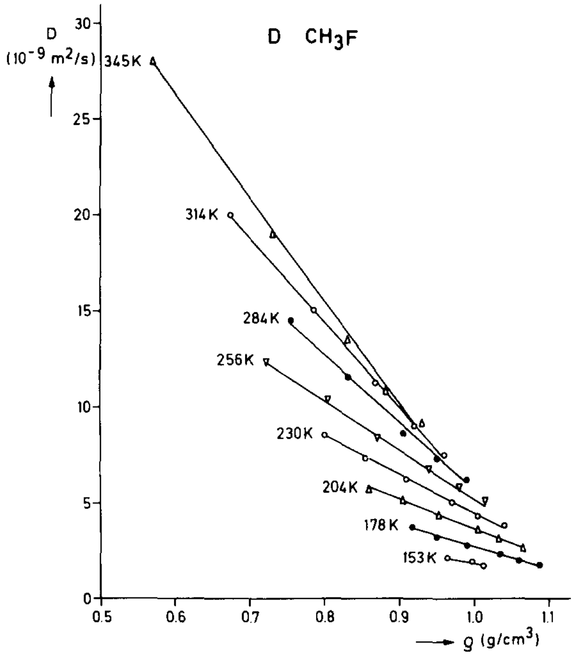

Fig. 4. Isotherms of the self diffusion coefficient of $CH_3F$ as a function of the density.

Table I

Evaluation of $D$ with the RHS model

| | $CH_3F$ | $CF_3H$ | $CH_3Cl$ | $CH_2Cl_2$ | $CHCl_3$ |
|---|---|---|---|---|---|
| $T$(K) | 150–440 | 142–250 | 185–440 | 186–406 | 230–400 |
| $d$(nm) | 0.35 | 0.39 | 0.40 | 0.44 | 0.48 |
| $A$ | 0.4–1.0 | 0.4–0.6 | 0.5–0.7 | 0.4–0.7 | 0.5–0.9 |

liquids the degree of rotation–translation coupling caused either by deviation from spherical shape or by attractive interactions. Since in the range of normal liquid densities the linear term dominates in eq. (2) one expects in a $D$ vs $\rho$ plot almost linear isotherms, their slope increasing with rising temperature. Fig. 4 gives the results obtained from $CH_3F$ in this representation. From these curves $d$ and $A$ can be derived [3]. They are compiled together with the parameters obtained for $CF_3H$, $CH_3Cl$, $CH_2Cl_2$ and $CHCl_3$ in table I. The rough hard sphere diameter $d$ is almost independent of temperature, even if a temperature interval of ~300 K is covered by the data ($CH_3F$, $CH_3Cl$). In the proximity of the melting temperature the coupling parameter $A$ is close to 0.5. It increases with rising temperature. Obviously it seems to approach 1 if the temperature could be raised sufficiently. For $CH_3Cl$ and $CH_2Cl_2$ the increase of $A$ with temperature is less pronounced than for the other three substances. No explanation can be given for this finding until now.

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