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ON THE MOLECULAR REORIENTATION IN LIQUID METHYL IODIDE*

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For liquid CH_3I within the temperature range of 223–303 K the dielectric permittivity for frequencies of 1 kHz, 9.54 and 26.5 GHz as well as the viscosity were measured. The correlation times for single dipole moment reorientations obtained from these measurements were in very good agreement with appropriate Raman correlation times. It was found also that the long time behaviour of this reorientation could be described successfully within the model of Hu and Zwanzig. For a discussion of the CD_3I molecules reorientation about its symmetry axis experimental results from the literature were used. For the second cumulant approximation of the friction model seems very suitable.

1. Introduction

The reorientation of CH_3I molecules in the liquid state was extensively investigated using NMR and Raman scattering techniques. The most important results were obtained by Campbell et al. [1]. They measured the Raman correlation times of the 525 cm^{-1} band and the deuterium magnetic resonance (DMR) for CD_3I at 273–363 K and pressures up to 2.5 Kb. Then, using the rotational diffusion model and the Langevin model, as modified by Woessner and Snowden [2], they calculated the coordinates $D_\perp$ and $D_\parallel$ of the rotational diffusion tensor and reached the conclusion that the reorientation of the CD_3 group about the molecular symmetry axis is somewhere in between an inertial reorientation process and diffusional reorientation.

The dielectric relaxation measurements as far as we know, were used to investigate the CH_3I reorientation only by Gillen et al. [3] and in a very limited way. They obtained $D_\perp$ using the dielectric relaxation time measurements for only one temperature and viscosity, η, for various temperatures.

The aim of this paper is to use the dielectric relaxation times and viscosity data obtained in our laboratory as well as DMR relaxation times taken from the literature [3] in order to study the CH_3I reorientation from 223–303 K.

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2. *Experimental*

The dielectric permittivity, ε', and loss factor ε'', of liquid CH_3I were measured at 9.54 GHz (3.14 cm) and 26.5 GHz (1.13 cm) using a method similar to that described by Van Loon and Finsy [4]. The power reflected from a variable length dielectric filled wavequide terminated by a shorting plunger was recorded. The theory of such measurements was described in [4, 9]. Nonideal properties of a short-circuit plunger were taken into account but a constant plunger reflection coefficient was assumed. To determine the dielectric permittivity and loss factor, the reflected power profile was analized by a computer. The best fitting of the propagation constant and attenuation were made to compute the dielectric permittivites and loss factors. The static dielectric permittivity was determined from capacity measurements at 1 kHz using an automatic C-bridge.

TABLE I

T [K]	223	233	243	253	263	273	283	293	303
$\varrho[\mathrm{kgm}^{-3}]\times 10^6$	2.472	2.444	2.419	2.391	2.365	2.336	2.309	2.280	—
$\eta[\mathrm{P}]\times 10^{-2}$	1.15	0.97	0.86	0.75	0.67	0.59	0.54	0.49	0.46
ε_0	9.31	8.79	8.43	8.12	7.83	7.54	7.27	6.97	6.73
ε' (9.54 GHz)	7.04	7.24	7.32	7.29	7.20	7.08	6.92	6.74	6.56
ε'' (9.54 GHz)	3.00	2.67	2.32	2.02	1.76	1.45	1.23	1.05	0.85
ε' (26.5 GHz)	4.29	4.56	4.77	5.01	5.17	5.39	5.46	5.55	5.61
ε'' (26.5 GHz)	2.52	2.74	2.63	2.64	2.49	2.37	2.24	2.06	1.88
ε_∞	3.03	2.98	2.93	2.87	2.85	2.80	2.70	2.60	2.48
τ_D [ps]	12.3	10.4	8.81	7.63	6.74	5.65	4.86	4.23	3.77
τ_{10} [ps]	16.2	13.6	11.6	9.76	8.55	7.11	6.06	5.27	4.66
K	0.760	0.763	0.769	0.779	0.788	0.795	0.802	0.802	0.809
n_D*	1.577	1.570	1.564	1.557	1.551	1.544	1.538	1.531	1.524

* Experimental value n_D for 293 K is taken from [24]. Other values n_D are taken from linear interpolation.

Viscosities were measured with an Ubbelohde viscosimeter. The estimated errors for ε' and ε'' are 1% and 2% and for static dielectric permittivities, ε_0, they are about 0.5% and for viscosities they are 2%. Before measurements liquid CH_3I was dried with phosphoric oxide P_2O_5 and fractionally distillated twice. Pertinent experimental data are given in Table I.

3. *Dielectric relaxation times*

The permanent dipole moment of the CH_3I molecule lies along the symmetry axis. Therefore, we may expect a typical Debye semicircle diagram for ε' and ε'' if measurements are done in a low frequency range [5]. We mean within a frequency range not too close to the far infrared domain. Indeed, all experimental values of ε' and ε'' are easily placed on the Debye semicircles (Fig. 1) with extrapolated values of ε_∞ given in Table I. Calculated on the basis using the standard method [6], the dielectric relaxation times, τ_D, are shown in the Table I. The relative error of τ_D does not exceed 5 per cent.

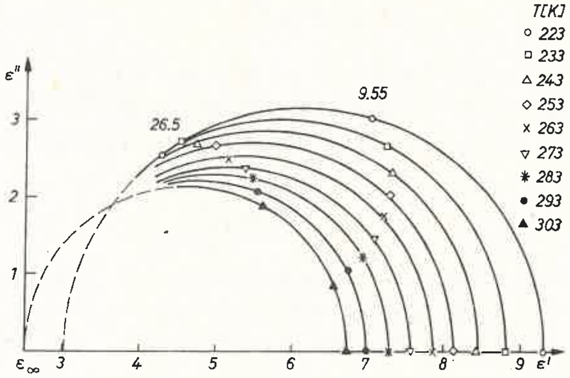

Fig. 1. Cole-Cole plot for liquid methyl iodide

4. *Dipole moment reorientation*

If we want to discuss the molecular reorientation problem then single molecule correlation times (SMCT) are needed. In the case of dielectric relaxation for top symmetric molecules the SMCT of interest must be written according to the spherical harmonics scheme [13], as τ_{10}. This may be related to τ_D in the following way [7, 19]:

$$\tau_{10} = K^{-1}\tau_D, \tag{4.1}$$

where K denotes Kirkwood's coefficient. The relation (4.1) is in agreement with the theory presented by Kivelson and Madden [7] if dynamical correlations are neglected. On the other hand [19], it was shown that for such high symmetry the dynamical correlations do not enter relation (4.2). Instead [19] an additional factor connected with local field appears. But in practice this factor approaches unity. If the molecule is modelled as an ellipsoide then the Kirkwood coefficient, K, takes the form

$$K = \frac{kT\varepsilon\ (\varepsilon_0-\varepsilon_\infty)\,(2\varepsilon_0+\varepsilon_\infty)}{N\mu_s^2\ (\varepsilon_0[1+D(\varepsilon_\infty-1)]^2}\ , \tag{4.2}$$

where D stands for the depolarisation factor along the symmetry axis, μ_s is a gas dipole moment of the molecule and N is the number of molecules in a unity volume.

Using the ellipsoide ratio of the short axis against the long axis 0.62 as proposed previously [16] we obtain for the CH_3I molecule $D = 0.217$. Putting $\varepsilon_\infty = n^2$ and $\mu_s = 1.64$ [20] it is found that K changes linearly from 0.760 at 223 K to 0.809 at 303 K. The exact values of K are given in Table I. The correlation time, τ_{10}, characterises the molecular axis reorientation. Similarly, the rotational correlation time, τ_{20}, corresponds to the Raman correlation time obtained for the 525 cm^{-1} band. If reorientation has a diffusive nature then the Hubbard relations [13] lead to $\tau_{10} = 3\tau_{20}$. And we shall expect the identical temperature dependence for both correlation times discussed.

Let us assume the Eyring activation model [14] which for viscosity provides the following temperature dependence:

$$\eta = \eta_0 e^{\frac{\Delta H}{RT}}, \tag{4.3}$$

where ΔH is the activation enthalpy and η_0 does not depend on temperature.

On the other hand the hydrodynamics models of reorientation [15] provide the relation between the elementary correlation time, τ_{lm}, [13] and viscosity as follows:

$$\tau_{lm} = C_{lm} \frac{\eta}{T}, \tag{4.4}$$

where C_{lm} is a constant independent on temperature. Using (4.3) and (4.4) we see that $\ln (T\tau_{lm})$ is a linear function of T^{-1}. On Fig. 2 such functions for τ_D and $3\tau_{RAM}$ are plotted using our dielectric data and Raman data from the literature [11, 12]. Also the function, $\ln (C_{H-Z}\eta)$, with $C_{H-Z} \doteq 1.93 \times 10^3$ psK(cP)$^{-1}$ calculated on the basis of the Hu and Zwanzig theory by Bauer et al. [16] is shown. As shown in Fig. 2 the enthalpies are lower than those previously reported [3, 11, 12]. The differences come from the use of the Arhenius relation for τ_{lm}, whereas we use this relation for viscosity (4.3). The values of enthalpy obtained from dielectric, Raman scattering and viscosity measurements are in very good agreement. The enthalpy obtained from viscosity should be greater than enthalpies obtained from dielectric or Raman spectroscopies. This is because viscosity depends not only on the reorientational motion characterised by times τ_{10} or τ_{20}, but it depends also on other motions. Good agreement between the enthalpies discussed indicates that the other motions have little importance for viscosity. Particulary this must be true for motion about the symmetrical axis of the CH_3I molecule.

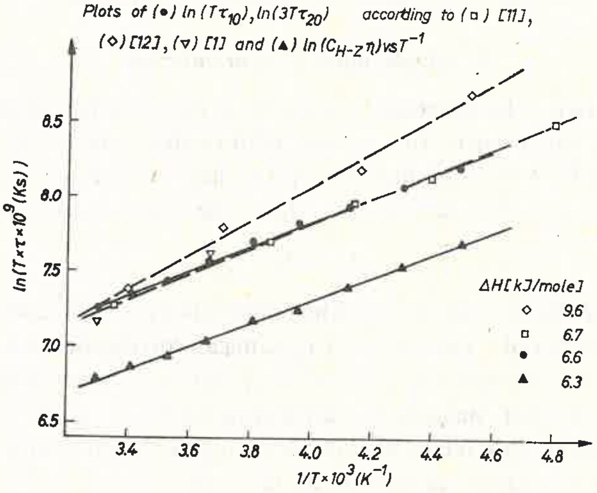

Fig. 2

Bauer et al. [16] proposed some generalisation for formula (4.4) adding to its right-hand side time τ^0_{lm}. According to their interpretation, τ^0_{lm}, characterises the short time inertial motion of the molecule. Such an assumption very often formally explains the observed experimental dependence of τ_{lm} on ηT^{-1} where the linear extrapolation for $\eta \to 0$ leads to $\tau^0_{lm} > 0$. This generalisation was criticised by Cheung et al. [17] because of its inconsistency with the rotational diffusion model. Moreover, using the Rayleigh and Raman scattering correlation times they found for CH_3I to be within experimental error $\tau^0_{20} = 0$.

The criticised generalisation for formula (4.4) can be expressed for the correlation time of perpendicular coordinate of angular velocity in the following form:

$$\tau_{\perp}^{-1} = \frac{2kC_{10}}{I}\eta + \tau_{\perp 0}^{-1}, \tag{4.5}$$

where C_{10} is the constant C_{lm} for $l = 1$ and $m = 0$, k is the Boltzman constant and $I_{\perp}$ denotes the proper coordinate of the inertia tensor for the CH_3I molecule where $I = 111.8 \times 10^{-47}$ kgm^2 [3]. In Fig. 3 the experimental dependence of $\tau_{\perp}^{-1}$ on η obtained from τ_D (Table I) using the Hubbard relation

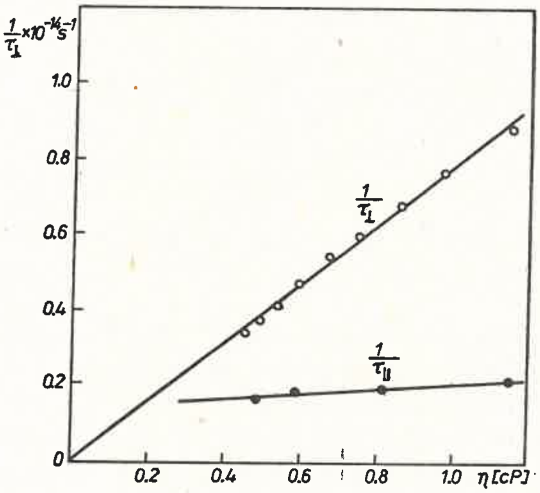

Fig. 3. Plots of $\tau_{\perp}$ obtained using Hubbard's relation from τ_{10} and $\tau_{||}$ vs η

$$\tau_{10} = \tfrac{1}{2}\frac{I_{\perp}}{kT}\tau_{\perp}^{-1} \tag{4.6}$$

is shown. This dependence shows that $\tau_{\perp 0}^{-1}$ or $(\tau^0_{10}) = 0$ which agrees with Cheung et al. [17].

However, the argument concerning the inconsistency of formula (4.5) with the rotational diffusion model proves nothing. It is well known that the experimental results are partly inconsistent with the model described. For example the Raman rotational correlation function for many liquids has a non-exponential short time behaviour. Therefore, we suggest that relation (4.5) together with $(\tau_{\perp 0})^{-1} \neq 0$ is quite probable. Recently Hynes et al. [23] presented some important arguments suggesting that the $\tau_{\perp 0}$ order of magnitude should be $\left(\frac{I_\perp}{kT}\right)^{1/2}$ but the value of $\tau_{\perp 0}$ has no particular physical significance.

The experimental value of C_{10} obtained from the data shown in Fig. 3 equals 3.25×10^3 ps K(cP)$^{-1}$. This value is in very good agreement with $C_{20} = 1.09 \times 10^3$ ps K(cP)$^{-1}$ reported by Cheung et al. [17] ($C_{10} = 3C_{20}$), but both differ from the theoretical value $C_{H-Z} = 1.93 \times 10^3$ ps K(cP)$^{-1}$ [16]. However, Cheung et al. [17], employing an uncertainty of modeling ellipsoid size for CH_3I, calculated that $C_{H-Z} = 2.1 \pm 1.2 \times 10^3$ ps K(cP)$^{-1}$.

5. *Reorientation about the symmetry axis*

Using the rotational diffusion model, every rotational correlation time, τ_{lm}, for symmetrical top molecules can be expressed by the correlation times $\tau_\perp$ and $\tau_{||}$ for perpendicular and paralell coordinates of angular velocity. Therefore, the effective correlation time, τ_2, which is related to the nuclear magnetic relaxation time, T_1, for nuclei D, in the CD_3I molecule has the form [21, 3]:

$$\tau_2 = \left(\frac{3\cos^2\vartheta-1}{2}\right)^2 \frac{1}{6\dfrac{kT}{I_\perp}\tau_\perp} + 3\sin^2\vartheta\cos^2\vartheta\,\frac{1}{5\dfrac{kT}{I_\perp}\tau_\perp+\dfrac{kT}{I_{||}}\tau_{||}} + \frac{3\sin^4\vartheta}{4}\,\frac{1}{2\dfrac{kT}{I_\perp}\tau_\perp+4\dfrac{kT}{I_{||}}\tau_{||}}, \tag{5.1}$$

where ϑ denotes the angle between the molecular symmetry axis and the symmetry axis of the electric field gradient tensor coupled to the quadrupole of the D nucleus. $I_{||}$ stands for the inertia moment related to the symmetry axis of the CD_3I molecule ($I_{||} = 11 \times 10^{-47}$ kgm^2 [3]). Taking τ_2 from paper [3] and our dielectric relaxation data the correlation times $\tau_\perp$ and $\tau_{||}$ using (4.6) and (5.1) were obtained. The results for $\vartheta = 107.6°$ (the D–C–I angle) and $\vartheta = 111.4°$ are shown in Fig. 4. The last value of ϑ has been proposed previously in [1] where a number of arguments supporting such a choice may be found. An unexpected feature clearly shown in Fig. 4 is the lack of a substantial difference between $\tau_\perp$ and $\tau_{||}$. Taking into consideration the shape of the CD_3I or CH_3I molecules, it would be reasonable to obtain $\tau_\perp \ll \tau_{||}$. Such results suggest the unaplicability of the rotational diffusion model to describe the CD_3 group motion in liquid CD_3I even in a relatively low range of temperatures. Similar conclusions were reached by Campbell et al. [1] for a temperature region above 273 K. Therefore, after Woessner and Snowden [2] they tried to apply the model of reorientation based on the Langevin equation. This model is equivalent to the friction model if angular position correlation functions are calculated in the second cumulant approximation [22, 23, 24]. Its limit for short angular velocity correlation times, $\tau_\perp$ and $\tau_{||}$, leads to the rotational diffusion model.

Let us discuss some details of the friction model for symmetrical top molecules. Woessner and Snowden [2] assumed in their final calculations that groups CH_3 or CD_3 rotate freely unless they are influenced by some intermolecular potentials. But this is not the case for liquids where strong intermolecular interactions must be taken into consideration. We may say that the limit discussed by Woessner and Snowden is a gas limit. To obtain the formula for relatively long, $\tau_{||}$, for liquids we start with the reduced angular position correlation time, τ^*_{lm}, which can be expressed using Eq. (3)–(5) from [22] and [18]

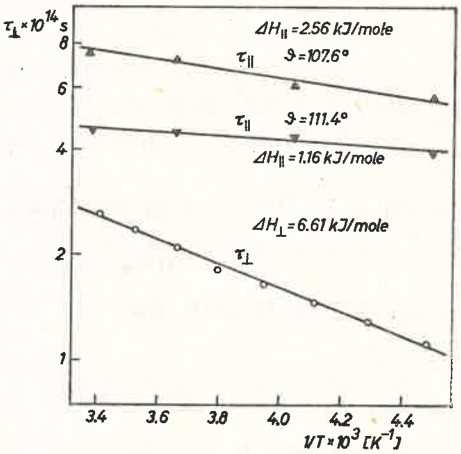

Fig. 4. Semilogarithmic plots of $\tau_\perp$ and $\tau_{||}$ (for $\vartheta = 107.6°$ and $111.4°$) which are obtained from τ_D and DMR data [3] vs T^{-1} if the diffusion model is applied

$$\tau^*_{lm} = \int\limits_0^\infty \exp\left\{-[l(l+1)-m^2]\int\limits_0^\infty (t^*-t^{*\prime})f_\perp(t^{*\prime})dt^{*\prime}\right.$$

$$\left. -m^2\frac{I_\perp}{I_{||}}\int\limits_0^t (t^*-t^{*\prime})f_{||}(t^{*\prime})dt^{*\prime}\right\} dt^*, \tag{5.2}$$

where

$$f_{\perp,||}(t^*) = \frac{\langle\omega_{\perp,||}(t^*)\omega_{\perp,||}(0)\rangle}{\langle\omega^2_{\perp,||}(0)\rangle} \tag{5.3}$$

are the angular velocity correlation functions for perpendicular ($\omega_\perp$) and parallel ($\omega_{||}$) coordinates of angular velocity. The reduced time, t^*, is expressed in $(I_\perp/kT)^{1/2}$ units. To obtain expressions (5.2), $\omega_\perp(t)$ and $\omega_{||}(t)$ are assumed to be stationary stochastic processes.

If $\tau^*_\perp \leqslant 1$ is in agreement with the Langevin equation:

$$f_{||}(t) = e^{-t^*/\tau_{||}^*}, \tag{5.4}$$

then

$$\tau_{lm}^{*} = \int_{0}^{\infty} \exp\left\{-[l(l+1)-m^{2}]\tau_{\perp}^{*}t^{*} - m^{2}\frac{I_{\perp}}{I_{\|}}\tau_{\|}^{*2}\left(\frac{t^{*}}{\tau_{\|}^{*}} + e^{-t^{*}/\tau_{\|}^{*}} - 1\right)\right\} dt^{*}. \qquad (5.5)$$

Contrary to expression (5.5) the gas-like limit for reorientation about the symmetrical axis may be obtained if the last term in the exponential function of (5.5) is replaced by $\frac{1}{2}(-m^{2}I_{\perp}/I_{\|}t^{*2})$. In such a case, after integration Woessner and Snowden's results are recovered.

Generally if the integration in Eq. (5.5) is performed [26]

$$\tau_{lm}^{*} = \tau_{\|}^{*}e^{a_{m}\tau_{\|}^{*}}(a_{m}\tau_{\|}^{*})^{-b_{lm}\tau_{\|}^{*}}\gamma(b_{lm}\tau_{\|}^{*}, a_{m}\tau_{\|}^{*}), \qquad (5.6)$$

where γ denotes the incomplete gamma function and

$$a_{m} = m^{2}\frac{I_{\perp}}{I_{\|}}\tau_{\|}^{*}, \quad b_{lm} = [l(l+1)-m^{2}]\tau_{\perp}^{*} + m^{2}\frac{I_{\perp}}{I_{\|}}\tau_{\|}^{*}. \qquad (5.7)$$

Now the effective DMR correlation time, τ_{2}, is given as:

$$\tau_{2} = \left(\frac{3\cos^{2}\vartheta - 1}{2}\right)^{2}\tau_{20} + 3\sin^{2}\vartheta\cos^{2}\vartheta\tau_{21} + \frac{3\sin^{4}\vartheta}{4}\tau_{22}, \qquad (5.8)$$

where τ_{2m} must be calculated according to (5.6). The results of applying formula (5.7) to obtain $\tau_{\|}$ are shown in Fig. 5. Suprisingly, the difference between $\tau_{\|}$ and $\tau_{\perp}$ is still small and the difference between the activation enthalpies is even smaller than for pure diffusive

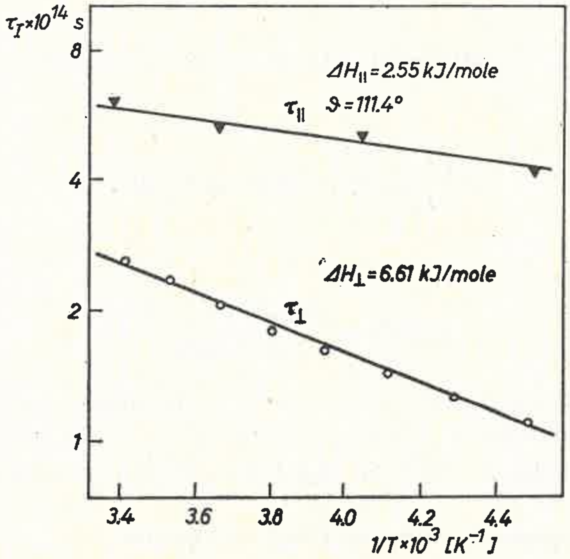

Fig. 5. Semilogarithmic plots of $\tau_{\perp}$ and $\tau_{\|}$ (for $\vartheta = 111.4°$) which are obtained from τ_{D} and DMR data [3] vs T^{-1} if formulae (5.7) and (5.6) are used

motion. Therefore, it appears that the motion about the symmetry axis of CH_3I in the temperature range of 222–293 K is not very different from diffusive motion. But the plot of $\tau_{\parallel}^{-1}$ against viscosity, η, in Fig. 3 shows a lack of dependence of $\tau_{\parallel}$ on η. To obtain information on the molecular motion about the symmetry axis for higher temperatures we have used the data from [1] where the Raman reorientational correlation times, $\tau_{RAM} = \tau_{20}$, of the 525 cm^{-1} band of CH_3I and the DMR correlation times (τ_2) of CD_3I for a wide range of temperature (273–363 K) and pressure (up to 2.5 Kb) are given. The

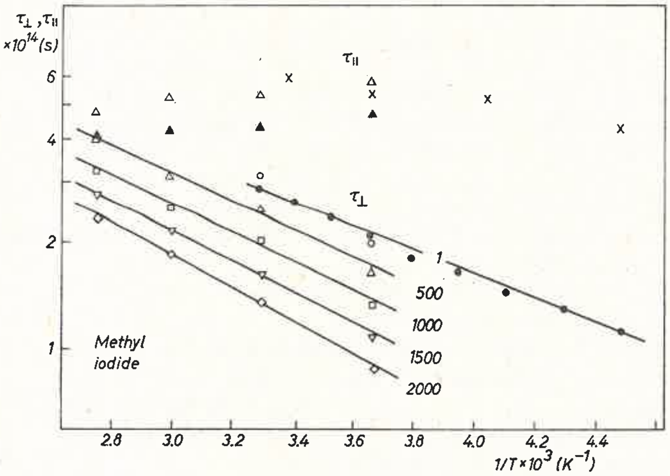

Fig. 6. $\tau_\perp$ and $\tau_{\parallel}$ for methyl iodide (CD_3I) vs T^{-1}. The experimental data are marked by (●, ×) and taken from [3] and Table 1. The other experimental data are taken from [1]

results are shown in Fig. 6. They are quite consistent with those for the lower range of temperature presented in Fig. 5. However, we can see clearly the change of the temperature behaviour of $\tau_{\parallel}$. For higher temperatures $\tau_{\parallel}$, decreases if the temperature increases which is not typical for a liquid state. The reduced correlation times, $\tau_{\parallel}^{*}$, in the range of temperatures and pressures shown in Fig. 6 are quite high. They change from 0.33 to 0.39 which is clearly not the range where the Hubbard relation behaves linearly on a logarithmic scale. Therefore, we can say that for higher temperatures the reorientation about the symmetrical axis is neither a diffusive motion nor a free rotation of the CD_3 group. The same conclusion was reached in a different way by Campbell et al. [1].

6. *Conclusions*

The measurements of ε', ε'' and viscosity for CH_3I in the range 223–303 K together with other data taken from literature lead us to the following conclusions:

1. The correlation times, τ_{10}, obtained from dielectric relaxation measurements using formula (4.1) agree within the limits of experimental error with $3\tau_{20}$ measured using Raman scattering (Fig. 2).

2. The constant, C_{10} Eq. (4.3), estimated on the basis of Hu and Zwanzig's theory [15] by Cheung et al. [17] agrees with those obtained from dielectric relaxation and viscosity measurements (§4) if the uncertainty of the modelling ellipsoid is taken into account. Also τ_{10}^{-1} (or τ_{10}^{0}) equals zero.

3. The activation enthalpies estimated from τ_{10}, τ_{20} and viscosity are in very good agreement (Fig. 2).

4. The motion of the CD_3 group about the symmetry axis is neither diffusive motion nor free rotation ($0.33 \leqslant \tau_{||}^{*} \leqslant 0.39$ (§5)).

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