Ultrasonic Absorption and Vibrational Relaxation in Liquid Tribromomethane

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In the present investigation the ultrasonic absorption in tribromomethane has been measured at temperatures from 10 to 50 °C. The absorption measurements were made by a pulse method over the frequency range 12 to 208 MHz.

A pronounced relaxation is found and this is associated with the time delay in deactivation of one of the vibrational modes. The residual absorption, which is greater than the Stokes value, suggests a second relaxation at higher frequencies.

A comparison of the experimental value of the absorption per wavelength $\mu'_{\max}$ with values calculated from the Raman fundamentals appears to indicate that the ultrasonic relaxation in tribromomethane is associated with the degenerate CBr_3 deformation vibration.

In a very few examples of vibrational relaxation in liquids it has been possible to account for the observed relaxation by the specific heat associated with vibrational modes of the molecules. The absorption of ultrasonic waves in carbon disulphide¹ is thus due to a relaxation of the total vibrational specific heat which is described by a single relaxation time. The observed relaxation in dichloromethane^{2–4} on the other hand cannot be accounted for by the specific heat associated with all the vibrational modes. In this case the experimental values are predictable if the specific heat is assumed to be divided in two parts, where one comprising all the vibrational modes except the mode of lowest wave-number is associated with a frequency of relaxation of 171 MHz at 25 °C. The specific heat corresponding with the mode of lowest wave number is associated with a relaxation at higher ultrasonic frequencies.

Measurements of the ultrasonic absorption in

tribromomethane^{5,6} and trichloromethane^{5,7} at lower frequencies did not give evidence of vibrational relaxation in these liquids. Relaxational behavior has, however, been detected later by measurements at higher frequencies.^{8,9}

Commercially available tribromomethane and trichloromethane are stabilized by admixture of approximately 1 % ethanol and it is thus to be expected that this impurity might strongly influence the ultrasonic absorption and the relaxation frequency.

In the present investigation the absorption of ultrasonic waves has been measured in tribromomethane with very low contents of ethanol in the frequency range 12 to 208 MHz and the temperature range 10 to 50 °C. The values of the absorption calculated from the measurements are considerably increased and they are dependent on frequency thus indicating ultrasonic relaxation in tribromomethane in the investigated frequency range.

EXPERIMENTAL

The ultrasonic absorption measurements have been made by a "pulse" method.^{10–12}

The tribromomethane was Bromoform reinst Merck, which is stabilized by about 1 % ethanol. The ethanol was removed from the samples by repeated shaking with water, followed by drying with anhydrous calcium chloride and fractionated distillation in vacuum. The "pure" tribromomethane decomposes gradually acquiring a yellow color. The influence of light and oxygen accelerate the decomposition and the purified samples were therefore handled with the necessary precaution. GLC^{13,14} on a column of 20 % diethylhexylsebacate, 5 % sebacic acid and 75 % celite C 22 showed that the ethanol

was almost completely removed by this procedure.

The viscosity of the tribromomethane was measured with a Raaschou capillary type viscometer¹⁶ relative to water, which was assumed to have a viscosity 17.938 mP at 0 °C and 8.949 mP at 25 °C.¹⁶ The accuracy of measurement is considered to be of the order of 1 %.

The boiling point of bromoform is 150.5 °C at 760 mmHg and 34.0 °C at 10 mmHg. The melting point is 8.05 °C and $n_D^{20} = 1.5976$. The samples distilled at 34.1 °C at 10 mmHg and had the refractive index $n_D^{20} = 1.5973$.

EXPERIMENTAL RESULTS

Absorption measurements were made over the frequency range 12 to 208 MHz for a number of temperatures between 10 and 50 °C. The results obtained show that the major part of the measured absorption is due to a relaxation process in the frequency region 76 to 106 MHz.

Fig. 1. Ultrasonic absorption in liquid tribromomethane; purified samples: ○ 25 °C (this work), △ 23–25 °C (Rasmussen²¹); commercial samples: ● 25 °C (this work), ▲ 23–25 °C (Rasmussen), ▼ 25 °C (Heasell and Lamb⁵), □ 26–27 °C (Andreae and Joyce⁶), ▽ 20 °C (Plass^{8,22}).

The experimental results obtained at 25 °C are shown in Fig. 1. The smooth curve of Fig. 1 was calculated from the equation

$$\alpha/f^2 = A/[1 + (f/f_c)^2] + B \quad (1)$$

which represents the absorption caused by a single relaxation process; α is the ultrasonic absorption coefficient, f is the frequency of the

sound wave and f_c the relaxation frequency. A and B are frequency-independent parameters. The parameters A , B , and f_c are, however, generally expected to be depending upon temperature. The term B represents the absorption at frequencies well above the investigated region of relaxation and includes the classical absorption, due to the effects of shear viscosity. The classical absorption (Stokes)

$$(\alpha/f^2)_{cl} = 8\pi^2\eta/3\rho v_u^3 \quad (2)$$

has the values given in Table 1 in the temperature range considered. In the table are also listed the viscosity, density, and ultrasonic velocity v_u .¹⁷

The values of the adjustable parameters A , f_c , and B , which agree with the best fits to the experimental data, have been estimated on an IBM 360 computer by use of a non-linear least squares program.* In Table 3 are the values of the parameters and also the values of the "relaxation strength" r , defined as the ratio of the relaxing part ($\delta\kappa_s$) of the adiabatic compressibility divided by the value (κ_s) which the latter assumes at low frequencies, together with the relaxation time $\tau_{p,s}$. r and $\tau_{p,s}$ are calculated from the formulas¹⁸

$$r = Av_u f_c / \pi - \frac{1}{2}(1 + 2B/A)(Av_u f_c / \pi)^2 - \dots \quad (3)$$

$$\text{and } f_c = [2\pi\tau_{p,s}(1 - r)^{\frac{1}{2}}]^{-1} \quad (4)$$

which are valid since the values of r and Z/τ are much less than unity. Z represents the additional effects when the attention is confined to frequencies in the neighbourhood of the relaxation region in question.

From eqn. (1) it follows that the ultrasonic absorption per wavelength $\mu = \alpha v_u / f$ is composed of two terms; the one equal to Bv_u / f represents the effects of relaxations at higher frequencies and shear viscosity, the other

$$\mu' = \frac{Av_u f}{1 + (f/f_c)^2} = 2\mu'_{\max} \frac{(f/f_c)}{1 + (f/f_c)^2} \quad (5)$$

is the absorption per wavelength corresponding to the relaxing component of the specific heat $C_p(a)$, which has the relaxation time $\tau_{p,s} = \tau_a$ such that $\omega\tau_a \approx 1$, where $\omega = 2\pi f$. The maximum

* The program (Shares DA 3094) is written in Fortran and adapted by Finn Johnsen, Technical University of Denmark.

Table 1. The classical absorption (Stokes) in liquid tribromomethane in the temperature range 10 to 50 °C.

θ °C	η mP ^a	ρ g cm ⁻³ ^b	v_u m s ⁻¹ 500 KHz ^b	v_u m s ⁻¹ 4 MHz ^a	$10^{17} \times (\alpha/f^2)_{cl}$ cm ⁻¹ s ²
50	14.57	2.8118	866	866	21
40	16.41	2.8377	888	891	22
30	18.77	2.8639	910	910	23
25	20.85	2.8772		920	24
20	22.29	2.8904	931	929	25
10	25.34	2.9159	953	952	26

^a This work. ^b Lagemann *et al.*¹⁷

Table 2. Experimental values of α/f^2 ($\times 10^{17}$ cm⁻¹ s²) in tribromomethane.

Fre- quency MHz	50 °C	40 °C	30 °C	25 °C	20 °C	10 °C
12	2698	2423	2365	2194	1961	1737
20	2546	2372	2254	2062	2081	1737
36	2241	2223	2028	1857	1772	1536
54	1903	1855	1661	1624	1528	1374
70	1690	1639	1502	1375	1260	
76	1445	1349	1213		1125	1141
94	1313	1300	1178	1168	1027	
98	1236	1142	1065	1078	1001	991
119	1083	958	919	856	831	819
140	862	803	773	736	728	623
162	797	790	611	579	548	534
184	690	711	595		488	492
208	600	551	501	502	445	344

absorption per wavelength $\mu'_{\max} = \frac{1}{2} A v_u f_c$ is attained at the frequency $f = f_c$.

It has been shown that values of $\mu'_{\max}$ can be computed from the formula ¹⁹

$$\mu'_{\max} = \frac{\pi (C_{p0} - C_{v0}) C_{ia}}{2 [C_{p0}(C_{p0} - C_{ia}) C_{v0}(C_{v0} - C_{ia})]^{\frac{1}{2}}} \quad (6)$$

where C_{ia} is the relaxing specific heat. C_{p0} and C_{v0} are the "static" specific heats, and it is

Fig. 2. The absorption per wavelength μ' due to the relaxation process in tribromomethane. The curves are theoretical and the points experimental.

Table 3. Absorption parameters and relaxation time for liquid tribromomethane.

θ °C	$10^{17} A$ cm ⁻¹ s ²	$10^{17} B$ cm ⁻¹ s ²	f_c MHz	$\mu'_{\max}$	r	$10^{10} \tau_{p,s}$ s	Z/τ
10	1732	20	106	0.088	0.055	15.2	0.0006
20	1891	191	83	0.073	0.046	19.4	0.0045
25	2007	175	88	0.081	0.051	18.3	0.0043
30	2141	260	77	0.075	0.047	20.9	0.0056
40	2220	291	81	0.080	0.050	19.9	0.0064
50	2357	356	76	0.078	0.049	21.2	0.0072

assumed that C_{po} apply at frequencies below the present relaxation range. μ' is plotted versus frequency in Fig. 2 at the temperatures 10 and 50 °C. The curves are calculated from the relaxation parameters, the points correspond to the values of $\alpha'/f^2 = (\alpha/f^2 - B)$.

DISCUSSION OF RESULTS

A comparison of the present results with those recently reported for tribromomethane and those for dichloro- and dibromomethane^{20,21} suggests that the behavior of tribromomethane is associated with the time-delay in deactivation of one or more vibrational modes, *i.e.* an ultrasonic relaxation which involves either a part or the whole of the vibrational specific heat.²² Tribromomethane has a symmetry which belongs to the symmetry group C_{3v} and in agreement with that expected on the symmetrical model there are six Raman fundamentals. The components of the vibrational specific heat C_i can be calculated from the Planck-Einstein relation²³

$$C_i = gR x^2 [e^{-x} / (1 - e^{-x})^2] \quad (7)$$

where $x = h\nu/kT$ and g is the degeneracy.

The fundamental vibration frequencies²⁴ are arranged in Table 4 together with the contributions from the six normal modes of vibration

Table 4. Calculation of the maximum absorption per wavelength $\mu'_{\max}$ for liquid tribromomethane at 25 °C.

Assignment	ν_i cm ⁻¹	$x = h\nu/kT$	C_i
$\nu_1(\text{CH})A_1$	3023	14.59	0.000
$\nu_2(\text{CBr})A_1$	538.6	2.60	1.164
$\nu_3(\text{CBr}_2)A_1$	222.3	1.07	1.808
$\nu_4 E$	1142	5.51	0.492
$\nu_5(\text{CBr})E$	656	3.17	1.828
$\nu_6(\text{CBr}_2)E$	153.8	0.74	3.797
ΣC_i	C_{ia} cal mol ⁻¹ deg ⁻¹	$\mu'_{\max}$	
1. C_3	1.808	0.037	
2. C_6	3.797	0.085	
3. C_{123}	2.972	0.064	
4. C_{456}	6.117	0.151	
5. C_{total}	9.089	0.263	
$\mu'_{\max}(\text{exp.})$		0.081	

to the vibrational specific heat C_{ia} . In the table are also the values of $\mu'_{\max}$ calculated from eqn. (6) using the different values for the specific heat.

The first division is the contribution to the specific heat from the symmetrical vibrational mode of species A_1 having the lowest frequency ($\nu_3 = 222.3$ cm⁻¹). The second division corresponds to the degenerate mode of species E having the lowest frequency ($\nu_6 = 153.8$ cm⁻¹). In the third and fourth divisions the modes 1, 2, 3 of species A_1 and 4, 5, 6 of species E are combined in possible specific heats. Finally is given the total vibrational specific heat.

In Table 5 is given an account of the thermal properties of liquid tribromomethane used for the computations in Table 4.

A comparison of the calculated values of $\mu'_{\max}$ with the experimental value derived from the absorption measurements entail the conclusion, that it is probable that the ultrasonic relaxation in tribromomethane is associated with the degenerate CBr_2 deformation vibration ν_6 , which is the vibrational mode with the lowest frequency. A relaxation time τ_1 is then associated with the deactivation of this mode. The value of the parameter B is equal to the Stokes value at 10 °C and there are no additional effects at this temperature. The value of B increases, however, with increased temperature and the percentage of absorption associated with the relaxation time τ_1 decreases. The experimental behavior suggests that additional effects have to be taken into consideration when the temperature is increased. By analogy with the mechanism proposed for polyatomic gases²⁶⁻²⁹ an additional effect might be a relaxation at a very high frequency associated with a complex transition probability, *e.g.* involving the modes ν_6 and ν_3 .

Absorption measurements in trichloromethane³⁰ have in a similar way given results which suggest that the relaxation in this case is associated with the symmetrical CCl_3 deformation vibration ($\nu_3 = 365.9$ cm⁻¹) rather than the degenerate deformation vibration of lowest frequency ($\nu_6 = 262.0$ cm⁻¹). It is rather difficult to appraise the apparent distinction in behavior between these halogenated methanes, but it might be of importance, that the measurements in tribromomethane have been carried out at temperatures rather close to the melting point,

Table 5. Thermal properties of liquid tribromomethane.

Thermal expansion coefficient	$\alpha \text{ deg}^{-1}$	0.000907 ^a
Specific heat (constant pressure)	$C_{p0} \text{ cal mol}^{-1} \text{ deg}^{-1}$	32.10 ²⁵
Ratio of specific heats	$\gamma = C_{p0}/C_{v0}$	1.390 ^b
Specific heat (constant volume)	$C_{v0} \text{ cal mol}^{-1} \text{ deg}^{-1}$	23.09

^a Calculated from the densities at different temperatures and the formula $\alpha = -(1/\rho) d\rho/dT$.¹⁷ ^b Calculated from the formula $\gamma - 1 = Mv_u^2 \alpha^2 T / C_{p0}$; the molecular weight $M = 252.75$.

whereas the measurements in trichloromethane are at temperatures rather close to the boiling point.

The about 1 % ethanol in the commercial tribromomethane has an effect, which means that the relaxation frequency is displaced to higher frequencies and that the loss decreases as a consequence of higher efficiency of collisions in the deactivation of the molecules. The measurements of Plass ⁸ support this view.

Several authors have reported values of the ultrasonic absorption in commercial samples of bromoform. From Fig. 1 it can be seen that the values are undoubtedly in disagreement. When the lowest values are found in samples with the highest concentration of ethanol, they are obviously dependent on concentration. Andreae and Joyce have evaluated the relaxation frequency 124 MHz from the measurements, which is reported without further comments. Plass on the other hand has estimated the relaxation frequency to 814 MHz, which gives a relaxation time of $\tau_{\text{obs}} = 2.0 \times 10^{-10} \text{ s}$. The relaxation is considered as vibrational and the vibrational specific heat calculated from the normal mode spectrum is compared with the value obtained from the ultrasonic absorption measurements. When the values disagree it is suggested that an additional mechanism of energy exchange between degrees of freedom must be supposed. The influence of the ethanol on the measured absorption values has not been taken into consideration.

The commercial samples are in fact dilute solutions of ethanol in bromoform, where the less absorbing component ethanol is associated.

The ultrasonic absorption in solutions of alcohols, e.g. propanol, butanol, *t*-butanol, and phenol in the non-polar solvents carbon tetra-

Fig. 3. Ultrasonic absorption in diluted solutions of ethanol in carbon tetrachloride.

chloride and cyclohexane has been reported by several workers ³³⁻³⁵ and in some of these cases it has been shown, that the curve of α/f^2 plotted against the concentration of alcohol has a maximum at low concentrations of alcohol. The ultrasonic relaxation spectra of solutions of this type have been attributed to the association of the alcohols by hydrogen bonding and the experiments are described by a multistep mechanism.^{36,37} Measurements on solutions of ethanol in carbon tetrachloride,³⁸ however, have not revealed any absorption maximum at low concentration and 25 °C. In Fig. 3 is shown the absorption of ultrasonic waves at 55 MHz and 25 °C in diluted solutions of ethanol in carbon tetrachloride. The absence of the maximum could be a question of too high a temperature so the complexes are depolymerized. It might then be possible to reveal a maximum by measurements at lower temperatures.

In the solutions of alcohols in inert solvents the interactions between the alcohol molecules (monomers and polymers) and the solvent molecules are negligible; this is, however, not the case in polar solvents, e.g. benzene, chloroben-

zene or solvents, e.g. chloroform, bromoform, where hydrogen bonding between the alcohol complexes and solvent molecules is to be expected.^{39,40} In these cases the absorption maximum decreases and is displaced to higher alcohol concentration or vanish completely.

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