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ULTRASONIC AND HYPERSONIC INVESTIGATIONS OF VIBRATIONAL RELAXATION IN LIQUID THIOPHENE

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The measurements of hypersonic wave propagation velocity in the frequency range 2-7 GHz and ultrasonic wave absorption coefficient in the frequency range 10-60 MHz in thiophene have revealed the existence of two relaxation regions associated with vibrational specific heat: the first one associated with the first mode (ν_1) of molecule vibrations and the second, associated with the remaining modes excluding the first one. It follows from the experimental values of hypersonic wave absorption coefficient that the bulk viscosity coefficient in this frequency range $\eta_{\gamma,\infty}$ exceeds by a factor 2.5 the laminar viscosity coefficient η_S.

1. Introduction

The results of previous investigations of vibrational relaxation in simple organic liquids such as benzene, toluene, thiophene and the like were analysed in terms of a single relaxation process [9, 10]. This approach was primarily based on the data on the ultrasonic wave absorption coefficient. On the other hand, Hunter [5], who measured the values of ultrasonic wave absorption coefficient using pulse technique and the values of hypersonic wave propagation velocity by stimulated Mandelstam-Brillouin scattering, came to a conclusion that there exist two relaxation processes in benzene: the first one associated with the specific heat of all types of vibrational modes except the first mode and the second – associated with the specific heat of the first mode Takagi [13] came to similar conclusions on the basis of the data on hypersonic wave propagation velocity in benzene in the frequency range 2–5 GHz.

In his theory Hunter [5] argues (cf. also Kleszczewski [6]) that the results based on the measurement of ultrasonic wave absorption coefficient do not include relaxation of all vibrational modes since the assumption of a single relaxation time leads to the description which is inconsistent with the results of velocity measurements in hypersonic range (Mandelstam-Brillouin scattering).

A consistent interpretation of the results on ultrasonic absorption and hypersonic wave propagation velocity is feasible in terms of two relaxation regions.

Beste [1, 2] attributes the relaxation process in the vapours of benzene and of its derivatives, i.e. in C_6H_5F, C_6H_5Cl, C_6H_5Br, C_6H_5J to the specific heat of a vibrational mode of the lowest frequency. From the determined mean collision time he determines the transition probability for vibrational quanta. This probability decreases with an increase of molecule vibration frequency [2]. Each vibrational mode can be associated with a single relaxation time. However, ultrasonic measurements reveal the existence of a single relaxation process, also in the case of compound molecules. In the case of a continuous excitation, such as at generation of acoustic waves in the medium, a strong coupling of the modes occurs. Therefore the relaxation process will proceed through excitation of the modes of the lowest frequency. The relaxation time of these modes and their frequency both decrease with an increase of molecular weight [2].

The present paper describes the investigations of thiophene in the range of hypersonic frequencies. The measurements of hypersonic wave propagation velocity made it possible to draw conclusions on the nature of vibrational relaxation in thiophene.

The measurements of ultrasonic wave absorption coefficient in thiophene, shown in Fig. 1, indicate that in the frequency range 20-5000 MHz a single relaxation process occurs with a relaxation time $\tau = 5.7 \times 10^{-10}$ s.

These results made it possible to determine the acoustic relaxation contribution to the vibrational specific heat, amounting to $C_{ak} = 35.58$ J(mole·deg).

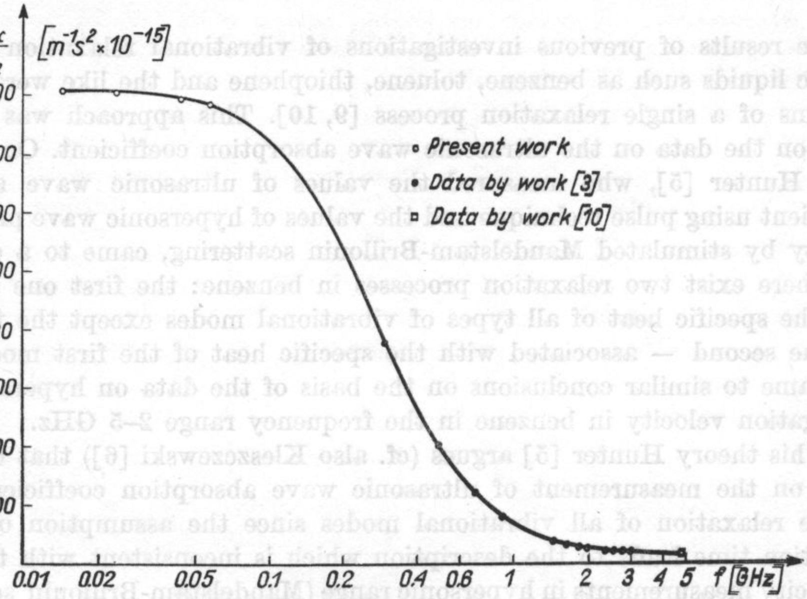


Fig. 1

On the other hand, the analysis of the results of the investigations of molecular spectra and the Planck-Einstein formula

$$C_{\mathrm{osc}} = \sum g_i \frac{(h\nu_i/kT)^2}{e^{h\nu_i/kT}(1-e^{-h\nu_i/kT})^2}, \tag{1}$$

where g_i is the degeneracy multiplicity, h – the Planck constant, k – the Boltzmann constant, T – the absolute temperature, ν_i – the i-th frequency of molecule modes, makes it possible to calculate the part of specific heat associated with intramolecular oscillations C_{osc}. The frequencies of vibrational modes for thiophene [12] are summarized in Table 1.

Table 1. Wave numbers of vibrational modes in thiophene [cm^{-1}]

ν_1	ν_2	ν_3	ν_4	ν_5	ν_6	ν_7	ν_8	ν_9	ν_{10}	ν_{11}	ν_{12}	ν_{13}	ν_{14}
450	603	710	748	832	1031	1078	1250	1357	1408	1588	1773	2998	3110

The value for thiophene calculated in this way equals to $C_{\mathrm{osc}} = 41.149$ J/mole deg. The difference $C_{\mathrm{osc}} - C_{\mathrm{ak}} = 5.5674$ J/(mole. deg). Thus, a past of the specific heat is associated with relaxation at a higher frequency. Following the Hunter's assumption this is the frequency of the first type of vibrational mode, which in thiophene amounts to $\nu_1 = 450\ \mathrm{m}^{-1}$ $(13.56\cdot 10^{12}\ \mathrm{Hz})$. The specific heat for this type of vibration amounts to $C_{\mathrm{osc}} = 5.599$ J/(mole·deg), and thus equals to the difference $C_{\mathrm{osc}} - C_{\mathrm{ak}}$.

The aim of the paper was thus to find the second relaxation range in the range of high frequencies, corresponding to the first type of vibrational mode ν_1.

2. Theory

The general form of the velocity dispersion equation for a single vibrational relaxation process [4] is

$$v^2 = v_0^2\left\{1+\frac{C_p-C_v}{C_p}\,\frac{C_{\mathrm{osc}}}{C_v-C_{\mathrm{osc}}}\,\frac{(f/f_r)^2}{1+(f/f_r)^2}\right\}, \tag{2}$$

where C_{osc} is the specific heat of all types of oscillation modes, calculated from (1), v – acoustic wave propagation velocity, v_0 – acoustic wave propagation velocity for $f\to 0$, f – frequency, f_r – relaxation frequency, C_p – specific heat at constant pressure, C_v – specific heat at constant volume.

The value of the velocity at the highest frequencies follows from equation (2) under the assumption $f \gg f_r$. Then

$$v_\infty^2 = v_0^2\,\frac{C_v(C_p-C_{\mathrm{osc}})}{C_p(C_v-C_{\mathrm{osc}})}. \tag{3}$$

On the other hand, if the process is described by two relaxation times, one can write [13]

$$v^2 = v_0^2\left\{1+\frac{C_p-C_v}{C_p}\cdot\frac{C_1}{C_v-C_1}\cdot\frac{(f/f_1)^2}{1+(f/f_1)^2}+\right.$$
$$\left.+\frac{C_p-C_v}{C_p}\cdot\frac{C_2}{C_v-C_1}\cdot\frac{C_v}{C_v-C_{\mathrm{osc}}}\cdot\frac{(f/f_2)^2}{1+(f/f_2)^2}\right\}, \tag{4}$$

where C_1 is the past of the specific heat associated with the relaxation at the frequency f_1, C_2 – the part of the specific heat associated with relaxation at the frequency $f_2 > f_1$, whereas $C_{\mathrm{osc}} = C_1 + C_2$.

The theory of double relaxation, proposed by Hunter, assumes that the first type of vibrational mode is associated with relaxation at a higher frequency f_2 and the remaining types of modes-with relaxation at a lower frequency f_1.

If two relaxation processes are sufficiently separated on the frequency scale, one can write an expression for the intermediate velocity values expected above the frequency corresponding to the process of first single relaxation. By virtue of equation (4) we have

$$v_i^2 = v_0^2\,\frac{C_v(C_p-C_1)}{C_p(C_v-C_1)}, \tag{5}$$

while, in region $f \cong f_1$, equation (4) assumes the form

$$\frac{v_i^2-v_0^2}{v_i^2-v^2} = 1+\left(\frac{f}{f_2}\right)^2. \tag{6}$$

It follows from this equation that the dependence of $(v_i^2-v_0^2)/(v_i^2-v^2)$ on f^2 is a straight line with a slope $(1/f_1^2)$. This relation makes it possible to estimate the first relaxation frequency f_1.

A similar equation for higher frequencies,

$$\frac{v_\infty^2-v_i^2}{v_\infty^2-v^2} = 1+\left(\frac{f}{f_2}\right)^2, \tag{7}$$

makes it possible to determine f_2.

The relaxation forces which are a measure of the influence of vibrational degrees of freedom are determined [13] by the relations

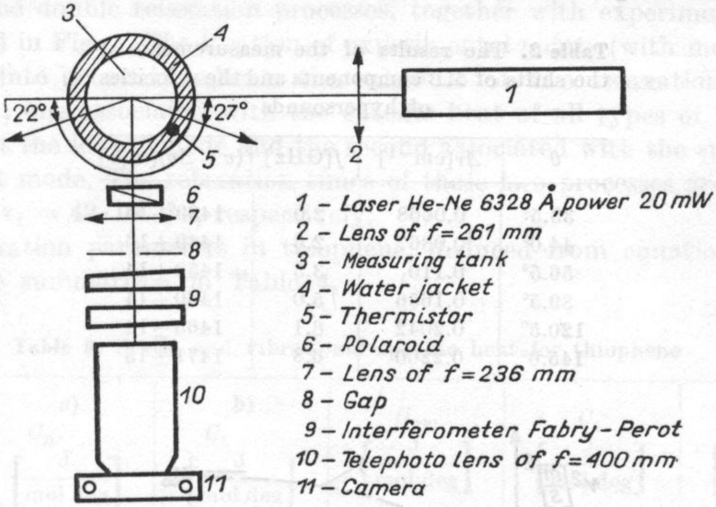
$$v_1 = \frac{v_i^2-v_0^2}{v_i^2} = \frac{C_p-C_v}{C_v}\cdot\frac{C_1}{C_p-C_1}, \tag{8}$$

$$v_2 = \frac{v_\infty^2-v_1^2}{v_\infty^2} = \frac{C_p-C_v}{C_v-C_1}\cdot\frac{C_2}{C_p-C_{\mathrm{osc}}}, \tag{9}$$

respectively, for particular relaxation processes.

3. Experiment

The hypersonic wave propagation velocity was determined from the shift of the components of the fine structure of the light scattered in the Mandelstam-Brillouin scattering process. The detection of light scattered at any angle mode it possible to measure the hypersonic wave propagation velocity at various frequencies. The measurement system is shown schematically in Fig. 2.



1 – Laser He-Ne 6328 Å, power 20 mW
2 – Lens of f=261 mm
3 – Measuring tank
4 – Water jacket
5 – Thermistor
6 – Polaroid
7 – Lens of f=236 mm
8 – Gap
9 – Interferometer Fabry-Perot
10 – Telephoto lens of f=400 mm
11 – Camera

Fig. 2

The hypersound velocity was determined from the formula

$$v_h = \frac{\Delta\nu\, c\, \lambda}{2n_D \sin\theta/2}, \tag{10}$$

where $\Delta\nu$ is the change of light-wave frequency in cm^{-1}, C – the velocity of light, λ – wave length of the light, n_D – refraction index for light, θ – scattering angle.

The hypersound velocity was measured with an accuracy of 1%. The exposure time of photographic plate was about 1.5 h. The distance between the mirrors of the Fabry-Perot interferometer was fixed at $d = 10$ mm. The registered spectrum of scattered light was scanned photometrically using an automatic IFO 451 microphotometer. The investigated liquid specified as analytically pure was additionally distilled twice. The temperature of the liquid was kept constant with an accuracy of 0.1°C and monitored using a platinum temperature sensor.

The measurements of ultrasonic wave absorption coefficient in the range 10-60 MHz were performed using the US-4 High-Frequency Set manufacture by the Institute of Fundamental Technological Research of the Polish Academy of Sciences.

4. Experimental results and discussion

The results of measurements of hypersound velocity in thiophene at $t = 20°C$ are summarized in Table 2.

Under the assumption of a single relaxation time the relation $v^2 = f(f)$ was plotted (Fig. 3). The values of the velocity of ultrasonic wave propagation at the lowest frequency v_0 was obtained from (2) and the values of the velocity at the highest frequency v_∞ from (3). The value of relaxation frequency was

Table 2. The results of the measurements of the shifts of MB components and the velocities of hypersounds

θ	$\Delta\nu[\mathrm{cm}^{-1}]$	f[GHz]	$(v \pm \Delta v)$[m/s]
33.5°	0.0668	2.0	1439 ± 15
44.0°	0.0867	2.6	1449 ± 16
56.5°	0.110	3.3	1450 ± 14
89.5°	0.1656	5.0	1460 ± 14
120.5°	0.2042	6.1	1465 ± 14
145.0°	0.2260	6.8	1471 ± 15

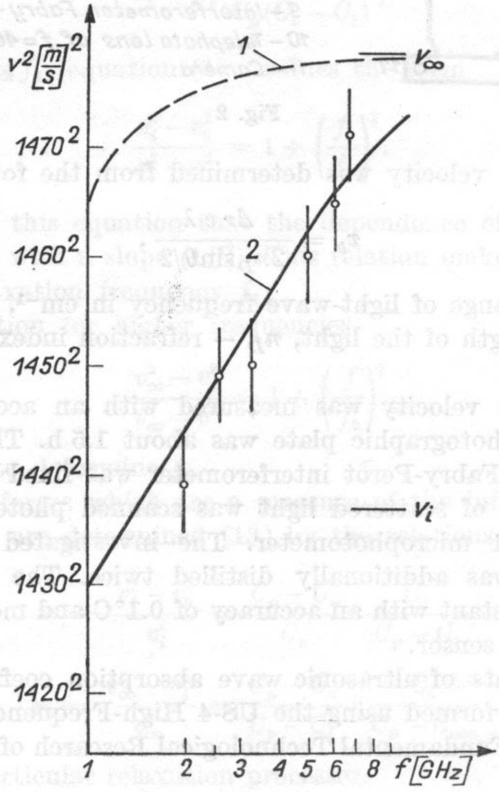


Fig. 3

assumed to be $f_r = 280$ MHz on the basis of the relation $a/f_2 = f(f^2)$ presented in Fig. 1. The data from Table 3 were used.

The theory of double relaxation made it possible to determine relaxation frequency f_2 in the high-frequency range from the dependence of $(v_\infty^2 - v_i^2)$ $(v_\infty^2 - v^2)-1$ on f^2.

By making use of equation (4) the theoretical relation $v^2 = f(f)$ was plotted assuming double relaxation. Both theoretical relations $v^2 = f(f)$ for the single and the double relaxation processes, together with experimental points are presented in Fig. 3. The location of experimental points (with measurement error taken into accuont) indicate the existence of two relaxation processes in thiophene; one associated with the specific heat of all types of vibrational modes except the lowest mode and the second associated with the specific heat of the lowest mode. The relaxation times of these two processes are $\tau_1 = 5.7 \cdot$ $\cdot 10^{-10}$ s and $\tau_2 = 42 \cdot 10^{-10}$ s, respectively.

The relaxation parameters in thiophene, deduced from equations (7), (9) and (10) are summarized in Table 4.

Table 3. Static and vibrational specific heat for thiophene

T [°C]	a) C_p $\left[\frac{\text{J}}{\text{mol deg}}\right]$	b) C_v $\left[\frac{\text{J}}{\text{mol deg}}\right]$	C_{osc} $\left[\frac{\text{J}}{\text{mol deg}}\right]$	C_1 $\left[\frac{\text{J}}{\text{mol deg}}\right]$	C_2 $\left[\frac{\text{J}}{\text{mol deg}}\right]$
20	125.106	84.319	41.149	35.550	5.599

a) – from [8], p. 528; b) – from the ratio $C_p/C_v = 1.46$ cited in [11].

Table 4. Relaxation parameters in thiophene

(a)

T [°C]	v_0 [m/s]	v_i [m/s]	v_∞ [m/s]	$\left(\frac{a}{f^2}\right)_0$ $[10^{-15} \text{m}^1 \text{s}^2]$	$\left(\frac{a}{f^2}\right)_\infty$ $[10^{-15} \text{m}^{-1} \text{s}^2]$
20	1296	1437	1478	1600	22

(b)

T [°C]	f_1 [MHz]	r_1	f_2 [MHz]	r_2
20	280	0.187	3800	0.0543

5. Conclusions

The results of the measurements of hypersonic wave propagation velocity and ultrasonic wave absorption coefficient in thiophene reveal the existence of two relaxation processes. A comparison of the values of the specific heats obtained from an analysis of the results of the investigations of molecular spectra (C_{osc}) and the values obtained from acoustical measurements (C_{ak}) indicates that the first relaxation process in the range of ultrasonic frequencies is associated with the specific heat of all types of vibrational modes except the lowest frequency mode ν_1, whereas the second one is associated with the specific heat of the lowest frequency mode.

The existence of the second relaxation process in thiophene is confirmed by the value of the ratio of bulk viscosity coefficient at hypersonic frequencies $\eta_{v,\infty}$ to the laminar viscosity coefficient η_s. The bulk viscosity coefficient has been determined from the formula

$$\left(\frac{\alpha}{f_2}\right)_\infty = \frac{2\pi^2(4\eta_s/3+\eta_{v,\infty})}{\varrho v_0^3}. \tag{11}$$

It has been assumed [11] that $(\alpha/f^2)_\infty = 22\cdot 10^{-15}$ [$\mathrm{m^{-1}\,s^2}$], laminar viscosity coefficient $\eta_s = 664\cdot 10^{-6}$ [$\mathrm{m^{-1}\,kg\,s^{-1}}$], density $\varrho = 1.0644\cdot 10^3$ [$\mathrm{kg/m^3}$]; $v_0 = 1296$ [m/s]. All above values refer to $t = 20°C$. The value of $\eta_{v,\infty}$, calculated from equation (11), makes it possible to estimate the ratio $\eta_{v,\infty}/\eta_s$ which turns out to be 2.5. This is greater than unity and thus indicates the existence of a relaxation process in the hypersonic range. Its character has been described above.

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