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ACOUSTICAL RELAXATION IN HETEROCYCLIC LIQUIDS

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Measurements of ultrasonic velocity and ultrasonic absorption coefficient have been carried out for several organic liquids in the frequency range from 10 to 1300 MHz at 293 K temperature.

The ultrasonic measurements and the infrared spectra of the liquids have been used for determination of vibrational degrees of freedom which take part in acoustical relaxation process.

1. Introduction

Based on the Kneser acoustical relaxation times measured by the authors [1] and using published data of optical frequencies, the active vibrational degrees of freedom were determined for thiazole [2] and pirimidine [3]. The lack of complete IR spectra for α-picoline, tetrahydrofuran and piperidine [11, 12] prevented a similar analysis for these substances.

Comparing these in complete IR data and the measured acoustical results, it has been possible to show that not all the degrees of freedom are active within the acoustical relaxation processes observed.

2. Experiment

The ultrasonic absorption spectra $\alpha/f^2(f)$ were measured by the ultrasonic pulse method from 10 to 1300 MHz [4, 5] and ultrasonic velocities were obtained using an ultrasound pulse-phase interferometer [4]. The temperature was stabilized with an accuracy of 0.01 K.

The measuring errors ranged from 7 to 4 per cent for attenuation in the frequency range 10-60 MHz, and from 3.5 to 5.5 per cent in the frequency range 400-1300 MHz.

The liquids used (made by Fluka AG, Bucks IG) were of analytical purity and were used after distillation.

3. Theory

In the case of acoustical relaxation the $\alpha/f^2(f)$ and $\mu(f)$ absorption curves can be described as follows

$$\frac{\alpha}{f^2} = \frac{A}{1+(\omega\tau)^2} + B, \tag{1}$$

$$\mu = \alpha\lambda = \left(\frac{A}{1+(\omega\tau)^2} + B\right) fc, \tag{2}$$

when the process is characterized by a single relaxation time. (Where A is the relaxational absorption, B the residual absorption after the process has relaxed, and $\tau = 1/2\pi fc$.)

The determination of the internal vibrational degrees of freedom involved in the acoustical relaxation process is possible using the Herzfeld formula [6]

$$\tau_i = \frac{C_p - C_i}{C_p}\tau_{\text{opt}}, \quad \tau_{\text{opt}} = \frac{Ac}{2\pi^2}\frac{C_p C_v}{(C_p - C_v)C_i}, \tag{3}$$

(where c is the velocity of ultrasound, C_i is the vibrational specific heat, C_p and C_v are the specific heats at constant pressure and volume); and the Planck-Einstein formula

$$C_i = R\sum \frac{\left(\frac{h\nu_i}{kT}\right)^2}{\exp\left(\frac{h\nu_i}{kT}\right)\left[1 - \exp\left(\frac{h\nu_i}{kT}\right)\right]^2}, \tag{4}$$

using the frequencies of fundamental vibrations ν_i measured from the infrared spectra.

Comparing τ_{ac} and τ_{opt} one can determine the degrees of freedom active in the process [7].

4. Results and discussion

Pirimidine

The variations of sound absorption $\alpha/f^2(f)$ and $\mu(f)$ for pirimidine are shown in Figs. 1 and 2 and can be described by equations (1) and (2). In these figures the solid lines represent curves of a single relaxation.

The relaxation time τ_{ac} determined from the acoustical measurements is $1.2\cdot10^{-10}$s whereas the value of τ_{opt} calculated according to formula (3) is smaller and is equal to $0.3\cdot10^{-10}$s. Hence it is possible to conclude that in the given range of frequencies of ultrasound and hypersound waves not all of the internal degrees of freedom take part in the energy transfer between vibrational and

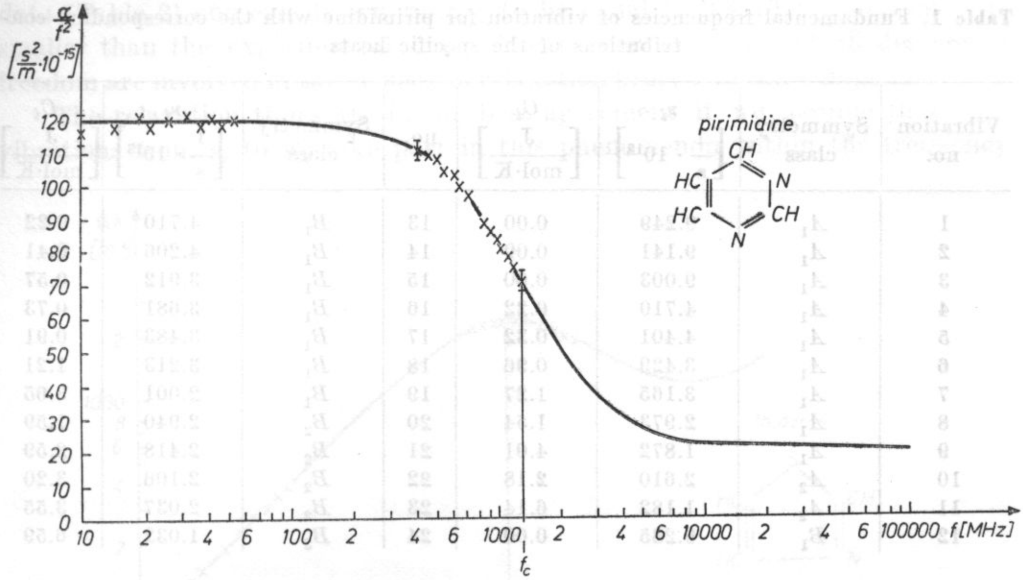

Fig. 1. Frequency dependence of the ultrasound absorption α/f^2 in pirimidine at 293 K temperature

in Figs. 1-5: — calculated, × — measured

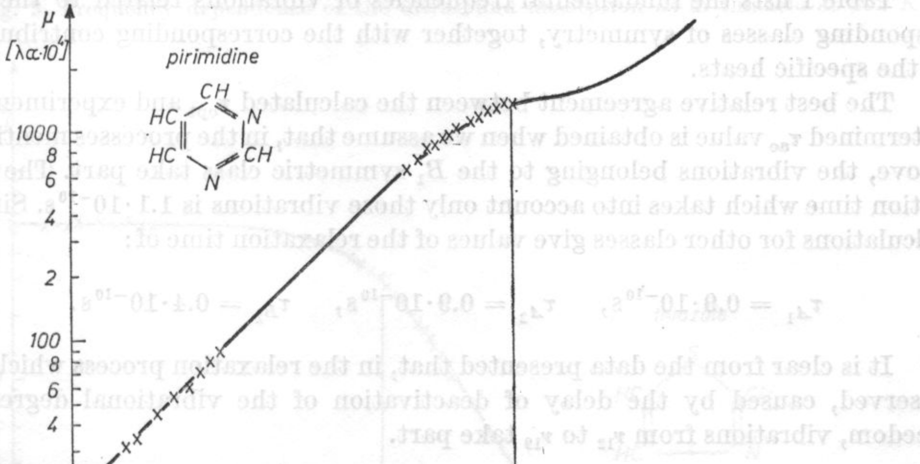

Fig. 2. Absorption μ measurements as a function of frequency in pirimidine

Table 1. Fundamental frequencies of vibration for pirimidine with the corresponding contributions of the specific heats

Vibration no.	Symmetry class	ν_i $\left[\frac{1}{s}\cdot 10^{13}\right]$	C_i $\left[\frac{J}{mol\cdot K}\right]$	no.	Symmetry class	ν_i $\left[\frac{1}{s}\cdot 10^{13}\right]$	C_i $\left[\frac{J}{mol\cdot K}\right]$
1	A_1	9.249	0.00	13	B_1	4.710	0.22
2	A_1	9.141	0.00	14	B_1	4.206	0.41
3	A_1	9.003	0.00	15	B_1	3.912	0.57
4	A_1	4.710	0.22	16	B_1	3.681	0.73
5	A_1	4.401	0.32	17	B_1	3.483	0.91
6	A_1	3.429	0.96	18	B_1	3.213	1.21
7	A_1	3.165	1.27	19	B_1	2.001	3.65
8	A_1	2.973	1.54	20	B_2	2.940	1.59
9	A_1	1.872	4.01	21	B_2	2.418	2.59
10	A_2	2.610	2.18	22	B_2	2.106	3.20
11	A_2	1.182	6.14	23	B_2	2.037	3.55
12	B_1	9.285	0.00	24	B_2	1.032	6.59

translational degrees of freedom, or in other words, the relaxation times of different degrees of freedom are different.

The complete spectroscopic data of IR for pirimidine listed in Table 1 [3] gives the possibility of determining, with a high probability, which of the vibrational degrees of freedom take part in the observed acoustical relaxation process.

Table 1 lists the fundamental frequencies of vibrations related to the corresponding classes of symmetry, together with the corresponding contributions of the specific heats.

The best relative agreement between the calculated τ_{opt} and experimentally determined τ_{ac} value is obtained when we assume that, in the processes mentioned above, the vibrations belonging to the B_1 symmetric class take part. The relaxation time which takes into account only those vibrations is $1.1\cdot 10^{-10}$ s. Similar calculations for other classes give values of the relaxation time of:

$$\tau_{A_1} = 0.9\cdot 10^{-10}\,\mathrm{s}, \quad \tau_{A_2} = 0.9\cdot 10^{-10}\,\mathrm{s}, \quad \tau_{B_2} = 0.4\cdot 10^{-10}\,\mathrm{s}.$$

It is clear from the data presented that, in the relaxation process which was observed, caused by the delay of deactivation of the vibrational degrees of freedom, vibrations from ν_{12} to ν_{19} take part.

Thiazole

The results obtained for thiazole are presented in Figs. 3 and 4. The acoustical relaxation process observed in this liquid can be also described by equations (1) and (2). The experimental results are in good agreement with the theoretical ones.

The relaxation time τ_{ac} estimated on the basis of the experimental results is equal to $2.7\cdot 10^{-10}$ s. Using the fundamental vibrational degrees of freedom data (Table 2) one can determine τ_{opt} to be equal to $2.3 \cdot 10^{-10}$ s, so that it is smaller than the experimental one. We can conclude that not all degrees of freedom are involved in the acoustical relaxation process in this compound.

The relaxation times are in the best agreement if we assume that only vibrations from ν_2 to ν_{18} take part in this phenomenon within the frequency

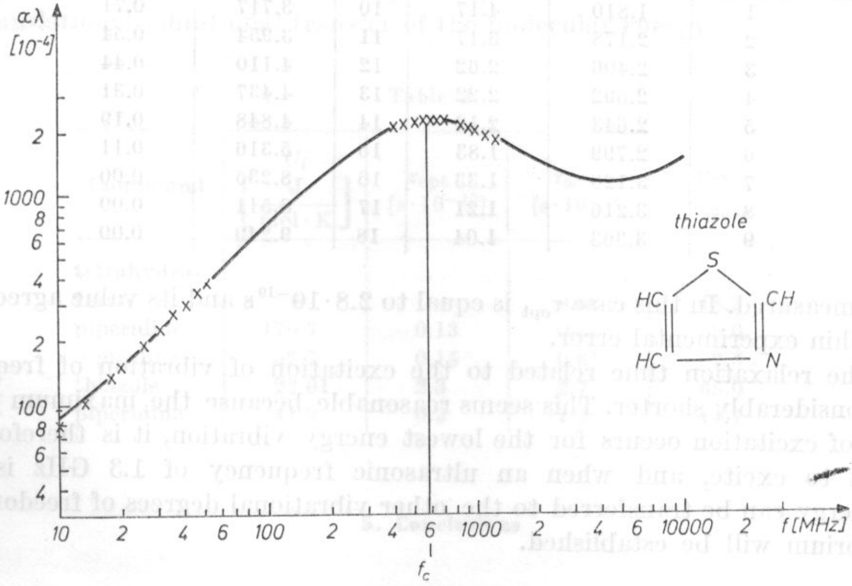

Fig. 3. Frequency dependence of the ultrasound absorption $\alpha\lambda$ in thiazole at 293 K

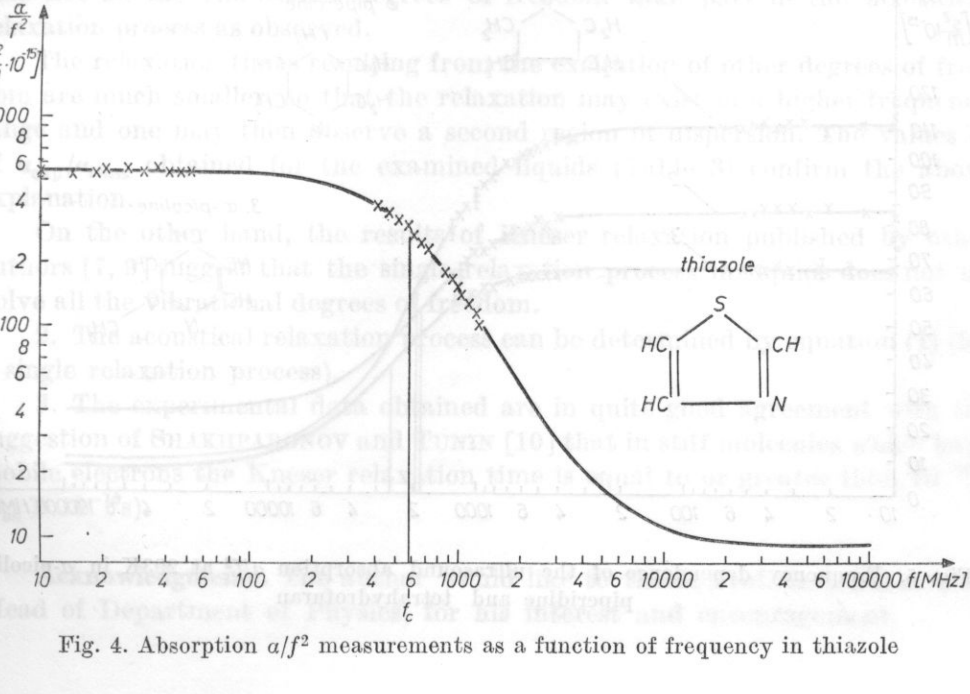

Fig. 4. Absorption α/f^2 measurements as a function of frequency in thiazole

Table 2. Fundamental frequencies of vibration for thiazole with the corresponding contributions of the specific heats

Vibration no.	ν_i $\left[\frac{1}{s}\cdot 10^{13}\right]$	C_i $\left[\frac{J}{mol\cdot K}\right]$	no.	ν_i $\left[\frac{1}{s}\cdot 10^{13}\right]$	C_i $\left[\frac{J}{mol\cdot K}\right]$
1	1.810	4.17	10	3.717	0.71
2	2.178	3.17	11	3.954	0.54
3	2.406	2.62	12	4.110	0.44
4	2.592	2.22	13	4.437	0.31
5	2.643	2.12	14	4.848	0.19
6	2.799	1.83	15	5.316	0.11
7	3.120	1.33	16	8.235	0.00
8	3.216	1.21	17	8.511	0.00
9	3.363	1.04	18	9.249	0.00

range measured. In this case τ_{opt} is equal to $2.8\cdot 10^{-10}$ s and its value agrees with τ_{ac} within experimental error.

The relaxation time related to the excitation of vibration of frequency ν_1 is considerably shorter. This seems reasonable because the maximum probability of excitation occurs for the lowest energy vibration, it is therefore the easiest to excite, and when an ultrasonic frequency of 1.3 GHz is used the energy can be transferred to the other vibrational degrees of freedom and equilibrium will be established.

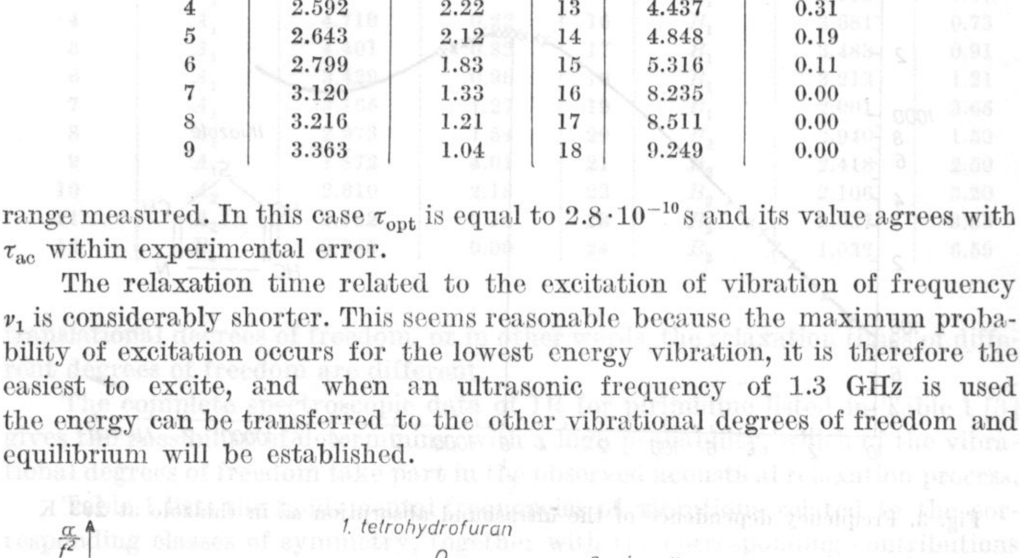

Fig. 5. Frequency dependence of the ultrasound absorption α/f^2 at 293K in α-picoline, piperidine and tetrahydrofuran

In these liquids the inflection points of the curves $\alpha/f^2(f)$ occur outside the measurement frequency range experimentally available, but they can be calculated from equation (1) [8].

It seems from the comparison of the values of τ_{ac} obtained from the acoustical measurements with the calculated τ_{opt} (Table 3) that the observed region of dispersion results from a Kneser process, and the relaxations are caused by the translational-vibrational transfer of the molecular energy.

Table 3

Compound	C_i $\left[\frac{J}{mol \cdot K}\right]$	τ_{opt} $[s \cdot 10^{-10}]$	τ_{ac} $[s \cdot 10^{-10}$	$\frac{\alpha_{exp}}{\alpha_{class}}$
tetrahydrofuran	—	—	0.82	18.3
piperidine	170.7	0.13	0.86	5.0
α-picoline	52.7	0.15	0.61	7.5
thiazole	22.01	2.3	2.7	65.0
piperidine	41.9	0.3	1.2	14.7

5. Conclusions

1. From the above considerations it appears that in the compounds examined not all the vibrational degrees of freedom take part in the acoustical relaxation process as observed.

The relaxation times resulting from the excitation of other degrees of freedom are much smaller, so that the relaxation may exist in a higher frequency range and one may then observe a second region of dispersion. The values of of $\alpha_{exp}/\alpha_{class}$ obtained for the examined liquids (Table 3) confirm the above explanation.

On the other hand, the results of Kneser relaxation published by other authors [7, 9] suggest that the single relaxation process in liquids does not involve all the vibrational degrees of freedom.

2. The acoustical relaxation process can be determined by equation (1) (for a single relaxation process).

3. The experimental data obtained are in quite good agreement with the suggestion of SHAKHPARONOV and TUNIN [10] that in stiff molecules which have mobile electrons the Kneser relaxation time is equal to or greater than 10^{-10} s ($\tau_{ac} \geqslant 10^{-10}$s).

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References

[1] B. Linde, A. Śliwiński, *Ultrasound attenuation of benzene-similar and heterocyclic liquids within the frequency range 10 - 1300 MHz,* Acoustics Letters, **2**, 65-68 (1978).

[2] G. Davidovics, Ch. Garrigou-Lagrange, J. Chouteau, J. Metzger, *Contribution á l'ètude des spectres de vibration du thiazole,* Spectrochimica Acta, **23A**, 1477-1487 (1967).

[3] L.M. Sverdlov, M.A. Kovner, E.A. Karainov, *Kolebatelnyie spektry mnogoatomnykh molekul,* Nauka, Moskva 1979.

[4] J. Wehr, *Measurements of velocity and damping of ultrasound* (in Polish), PWN, Warsaw 1972.

[5] L.A. Davidovich, S. Makhmakov, L. Pulatova, P. K. Khabibulaiev, M. G. Khaliulin, *Isledovanie akusticheskikh svoistv nekotorykh organicheskikh zhidkostei na chastotakh 0.3-3 GHz,* Akust. Zh., **XVIII**, W 2, 318-320 (1972).

[6] K.F Herzfeld, T.A. Litowitz, *Absorption and dispersion of ultrasonic waves,* Academic Press, New York and London, 1959.

[7] A.S. Lagunov, B.A. Belinskii, *Isledovanie akusticheskikh svoistv zhidkikh: benzola, piridina, pirola i phurana v diapazonie chastot 6-900 MHz,* Uchonyie Zapiski, Primenenie ultraakustyki k isledovaniu veshchestva, **XXII**, 85-96 (1967).

[8] W. Boch, *Investigations of zinc chloride solutions in methyl alcohol by methods of molecular acoustics* (in Polish), Poznań 1975.

[9] Z. Kleszczewski, *Thermal relaxation processes in some organic liquids* (in Polish), Archiwum Akustyki, **11**, 1, 59-66 (1976).

[10] M.I. Shakhparonov, M.S. Tunin, *Giperakusticheskiie svoistva zhidkosti i struktura molekul,* Primenenie ultraakustiki k isledovaniu veshchestva, **XV**, 19-29 (1961).

[11] *Arbeitsatlas der Infrarotspektroskopie,* Butterworth-Verlag Chemie, London – Weinheim 1972.

[12] J.H.S. Green, W. Kynaston, H.M. Paisley, *Vibrational spectra of monosubstituted pyridines,* Spectrochimica Acta, **19**, 549 (1963).

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