Hypersonic Velocity, Absorption and Relaxation in Molten $CsNO_3$

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Brillouin spectra of molten $CsNO_3$ were investigated for scattering angles between 40 and 140° and in a temperature interval of 420–520 °C. An Ar^+ singlemode laser was used for excitation and the total instrumental width was ~265 MHz. The measured frequency shifts and linewidths of the Brillouin components were used to determine velocities and attenuations of thermal sound waves in the frequency range 2.3–7.0 GHz. A dispersion of 4–5% was found between the present hypersonic velocities and reported ultrasonic velocities. A considerable decrease in attenuation with frequency was observed in the investigated frequency range, with the value at high frequency approaching the classical attenuation. The results are in good agreement with Mountain's theory of a single relaxation time. The relaxation time of the bulk viscosity coefficient was calculated to 1.2×10^{-10} s.

Introduction

The present study of molten $CsNO_3$ is a continuation of the experimental investigation of relaxation phenomena in molten nitrates [1–3]. Earlier measurements in molten $CsNO_3$ [4] performed in this laboratory have revealed a different velocity in the hypersonic than in the ultrasonic region. The purpose of this work was to investigate the frequency dependence of

i the hypersonic velocity and
ii the sound absorption.

From such a study conclusions can be drawn concerning possible relaxation effects between the ultrasonic and hypersonic frequency regions.

Thermal sound waves have been examined in the hypersonic frequency region (>1 GHz) by using Brillouin scattering spectroscopy. In these measurements the velocity and absorption have been determined from the shift and width of the Brillouin components and the results have been compared with corresponding ultrasonic data [5]. The scattering angle, which determines the frequency of the investigated sound waves, was varied between 40° and 140°, giving a frequency range above the relaxation frequency. Hence the hypersonic velocity should be higher than the ultrasonic velocity as is actually observed. Furthermore, the temperature dependence of the velocity and absorption was studied over the range 420 – 520 °C. A simplified relaxation theory based on a single relaxation time [6, 7] has been used in analyzing the hypersonic results. The experimental arrangement is essentially the same as that used earlier in this laboratory [8]. In evaluating the Brillouin spectrum the convolution technique described in Ref. [2] has been used.

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Hypersonic Velocity Measurements

Brillouin spectra of molten $CsNO_3$ were recorded in a temperature range of 100 °C above the melting point. The scattering light was analyzed at four different scattering angles, 39.8°, 65.0°, 115.2°, and 140.5° corresponding to sonic frequencies ranging from 2.3 to 7.0 GHz. An interorder separation of 9.95 GHz was selected to suit all the frequency shifts which was possible by working with overlapping orders at 115° and 140°. The spectroscopic determination of the frequency shift f made it possible to calculate the hypersonic velocity v from Bragg's law:

$$v = f \cdot \lambda / (2\, n \sin \Theta/2) \,. \qquad (1)$$

Here λ is the wavelength of the incident light, n is the refractive index of the scattering medium and Θ is the scattering angle. The observed hypersonic frequency shifts and velocities at each temperature are tabulated in Table I. The refractive indices in this table are calculated from the data given by Karawacki et al. [9].

The velocities obtained at the different scattering angles did not differ within the experimental error ($< \pm 1\%$), i. e. no frequency dependence of the velocity could be observed in this frequency region. Moreover, present results are in agreement with earlier hypersonic velocity data reported from this

Table I. Velocity data for molten $CsNO_3$.

Scattering angle	Temperature (°C)	Refractive index [a]	Shift (GHz)	Hypersonic velocity (m/s)	Ultrasonic velocity (m/s)
39.8°	420.0	1.4382	2.56	1274	1215
	438.7	1.4350	2.51	1253	1196
	458.3	1.4316	2.47	1235	1176
	500.0	1.4244	2.38	1200	1133
	520.0	1.4209	2.34	1178	1113
65.0°	419.7	1.4383	3.99	1259	1215
	458.3	1.4316	3.85	1223	1176
	519.9	1.4209	3.65	1168	1113
115.2°	419.9	1.4383	6.29	1264	1215
	458.2	1.4316	6.09	1230	1176
	519.7	1.4210	5.78	1176	1113
140.5°	419.9	1.4383	7.01	1264	1215
	438.7	1.4350	6.90	1246	1196
	458.2	1.4316	6.78	1227	1176
	479.8	1.4279	6.65	1208	1154
	500.1	1.4244	6.54	1191	1133
	520.2	1.4209	6.43	1173	1112

[a] Ref. [9].

laboratory [4]. However, the hypersonic velocities were all higher than the corresponding ultrasonic ones, which can be seen in Table I. The measured dispersion between hypersonic and ultrasonic velocities was 4 – 5% in the temperature range 420 – 520 °C. Since the obtained hypersonic velocity was frequency insensitive, the calculated velocity may be taken as the velocity at infinite frequency, v_∞ [6, 7].

The temperature dependence of the velocity in different frequency regions can be summarized as follows:

hypersonic velocity (present results)

$$v = 1647 \quad - 0.91 \quad T,$$

hypersonic velocity (earlier results [4])

$$v = 1645 \quad - 0.93 \quad T,$$

ultrasonic velocity [5] $\quad v = 1645.5 - 1.025\,T$;

v is the velocity in ms^{-1} and T is the temperature in °C.

Absorption Measurements

The broadening of the Brillouin components, $\Delta\nu_B$, due to damping of the thermal sound waves is related to the acoustic absorption coefficient, α, according to:

$$\Delta\nu_B = \alpha\, v/\pi\,. \qquad (2)$$

If both the Brillouin and Rayleigh components are Lorentzian the broadening of the Brillouin line can be calculated as the difference between these two components. Then the Rayleigh width is assumed to be identical to the instrumental line width. However, when analyzing the Rayleigh line shape it showed both a Gaussian and a Lorentzian character. Therefore, a Voigt function, i. e. a convolution of a Gaussian and a Lorentzian function was matched to the experimentally obtained Rayleigh line. This total instrumental line was then convoluted with the Lorentzian response function of molten $CsNO_3$ and the Brillouin line broadening was obtained. The observed Rayleigh and Brillouin linewidths, $\Delta\nu_R$ and $\Delta\nu_{OBS}$, are given in Table II together with the calculated Brillouin line broadening, $\Delta\nu_B$. The Rayleigh width is a measure of the spectroscopic resolution of the system. In these measurements the Rayleigh width varied between 254 and 282 MHz, and each tabulated value is an average of at least six different spectral orders at each frequency and temperature.

The observed attenuation (α/f^2) at different frequencies and temperatures are given in Table II and are graphically represented as solid curves in Figure 1. The dashed curves show the classical and the ultrasonic attenuations. The classical expression

Table II. Experimental data of Brillouin linewidths and attenuations in molten $CsNO_3$.

Scattering angle	Temperature (°C)	Frequency (GHz)	Rayleigh linewidth $\Delta\nu_R$ (MHz)	Observed linewidth $\Delta\nu_{OBS}$ (MHz)	Brillouin linewidth $\Delta\nu_B$ (MHz)	Attenuation α/f^2 (10^{-15} m^{-1} s^2)
39.8°	420.0	2.56	263	335	95	36
	438.7	2.51	266	340	97	39
	458.3	2.47	263	340	100	42
	500.0	2.38	282	358	100	46
	520.0	2.34	260	359	126	62
65.0°	419.7	3.99	265	390	157	25
	458.3	3.85	265	381	148	26
	519.9	3.65	265	374	138	28
115.2°	419.9	6.29	267	534	315	20
	458.2	6.09	259	485	270	19
	519.7	5.78	254	500	289	23
140.5°	419.9	7.01	268	601	387	20
	438.7	6.90	271	586	368	20
	458.2	6.78	259	541	330	18
	479.8	6.65	263	533	318	19
	500.1	6.54	273	547	324	20
	520.2	6.43	264	525	308	20

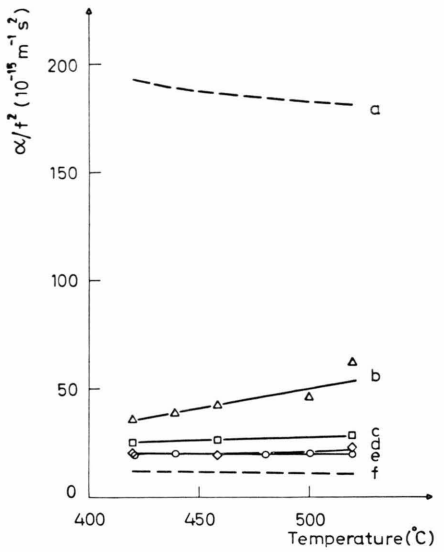

Fig. 1. Graphs of attenuation (α/f^2) versus temperature for molten $CsNO_3$. Present measurements at $\Theta=40°$ are labelled: △, at $\Theta=65°$: □, at $\Theta=115°$: ◇, and at $\Theta=140°$: ○. The dashed curves represent values at (a) low frequencies—ultrasonic values calculated according to Eq. (4), and (f) high frequencies — the classical values calculated according to Equation (3). The solid curves (b), (c), (d) and (e) represent values at 40°, 65°, 115° and 140° scattering angle, respectively — the present hypersonic values.

for the attenuation (α_{class}/f^2) due to the shear viscosity, η_S, is [10]

$$\alpha_{class}/f^2 = 8\pi^2\eta_S/(3\varrho v^3) . \quad (3)$$

Here ϱ is the density and v is the sonic velocity. The ultrasonic absorption is considerably larger than that predicted by Eq. (3) and this is accounted for by assuming the existence of a bulk viscosity term, η_B, in addition to the shear viscosity:

$$\alpha/f^2 = 2\pi^2/(\varrho v_0^3)\,[4/3\,\eta_S + \eta_B] \quad (4)$$

where v_0 is the low frequency velocity.

For single relaxation behaviour the equation for the excess attenuation, (α_{η_B}/f^2), valid at any frequency is [11]

$$\alpha_{\eta_B}/f^2 = 2\pi^2/(\varrho v_0^3)\,[\eta_{B_0}/(1+4\pi^2 f^2\tau^2)] . \quad (5)$$

τ is the relaxation time of the bulk viscosity coefficient.

From Fig. 1 it is obvious that the attenuation is very sensitive to frequency changes in the measured frequency range. In fact, the obtained attenuation is decreasing with increasing frequency in accordance with Mountain's theory. Furthermore, the present results are close to the classical limit indicating that the measurements were performed above the relaxation frequency. When calculating the classical and ultrasonic attenuations, density and shear viscosity data were taken from Ref. [12] and values of the ultrasonic velocity are from Reference [5]. The bulk viscosity coefficient at low frequencies, η_{B_0}, was extrapolated from data given in Ref. [13], where a linear relationship between η_{B_0}/η_S and the cation volume for molten nitrates is reported.

The measured frequency dependence of the attenuation made it possible to calculate the relaxation time by using Equation (5). No temperature dependence of the relaxation time was found and the results at different frequencies and at a temperature of 458 °C are tabulated in Table III together with the corresponding relaxation frequencies $(1/2\pi\tau)$. Moreover, the relaxation time could be calculated from the velocity measurements according to

$$\tau = \eta_{B_0}/[\varrho(v_\infty^2 - v_0^2)] \quad (6)$$

since the obtained hypersonic velocity may be taken as the velocity at infinite frequency, v_∞. The values of the relaxation time and relaxation frequency from the velocity measurements are also given in Table III.

Table III. Experimental data of the relaxation time for molten $CsNO_3$.

Temperature (°C)	Hypersonic velocity (m/s)	Frequency (GHz)	Relaxation time (10^{-10} s)	Relaxation frequency (GHz)
458.3	1235	2.47	1.4 [a]	1.2 [a]
458.3	1223	3.85	1.4 [a]	1.2 [a]
458.2	1230	6.09	1.2 [a]	1.3 [a]
458.2	1227	6.78	1.1 [a]	1.4 [a]
458	1230	∞	1.1 [b]	1.5 [b]

[a] Calculated from absorption data.
[b] Calculated from velocity data.

A typical relaxation curve, based on a single relaxation theory, is shown in Fig. 2 where the attenuation (α/f^2) is plotted as a function of frequency ($\log f$). The physical constants used in these calculations are represented in Table IV. The solid curve is obtained from the absorption measurements and the dashed curve from the hypersonic velocity data. The dotted line represents the classical limit of the attenuation at infinite frequency.

Table IV. Physical constants of molten $CsNO_3$ at 458 °C.

Refractive index n	1.4316 [a]
Density ϱ	2.768 gcm^{-3} [b]
Shear viscosity η_S	1.89 cP [b]
Low-frequency bulk viscosity η_{B_0}	39 cP [c]
Ultrasonic velocity v_0	1176 ms^{-1} [d]
Classical attenuation α_{class}/f^2	11×10^{-15} m^{-1} s^2
Low-frequency attenuation $\alpha/f^2 (f\to 0)$	182×10^{-15} m^{-1} s^2

[a] Ref. [9]. [b] Ref. [12]. [c] Extrapolated from Ref. [13]. [d] Ref. [5].

From Fig. 2 it is clear that the experimentally determined attenuations at the four different frequencies at 458 °C were in agreement with the single relaxation curve. Also, Fig. 2 and Table III demonstrates the good agreement between the relaxation times from two independent measurements: 1) the sonic velocity and 2) the Brillouin line broadening measurements. The absorption data revealed a significant frequency dependence of the attenuation and consequently the measurements were performed in a relaxation region. Then relaxation effects should also appear in the velocity data. However, no frequency dependence of the velocity in the investigated frequency range was found. This is mainly due to the fact that the investigated frequency range corresponded to the end of the relaxation region and that the total velocity dispersion over the whole relaxation region was small (4 – 5%).

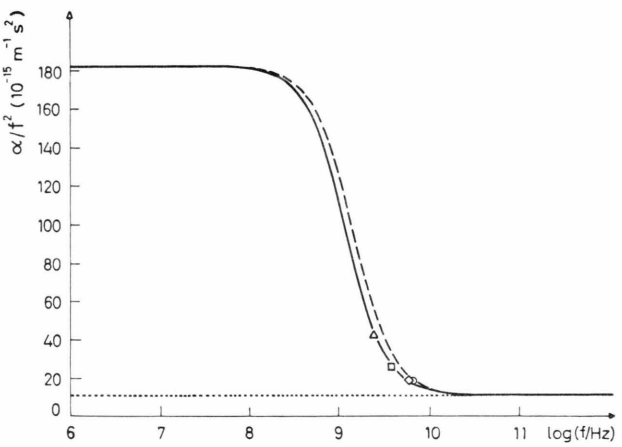

Fig. 2. Graphs of attenuation (α/f^2) versus frequency ($\log f$) for molten $CsNO_3$ at 458 °C. Present measurements at $\Theta=40°$ are labelled: △, at $\Theta=65°$: □, at $\Theta=115°$: ◇, and at $\Theta=140°$: ○. The solid and dashed curves represent theoretical values based on the assumption of a single relaxation time for the absorption and velocity measurements, respectively. The dotted curve represents the classical attenuation.

Conclusions

The present hypersonic velocities, obtained by Brillouin scattering experiments in molten $CsNO_3$, are all higher than corresponding ultrasonic velocities in a temperature interval of 420 – 520 °C. No frequency dependence of the velocity was found between 2.3 – 7.0 GHz. These results yield a relaxation time of 1.1×10^{-10} s corresponding to a relaxation frequency of 1.5 GHz. A significant frequency dependence of the attenuation in the investigated frequency region was found. The relaxation time calculated from absorption data is 1.3×10^{-10} s and the corresponding relaxation frequency is 1.3 GHz. The agreement between the independently calculated relaxation times demonstrates the applicability of Mountain's theory based on a single relaxation time. Finally, the present study has shown the importance of analyzing the proper shape of the spectral components when Brillouin line broadening is to be determined.

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