Determination of the Hypersonic Velocities in the Molten Salts $NaNO_3$ and KNO_3

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Hypersonic velocities in the molten salts $NaNO_3$ and KNO_3 have been obtained by Brillouin scattering measurements. A He-Cd laser, 4416 Å, was used as a radiation source and the scattered light was analyzed with a pressure-scanned Fabry-Perot spectrometer. The temperature dependence of the sound velocity was determined in a temperature range covering some 100° above the melting point of the investigated salts. The obtained hypersonic velocity for $NaNO_3$ was about the same and for KNO_3 greater than reported ultrasonic velocities indicating that the measurements are performed in a frequency region below any possible relaxation frequency for $NaNO_3$ and above some possible relaxation frequencies for KNO_3.

Introduction

Brillouin spectroscopy has long been used when studying acoustic properties of thermal waves in liquids in the hypersonic region. In this laboratory Brillouin scattering measurements have been performed previously in several liquids at room temperature [1, 2] and at present in molten salts at high temperatures.

A comparison of the measured hypersonic velocity data with ultrasonic data provides evidence for some properties of the liquids such as relaxation processes. In pure liquids two types of relaxation phenomena are known to produce velocity dispersion [3, 4]: thermal and structural relaxation. Thermal relaxation is due to the exchange of external and internal degrees of freedom, that is, an irreversible exchange of energy between the translational and vibrational or (and) rotational degrees of freedom. The structural relaxation is due to slow structural changes caused by the passage of the sound wave which disturbes the equilibrium degree of order. The disturbed system is restored to equilibrium but a delay in this equalization leads to dispersion in the sound velocity.

In nonassociated liquids the thermal relaxation processes are dominant whereas structural relaxation predominates in associated liquids. The present paper reports on molten alkali nitrates which may be expected to behave like associated liquids because of the strong attractive Coulomb interaction between the positively and negatively charged ions in the salts. In these investigations the hypersonic velocities of molten $NaNO_3$ and KNO_3 and their temperature dependence have been measured and compared with earlier ultrasonic data obtained by Higgs and Litovitz [5] and by Bockris and Richards [6]. KNO_3 has not previously been investigated in the hypersonic frequency region, whereas measurements on $NaNO_3$ have recently been performed by Reinsborough and Valleau [7].

Experimental

The experimental arrangement and method are essentially the same as already described in earlier reports from this laboratory [1, 2]. The light from a 4416 Å Spectra Physics He-Cd laser scattered by thermal phonons was analyzed by a pressure-scanned Fabry-Perot spectrometer and detected by a photomultiplier kept at a low working temperature with the aid of water cooled peltier elements. Investigations of molten salts require a high temperature thermostat (see Figure 1). It consists of an Al/Stain-

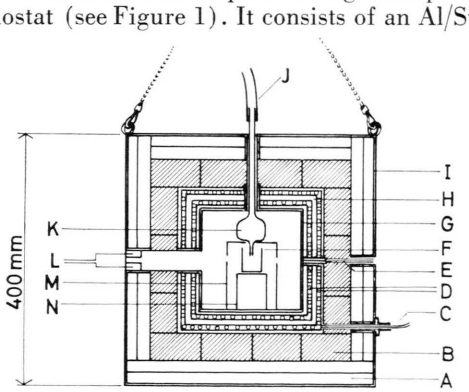

Fig. 1. Cross section of the furnace.
A: High temperature block; B: Insulating fire brick; C: Resistor of the temperature regulator; D: Kanthal windings; E: Cerafelt, a fiber felt between upper and lower part of the furnace; F: Scattering cell; G: Stainless steel furnace cube; H: Ceramic frame; I: Aluminium furnace case; J: Pressure gas pipe; K: Salt reservoir; L: Asbestos plug with an opening for scattered light; M: Aluminium envelope; N: Aluminium support.

less steel cube which was constructed in two parts with a double layer of Kanthal windings connected serially between the parts. The power input was regulated by a proportional temperature regulator, Swema TK65 U, making an excellent temperature stability possible. Three hours after a 10° change of the temperature the liquid could be maintained to within ±0.1° for a period of 45 min in the range 250 – 550 °C. The fixed scattering angle was kept at 90°, as the furnace is constructed with right angle scattering light ports. The upper part of the furnace can be raised by a lift which facilitates the adjustment of the scattering cell inserted into the furnace at room temperature.

The cylindrical sample cell was carefully centered at the scattering point by introducing a needle of 0.5 mm diameter along the axis of the cell, which was correctly positioned if the image of the needle could be seen sharp at the entrance aperture of the detector system. The cell was enclosed by a cylindrical Al-envelope, partly to equalize the temperature, partly to protect the cell from movements when the salt reservoir together with the upper part of the furnace was lowered after the optical arrangement had been adjusted (see Figure 2). To get rid of residual water the temperature of the central region of the furnace was kept below the melting point of the salt for at least three days. According to Bockris and Richards [4] the effects of traces of water in the salts on the velocity of sound is however negligible as the error is less than the experimental reproducibility. The temperature was slowly raised over the melting point and by applying an excess pressure of argon gas in the reservoir the salt was forced into the cell through a Millipore filter used to minimize the Tyndall scattering. The salts were of analytic grade without further purification. The temperature was registered by a DC differential voltmeter Hewlett-Packard model 3420B and a platinel-platinel thermocouple, which was in direct contact with the melt just above the scattering point (see Figure 2).

When evaluating the hypersonic shift from the spectrum the result depends on the ratio of the shift and the free spectral range. If the spectral lines are of equal intensity, this ratio, the so called fractional order, should be kept as close to 0.33 as possible to avoid any pulling effect [8] between the different lines. The Fabry-Perot etalon spacer was chosen to give a convenient fractional order to minimize this shrinkage effect. The same spacer could be used over the entire temperature range for each of the molten salts as the shifts varied less than 1 GHz. A spacer of 6.065 mm was used, giving a free spectral range of 24.73 GHz.

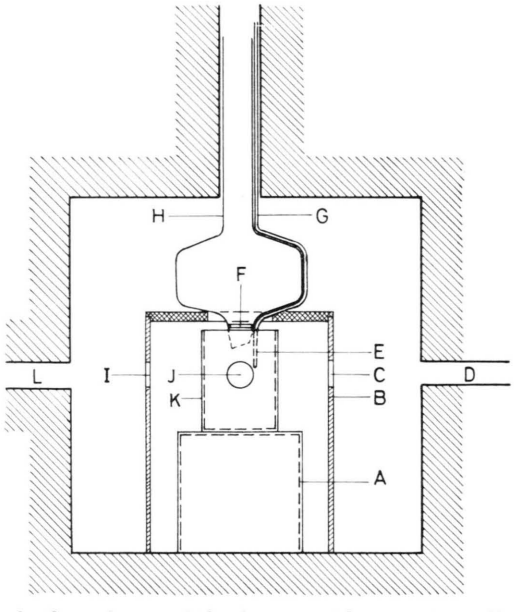

Fig. 2. Central part of the furnace with scattering cell and filling device in position.
A: Aluminium support; B: Aluminium envelope; C: Light outlet; D: Light trap; E: Platinel-platinel thermocouple enclosed by a quartz tube: F: Millipore filter; G: Platinel-platinel thermocouple enclosed by high temperature insulation; H: Salt reservoir of pyrex; I: Light inlet; J: Outlet of scattered light; K: Quartz cell; L: Light port, inlet.

Results and Discussion

The hypersonic velocity of thermal waves was determined in the molten salts $NaNO_3$ and KNO_3. The temperature dependence of the sound velocity was measured in a temperature range covering some 100° above the melting point, see Table I and II. The standard deviations of the hypersonic velocity data were less than 1% for both salts. The quoted uncertainties in the velocities at a fixed temperature represent average deviations over two separate measurements, each running over seven successive spectral orders. A comparison of the obtained hypersonic velocities with earlier ultrasonic data in the actual temperature range is shown in Figure 3. The temperature coefficient of the hypersonic velocity appeared to be the same as that of ultrasound for $NaNO_3$, furthermore the hypersonic and ultrasonic velocities agreed within experimental errors, indicating no dispersion at the measured frequencies, which consequently should be below any relaxation frequency. The data of KNO_3 however showed a different temperature coefficient of hypersound and ultrasound. In addition, the measured hypersonic velocities are all higher than the ultrasonic ones showing

Table 1. Hypersonic velocities in molten $NaNO_3$.

Temperature (°C)	Index of refraction	Frequency shift (GHz)	Hypersonic velocity (m/s)
308.5	1.4430	8.46	1830±11
312	1.4425	8.42	1822±13
322	1.4410	8.36	1812± 9
333.5	1.4394	8.28	1795± 9
344.5	1.4377	8.22	1785± 8
355	1.4362	8.16	1775± 8
366	1.4346	8.10	1763± 8
374.5	1.4332	8.05	1753±11
384.5	1.4318	8.01	1746±10
394.5	1.4303	7.95	1736±12
404.5	1.4289	7.86	1719±15
415	1.4273	7.82	1711±11
424.5	1.4259	7.75	1697± 8
434	1.4245	7.69	1685± 7
444	1.4230	7.64	1676± 9
453	1.4217	7.59	1667± 7
462	1.4204	7.56	1661± 6

Table 2. Hypersonic velocities in molten KNO_3.

Temperature (°C)	Index of refraction	Frequency shift (GHz)	Hypersonic velocity (m/s)
336	1.4284	8.52	1862±12
341	1.4276	8.47	1852±14
341	1.4276	8.44	1847±10
351	1.4260	8.38	1834±10
351	1.4260	8.34	1827±11
361.5	1.4243	8.26	1812±19
362	1.4242	8.30	1821± 9
372	1.4226	8.19	1798±10
381.5	1.4211	8.11	1781±13
391	1.4196	8.07	1775±10
392	1.4194	8.08	1777±14
401	1.4180	8.00	1763±12
402	1.4178	7.96	1753±10
412	1.4160	7.88	1737± 8
421	1.4146	7.88	1739±12
431	1.4130	7.73	1708±16
440	1.4115	7.70	1704± 8
441	1.4114	7.74	1713±17
450	1.4098	7.60	1682±10
459	1.4084	7.58	1680±15
478	1.4054	7.43	1650±12

that some relaxation region appears at or lies below the frequency range of the sound velocities measured. It should be pointed out that Higgs et al.[5] in the ultrasonic region found KNO_3 to differ from $NaNO_3$ when measuring absorption as a function of frequency at different temperatures. The ultrasonic absorption in polyatomic liquids is not only due to the shear viscosity but also to the bulk viscosity, giving a larger absorption than that predicted by Stokes[9]. In the report of Higgs et al.[5] the bulk viscosity of KNO_3 turned out to be about three times that of $NaNO_3$. The present results do not give any explanations of the details of the structural relaxation but indicate a different behaviour of $NaNO_3$ and KNO_3 in the hypersonic region. For KNO_3 the dispersion was 5% at 300 °C and only 3% at 450 °C, when comparing present results with the ultrasonic data reported by Higgs et al.[5]. The temperature dependences of the velocities of the molten salts are summarized in Table III.

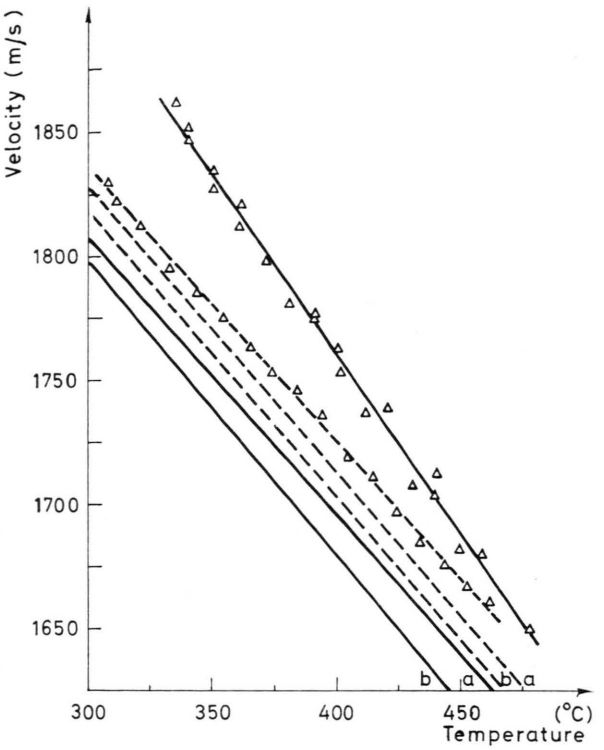

Fig. 3. The temperature dependence of the hypersonic and ultrasonic velocities in molten $NaNO_3$ (dashed lines) and molten KNO_3 (solid lines). Present hypersonic measurements are labeled △, ultrasonic measurements are from Ref. 5(a) and Ref. 6(b).

Table 3. Velocity data as a function of temperature for pure molten salts (meter/sec).

Pure salt	Hypersonic velocity Present research	Ultrasonic velocity Higgs and Litovitz[5]	Bockris and Richards[6]
$NaNO_3$	$2166-1.10\,T$ [a]	$2175-1.155\,T$	$2164-1.15\,T$
KNO_3	$2342-1.45\,T$	$2144-1.12\,T$	$2157-1.194\,T$

a) T is the temperature in °C.

To evaluate the hypersonic velocities the refractive indices of the molten salts at 4416 Å had to be known. Recently, Gustafsson and Karawacki[10] have measured the refractive indices for a number of

molten salts at five different wavelengths and at different temperatures. These results were used to extrapolate the refractive indices at 4416 Å at the actual temperatures using the expression [11]

$$\Phi(T) = (n_\lambda^2(T) - 1)/(n_\lambda^2(T) + 2)$$

where $n_\lambda(T)$ is the refractive index for a particular wavelength λ and temperature T. A plot of $(1/\Phi(T))$ vs $(1/\lambda^2)$ gives a straight line and the desired refractive index at that particular temperature. Linear relationship between refractive index and temperature was obtained. The extrapolated refractive indices are given in Table I and II.

Conclusions

Brillouin spectroscopy has for the first time been used to obtain the hypersonic velocities of thermal phonons in KNO_3. Measurements at three different temperatures for $NaNO_3$ with a He-Ne gas laser as a radiation source have earlier been performed by Reinsborough and Valleau [7]. In spite of the extension of the frequency range from previous ultrasonic to present hypersonic measurements no dispersion could be observed for $NaNO_3$, whereas for KNO_3 the measured velocities correspond to frequencies above at least one relaxation frequency as indicated by higher hypersonic velocities and a different temperature dependence.

Acknowledgement

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