Brillouin Scattering in Liquids at 4416 Å and 4765 Å

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An argon ion laser operating at 4765 Å and a helium-cadmium laser operating at 4416 Å have been used as radiation sources to study Brillouin scattering in seven organic liquids. The Brillouin spectra were investigated at 90° with a pressure-scanned Fabry-Perot spectrometer. The measured frequency shifts between the Stokes and anti-Stokes lines were used to determine the hypersonic velocities of thermal waves at frequencies between 4.8 and 7.2 GHz. No dispersion of the hypersound could be detected.

Introduction

According to the very first predictions by Brillouin[1] the spectrum of light scattered from thermal density fluctuations in liquids should in addition to a Rayleigh component consist of two symmetrically Doppler shifted components, the Stokes and anti-Stokes lines, also known as Brillouin lines. This frequency shift from the central line is the frequency of the phonon and is given by

$$\Delta\nu = 2\,\nu_0\,n\,(v/c)\,\sin\Theta/2 \qquad (1)$$

where ν_0 is the incident light frequency, v is the sonic velocity, n is the index of refraction, c is the velocity of light, and Θ is the scattering angle. Brillouin scattering has almost exclusively been investigated in liquids with the 6328 Å radiation of He-Ne lasers. In these experiments a 50 mW Spectra Physics Model 185 helium-cadmium laser and a 30 mW Spectra Physics Model 141 argon ion laser operating at 4416 Å and 4765 Å respectively have been used. The most immediate advantage with these light sources compared with the helium-neon laser is that the scattered intensity can be expected to increase by a factor 4 when changing from 6328 Å to 4416 Å according to the $\nu_0{}^4$-dependence in the relation[2]

$$I \propto (\nu_0{}^4/r^2)\,\langle(\Delta\varepsilon)^2\rangle \qquad (2)$$

where r is the distance from the scattering sample to the point of observation, and $\langle(\Delta\varepsilon)^2\rangle$ is the mean-square fluctuation of the dielectric constant. Photo cathodes are also more sensitive in the blue than in the red light. Furthermore the hypersonic velocities are determined at on the average 1.4 times higher frequencies compared with measurements at 6328 Å. This is intelligible from Eq. (1), where the shift is shown to be directly proportional to the frequency of the radiation source. The disadvantage with these lasers is that they are running multimode at present, which prevent us from a more detailed analysis of the scattered spectrum. However, by a proper choice of the free spectral range it is possible to determine the hypersonic velocities with high precision as shown below.

Apparatus and Experimental Method

Radiation from the He-Cd (Ar^+) laser was incident on the liquid sample placed in a cylindrical quartz cell with optical windows. Light scattered at 90° was collected by a lens and passed through a pressure scanned[3] Fabry-Perot interferometer. To obtain the scattering angle we used a right angle prism, giving a precision of ±0.5°. A diagram of our apparatus is shown in Fig. 1 where it can be seen that the basic layout of the equipment is that used by Chiao and Stoicheff[4]. To minimize extraneous stray light[5] a pinhole A_1 was placed in the focus of the collecting lens L_2 (Fig. 1). Black-painted boxes enclosed the apparatus from the pinhole to

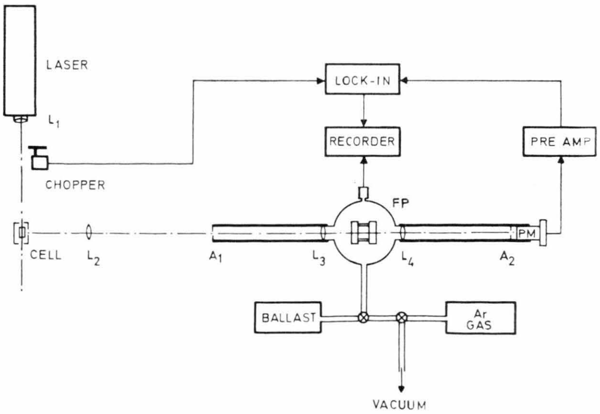

Fig. 1. Experimental arrangement for 90° scattering. L_1, L_3 and L_4, 50-cm UV-achromate lenses; L_2, 20-cm lens; A_1 and A_2, 1,0-mm apertures.

the photomultiplier. A typical trace of the Brillouin spectrum from one of our samples is given in Figure 2. The widths of the spectral components are influenced by several experimental factors. The largest contribution to the experimental line width is in this case due to the laser line. The angular aperture of observation gives a contribution determined by the diameter of the lens L_2 (Fig. 1) and was chosen to approximately ± 3°. The diameter of the aperture covering the photomultiplier also adds to the experimental line width. The influence from an aperture of radius R for scanning the interference pattern at the photomultiplier[3] is given by

$$\Delta\nu_R/\nu \cong \tfrac{1}{2} R^2/f^2 \tag{3}$$

where $\Delta\nu_R$ is the instrumental width in wave number, ν is the frequency of the light, and f is the focal length of the lens used. The diameter of the aperture A_2 (Fig. 1) in front of the photomultiplier was chosen to keep the total instrumental width unaffected.

The contribution to the line width from the limited finess of the Fabry-Perot interferometer is in our case negligible compared to that of the laser line. The interferometer consists of quartz plates, with a diameter of 60 mm and a flatness of $\lambda/200$, that were dielectrically coated to a reflectivity of 96 percent at 4416 Å. The free spectral range of the interferometer was 18.58 GHz with a quartz spacer of 8.075 mm. Linear pressure scanning in the interferometer housing was obtained by using a driving pressure of 2 atm and a needle valve[6]. The maximum corrections caused by the nonlinearity of the flow are less than 1% over the range of 0 – 0.5 atm and less than 3% between 0 – 1 atm. Corrections for nonlinearities were made in analyzing the spectral traces[7] (see below).

An RCA C 31 000 A photomultiplier in connection with ac-detection was used and the output was displayed on one of the two channels of a chart recorder, Hewlett Packard 7100 b. A Statham Pressure Transducer Model PA 731 TC-25-350 was connected to the other channel to show the pressure of the Fabry-Perot interferometer housing as a function of time.

Results and Discussion

Seven liquids, all of spectroscopic quality, were investigated. The cylindrical sample cell was placed in a box, which was temperature controlled to ± 0.1° and kept close to 23 °C. Great care was taken in centering the cell, as a difference in the velocity was registered when the cell was displaced a few mm.

The hypersonic velocities observed are shown in the fifth and ninth column of Table 1. The tenth column of this table gives ultrasonic velocities taken from the literature. The standard deviations in the measurements of the hypersonic velocities are less than 2% and are calculated from the spectra of four to six successive spectral orders. These calculations do not include possible errors in the measurements of fringe centers. In order to minimize disturbing effects due to small nonlinearities in the pressure scanning an averaging method in evaluating the

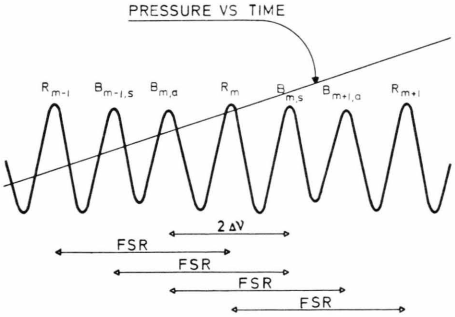

Fig. 2. Spectrum of light scattered from toluene at 22.6 °C. R_m: Rayleigh component, m-th order; $B_{m,\mathrm{a}}$ and $B_{m,\mathrm{s}}$: anti-Stoke and Stoke Brillouin component, m-th order.

Table 1. The observed shifts and velocities of sound in seven liquids.

Liquid	$\lambda = 4416$ Å T (°C)	shift (GHz)	refr. index	hypersonic velocity (m/s)	$\lambda = 4765$ Å T (°C)	shift (GHz)	refr. index	hypersonic velocity (m/s)	ultrasonic velocity (m/s)
Benzene	23.1	7.13	1.523[8]	1462 ± 15	23.1	6.66	1.515[8]	1481 ± 15	1324[10]
Carbon disulfide	22.7	6.59	1.672[8]	1231 ± 15	23.8	6.07	1.656[8]	1235 ± 14	1158[10]
Toluene	22.6	6.33	1.516[8]	1304 ± 9	23.2	5.82	1.509[8]	1299 ± 20	1324[10]
Acetone	22.4	5.10	1.367[8]	1165 ± 17					1190[10]
Chloroform	22.9	4.80	1.457[8]	1029 ± 8					1001[10]
Methylene chloride	22.7	5.10	1.434[9]	1110 ± 5					1093[10]
n-Hexane	22.8	4.83	1.383[8]	1090 ± 4					1113[11]

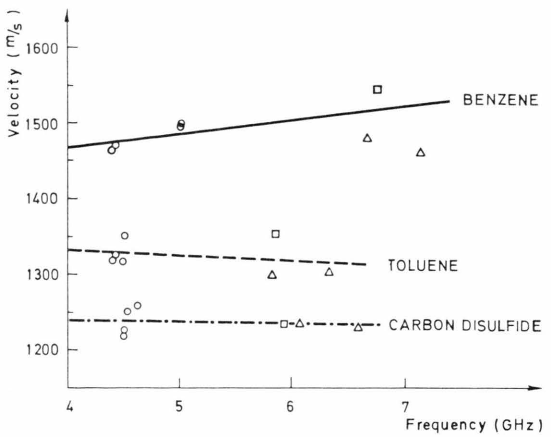

Fig. 3. Graphs of velocity vs. frequency for benzene, toluene and carbon disulfide. Our measurements at 4416 Å and 4765 Å are labeled △, measurements at 4880 Å: □, and those at 6328 Å: ⊙.

spectra was used: measurements of the distances (Fig. 2) between R_{m-1} and R_m, $B_{m-1,s}$ and $B_{m,s}$, $B_{m,a}$ and $B_{m+1,a}$ and finally R_m and R_{m+1} give a mean value of the free spectral range of the m-th order. The corresponding shift is given by half the distance between $B_{m,a}$ and $B_{m,s}$.

The velocity measurements of the liquids are compared in Table 2 with those obtained with an Ar^+ laser at 4880 Å and He-Ne lasers at 6328 Å by other groups. The present data, at 4416 Å and 4765 Å, agree within experimental errors with those obtained at 6328 Å by other investigators if a negligible temperature dependence is assumed. The weak temperature dependence, less than $-0.5\%/^\circ$C for all liquids, makes it possible to favourably compare the results obtained at slightly different temperatures. The values in Table 2 do not indicate any relaxation frequency even in the expanded frequency range. The frequency dependence of the velocities for three liquids is displayed in Figure 3. In spite of the extended frequency range (6328 Å ÷ 4416 Å) no dispersion of the hypersound could be observed. Work is now in progress to further extend the frequency range by using larger scattering angles and the UV-radiation (3250 Å) of the He-Cd laser.

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Table 2. Brillouin shifts and acoustic velocities in seven liquids.

Liquid	present				other			
	$\lambda = 4416$ Å shift (GHz)	hypersonic velocity (m/s)	4765 Å shift (GHz)	hypersonic velocity (m/s)	4880 Å shift (GHz)	hypersonic velocity (m/s)	6328 Å shift (GHz)	hypersonic velocity (m/s)
Benzene	7.13	1462	6.66	1481	6.75	1546[12]	5.004	1495[13]
							5.01	1500[7]
							4.39	1464[16]
							4.42	1471[17]
Carbon disulfide	6.59	1231	6.07	1235	5.93	1236[12]	4.496	1225[13]
							4.62	1258[14]
							4.53	1250[7]
							4.496	1217[15]
Toluene	6.33	1304	5.82	1299	5.85	1354[12]	4.50	1350[7]
							4.48	1316[15]
							4.39	1317[16]
							4.42	1326[17]
Acetone	5.10	1165					3.60	1190[7]
							3.51	1137[15]
							3.47	1144[16]
Chloroform	4.80	1029			4.60	1112[12]	3.4	1055[17]
Methylene chloride	5.10	1110			4.33	1028[12]	3.53	1113[17]
n-Hexane	4.83	1090					3.42	1110[7]

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Force Constants and Mean Amplitudes of Vibration of the Metal-Hexahalo Species of Group IV—VI

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The general valence force constants and vibrational amplitudes have been evaluated for the metal hexahalo species of groups IV—VI elements using recent infrared and Raman spectral data. The results are employed to study the trend of variation among different species as well as the influence of cations on the relative stiffness of the chemical bonds. It has been found that the chemical bonds in the environment of a cesium cation are stronger than those of a tetraethylammonium cation.

Recently Bronswyk et al.[1] have recorded the infrared and laser Raman spectra of the metal-hexahalo species $R_2M^{IV}X_6$, $RM^{V}X_6$ [$R = (C_2H_5)_4N$ or Cs; M^{IV} = Ti, Zr or Hf; M^{V} = Nb, Ta; X = Cl or Br] and WCl_6 and interpreted the fundamental frequencies on the basis of octahedral symmetry. They have also reported the force constants using the modified Urey-Bradley force field (MUBFF) and the generalized valence force field (GVFF). In order to calculate the complete set of force constants in the GVFF model they have set a few interactions equal to zero and $f_{rr'} = 4/3\, f_{rr}$. In the present paper it is aimed to compute a complete set of force constants employing the GVFF model without the above constraints and the mean amplitudes of vibration. The results will be used to study the trend of variation in force constants as well as the influence of cations on the relative stiffness of the chemical bonds.

The anions of the type MX_6 possessing octahedral symmetry give rise to six fundamental frequencies which are distributed among different species as

$$1\,a_{1g} + 1\,e_g + 2\,f_{1u} + 1\,f_{2g} + 1\,f_{2u}$$

where $\nu_1(a_{1g})$, $\nu_2(e_g)$ and $\nu_5(f_{2g})$ are Raman active, $\nu_3(f_{1u})$ and $\nu_4(f_{1u})$ are infrared active and $\nu_6(f_{2u})$ is inactive in both. The inactive $\nu_6(f_{2u})$ is permitted as binary combination bands. The only fundamental to show appreciable dependence on the cation is $\nu_3(f_{1u})$.

Wilson's GF matrix method[2] was employed to calculate the force constants in the GVFF model. The mean amplitudes of vibration were evaluated at 0 °K, 298 °K and 500 °K using Cyvin's secular equation[3] $|\Sigma G^{-1} - \Delta E| = 0$, where the symbols have their usual meaning. F and G matrix elements, and analytical expressions for mean amplitudes of vibration were taken from Cyvin's book[3]. The two dimensional equations occuring in f_{1u} species were solved by Müller's method[4, 5, 6]. The fundamental fre-

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