BRILLOUIN SCATTERING IN LIQUID SULFUR DIOXIDE

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**Abstract**: Ultrasound attenuation in nonassociating liquids is mainly due to the delayed exchange of energy between the external (translational and rotational) and internal (vibrational) degrees of freedom. With increasing sound frequency, the energy distribution among the internal degrees of freedom can no longer follow the variations of the translational temperature. At very high sound frequencies, the distribution of the vibrational modes of the molecules corresponds to the average temperature of the liquid. Both, the increase of sound speed and the decrease of sound damping, can be characterized by a relaxation time, which in turn may be discussed in terms of relaxing bulk viscosity and/or relaxing vibrational specific heat capacities.

Sulfur dioxide is a nonlinear, polar, triatomic molecule of considerable practical and theoretical interest. There are three fundamental eigenmodes: the symmetrical stretching mode with 1152 cm\(^{-1}\), the antisymmetrical stretching mode with 1362 cm\(^{-1}\), and the bending mode with 518 cm\(^{-1}\). Liquid sulfur dioxide has a vibrational relaxation step in the low MHz frequency range, which was firmly attributed to the relaxation of two of the three vibrational modes of the SO\(_2\) molecule. The relaxation of the third mode (518 cm\(^{-1}\)) was presumed to occur at substantially higher frequencies in the GHz region. This type of double relaxation has only been found in very few other liquids, such as dichloromethane, dibromomethane, benzene and pyridine. However, to the best of our knowledge, such a well-separated relaxational behavior (22MHz compared to 1.5 GHz) has been found only for liquid SO\(_2\) [1-3].

For the determination of the relaxation time of the single remaining molecular vibrational eigenmode, we performed Brillouin experiments on orthobaric liquid SO\(_2\) between 274.7 K and 313.2 K. The liquid was contained in a quadratic quartz cuvette with windows of 6 mm thickness for 90\(^\circ\), a hexagonal cuvette for 60\(^\circ\) and 120\(^\circ\), and an octagonal cuvette for 45\(^\circ\) and 135\(^\circ\) scattering geometry. All cuvettes were thermostatted to within 0.1 K. The scattering angle is known with an imprecision of 10\(^\prime\). An electronically stabilized three-pass Fabry-Perot interferometer with a free spectral range of 15 GHz and a finesse of about 35 was used. Due to the high contrast and the resolution our instrument did allow more precise measurements than before.

The physical quantities necessary for data evaluation were obtained from critically selected literature data: vapor pressure, density, isobaric expansivity, isothermal compressibility, ultrasonic speed and sound damping, molar heat capacities at constant pressure and at constant volume, shear viscosity, thermal conductivity and refractive index [4], all for orthobaric conditions in the temperature range considered.

The hypersound speeds and the relaxation times were determined from each experimental Brillouin spectrum by fitting theoretical Brillouin spectra to it, considering the influence of the instrumental halfwidth of the Fabry-Perot interferometer. For the fitting procedure Mountain’s theory based on the relaxing bulk viscosity \(\eta_v\) was used. The interpolated/extrapolated sound absorption data \(\alpha/f^2\) of Bass and Lamb [1], and Fenner et al. [2] from ultrasonic measurements were combined with our hypersonic absorption data obtained from the half width at half height of the Brillouin peaks. By appropriately fitting the double relaxation of sound attenuation, for the relaxation frequency associated with the second relaxation step \(f_2 = 1.6\) GHz is obtained, which corresponds to a relaxation time of about \(\tau_v,2 = 100\) ps. Two further results deserve special attention:
(I) the optimized average nonrelaxing bulk viscosity \( \eta_{v,nr} = 5.04 \times 10^{-3} \) P is essentially twice as large as the shear viscosity \( \eta_s = 2.57 \times 10^{-3} \) P (P = 0.1 Pa·s), whence no relaxation of shear viscosity needs to be invoked to present adequately our data, as recently conjectured by us [3];

(II) the relaxing heat capacity extracted from our experimental results is in good agreement with the Planck-Einstein value of \( C_{vib,2} = 4.92 \text{ J·K}^{-1}·\text{mol}^{-1} \).

\[ \text{LIQUID SULFUR DIOXIDE, } T = 293.15 \text{ K} \]

Fig. 1. Brillouin spectrum of orthobaric liquid SO\(_2\) at 293.15 K. The scattering angle is \( \theta = 90^\circ \), the free spectral range is 15.00 GHz, the finesse is about 35. The experimental Brillouin spectrum was fitted with a theoretical spectrum (calculated from Mountain’s theory based on a relaxing bulk viscosity \( \eta_v \)) convoluted with the instrumental function of the Fabry-Perot interferometer.

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Fig. 2. Sound absorption \( \alpha/f^2 \) of orthobaric liquid SO\(_2\) as function of the sound frequency \( f \) at 293.15 K. Included are the interpolated/extrapolated values obtained from the ultrasonic work of Bass and Lamb [1], and of Fenner et al. [2] at low frequencies, that is between 3MHz and 90 MHz.