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APPLICATION OF DIGITAL TECHNIQUE TO THE SPECTRAL ANALYSIS OF MANDELSHTAM-BRILLOUIN SCATTERED LIGHT

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The experimentally recorded Mandelshtam-Brillouin type light scattering function is in general a convolution of the real scattering function and the overall instrumental function, accounting for all the deformations introduced by the measuring arrangement. We propose an algorithm for the numerical deconvolution of the spectrum applicable to the correction of the latter, and the deformation of the parameters of the scattering function. Results obtained when testing the computer program determining the Rayleigh line halfwidth $\Delta\nu_R$ as well as the shift $\delta\nu_{MB}$ halfwidth $\Delta\nu_{MB}$ of the Mandelshtam-Brillouin line are given, proving high degree of the effectivity of our numerical method.

Rejestrowana eksperymentalnie funkcja rozpraszania światła typu Mandelsztama-Brillouina jest w ogólności splotem rzeczywistej funkcji rozpraszania oraz całkowitej funkcji aparaturowej opisującej wszystkie zniekształcenia wnoszone przez układ pomiarowy. W pracy przedstawiono algorytm numerycznej metody dekonwolucji widma zastosowanej do korekcji widma i wyznaczenia parametrów funkcji rozpraszania. Przedstawiono również rezultaty testowania programu komputerowego wyznaczającego szerokość połówkową linii Rayleigha $\Delta\nu_R$ oraz przesunięcie $\delta\nu_{MB}$ i szerokość połówkową $\Delta\nu_{MB}$ linii Mandelsztama-Brillouina. Wyniki testu wykazały dużą przydatność zastosowanej metody numerycznej.

1. Theoretical foundations of Mandelshtam-Brillouin light scattering

Molecular light scattering by liquid media is due to time-dependent thermodynamical fluctuations of quantities such as temperature, pressure, and concentration. Mandelshtam-Brillouin scattering is a process of this kind. The fluctuations can be said to modulate the scattered light spectrum. Thus, in accordance with the Wiener-Kinchin theorem, their variations in time reflect the underlying stochastic ocurring in the scattering media.

Classically [1], the spectral intensity distribution of the light scattered is proportional to the Fourier transform of the autocorrelation function of fluctuations in density (concentration). This quantity is termed the structural factor, and is generally denoted by $S(\nu, q)$. Its analytical form is due to Mountain [2]:

$$S(\nu, q) = A\left\{(1-1/\gamma)\cdot\frac{\Delta\nu_R}{\nu^2+\nu_R^2}+(1/\gamma)\left[\frac{\Delta\nu_{MB}}{(\nu_0-cq)^2+\Delta\nu_{MB}^2}+\frac{\Delta\nu_{MB}}{(\nu_0-cq)^2+\Delta\nu_{MB}^2}\right]\right.$$
$$\left.+\frac{\Delta\nu_{MB}}{cq}\left[\frac{\nu+cq}{(\nu-cq)^2+\Delta\nu_{MB}^2}\frac{\nu+cq}{(\nu-cq)^2+\Delta\nu_{MB}^2}\right]\right\}. \quad (1)$$

The first three components of the scattered light spectrum are Lorentzian in form. These are: the Rayleigh line of frequency unchanged compared to the incident frequency, and the Mandelshtam-Brillouin doublet, disposed symmetrically on either side of the central line at a distance $\delta\nu_{MB} = \pm cq$. The fourth and fifth components give a non-Lorentzian correction to the Mandelshtam-Brillouin lines shifting them slightly (towards the central line) and causing them to become asymmetric. This correction is usually very small. However, it affects the positions of the lines perceptibility and has to be taken into account when interpreting the spectrum. With the shift measured amounting to ν_p and the linewidth equal to $\Delta\nu_{MB}$, the real position of the Mandelshtam-Brillouin has to be determined from the formula

$$\nu_{MB}^2 = \nu_p^2 + 2\Delta\nu_{MB}^2. \quad (2)$$

The preceding relations are valid for media in which no relaxational processes occur. Liquids with relaxation exhibit moreover a line referred to as the Mountain line [2].

The experimentally recorded scattered light spectrum is in general the convolution of several functions [3, 4]: the line corresponding to the light source with the spectral distribution $I(\nu)$ the line of the spectral analyzer with the distribution $T(\nu, \nu')$ and the scattering line with the distrubution $S(\nu, \nu')$. The notation $X(\nu, \nu')$ is meant to signify that the function X determines the intensity of the output radiation of frequency ν which has arisen in response to input radiation of unit intensity and of frequency ν'. Since all these distributions take non-zero values only in a narrow interval about the central frequency of the incident light wave we are justified in writing

$$S(\nu, \nu') = S(\nu-\nu'), \qquad T(\nu, \nu') = S(\nu-\nu'). \quad (3)$$

In this case, the spectrum observed is given by the formula

$$0(\nu) = \int_{-\infty}^{+\infty} T(\nu-\nu') \int_{-\infty}^{+\infty} S(\nu-\nu')\cdot I(\nu'')d\nu' d\nu'' = \mathscr{F}^{-1}\{\mathscr{F}[T(\nu)]\mathscr{F}[S(\nu)]\mathscr{F}[I(\nu)]\}, \quad (4)$$

with $\mathscr{F}$ the Fourier transform, and $\mathscr{F}^{-1}$ the inverse transform.

Thus, the scattering function can be determined from the following expression

$$S(\nu) = \mathscr{F}^{-1}\{\mathscr{F}[0(\nu)]/\{\mathscr{F}[T(\nu)]\mathscr{F}[I(\nu)]\}\}. \quad (5)$$

The preceding operation is referred to as deconvolution of the spectrum. It has to be performed in order to determine the "true" scattering function contributed by the scattering liquid and, consequently, such parameters as the shift in Mandelshtam-Brillouin line $\delta\nu_{MB}$ and its halfwidth $\Delta\nu_{MB}$.

Obviously, Eq. (5) is not accessible to strict solution, though a number of methods exist permitting approximate solutions of the problem. Here, we have in mind primarily the pseudodeconvolution method of JONES et. al. [5], as well as that of LEIDECKER and LAMACCHIA [4]. We shall discuss the former in more detail in Section 2.

2. The influence of the instrumental line on the recorded Mandelshtam-Brillouin scattered light spectrum

The deformations incurred when recording various spectra have long been the object of studies in the infrared, Raman and Mandelshtam-Brillouin spectroscopy. It has been established [3, 5, 6] that the deformation caused by the instrumental line can be neglected if the ratio of its halfwidth $\Delta\nu_I$ and that of the line investigated $\Delta\nu$ fulfils the condition $\Delta\nu_I/\Delta\nu \leqslant 0.2$. In most cases this condition is not fulfilled. Thus in order to obtain correct results, one has to have recourse to one of the methods evolved for correcting the experimentally recorded spectra.

In accordance with what has been said above, the instrumental line in the Mandelshtam–Brillouin case is the resultant of the Gaussian gas laser line [7], the Fabry-Pérot étalon line given by the Airy function [8], and the line due to the finite size of the scanning aperture described by a triangle function [4]. In practice, for the sake of simplicity, one usually makes use of the over-all instrumental function $A(\nu)$. The latter can be expressed as the product of a Gaussian and a Lorentz function:

$$A(\nu) = A_0[1+(1/\Delta\nu_L^2)(\nu-\nu_0)^2]\exp[-(1/\Delta\nu_G^2)(\nu-\nu_0)^2]. \tag{6}$$

Applying the over all instrumental function $A(\nu)$ alone, the experimentally recorded spectrum can be written in the following form:

$$O(\nu) = \int_{-\infty}^{+\infty} A(\nu-\nu')S(\nu')d\nu', \tag{7}$$

where $S(\nu)$ is the scattering function. Eq. (7) is an integral equation of the convolution type accessible to numerical solution by reduction to a set of linear equations:

$$O_i = \sum_{j=1}^{n} A_{ij}S_j, \qquad i = 1, 2, 3, \ldots, n. \tag{8}$$

0 and **S** are, respectively, vectors of the experimental points measured and the scattering function, whereas **A** is the transformation matrix of the instrumental function the matrix elements of which represent the values of the symmetric instrumental function measured at the same intervals $\Delta\nu$ as the values of $O(\nu)$. The matrix **A** fulfils the normalisation condition. For deconvolution of the spectrum, i.e. for determining the scattering function $S(\nu)$ from the experimental functions $S(\nu)$ and $A(\nu)$, we used one of the available methods of deconvolution (referred to as ψ-deconvolutions), namely that of JONES et. al. [4]. According to Jones, the transformation matrix of the instrumental function is constructed in the following form:

$$\begin{bmatrix} a_{11} & a_{12} & \dots & a_{1m} & 0 & 0 & 0 & \dots & 0 \\ 0 & a_{21} & a_{22} & \dots & a_{2m} & 0 & 0 & \dots & 0 \\ \dots & \dots & \dots & \dots & \dots & \dots & \dots & \dots & \dots \\ 0 & 0 & \dots & 0 & a_{m1} & a_{m2} & \dots & \dots & a_{mn} \end{bmatrix}.$$

The matrix is obtained as follows; having available n values of the scattering function $S(v_i)$ and n values of the instrumental function $A(v_i)$ we assume that the $2l$ values of the function $A(v_i)$ lying on the wings of the line are zero. Thus, the matrix **A** has $m = n-2l$ rows. In practice, the values of the matrix elements a_{ij} are determined by recording light scattering from a statistically homogeneous medium.

Jones' is an iterative method. As the zeroth approximation, one assumes the experimentally observed values of the scattering function

$$S_i^{(0)} = S_i, \quad i = 1, 2, \dots, n. \tag{9}$$

The k-th step of the iteration procedure consists of 4 stages. In the first, one determines the vector $\mathbf{B}(B_1, B_2, \dots, B_m)$ from the formula

$$\mathbf{B}^{(k)} = \mathbf{A}\cdot\mathbf{S}^{(k-1)} \tag{10}$$

In the second — the vector $\mathbf{R}(R_1, R_2, \dots, R_m)$

$$R_i = S_{1+i}/B_i, \quad i = 1, 2, \dots, m. \tag{11}$$

In the third stage, one finds the next $(k+1)$-st approximation of the vector **S**:

$$S_i^{(k+1)} = S_i^{(k)}\cdot R_1, \quad i = 1, 2, \dots, l \tag{12}$$

$$S_i^{(k+1)} = S_i^{(k)}\cdot R_{i-1}, \quad i = l+1, l+2, \dots, l+m \tag{13}$$

$$S_i^{(k+1)} = S_i^{(k)}\cdot R_m, \quad i = l+m+1, l+m+2, \dots, n \tag{14}$$

The equations (12) and (14) describe the wings of the line. In the fourth stage we determine the value of

$$\delta^{(k)} = \sum_{i=1}^{n} |S_i^{(k)} - S_i^{(k-1)}|. \tag{15}$$

One continues the iterative procedure until the following condition is fulfilled

$$|\delta^{(k)} - \delta^{(k-1)}| \leqslant \varepsilon, \tag{16}$$

where the parameter ε is a prescribed number. For practical purposes a sufficient approximation is achieved after some 10–20 iterations.

On having determined the function $S(v)$ by deconvolution, one can proceed to determine the parameters of the spectrum: the halfwidth of the Rayleigh line Δv_R, that of the Mandelshtam-Brillouin line Δv_{MB}, and the Mandelshtam-Brillouin shift

$\delta\nu_{MB}$. To this aim, we made use of the procedure consisting in fitting the theoretical curve of eq. (1) to the „experimentally" determined points of the function $S(\nu)$ by the least squares method.

3. Testing the numerical procedure. The design of a measuring stand for the digital recording of Mandelshtam-Brillouin scattered light spectra

On the basis of the preceding Jones' algorithm we wrote in PASCAL language a program for deconvolution of the spectrum and the determination of the parameters of the Mandelshtam-Brillouin scattering spectrum recorded. The functioning of the fitting procedure was checked on data generated on the basis of Eqs. (1) and (6). Fig. 1 shows the instrumental line of Eq. (6). Its parameters amount to:

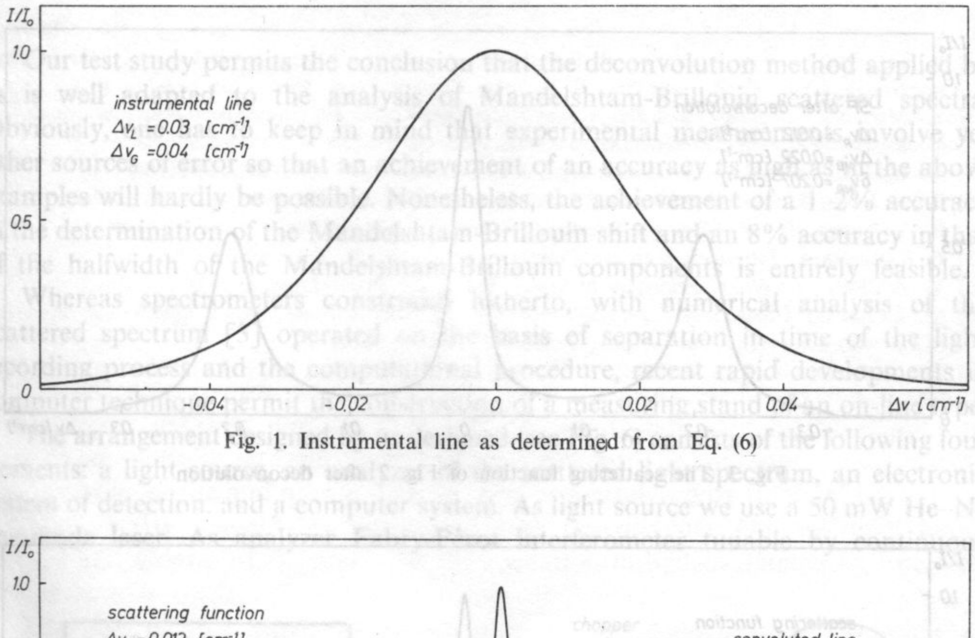

Fig. 1. Instrumental line as determined from Eq. (6)

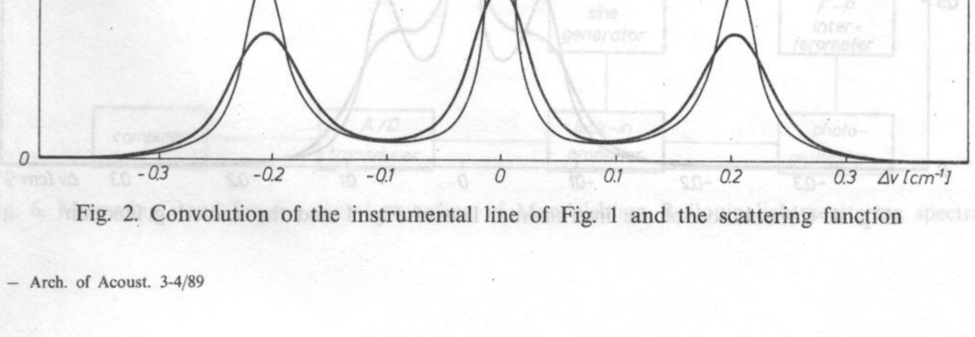

Fig. 2. Convolution of the instrumental line of Fig. 1 and the scattering function

$\Delta\nu_L = 0.03\ \mathrm{cm}^{-1}$, and $\Delta\nu_G = 0.04\ \mathrm{cm}^{-1}$. Its convolution with the scattering function, of parameters equal to $\Delta\nu_R = 0.012\ \mathrm{cm}^{-1}$, $\Delta\nu_{MB} = 0.022\ \mathrm{cm}^{-1}$ and $\delta\nu_{MB} = 0.207\ \mathrm{cm}^{-1}$, is shown in Fig. 2, where one notes a lowering of the maxima and a broadening of all the lines. The result of the deconvolution and fitting procedure is shown in Fig. 3. Obviously, agreement between the parameters assumed and those obtained is very good.

A case of greater interest is shown in Fig. 4. Here convolution of the instrumental line of Fig. 1 and a scattering function with the parameters $\Delta\nu_R = 0.012\ \mathrm{cm}^{-1}$, $\Delta\nu_{MB} = 0.023\ \mathrm{cm}^{-1}$ and $\delta\nu_{MB} = 0.073\ \mathrm{cm}^{-1}$ led to complete obliteration of the hyperfine structure, so that an analysis of the spectrum by traditional methods was not possible. However, the result of deconvolution of this spectrum is illustrated in Fig. 5 where, quite obviously, the hyperfine structure is reconstituted and the values of the parameters are in excellent agreement with those assumed.

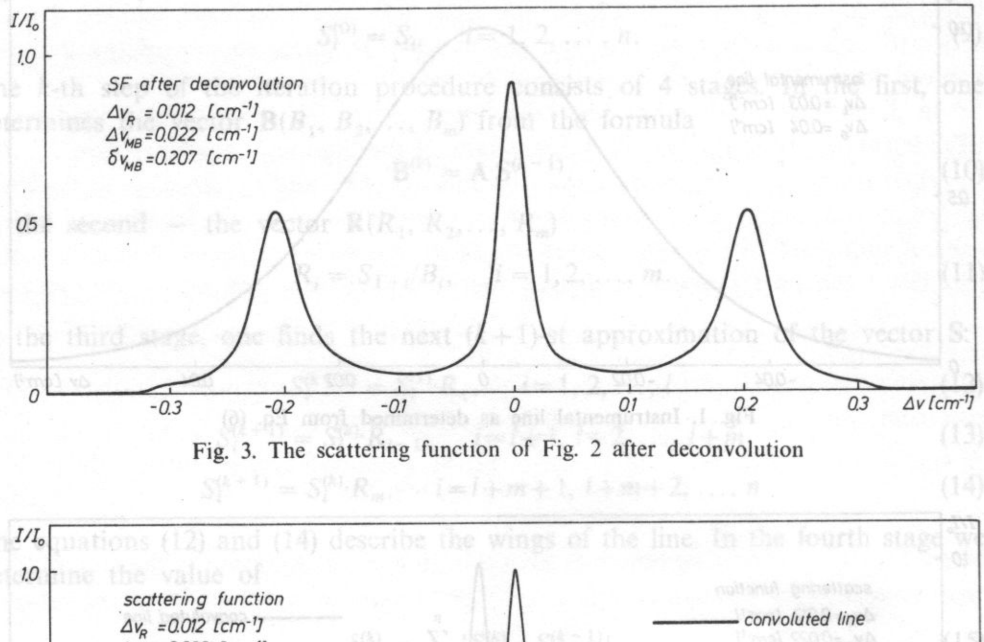

Fig. 3. The scattering function of Fig. 2 after deconvolution

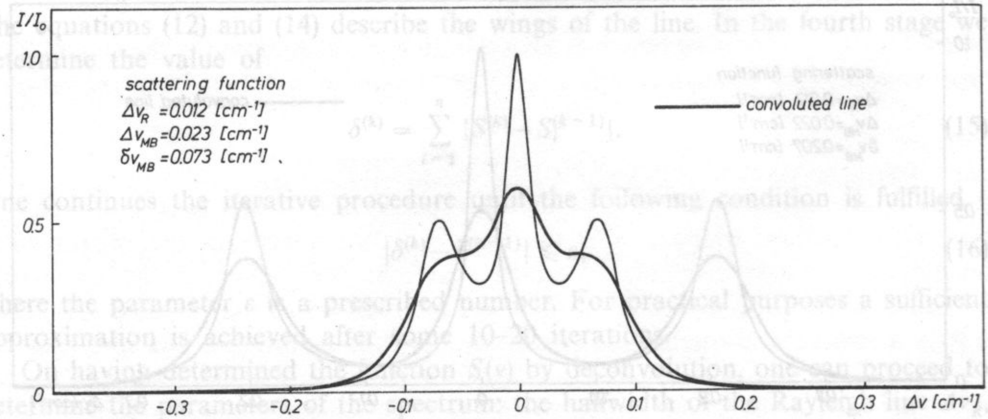

Fig. 4. Convolution of the instrumental line of Fig. 1 and the scattering function

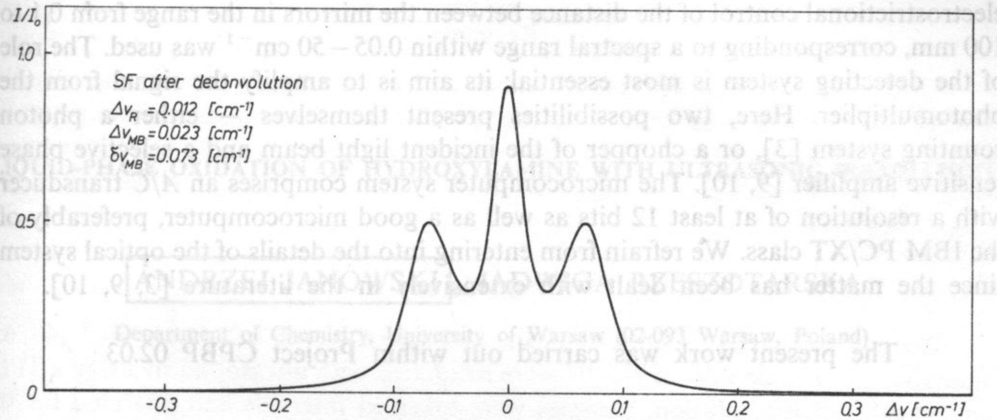

Fig. 5. The scattering function of Fig. 4 after deconvolution

Our test study permits the conclusion that the deconvolution method applied by us is well adapted to the analysis of Mandelshtam-Brillouin scattered spectra. Obviously, one has to keep in mind that experimental measurements involve yet other sources of error so that an achievement of an accuracy as high as in the above examples will hardly be possible. Nonetheless, the achievement of a 1–2% accuracy in the determination of the Mandelshtam-Brillouin shift and an 8% accuracy in that of the halfwidth of the Mandelshtam-Brillouin components is entirely feasible.

Whereas spectrometers construed hitherto, with numerical analysis of the acattered spectrum [3] operated on the basis of separation in time of the light recording process and the computational procedure, recent rapid developments in computer technique permit the construction of a measuring stand of an on-line type.

The arrangement designed by us designed (see Fig. 6) consists of the following four elements: a light source, an analyzer of the scattered light spectrum, an electronic system of detection, and a computer system. As light source we use a 50 mW He–Ne one-mode laser. As analyzer Fabry-Pérot interferometer tunable by continuous

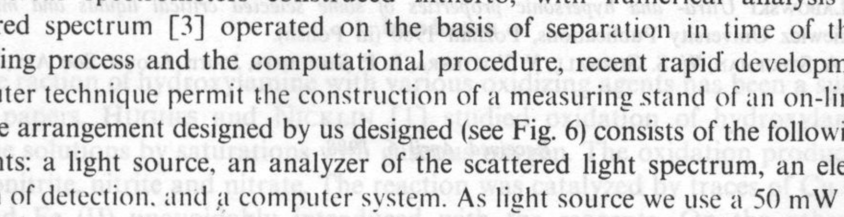

Fig. 6. Measuring stand for the digital recording of Mandelshtam–Brillouin light scattering spectra

electrostrictional control of the distance between the mirrors in the range from 0.1 to 100 mm, corresponding to a spectral range within 0.05 – 50 cm^{-1} was used. The role of the detecting system is most essential: its aim is to amplify the signal from the photomultiplier. Here, two possibilities present themselves — either a photon counting system [3], or a chopper of the incident light beam and a selective phase sensitive amplifier [9, 10]. The microcomputer system comprises an A/C transducer with a resolution of at least 12 bits as well as a good microcomputer, preferably of the IBM PC/XT class. We refrain from entering into the details of the optical system since the matter has been dealt with extensively in the literature [3, 9, 10].

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