



# INCLUSION OF THE INFLUENCE OF INTERMOLECULAR INTERACTIONS ON THE VIBRATIONAL SPECTRA OF MOLECULES AND THE DETECTION OF ROTATIONAL SWINGS IN INVESTIGATION OF THE STRUCTURE OF CONDENSED SYSTEMS

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## Abstract

In this study we investigate vibrational and rotational relaxation of a bromobenzene molecule in the broad spectral region at the room temperature using the Raman scattering spectroscopy method. Experimentally, and by using quantum-chemical calculation, it has been shown that hydrogen atom can have *H* – bond with carbon atom both inside the molecule, as well as between bromobenzene molecules. Intense lines of the Raman scattering can be observed in the low frequency region of the spectrum, which opens the possibility for observation of the detection of rotational swings of the separate atomic groups in complex molecules.

**Keywords:** spectrum, Raman scattering, bromobenzene, intermolecular interaction, rotational-shaking motion.

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## 1. Introduction

Combinational or Raman scattering of light (RSL) – is still continuing to be one of the informative methods in the study of the subtle processes in condensed matter systems [1-11].

Despite the rather extensive experimental information on the behavior of various physical characteristics of monohalogenated benzenes, there is currently no unified idea of the processes occurring in these liquids at the molecular level.

This situation stimulates further studies of these promising objects. In this work we present results of investigation of vibrational and rotational relaxation of the bromobenzene molecule – C<sub>6</sub>H<sub>5</sub>Br in the broad spectral range.

The bromobenzene molecule belongs to the group of monohalogenated benzenes. Regarding the geometric structure of monohalobenzenes, there is no consensus in the literature. The most common model is a planar structure with a benzene ring in the form of a regular hexagon (Fig. 1).

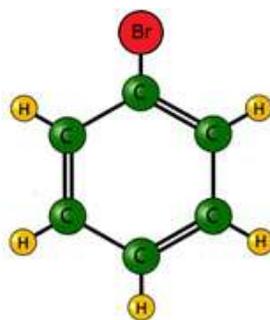


Figure 1. Structure formula of the bromobenzene molecule.

### Experimental part

It is known, that the existence of various impurities in the investigating substances, which is able to interact with molecules of the medium leads to a distortion of the pattern of inter-molecular interactions as well as changes in Raman scattering spectra, and correspondingly, lead to misinterpretations of the changes in spectra and quantitative results based on them. In this regard, a serious problem arises in the study using the RSL for the choice of methods for cleaning the scattering medium. Bromobenzene, depending on the grade of purity of the initial product, was purified according to refs [12-16]. The degree of purity of the object was controlled by the ratio of the intensities of the shifted and unshifted Mandelstam-Brillouin components of the polarized part of molecular light scattering and by the boiling point. The Raman spectra were obtained with a laser scanning confocal microscope (Fig. 2.). The STR250 laser Raman spectrometer with confocal

microscopy is a very compact and flexible system with high sensitivity for measuring weak Raman scattering from different materials. The system consists of a spectrometer (07) with a focal length of 250 mm, a Czerny-Turner scanning mechanism in the spectral region 50-7000 cm<sup>-1</sup>, three different diffraction gratings (number of lines per 1 mm are 600; 1200; 1800, respectively) which can interchange automatically, with a resolution of 1 cm<sup>-1</sup>, with antistatic effect and CCD camera (08) with cooling to a temperature of -60°C. The set includes an optical microscope (03) for a small sample with a spatial resolution of <1 mm and an excitation laser (01) for the visible region (532 nm). The system includes user-friendly management and data processing software based on the Windows platform. The Raman spectra were measured in a 180° geometry, i.e., radiation was recorded at an angle of 180° with respect to the incident light.

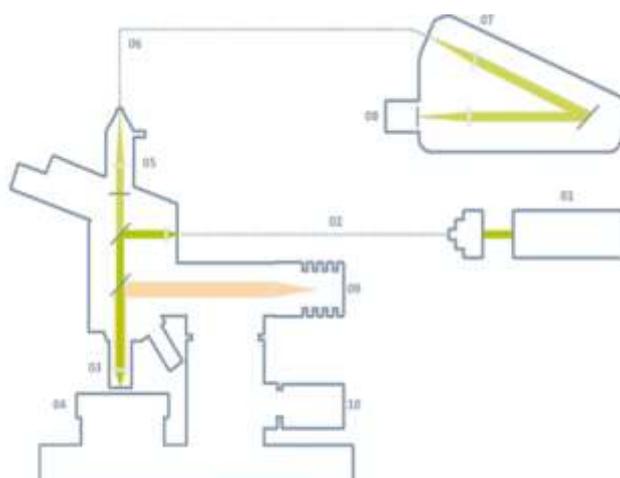


Figure 2. Scheme of the experimental setup for recording the spectra of Raman scattering of light 01

- exciting laser; 02, 06 - optical fiber connection with a bandwidth of up to 90%; 03 - tuned lens; 04 - microscope stage; 05 - set of filters; 07 - STR250 spectrometer; 08 - piezoelectric detector; 09 - white lighting; 10 - focus screw. The experiment was set up as follows: a quartz cuvette was used to study bromobenzene. A quartz cuvette with liquid was placed on the microscope stage and a laser beam was focused into it. The scattered light was collected by the same lens. Setup consists of spectrometer with scanning mechanism in the spectral range 50-700  $\text{cm}^{-1}$ , three diffraction grating with 600, 1200, 1800 lines per mm, which can interchange positions automatically. Measurements of RSL spectra were performed under the angle of  $180^\circ$  to the incident light. To obtain reliable information about intramolecular processes and intermolecular interactions in liquids from the spectra of the Raman band contours, the contour recorded by the recording device must be corrected for the distorting influence of the spectral device. The contour of the Raman line, obtained experimentally, can differ significantly from the true contour, both in shape and in width. The greatest effectiveness and result efficiency among existing methods for determining the true width of the Raman line from the half-width of the observed width of the contour can be obtained by the formula (1) shown below proposed in [18]

$$\sigma_{\text{true}} = \sigma_{\text{obs}} \left[ 1 - \left( \frac{\Delta_{\text{app}}}{\sigma_{\text{obs}}} \right)^2 \right] \quad (1)$$

where  $\sigma_{\text{true}}$  – true halfwidth of the RSL contour,  $\Delta_{\text{app}}$  – halfwidth of hardware function,  $\sigma_{\text{obs}}$  – line width obtained experimentally. The linewidth values obtained by this method are in good agreement with other methods.

## 2. Results and discussion

The Raman spectrum of bromobenzene recorded in the region of intramolecular interactions at room

temperature in the spectral frequency range 50 ÷ 3200  $\text{cm}^{-1}$  is shown in Fig. 3. According to the spectrum shown in Fig.3, a large number of lines are present in the low-frequency region of the Raman spectrum, the most intense of which has a frequency value of 266  $\text{cm}^{-1}$ , close to the value calculated by the quantum chemical method. In addition, the spectrum contains intense lines with frequency values of 133  $\text{cm}^{-1}$  and 624  $\text{cm}^{-1}$ . In general, significantly more lines are found in the observed spectrum than in the literature data on the Raman spectra for the object under discussion. An analysis of works on the investigations of the Raman spectra of liquids in the low frequency range showed that such works are very limited. Nevertheless, observations of rotational swings in the Raman spectra of methyl and heavier atomic groups are known. Note that a direct observation of spectral lines caused by rotational swings greatly facilitates the determination of the thermodynamic functions of molecules by means of statistical calculations. In this regard, special attention was paid to the observation of rotational swings of molecules. The interpretation of the observed Raman lines, in particular, the assignment of some of the lines to rotational oscillations, is difficult without a special theoretical analysis, because the low-frequency spectrum of bromobenzene is rich in lines. This means that deformation oscillations are also observed along with rotational oscillations. For molecules containing heavier groups, as in our case, bromobenzene, the lines lying in the lowest frequency range of the spectrum are usually referred to as rotational swings. If the height of the potential barrier of rotational oscillations is known, it is quite easy to determine the corresponding frequency ( $\nu \sim \sqrt{U}$ ), and by comparing the calculated values of the frequencies with those observed in the experiment, one can select the frequencies of rotational oscillations.

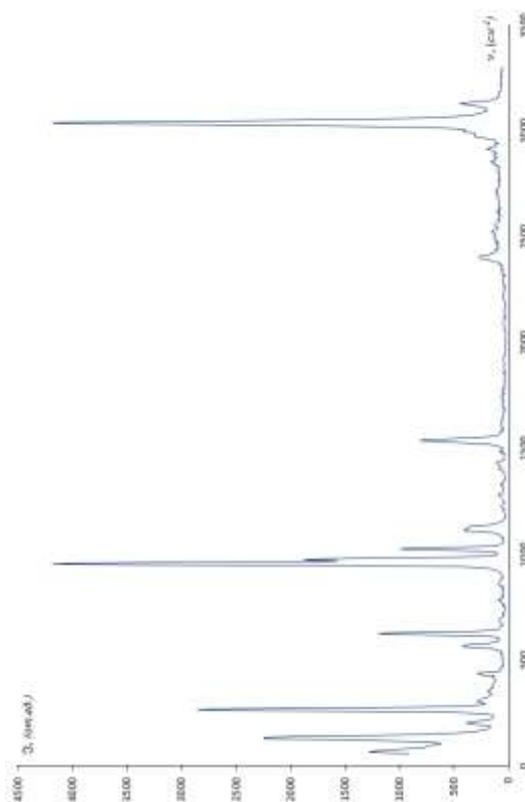


Figure. 3. Raman spectrum of bromobenzene at room temperature in the frequency range  $50 \div 3200 \text{ cm}^{-1}$

We calculated potential barriers using the methodology described in works [11,17]. To determine the height of potential barriers, we need structural data values with high accuracy, such as bond length and angles between bonds of

bromobenzene atoms, determined by quantum chemical calculations. The results of such calculations, considering the intramolecular interaction of bromobenzene, are shown in Fig. 4.

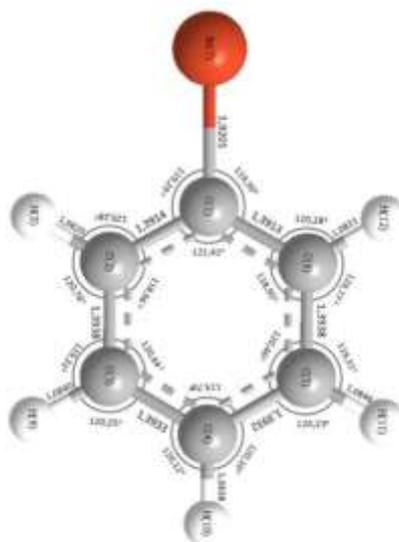


Fig.4. Calculated structure of bromobenzene

The results of the calculation of potential barriers, the calculated and experimental values of the frequencies for the most intense line of rotational

oscillations of the RSL for the bromobenzene molecule are presented in Table 1.

Table 1.

Substance	U, cal/mole (calculated)	$\nu$ , $\text{cm}^{-1}$	
		Calculated	Experimental
$\text{C}_6\text{H}_5\text{Br}$	5500	240	266

An analysis of the table shows that, according to our estimates, the accuracy of determining the potential barrier does not exceed  $\pm 26 \text{ cm}^{-1}$ . From the data we obtained on the low-frequency Raman spectra of bromobenzene, it can be seen that we could establish the observation of rotational swings of atomic groups in the spectrum. From our point of view, the low intensity of these lines, which is also confirmed by our early observations, and the region of the spectrum which is inappropriate for work, were the reasons for the lack of systematic studies of rotational oscillations by the Raman method. However, our studies show that with careful selection of the conditions for recording Raman spectra, it is possible to obtain frequencies in the region of  $150 \text{ cm}^{-1}$  and even lower.

### 3. Conclusion

Using Raman spectroscopy, we have recorded a spectrum in the low frequency range, which indicates the observation of rotational swings of individual atomic groups of bromobenzene. It is shown that the patterns observed in scattering data can be interpreted on the basis of the mechanism of intermolecular vibrations of molecules caused by specific interactions between molecules, for example, rotational vibrations of one part of the molecules relative to another, and deformation vibrations, etc. The observed spectral bands are assigned to the type of vibrations in the Raman spectrum in bromobenzene. Intense Raman lines are observed in the low-frequency range of the spectrum, which opens up the possibility of observing the manifestation of rotational swings of molecules.

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