

# Application of Raman scattering of light to study the structure of molecules

Bakhodir Eshchanov, Shavkat Otajonov, Khusnida Rakhmatillaeva

**Abstract**— The structure and shape of the bands for the vibrational Raman spectra of ethanol molecules in solutions with toluene are analyzed. The possibilities of their use to obtain information on the features of molecular interactions and their vibrational dynamics are shown.

**Index Terms**— Light scattering, Raman scattering, molecular liquids, vibrational motion, intermolecular interaction, solution, rotational oscillation, intramolecular vibration.

## 1 INTRODUCTION

The problem of establishing the nature and strength of intermolecular interactions (IMI) in condensed media and strongly fluctuates anisotropic molecules, as well as the most common regularities in the variation of the optical spectra of polyatomic molecules due to the influence of IMI of different nature, is an actual field in modern spectroscopy of condensed media [1-4].

A characteristic difference between the optical spectra of polyatomic molecules and atomic ones is that in all molecules consisting of not less than three atoms, the motion is more complex than in atoms, that is, together with the motion of electrons, an important role plays the oscillation (periodic change with respect to the location of the nuclei) and rotational (periodic change in orientation) motion of the molecule [5,6].

Oscillation spectroscopy is one of the most informative methods for studying the liquid state of a substance and makes it possible to obtain information that is often inaccessible to other experimental methods of investigation. Oscillation spectra of molecules are characterized by the position of the band maxima, their intensity and shape. The study of changes in these parameters under the influence of inter particle interactions allows obtaining information on the structure of liquids.

Rotational vibration of individual atomic groups in complex molecules is manifested in the low-frequency region of the oscillation spectra. Information on this spectral region is given by absorption spectra of long-wavelength infrared radiation and Raman spectra (Raman scattering) in the low-frequency region.

In this work a solution of toluene + ethanol is studied in a wide range of concentrations (1-0.2 molar solution of toluene).

Taking into account the great principled and practical importance of the study of rotational vibration, an experimental and theoretical study of low-frequency Raman spectra for a wide class of liquids is carried out.

## 2 EXPERIMENT SETUP

Raman spectra of objects were obtained with using a laser scanning confocal microscope (Fig. 1). 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 scanning mechanism for Czerny-Turner in the region of the wave number of 50-7000  $\text{cm}^{-1}$ , automatically changing places three different diffraction lattices (with number of strokes of 600, 1200, 1800 per 1 mm), with resolution of 1  $\text{cm}^{-1}$ , with an anti-static effect and a CCD (08) chamber with cooling at a temperature of  $-60^\circ\text{C}$ . It includes an optical microscope (03) for a small sample with a spatial resolution of  $<1\text{ mm}$  and an exciting laser (01) for the visible region (532 nm).

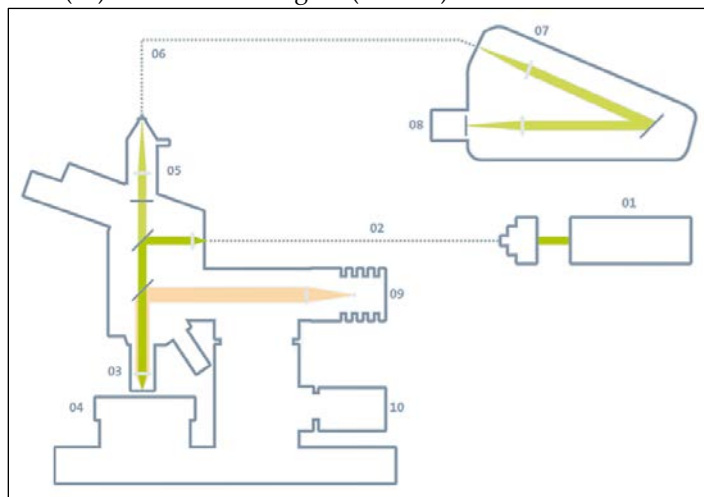


Fig.1

The system includes user-friendly software for managing and processing data based on the Windows platform. The

- Bakhodir Eshchanov is associate professor in National University of Uzbekistan, Uzbekistan, Tashkent, E-mail: bakhodir.eshchanov@gmail.com
- Shavkat Otajonov is professor in National University of Uzbekistan, Uzbekistan, Tashkent.
- Khusnida Rakhmatillaeva is student of masters degree in National University of Uzbekistan, Uzbekistan, Tashkent.

Raman spectra were measured in geometry of  $180^\circ$ , that is, radiation was detected at an angle of  $180^\circ$  in relation to the incident light.

The experiment was carried out as follows: a quartz cuvette was used to study benzene and its derivatives. A quartz cuvette with liquid was placed on a highly precise scan table (04) a laser beam was focused into it. Scattered light is collected by the same lens.

### 3 RESULTS AND DISCUSSION

As demonstrated in this document, the numbering for sections upper The bands of Raman scattering for ethanol in pure liquid and in solution with toluene are shown in Fig. 2. The spectrum is complex and highly variable in depending on the concentration of the mixture.

The results of experimental studies for the frequency shift  $\Delta\nu$  of the Raman scattering for the ethanol band of  $2941\text{ cm}^{-1}$  show that in the entire concentration range investigated in the experimental errors we observe a linear dependence of the value of  $\Delta\nu$  on the concentrations (Fig. 3).

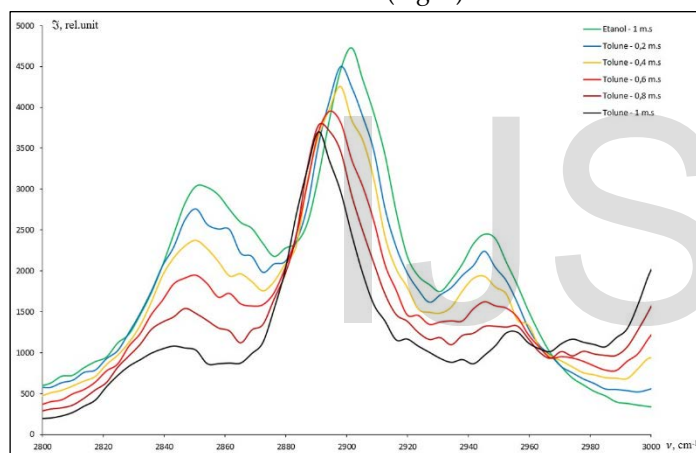


Fig 2.

We can see from Fig. 2 that dilution of ethanol in a solvent (toluene) leads to a strong line broadening. If the solution contains 0.8 molar solution of toluene the width of this band is almost one and a half times larger than the width of the band of pure ethanol.

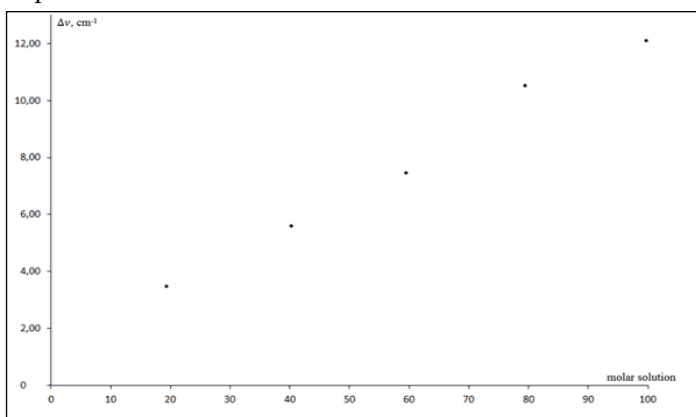


Fig 3.

The vibrational relaxation of molecules in liquids is deter-

mined mainly by intermolecular interaction. There are three mechanisms of relaxation of intramolecular vibrations. The first one is energy relaxation, i.e., dissipation of energy of intramolecular vibrations to all other degrees of freedom of movement, including the translational and rotational motion of molecules and other vibrational modes. The second one is phase relaxation, i.e., modulation of the phase of the intramolecular vibration by collisions with surrounding molecules, in other words, fluctuations of the local field. The third one is resonant energy exchange, i.e., the exchange of energy quanta of intramolecular vibrations between oscillators of the same type.

Resonant energy exchange can make a significant contribution to the shape of the band contours in pure liquids and solutions with sufficiently strong intermolecular interactions. Its manifestations in the vibrational spectra of liquids have been studied in a number of theoretical and experimental studies [7,8]. It was found that resonant energy transfer, in addition to broadening the band contours in liquids with strong intermolecular interactions, should cause the positions of the maxima of the bands of the same oscillation to not coincide in the spectrum of concentration Raman scattering. This effect of the mismatching between the frequencies of the maximum of the Raman band in ethanol + toluene solutions ( $\Delta\nu$  - negatively) is connected by the mechanism of resonant energy exchange.

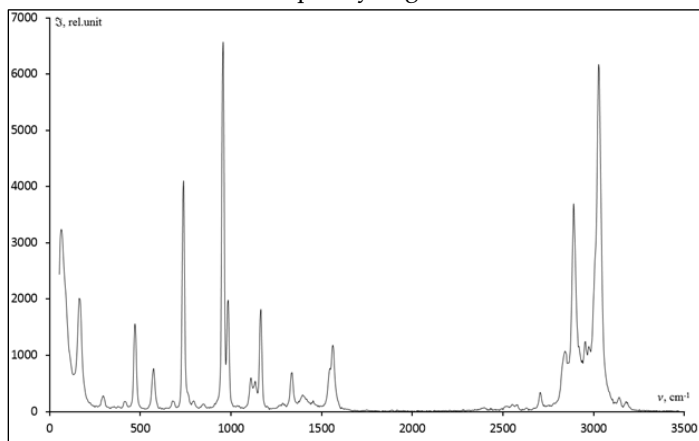
An analysis of the quantum and chemical calculations of the frequencies for normal vibrations of the complexes studied showed that for all configurations the values of the mismatching the vibration frequencies depend on the nature of the intermolecular interaction. Rotational vibration of individual atomic groups in complex molecules is manifested in the low-frequency region of the vibrational spectra.

The study of lines corresponding to the rotational vibration of atomic groups is of great importance for studying the forces acting in molecules between chemically unconnected atoms.

To study the rotational vibration of methyl groups in the Raman spectrum of low frequencies, a convenient object of study is toluene. According to the structural formula, in addition to the rotational oscillations of the group  $\text{CH}_3$  ( $215\text{ cm}^{-1}$ ,  $345\text{ cm}^{-1}$ ), deformation oscillations can be observed in the spectrum. The assignment of lines in the Raman spectra of toluene to rotational oscillations is complicated by the fact that the low-frequency spectrum in toluene have a lot of spectral lines. This means that, together with rotational oscillations, deformation vibrations ( $800\text{ cm}^{-1}$  and higher) are observed.

For molecules containing heavier groups, lines lying in the lowest frequency region of the spectrum are usually referred to as rotational vibration. In the case of rotational vibration of methyl groups, the corresponding lines can lie in a relatively wide spectral region, starting from the wing of the Rayleigh lines to  $600\text{ cm}^{-1}$  (Fig. 4). This is due to the fact that the moment of inertia for the methyl group is small.

In the low-frequency spectra of toluene, a significant number of lines of rotational oscillations were founded that have a comparatively low-intensity wing of the Rayleigh line [9], therefore, in the low-frequency region, we could record not



very intense Raman lines, already from 100  $\text{cm}^{-1}$ . The lines observed in the low-frequency region have different widths and intensities, but most of the lines are weak, their intensity is several units in the common scale.

Fig.4.

#### 4 CONCLUSION

Interpretation of these lines in the first approximation can be obtained if we imagine that the molecules studied bind rotational oscillations to one another. This assumption is a crude simplification of the problem, since the interactions of rotational vibration with other vibrations of the molecule are not taken into account. However, we can expect that these interactions are still not very large due to the considerable difference of the frequencies of the considered lines and the frequencies of other lines in the low-frequency region of the spectrum of the molecules studied.

According to the literature data, if the height of the potential barrier of rotational oscillations is known, the corresponding frequency can be found quite easily. Comparing the calculated value of frequencies with those observed in the experiment, one can classify these certain frequencies to rotational vibration.

Unfortunately, for methyl-substituted hydrocarbons, there is no reliable data on the height of potential barriers of rotational vibration.

#### ACKNOWLEDGMENT

We are very grateful to Matsumae international foundation (MIF, Gno: 16G14) for financing of scholarship for B. Eshchanov in 2016 in Tokai University (Japan).

Also we would like to say thanks Dr. Olga V. Karpova from Turin polytechnic university in Tashkent for fruitful discussion.

#### REFERENCES

- [1] B.Eshchanov, Sh.Otajonov, A.Isamatov, D.Babajanov, "Dynamics of relaxation processes in liquids: Analysis of oscillation and orientation spectra," *J. Mol. Liquids*, vol. 202, pp. 148-152, 2015.
- [2] M.Perrot, M.Besnard, J.Lascombe, M.Bouachir, "Orientational and induced depolarized Rayleigh scattering of some anisotropic molecules in their liquid state," *Canadian J. Phys.*, vol. 59, no. 10, pp.1481-1489, 1981.
- [3] A.Ismael, "Low-frequency isotropic and anisotropic raman spectra of aromatic liquids," *J. Chem. Phys.*, vol. 132, pp. 174503-174510, 2010.
- [4] G.C.Tabisz, W.R.Wall, D.P.Shelton, "Collision-induced light scattering from liquid  $\text{CCl}_4$  and  $\text{C}_6\text{H}_{12}$ ," *Chem. Phys. Let.*, vol. 15, pp. 387-391, 1972.
- [5] M.Born, J.R.Oppenheimer, "On the quantum theory of molecules," *Ann. Phys.* vol. 84-457, 1927.
- [6] M.Knap, E.Arrigoni, W.Linden, "Vibration-mediated correlation effects in the transport properties of a benzene molecule," *Physical review B*, vol. 88, pp. 054301-1-5, 2013.
- [7] J.Bukowska, "Raman and infrared studies of interactions between amides and ions," *J. Mol. Struct.* vol. 98, no. 1, pp. 1-10, 1983.
- [8] D.E.Logan, "The non-coincidence effect in the Raman spectra of polar liquids," *J. Chem. Phys.*, vol. 103, no. 2, pp. 215-225, 1986.
- [9] B.Eshchanov, Sh.Otajonov, A.Isamatov, "On possible models of thermal motion of molecules and temperature effect on relaxation of optical anisotropy in bromine benzene" *Ukraine Journal of Physics.*, vol. 56, no. 11, pp. 1178-1181, 2011.