https://doi.org/10.15407/ujpe65.4.284

B. ESHCHANOV,[1, 2] SH. OTAJONOV,[2] G. MUKHAMEDOV,[1] I. DOROSHENKO,[3]
O. KARPOVA,[4] SH. ALLAKULIEVA [2]

[1] Chirchik State Pedagogical Institute
(Uzbekistan; e-mail: bakhodir.eshchanov@gmail.com)
[2] National University of Uzbekistan
(Uzbekistan)
[3] Taras Shevchenko National University of Kyiv
(2, Prosp. Academician Glushkov, Kyiv 03022, Ukraine)
[4] Turin Polytechnic University in Tashkent
(Tashkent, Uzbekistan)

EXPERIMENTAL STUDY OF RAMAN SPECTRA OF SOME AROMATIC HYDROCARBONS[1]

The vibrational spectra of liquid aromatic hydrocarbons – bromobenzene, dioxane, toluene – are studied in a wide frequency range by means of Raman spectroscopy. The manifestation of torsional vibrations of individual groups of atoms is established from the obtained data on the low-frequency spectra. The possibility of using a semiempirical method for calculating the potential barriers of methyl and halide groups in benzene derivatives is shown.

Keywords: vibrational spectroscopy, bromobenzene, dioxane, toluene, deformational vibrations, torsional vibrations, potential barrier.

1. Introduction

Vibrational spectroscopy is one of the most informative experimental methods for studying the liquid state of substances. Using vibrational spectroscopy, one can obtain information that is often inaccessible to other experimental methods of research. There are many theoretical and experimental works [1–15] devoted to the investigation of contributions of intra- and intermolecular interactions to the contours of vibrational bands.

Vibrational spectra of molecules are characterized by the position of the maxima of the bands, their intensity, and shape. The study of changes in these parameters caused by intermolecular interactions makes it possible to obtain information about the structure of liquids and the presence of relatively long-lived intermolecular complexes and associates in them [16–18], as well as to study the molecular dynamics. Intermolecular interactions in liquids cause changes in the force constants of interatomic bonds in molecules. The dynamic nature of these interactions is the cause for the broadening of the bands in the vibrational spectra of liquids. However, if this disturbance keeps for a relatively long time, it leads to a change in the frequency of the vibrational band in the spectrum. This time should significantly exceed the relaxation time of intramolecular vibrations, which usually does not exceed tens of picoseconds in liquids. Therefore, the existence of a relatively long-lived local order in a fluid associated with the formation of various complexes and associates is manifested in a changing of the frequencies of intramolecular vibrations. These changes are observed most clearly in the bands corresponding to the vibrations of atoms, through which the interaction between the molecules in an associate takes place. The variety of such local environments leads to the fact that there are several discretely shifted bands in the spectrum, the number of which is determined by the number of types of associates formed in the liquid. The intensity of these bands depends on the concentration of associates of this type in the liquid [9, 10, 18, 19].

The low-frequency part of vibrational spectra contains, in particular, torsional vibrations of molecu-

© B. ESHCHANOV, SH. OTAJONOV,
G. MUKHAMEDOV, I. DOROSHENKO, O. KARPOVA,
SH. ALLAKULIEVA, 2020

---

[1] The paper was presented at XXIVth Galyna Puchkovska International School-Seminar "Spectroscopy of Molecules and Crystals" (August 25–30, 2019, Odesa, Ukraine).

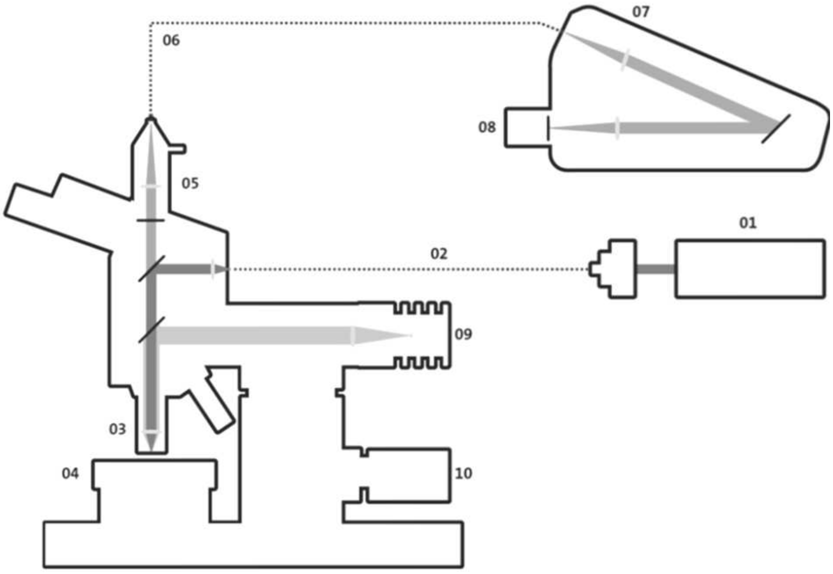

Fig. 1. Scheme of the experimental setup for the registration of Raman spectra: 01 – exciting laser; 02, 06 – connection of optical fiber with a capacity of up to 90%; 03 – tuned lens; 04 – microscope table; 05 – filter set; 07 – spectrometer STR250; 08 – piezoelectric detector; 09 – white light; 10 – screw focusing

les. It should be noted that the study of torsional vibrations of atomic groups of complex molecules is of great importance for understanding the forces acting in molecules. The data on torsional frequencies are necessary for the statistical calculation of the thermodynamic functions of molecules, and the exact values of thermodynamic functions are, in turn, required for solving various problems. Refining the frequency values or detecting the new lines in a low-frequency region plays an important role for the reliable interpretation of the entire vibrational spectrum, since low frequencies are very sensitive to small changes in force constants.

Despite the wide scientific and practical application, the study of the behavior of physical regularities associated with the manifestation of low-frequency Raman spectra, at the moment remains practically unlit in the scientific literature. There are only a few works devoted to these problems [20–22].

In the presented work, we study the intermolecular interactions in some liquid aromatic hydrocarbons such as bromobenzene (C_6H_5–Br), toluene (C_6H_5–CH_3), and dioxane ($C_4H_8O_2$) by analyzing their Raman spectra. All these molecules consist of a benzene ring, some atoms of which are substituted by other atoms or groups of atoms. So, in bromobenzene, one of hydrogen atoms is substituted by Br, in toluene – by methyl group CH_3. In dioxane, two carbon atoms of the benzene ring are substituted by oxygen atoms. The different nature of the attachment of methyl and halide groups to the benzene ring makes them interesting objects for studying the effect of a non-polar hydrocarbon substituent on the nature of the relaxation processes of molecules in the liquid phase [13, 23]. Such systematic study of entire classes of compounds with a gradually complicating structure of molecules is of particular importance. It can help to understand the role of the shape and size of molecules in the intermolecular interaction.

2. Experiment

The Raman spectra were recorded using a laser Raman spectrometer STR250 with a confocal microscope. This is a very compact flexible system with high sensitivity, which can be used for the registration of the weak Raman scattering. The scheme of the experimental setup is presented in Fig. 1.

The setup consists of a spectrometer (07) with a focal length of 250 mm with a scanning mechanism in the spectral range 50–7000 cm^{-1}, three different automatically changing diffraction lattices (600; 1200; 1800 number of lines per 1 mm), resolution of 1 cm^{-1},

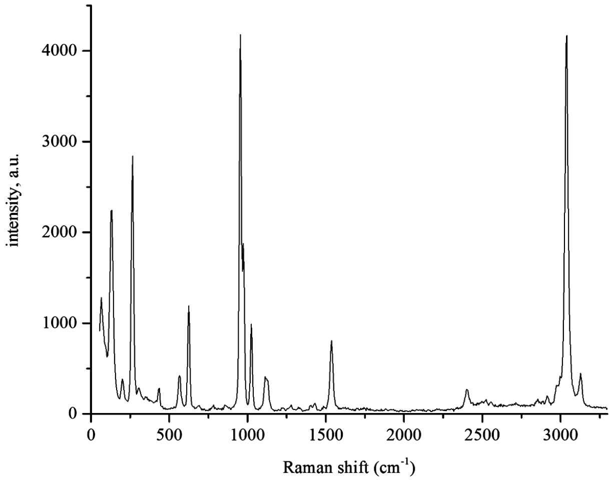

Fig. 2. Raman spectrum of liquid bromobenzene

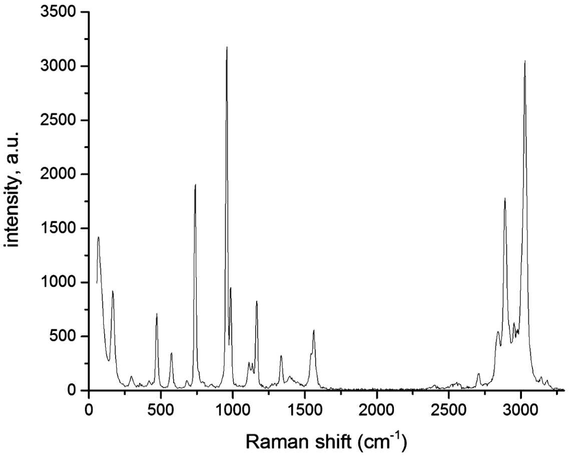

Fig. 3. Raman spectrum of liquid toluene

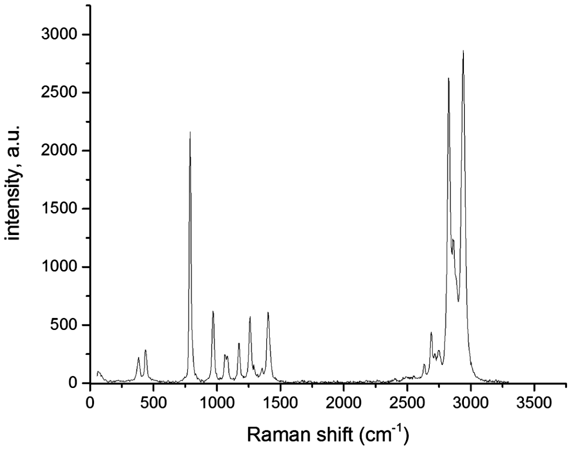

Fig. 4. Raman spectrum of liquid dioxane

and CCD (08) camera with cooling at –60 °C. It also 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 Raman spectra were recorded at an angle of 180 °C with respect to the incident light. The studied objects were thoroughly cleaned according to the procedures described in [24].

3. Results and Discussions

The general view of the registered Raman spectra of pure liquid bromobenzene, toluene, and dioxane in the spectral range 50–3300 cm^{-1} are presented in Figs. 2–4, respectively. The positions of the maxima for the registered bands of the investigated liquids and their intensities are presented in Table 1.

Table 1. **Maxima positions and intensities of Raman bands in the registered spectra of bromobenzene, dioxane, and toluene**

Bromobenzene – C_6H_5Br		Dioxane – $C_4H_8O_2$		Toluene – $C_6H_5(CH_3)$	
ν, cm^{-1}	$\Im$, (a.u.)	ν, cm^{-1}	$\Im$, (a.u.)	ν, cm^{-1}	$\Im$, (a.u.)
177	980	434	87	215	379
244	231	486	133	345	64
310	1745	835	1249	465	41
481	187	852	125	518	439
613	389	1016	305	620	165
668	696	1111	107	728	19
998	2530	1130	110	785	1300
1018	1592	1218	152	1002	2371
1068	826	1306	245	1030	650
1156	175	1338	58	1155	122
1165	344	1394	50	1179	105
1580	261	1443	235	1210	508
3077	1710	2671	77	1379	162
3142	196	2729	193	1586	136
		2785	121	1604	232
		2868	975	2442	102
		2902	464	2743	86
		2978	977	2876	216
				2931	763
				2993	258
				3019	186
				3065	1301
				3158	56
				3186	43

A characteristic difference between polyatomic and one-atomic molecules in the context of molecular spectroscopy is that, in all molecules consisting of no less than three atoms, the motion is more complex than that in atoms. In other words, along with the motion of electrons, the vibrational (periodic changes relative to the location of nuclei) and rotational (periodic changes in the orientation) movements of a molecule play an important role.

The vibrational relaxation of molecules in liquids is determined mainly by intermolecular interactions. Three mechanisms of relaxation of intramolecular vibrations are distinguished:

• energy relaxation which is the dissipation of the energy of intramolecular vibrations to all other degrees of freedom of the movement, including the translational and rotational motions of molecules and other vibrational modes;

• phase relaxation, i.e., the phase modulation of intramolecular vibrations by collisions with surrounding molecules or, in other words, local field fluctuations;

• resonant energy exchange – the exchange of energy quanta of intramolecular vibrations between oscillators of the same type.

In most liquids studied so far, the phase relaxation is the dominant mechanism of vibrational relaxation. The resonant energy exchange can make a significant contribution to the shape of the contours of bands in pure liquids with strong intermolecular interactions. Its manifestation in the vibrational spectra of liquids was studied in many theoretical and experimental works (for example, [25, 26]). It was found that, in addition to the broadening of the contours of bands in liquids with strong intermolecular interactions, the resonant energy transfer should cause a discrepancy between the positions of the maxima of bands of the same vibrations in the isotropic and anisotropic Raman scattering spectra. The frequency of the band maximum in the anisotropic spectrum (ν_{anis}) should be higher than in the isotropic one (ν_{is}, and the frequency difference $\Delta\nu = \nu_{\mathrm{anis}} - \nu_{\mathrm{is}}$ should be positive. This discrepancy effect was found in many liquids, and it has become generally accepted to explain it by the manifestation of the resonant energy exchange. The observed experimental value of $\Delta\nu$ usually does not exceed several wavenumbers.

According to our experimental data, the Raman bands of C–Br in bromobenzene, C–H in toluene, and C–O in dioxane are complex. For bromobenzene, four intense bands with frequencies of 177 cm^{-1}, 310 cm^{-1}, 998 cm^{-1}, and 3077 cm^{-1} can be roughly distinguished. The most intense line is 3077 cm^{-1}, against the background of which lies a band at 3142 cm^{-1} with relatively low intensity. This indicates that, despite the fact that all these bands are related to the same $C = H$ vibrations, their depolarization coefficients are different. When comparing the spectra of compounds with common structural features, it turned out that, in some cases, together with frequencies, the other band parameters – intensity, width and degree of depolarization – keep their value when moving from one molecule to another.

Our results showed that not every branching or other structural feature of molecules, repeated in a number of similar compounds, leads to the appearance of characteristic lines in their spectra. Only some specific groups of atoms or bonds (in some cases, individual atoms and bonds) have characteristic lines in the Raman spectra.

The special role of the characteristic structural elements is due to the fact that they are the structural units of molecules that actually manifest themselves in vibrations and, through vibrations, in Raman spectra. If there are several identical characteristic structural elements in the molecule under study, then the frequencies of the characteristic lines belonging to them coincide in many cases. Consequently, the intensities of the corresponding lines are proportional to the number of such structural elements. This phenomenon is well illustrated by the example of the lines belonging to the stretching vibrations of the CH_3 group of toluene, which has two $C = C$ bonds. In the spectrum of this compound, the intensity of the 1210-cm^{-1} line is equal to 508 relative units, whereas, in the spectra of dioxane with one $C = C$ bond, the intensity of the corresponding line is equal to 152 (see Table 1).

If, with a change in the molecule, the vibrations of the main characteristic structural element are disturbed, then the lines of the other characteristic elements appear in the spectrum more clearly. The identification of characteristic structural elements with their inherent sets of characteristic lines represents the first step toward establishing a correlation between Raman spectra and a molecule structure. The second step is to study the regularities of torsional vibrations of individual atomic groups in complex

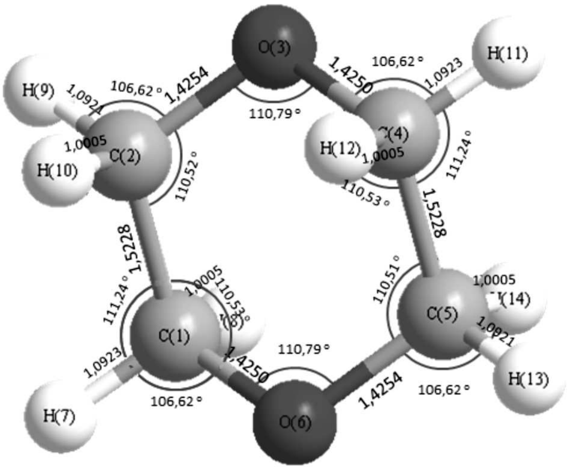

Fig. 5. Bond lengths and angles between bonds for a dioxane molecule

molecules. Torsional vibrations of individual atomic groups in complex molecules manifest themselves in the low-frequency region of vibrational spectra (from 50 to 500 cm^{-1}).

As is seen from Figs. 2–4, in the low-frequency region of the registered Raman spectra of the objects studied (100–600 cm^{-1}), a significant number of bands were registered. According to the structural formula, in addition to the torsional vibrations of the CH_3 group (177 cm^{-1}, 244 cm^{-1}, 310 cm^{-1} – for bromobenzene; 434 cm^{-1}, 486 cm^{-1} – for dioxane; 215 cm^{-1}, 345 cm^{-1}, 465 cm^{-1} – for toluene), deformational vibrations can be observed in the spectra.

The analysis shows that the interpretation of the observed bands, in particular, the assignment of low-frequency Raman bands to the torsional vibrations without special theoretical analysis is difficult, because the vibrational spectra of these liquids are very rich. Therefore, the calculation of the torsional frequencies of methyl groups in the studied liquids was carried out by a semiempirical method. If the height of a potential barrier of torsional vibrations is known, it is not difficult to find the corresponding frequency and, comparing the calculated values with experimentally observed ones, to determine the frequencies of torsional vibrations. For methyl-substituted molecules, there are no reliable data on the potential barrier height of torsional vibrations in the literature. Therefore, an attempt was made to theoretically calculate the potential barriers and the corresponding frequencies of torsional vibrations in xylenes [27].

Table 2. **Calculated end experimental frequencies of torsional vibrations**

Substance	ν, cm^{-1}	
	Experiment	Calculated
Bromobensene	266	254
Dioxane	382	369
Toluene	296	304

Semiempirical methods of calculation are based on the assumption that the height of the potential barrier is equal to the difference in the repulsion energies between both rotating parts of the molecule in the positions with the smallest and greatest repulsions. There are several methods of semiempirical calculation of barriers.

We used a semiempirical method to calculate potential barriers, but we have substantially changed this method by quantum chemical calculations in order to spread it to molecules that are more complex. For the studied molecules, the potential barriers were calculated using the potential repulsion proposed in [27]. We used also reliably determined barrier values from microwave data and accurate structural data (bond lengths and angles) determined by quantum chemical calculations. The results of quantum chemical calculations involving ithe intermolecular interaction for dioxane as an example are shown in Fig. 5.

The latter is very important because of a sharp change in the potential values with a change in the interatomic distance. Our calculation showed that the use of the repulsion function between hydrogen atoms for the molecules under study from [23]

$$U = 950.5\exp(-1.98r) - 1995\exp(-3.7r), \qquad (1)$$

where r is the distance between hydrogen atoms in angstroms, without consideration of the interaction between other atoms in the most cases gives a satisfactory agreement with experimental data. The calculated frequencies of torsional vibrations for the studied substances and the corresponding experimental values are presented in Table 2.

As is seen from Table 2, the calculated and experimental frequency values are in a satisfactory agreement. In this case, the relationship between the height of the potential barrier U and the frequency of torsional vibrations ν takes a particularly simple form

$$\nu = \frac{3}{2\pi c}\sqrt{\frac{U}{2}}. \qquad (2)$$

For the calculations, one should also know the reduced moment of inertia I_r for torsional vibrations. In the case where we have a molecule of the symmetric top type, the expression for the reduced moment of inertia is [28]

$$I_r = \mathfrak{I}_\varphi\left(1 - I_\varphi \Sigma i \frac{K_i^2}{I_i}\right), \qquad (3)$$

where i – 1, 2, 3; I_i – principal moments of inertia of the whole molecule; K_i – direction cosines of the angles formed by the axis of the top with the principal axes of inertia; I_φ – moment of inertia of the top in relation to the axis of rotation. The case of the reduced moment of inertia of torsional vibrations in the presence of several symmetric rotating groups was considered in [29].

4. Conclusion

Because the low frequency part of Raman spectra of the studied aromatic hydrocarbons – bromobenzene, dioxane, and toluene – consists of a large number of bands, it is rather difficult to assign the observed bands and to interpret the whole spectra without a special theoretical analysis. Such rich spectrum means that, along with torsional vibrations, deformational vibrations are also observed in this region. If, for molecules containing heavier groups, the bands lying in the lowest frequency region of the spectrum are usually assigned to torsional vibrations, in the case of the torsional vibrations of methyl groups, the corresponding bands can lie in a relatively wide spectral region up to 500 cm^{-1}. This is because the moment of inertia of a methyl group is small. Considering the experimental data, it is clear that it is difficult to distinguish a certain group of bands of the investigated substances by some distinctive features. The bands observed in the low-frequency region have different widths and intensities.

1. B.J. Ka, E. Geva. Vibrational energy relaxation of polyatomic molecules in liquid solution via the linearized semiclassical method. *J. Phys. Chem. A* **110**, 9555 (2006).
2. S.A. Kirillov, A. Morresi, M. Paolantoni. Recovery of the depolarization ratio of single lines fromoverlapping isotropic and anisotropic Raman profiles and assignment of molecular vibrations, with special reference to toluene and toluene-d$_8$. *J. Raman Spectrosc.* **38**, 383 (2007).
3. D. Wang, K. Mittauer, N. Reynolds. Raman scattering of carbon disulfide: The temperature effect. *Am. J. Phys.* **77**, 1130 (2009).
4. J. Lindner, P. Vohringer, M.S. Pshenichnikov, D. Cringus, D.A. Wiersma, M. Mostovoy. Vibrational relaxation of pure liquid water. *Chem. Phys. Lett.* **421**, 329 (2006).
5. H.J. Bakker, A.J. Lock, D. Madsen. Strong feedback effect in the vibrational relaxation of liquid water. *Chem. Phys. Lett.* **384**, 236 (2004).
6. A.J. Lock, H.J. Bakker. Temperature dependence of vibrational relaxation in liquid H_2O. *J. Chem. Phys.* **117**, 1708 (2002).
7. V. Pogorelov, L. Bulavin, I. Doroshenko, O. Fesjun, O. Veretennikov. The structure of liquid alcohols and the temperature dependence of vibrational bandwidth. *J. Mol. Struc.* **708**, 61 (2004).
8. L. Bulavin, I. Doroshenko, O. Lizengevych., V. Pogorelov, L. Savransky, O. Veretennikov. Raman study of molecular associations in methanol. In: *Proceedings of SPIE – The International Society for Optical Engineering* **5507**, 138 (2004).
9. F.H. Tukhvatullin, V.E. Pogorelov, A. Jumabaev, H. Hushvaktov, A. Absanov, A. Shaymanov. Aggregation of molecules in liquid methyl alcohol and its solutions. Raman spectra and ab initio calculations. *J. Mol. Struct.* **881**, 52 (2008).
10. F.H. Tukhvatullin, V.E. Pogorelov, A. Jumabaev, H. Hushvaktov, A. Absanov, A. Usarov. Polarized components of Raman spectra of O–H vibrations in liquid water. *J. Mol. Liquids.* **160**, 88 (2011).
11. F.H. Tukhvatullin, A. Jumabaev, G. Muradov, H. Hushvaktov, A. Absanov. Raman spectra of C–H vibrations of acetonitrile in aqueous and other solutions. Experimental results and ab initio calculations. *J. Raman Spectrosc.* **36**, 932 (2005).
12. Jr. C.W. Bauschlicher, A. Ricca. On the calculation of the vibrational frequencies of C_6H_4. *Chem. Phys. Lett.* **566**, 1 (2013).
13. 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. *Ukr. J. Phys.* **56**, 1178 (2011).
14. B. Eshchanov, Sh. Otajonov, A. Isamatov, D. Babajanov. Dynamics of relaxation processes in liquids: Analysis of oscillation and orientation spectra. *J. Mol. Liq.* **202**, 148 (2015).
15. Y. Takasu, S. Matsumoto, Y. Fujii, I. Nishio. Raman study of the low temperature behavior of tetrahydrofuran molecule in the cage of clathrate hydrate. *Chem. Phys. Lett.* **627**, 39 (2015).

16. V. Pogorelov, A. Yevglevsky, I. Doroshenko, L. Berezovchuk, Yu. Zhovtobryuch. Nanoscale molecular clusters and vibrational relaxation in simple alcohols. *Superlattices and microstructures* **44**, 571 (2008).
17. A. Vasylieva, I. Doroshenko, Y. Vaskivskyi, Y. Chernolevska, V. Pogorelov. FTIR study of condensed water structure. *J. Mol. Struct.* **1167**, 232 (2018).
18. V. Pogorelov, Y. Chernolevska, Y. Vaskivskyi. Structural transformations in bulk and matrix-isolated methanol from measured and computed infrared spectroscopy. *J. Mol. Liq.* **216**, 53 (2016).
19. I. Doroshenko, V. Balevicius, G. Pitsevich, K. Aidas, V. Sablinskas, V. Pogorelov. FTIR/PCA study of propanol in argon matrix: The initial stage of clustering and conformational transitions. *Fiz. Nizk. Temp.* **40**, 1384 (2014).
20. R.L. Redington. The infrared spectrum and barriers hindering internal rotation in H_2S_2, CF_3SH, and CF_3SD. *J. Mol. Spectr.* **9**, 469 (1962).
21. B. Eshchanov, Sh. Otajonov, Kh. Rakhmatullaeva. Application of Raman scattering of light to study the structure of molecules. *Intern. J. Sci. & Engin. Research.* **9**, 1532 (2018).
22. G.A. Pitsevich, I.Yu. Doroshenko, V.Ye. Pogorelov, E.N. Kozlovskaya, T. Borzda, V. Sablinskas, V. Balevicius. Long-wave Raman spectra of some normal alcohols. *Vibr. Spectroscopy.* **72**, 26 (2014).
23. Sh. Otajonov, B. Eshchanov, A. Isamatov. Manifestation of substance molecular structure in temperature effects of light scattering. *J. Chem. Chem. Engin.* **7**, 791 (2013).
24. A. Weissberger, jr., E.S. Proskauer, J.A. Riddik, E.E. Toops. *Organic Solvents, Physical Properties and Methods of Purification* (Interscience, 1955).
25. B. Desbat, P. Huong. Structure of liquid hydrogen fluoride studied by infrared and Raman spectroscopy. *J. Chem. Phys.* **78**, 6377 (1983).
26. D.E. Logan. On the isotropic Raman spectra of isotopic binary mixtures. *Mol. Phys.* **58**, 97 (1986).
27. V. Magnasco. An empirical method for calculating barriers to internal rotation in simple molecules. *Il Nuovo Cimento.* **24**, 425 (1962).
28. B.L. Crawford. The partition functions and energy levels of molecules with internal torsional motions. *J. Chem. Phys.* **8**, 273 (1940).
29. W.G. Fateley, F.A. Miller. Torsional frequencies in the far infrared – II: Molecules with two or three methyl rotors. *Spectrochim. Acta.* **18**, 977 (1962).

Received 06.10.2019

Б. Єшчанов, Ш. Отажонов, Г. Мухамедов,
І. Дорошенко, О. Карпова, Ш. Аллакулієва

ЕКСПЕРИМЕНТАЛЬНЕ ДОСЛІДЖЕННЯ СПЕКТРІВ КОМБІНАЦІЙНОГО РОЗСІЯННЯ СВІТЛА ДЕЯКИХ АРОМАТИЧНИХ ВУГЛЕВОДНІВ

Резюме

Досліджено коливальні спектри рідинних ароматичних вуглеводнів – бромбензолу, діоксану, толуолу – в широкому інтервалі частот методом комбінаційного розсіяння світла. З отриманих даних по низькочастотним спектрам встановлено прояв торсіонних коливань окремих груп атомів. Показано можливість використання напівемпіричного методу для розрахунку потенціальних бар'єрів метильної та галоїдної груп похідних бензолу.