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STUDY OF THE INFLUENCE OF SUBSTITUTED BROMINE ATOMS IN THE MOLECULAR STRUCTURE ON THE RAMAN SPECTRA OF THE MOLECULE

(Submitted by Uz AS academician K.M.Mukimov)

Introduction. Many studies have been conducted on aromatic substances with benzene as their molecular structure, unique physical properties, and wide industrial applications [1,2]. In this work [3], 1,2-dibromobenzene was studied by FT-IR and FT-Raman methods and vibrational analysis was performed. It was found that the wave numbers of C-C bond vibrations were shifted away from the expected range due to the presence of C-Br and C-Cl bonds [4]. Dibromobenzenes (1,2-, 1,3-, 1,4-$C_6H_4Br_2$) were studied using density functional theory (DFT) and second-order Mueller-Plesset theory (MP2), and the dipole moment and molecular orbital boundaries were determined. It was assumed that the electronegativity of bromine atoms in 1,4-$C_6H_4Br_2$ is more negative than in 1,2- and 1,3-$C_6H_4Br_2$ [5]. Despite the large amount of experimental data on the regularities of various physical properties of benzenes with the addition of halide elements, there is currently no consensus on the processes occurring in these liquids at the molecular level. This situation indicates the need for a more extensive study of these objects. This research work is also a logical continuation of work in this direction.

Object and methodology of the study. The objects of the study were purposefully selected bromobenzene–C_6H_5Br and o-dibromobenzene–$C_6H_4Br_2$ molecules, which are intended to study the contribution of atoms of the halogen group substituted in the benzene ring to the Raman spectrum and the regularities of relaxation processes.

The objects of the study were purchased from the American company "Sigma-Aldrich". The purity of the object of the study is of great importance when recording the Raman spectrum. It is necessary that it is completely free from the influence of foreign particles. Their purity is 99.5% and they were used to record the spectra without additional purification. The chemical structure of the bromobenzene and o-dibromobenzene molecules is presented in fig.1.

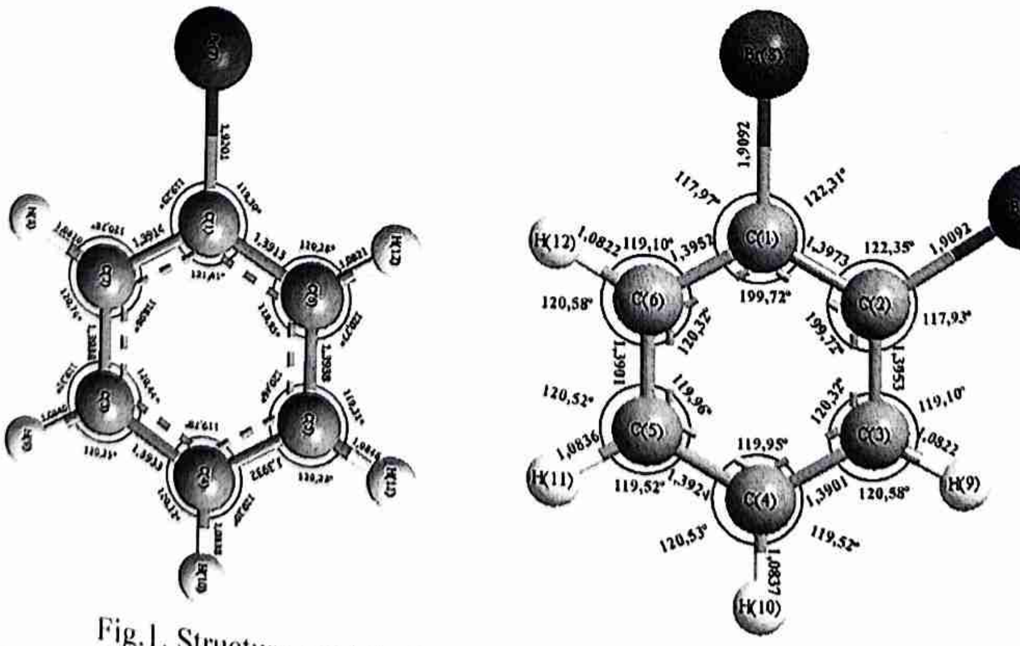


Fig.1. Structure model of bromobenzene and o-dibromobenzene molecules

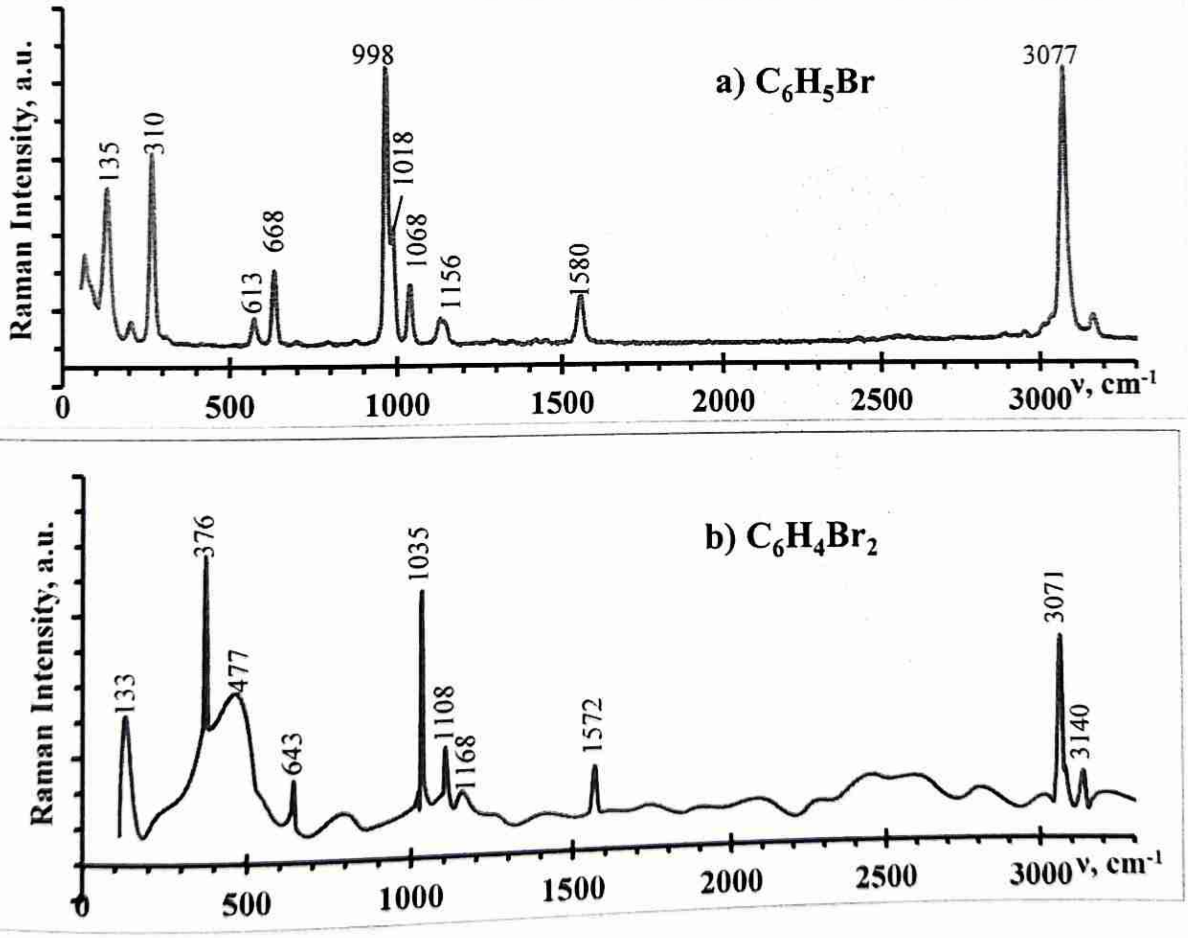
The Raman scattering spectrum of light was recorded on a spectrometer based on the Renishaw InVia Raman spectrometer. Laser radiation with wavelengths of 532 nm and 785 nm was used as a light source.

To determine the theoretical values of the optimal geometric parameters and normal vibration frequencies of the molecules, quantum-chemical calculations were performed using the ORCA program using the density functional theory (DFT) method and the (B3LYP) HF/6-311G** basis set.

Results and discussion.

Raman spectra were recorded for the research objects using laser radiation in the visible (λ=532nm) and near-infrared (λ=785nm) regions, the frequency distribution of the spectrum is shown in fig.2. According to the analysis of the images, the Raman spectrum of o-dibromobenzene was affected by the fluorescence effect, while the Raman spectrum of bromobenzene was not affected by the fluorescence effect.

The background of the fluorescence effect in the Raman spectrum of the o-dirombenzene molecule when excited by short-wavelength light can be explained by the fact that the difference between the molecular orbitals decreases as a result of the substitution of a pair of Br atoms in the halide group instead of two H atoms in the molecular structure. In this article, the spectrum obtained with a laser with a wavelength of 785 nm (fig.2c) was used for analysis.



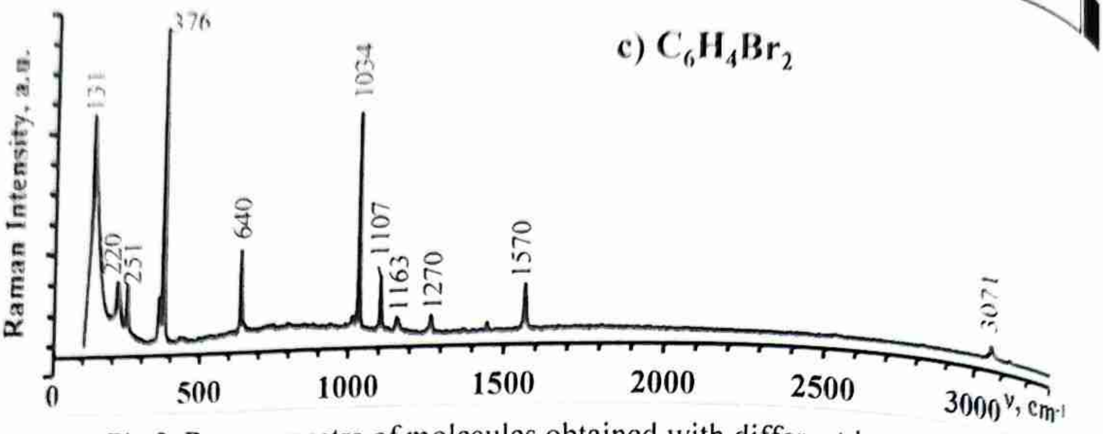


Fig.2. Raman spectra of molecules obtained with different lasers: a)532 nm; b)532 nm; c)785 nm

The spectral bands in the lower frequency range of the Raman spectrum appear as a result of deformation vibrations of the molecule and rotational vibrational motions of one part of the molecule relative to another. The experimental results obtained for the O-dibromobenzene molecule show that the intensity of the spectral band corresponding to the frequency of 376 cm^{-1} is much greater than that of the other spectral bands, and we consider the appearance of the spectrum to be associated with the laws of rotational vibrational motion associated with the C-Br bond. In the Raman spectrum of bromobenzene, the spectral band corresponding to the rotational vibrational motions of the molecule corresponds to the value of 310 cm^{-1}.

Of course, in order to come to a scientific conclusion that the appearance of the spectrum in the low frequency range is related to the rotational-vibrational motion of the molecule, we need to compare the values of the frequency determined through theoretical calculations with the values found in experiments.

An empirical method can be used to calculate the theoretical value of the optical spectrum frequency resulting from the rotational vibrational motion of the o-dibromobenzene molecule [6]. Based on this approach, theoretical values of the potential depth and frequency for bromobenzene, dioxane, and pyridine molecules have been determined [7,8].

The potential depth "U" of the o-dibromobenzene molecule is considered to be proportional to the difference in the escape energy of the molecules in rotational motion. Based on this approach, the potential depth value "U" found by theoretical calculations for the o-dibromobenzene molecule is "U"=4037 cal/mol, and the experimental value of the frequency is vexp. = 376 cm^{-1}, and the value found by theoretical calculations is vnaz. = 375 cm^{-1}. The experimental and theoretical values of the frequency are almost equal, the difference does not exceed 1 cm^{-1}. This suggests that the formation of the spectral band corresponding to the low frequency is due to the rotational-vibrational motion of the o-dibromobenzene molecule.

Since the laws of molecular motion are related to the arrangement of atoms, quantum chemical calculations have determined the arrangement of atoms in the aniline molecule, as well as the bond lengths and angles between them (fig.1). This information is of practical importance and may be useful in the synthesis of promising chemical substances.

When comparing the Raman spectra of the studied objects with the Raman spectrum of benzene given in the scientific literature, the formation of additional spectral bands and frequency shifts of the spectral bands were observed. For example, in the high-frequency region, the spectral band with a frequency of 3077 cm^{-1} associated with the symmetric valence vibrations of the C-H bond atoms of bromobenzene underwent a blue shift of 15 cm^{-1}. We assume that this shift is due to the hyperconjugation interaction of the monosubstituted heavy Br atom with the aromatic ring. The small difference in the blue shift of the spectral band associated with the symmetric valence vibrations of the C-H bond atoms in the Raman spectrum of o-dibromobenzene means that the above conclusion is valid only for mono-substitutions.

Conclusions. For the first time, the laws of mono- and di-substitution in the molecular structure were studied using the Raman spectrum in a wide spectral range (100÷3500 cm^{-1}), which reflects the laws of motion of bromobenzene and o-dibromobenzene molecules. Based on the experimental results and theoretical calculations, it was suggested that the high-intensity spectral band formed at low frequencies is associated with the rotational-vibrational motion of the molecule. It was found that the frequency shift of the spectral band associated with the C-H valence vibrations in the Raman spectrum of the molecule depends on the masses of the atoms in the substituted halide group, and this connection is relevant for mono-substitutions.

It was suggested that the mechanisms of formation of experimentally observed Raman spectra, including the regularities of rotational-vibrational, deformational, and valence vibrational motions, are related to the short- and long-range ordering of molecules that occurs as a result of intermolecular interactions in liquids.

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REFERENCES

1. Zaczek A.J., Catalano L., Naumov P., Korter T.M., Mapping the polymorphic transformation gateway vibration in crystalline 1,2,4,5-tetrabromobenzene. // Chem. Sci., 2018, Vol.10, pp.1332-1341.

2. Jeyavijayan S., Spectroscopic (FTIR, FT-Raman), molecular electrostatic potential, NBO and HOMO–LUMO analysis of P-bromobenzene sulfonyl chloride based on DFT calculations. // Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, 2015, Vol.136, Part B, pp.890-899, ISSN 1386-1425.

3. Shakila G., Periandy S., Ramalingam S. Molecular Structure and Vibrational Analysis of 1-Bromo-2-Chlorobenzene Using ab initio HF and Density Functional Theory (B3LYP) Calculations.// Journal of Atomic and Molecular Physics. 2011.

4. Shakila G., Periandy S., Ramalingam S.. Vibrational spectroscopic investigation (FT-IR and FT-Raman) on 1,2-dibromobenzene by HF and hybrid (LSDA and B3LYP) calculations. // Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, 2012, Vol.86, pp.449-455, ISSN 1386-1425.

5. Tsang-Hsiu Wang, Chen-Shuo Hsu, Wen-Lin Huang, Yih-Hsing Lo. Structures, molecular orbitals and UV–vis spectra investigations on Br2C6H4: A computational study. // Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, 2013, Vol.115, pp.866-875, ISSN 1386-1425.

6. Magnasco V., An empirical method for calculating barriers to internal rotation in simple molecules. // Nuovo Cimento, 1962, Vol. 24, P.425.

7. Eshchanov B., Otajonov Sh., Mukhamedov G., et al., Experimental study of Raman spectra of some aromatic hydrocarbons. // Ukrainian Journal of Physics, 2020, Vol.65, No.4, pp.284-290.

8. Khudoyberdieva D., Otajonov Sh., Eshchanov B., H.Eshquvatov, N.Abdullayev, Mechanisms of Raman scattering spectrum of light from pyridine molecule in the lower frequency range. // Results in Optics, 2024, 100685, ISSN 2666-9501. https://doi.org/10.1016/j.rio.2024.100685

MUNDARIJA

O'z FA akademigi U.A.Rozikov, I.T.Jo'rayev
Volterra operatorlarining idempotent o'lchovlar to'plamidagi dinamik sistemalari 3

A.B.Xasanov, U.O.Xudayorov
Davriy cheksiz zonali funksiyalar sinfida manbali Liuvill tenglamasi uchun aralash masala 8

X.M.Shadimetov, O.X.Gulomov
Tez tebranuvchi funksiyalarning integrallarini hisoblash uchun optimal kvadratur formulalar 14

A.Abdusattarov
Yemirilishni hisobga olgan holda takroriy-o‘zgaruvchan yuklanishlar ta`siridagi yupqa sterjen-quvurlarning deformatsiyalanishini chiziqsiz modeli 20

Ўз Р ФА академиги Р.А.Муминов, Х.Собиров, Ф.Г.Муллагалиева, У.М.Насимов, Т.З.Ахтамов
Қуёш элементларига асосланган фотоэлектрик тизимлар 27

Ш.Отажонов, Д.Б.Худойбердиева
Молекулалар структурасида ўрин алмашган бром атомларини молекуланинг раман спектрларига таъсирини тадқиқ қилиш 36

F.A.Rasulova
Gigant dipol rezonansning izospin kengayishi konsepsiyasini $^{96\text{-}98}$Mo yadrolarida (γ,p) reaksiyalarda sinab ko‘rish 41

O'zR FA academigi I.I.Sodiqov, T.B.Fayziyev, S.A.Boytelesov, F.R.Kungurov, Sh.A. Aliqulov, D.P. Tadjibayev
VVR-SM reaktorining faol zonasi uchun uran-235 ning o‘rtacha yonishiga bog‘liq holda samarali ko‘payish koeffitsientining xavfsiz ishlash chegaralarini aniqlash 46

L.O.Xajiyev, O'zR FA akademigi I.I.Sadikov, A.M.Abdukayumov, Z.O.Usarov
^{99m}Tc-PSMA-11 radiofarmatsevtik preparatining radiokimyoviy tozaligini aniqlashning analitik uslubini ishlab chiqish va validatsiya qilish 52

Sh.Yunusxonov, I.Dj.Kurbanbayev, Z.L.Abdurazakova
Turlararo duragaylar populyatsiyasidan yaxshilangan g’o’za navlarini tanlashni tezlashtirish uchun oqsil markerlarlaridan foydalanish imkoniyati 59

Н.И.Бозоров, Н.Ш.Ашуров, У.У. Жумартова, В.О.Кудышкин, А.А.Атаханов, ЎзР ФА академиги С.Ш.Рашидова
Полиакриламиднинг техник углерод билан ўзаро таъсири 64

D.S.Isomitdinova, G.A.Ixtiyarova, J.M.Sharopov
Apis mellifera xitozani asosida sintez qilingan xitozan/mis polimetallokompleksining strukturaviy xossalari 69

S.S.Omonova, U.J. Ishimov, V.U.Khujaev, Sh.M.Adizov, S. F. Aripova
O‘zbekistonning Farg‘ona vodiysida o‘sadigan *Heliotropium* turkumiga mansub o‘simliklarning alkaloidlari va ularning mass-spektrometrik tahlili 74

U.B.Xamidova, Ye.O.Terenteva, E.G.Yusupova, G.A.Piyakina, S.A.Ikramov, D.R.Mansurov, Sh.S.Azimova
Sintetik komplekslar orasida o‘smaga qarshi agentlarni izlash 82

O'zR FA akademigi A.S.Turayev, B.I.Muxitdinov, A.A.Boydedayev, H.H.Qirg'izbayev, D.M.Amonova, M.Sh.Karimov, N.S.Normahamatov
Gialuron kislotaning sulfat hosilalarini olish va ularning strukturalarini o’rganish 89

С.Б.Хайтметова, ЎзР ФА академиги А.С.Тураев, Г.А.Халилова, Д.С. Сагдуллаева, С.Р. Маккамбоева
Буғдой ўсимлиги иккиламчи хомашёсидан экстракция усулида мой ажратиб олиш 95

G.B.Sidrasulieva, A.E.Aytmuratova, N.T.Kattaev, H.I.Akbarov
O-g-C3N4/NiO nanokompozitining sintezi, identifikatsiyasi va termik barqarorligi 100