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VIBRATIONAL DYNAMICS AND RAMAN SPECTRA OF AROMATIC MOLECULES WITH HEAVY HALIDE ATOMS: BROMOBENZENE AND ORTHO-DIBROMOBENZENE

Annotation. *This study investigates the vibrational dynamics of heavy halide atoms in the structure of bromobenzene and ortho-dibromobenzene molecules, as well as their manifestation in Raman spectra. Using experimental Raman spectra, vibrational frequencies and intensities related to molecular symmetry were determined, and spectral differences between mono- and dihaloaromatic molecules were analyzed. In the ortho-dibromobenzene molecule, an increase in the number of spectral lines and a redistribution of intensities were observed as a result of the heavy atom effect. The results were interpreted using quantum chemical calculations and showed good agreement with experimental data. The results of the study will provide a scientific basis for a more thorough interpretation of the spectral properties of aromatic halogen compounds and an assessment of the heavy atom effect in molecular spectroscopy.*

Keywords: *Raman spectrum, heavy atom effect, molecular symmetry, bromobenzene, ortho-dibromobenzene.*

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OG'IR GALOID ATOMLI AROMATIK MOLEKULALARNING TEBRANISH DINAMIKASI VA RAMAN SPEKTRLARIDA NAMOYON BO'LISHI: BROMBENZOL VA ORTO-DIBROMBENZOL

Annotatsiya. *Ushbu tadqiqot brombenzol va orto-dibrombenzol molekulalari strukturasida og'ir galoid atomlarining tebranish dinamikasini hamda Raman spektrlarida namoyon bo'lish qonuniyatlarini o'rganishga bag'ishlangan. Eksperimental Raman spektrlari asosida molekulalarning simmetriyasi bilan bog'liq tebranish chastotalari va intensivliklari aniqlanib, mono- va digaloidli aromatik molekulalar orasidagi spektral farqlar tahlil qilindi. Ortodibrombenzol molekulasida og'ir atom effekti natijasida spektral chiziqlar sonining ortishi hamda intensivliklarning qayta taqsimlanishi kuzatildi. Olingan natijalar kvant-kimyoviy hisoblashlar yordamida izohlanib, eksperimental ma'lumotlar bilan yaxshi mos kelishini ko'rsatdi. Tadqiqot natijalari aromatik galoid birikmalarning spektral xususiyatlarini chuqurroq talqin qilishga va molekulyar spektroskopiyada og'ir atom ta'sirini baholashga ilmiy asos bo'ladi.*

Kalit so'zlar: *Raman spektri, og'ir atom effekti, molekulyar simmetriya, brombenzol, orto-dibrombenzol.*

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ДИНАМИКА КОЛЕБАНИЙ И СПЕКТРЫ РАМАНА АРОМАТИЧЕСКИХ МОЛЕКУЛ С ТЯЖЕЛЫМИ ГАЛОИДНЫМИ АТОМАМИ: БРОМБЕНЗОЛ И ОРТО-ДИБРОМБЕНЗОЛ

Аннотация. *Данное исследование посвящено изучению колебательной динамики атомов тяжелых галоидов в структуре молекул бромбензола и орто-дибромбензола, а также закономерностей их проявления в спектрах Рамана. На основе экспериментальных спектров Рамана были определены колебательные частоты и интенсивности, связанные с симметрией молекул, и проанализированы спектральные различия между моно- и дигалоидароматическими молекулами. В молекуле орто-дибромбензола наблюдалось увеличение числа спектральных линий и перераспределение интенсивностей в результате эффекта тяжелого атома. Полученные результаты были интерпретированы с использованием квантово-химических расчетов и показали хорошее соответствие экспериментальным данным. Результаты исследования обеспечат научную основу для более глубокой интерпретации спектральных свойств ароматических галоидных соединений и оценки эффекта тяжелого атома в молекулярной спектроскопии.*

Ключевые слова: *Рамановский спектр, эффект тяжелых атомов, молекулярная симметрия, бромбензол, орто-дибромбензол.*

Introduction. It is known that the study of physical laws associated with relaxation processes occurring in condensed media under the influence of electromagnetic radiation is currently one of the urgent problems of both fundamental and practical importance. As a result of such studies, it becomes possible to obtain scientifically sound information about the structure of the medium and develop important recommendations for practice on their basis. Raman scattering spectra of light are currently one of the most effective and informative methods for studying the vibrational-rotational motions of molecules of condensed media in energy levels and the laws of relaxation processes associated with them [1–11].

Despite the large amount of experimental data on the various physical properties of benzene derivatives containing halide compounds, there is currently no single, fully formed idea of the mechanism of processes occurring at the molecular level in these liquids. This indicates the need for a more in-depth and comprehensive study of this class of compounds. This work is a logical continuation of the research being conducted in this direction.

In this study, the molecules bromobenzene – C_6H_5Br and ortho-dibromobenzene - $C_6H_4Br_2$, which have asymmetric properties in terms of the polarizability tensor, were purposefully selected as objects, and the aim was to study the contribution of halogen atoms substituted in the benzene ring to the Raman spectrum and the laws of relaxation processes. The spatial structure model of the research objects is presented in Figure 1.

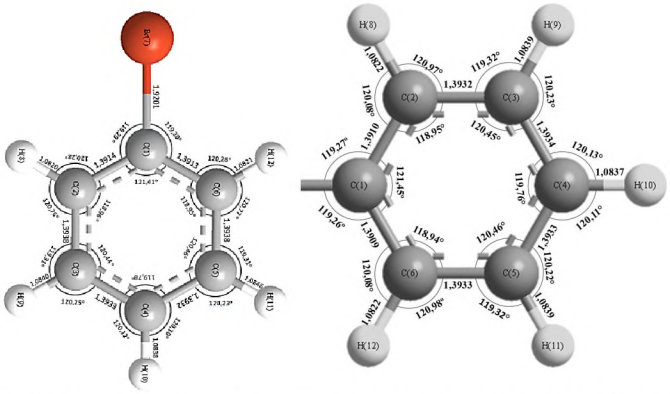


Figure 1. Model of the molecular structure of bromobenzene and ortho-dibromobenzene.

Research Methodology. The research objects were purchased from Sigma-Aldrich, USA. Their purity was 99.5% and they were used to record spectra without additional purification.

The Raman spectra of the research objects were recorded on a spectrometer (in the frequency range of 50–4000 cm^{-1}) based on the InVia Raman spectrometer of the Renishaw company. The spectral resolution of the Raman spectrometer was 0.3 cm^{-1}, and the spatial resolution was 0.25 μm. Lasers with a power of 100 mW and a wavelength of 785 nm were used as the light source. The optimal geometric parameters of the molecules and the theoretically calculated Raman spectrum were performed using the ORCA program, using the density functional theory (DFT) method and the (B3LYP) HF/6-311G** basis set [12].

Analysis and results. The frequency distribution of the Raman spectra recorded for the research objects is shown in Figure 2.

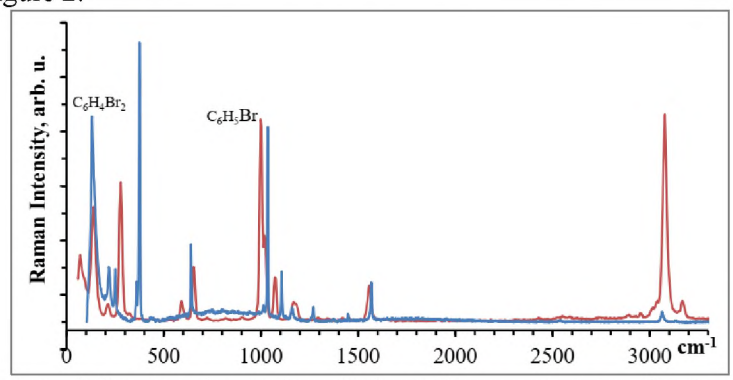


Figure 2. Overview of the experimentally obtained Raman spectrum for bromobenzene and ortho-dibromobenzene molecules.

The results of the study showed that several spectra with different intensities were observed in the frequency range of 100–3500 cm^{-1}. We are more interested in the spectral contours in the lower frequency range of 100–1100 cm^{-1}, since this region is considered the "fingerprint" region of the molecule in the Raman spectrum, and it is in this range that regularities associated with changes in the molecular structure are observed.

In the lower frequency region of the Raman spectrum of ortho-dibromobenzene, new spectral bands with frequency values of 222 cm^{-1} and 252 cm^{-1} were observed. The appearance of these spectral bands is associated with the out-of-plane and in-plane rotational-diffusion motions of the ortho-dibromobenzene molecule, respectively.

The optical spectrum corresponding to the lower frequency, which is formed by the rotational-oscillating motion of the molecule, has hardly been studied. In some literature, there is information that the lower frequencies correspond to the spectral range of 900 cm^{-1}. The spectrum in the spectral range smaller than 50–100 cm^{-1} is difficult to observe experimentally, since it is influenced by the Rayleigh scattering spectrum. It should be noted that the study of the rotational-oscillating motion vibrations of atomic groups of molecules is of great importance for understanding intermolecular forces.

The Raman spectrum of ortho-dibromobenzene differs significantly from that of bromobenzene in the intensity distribution of the spectral bands in the lower frequency range, due to the fact that the electron cloud of the molecule is significantly deformed due to the pair of halogen bromine atoms that are replaced in the structure. Due to this, this molecule has a higher polarizability compared to bromobenzene. The large electron cloud of heavy halogen atoms is more easily redistributed under the influence of an external electromagnetic field, which enhances the polarizability properties of the molecule.

Of course, in order to come to a scientific conclusion that the appearance of the spectrum in the lower frequency range is associated with the rotational-swinging motions of the molecule, we need to compare the values of the frequency determined by theoretical calculations with the values found in the experiment. Figure 3 shows the general appearance of the theoretically calculated Raman spectrum for the ortho-dibromobenzene molecule. According to the analysis of the experimentally obtained and theoretically calculated frequency values, small shifts in the frequencies associated with some vibrations were observed. Typically, theoretically calculated frequency values are higher than the corresponding experimentally obtained frequency values due to the influence of electron correlation and the shortcomings of the Hartree-Fock basis set.

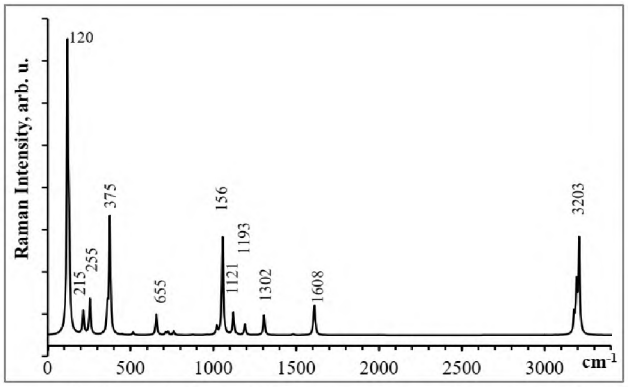


Figure 3. Overview of the theoretically calculated Raman spectrum for the ortho-dibromobenzene molecule.

To account for errors in the theoretical calculation of the frequency value, a "scaled" scale was used and multiplied by 0.9668, which was found to be in relatively good agreement with the experimental results. The total number of theoretically calculated spectra was consistent with the number of spectra obtained from the experiment.

Conclusion. In this study, the main results obtained by analyzing the vibrational dynamics of bromobenzene and ortho-dibromobenzene and their agreement with theoretical and experimental data are discussed in detail. In particular, the low-frequency rotational-diffusion vibrations associated with heavy bromine atoms are separately considered and their effect on the molecular structure and Raman spectral features is evaluated. Also, the molecular symmetry changes caused by the introduction of bromine atoms into the benzene ring and its effect on the vibrational frequencies and Raman intensities are clearly shown, which serves to further understand the dynamic behavior of molecules. These results will help to improve molecular models for dihalobenzene derivatives and more accurately assess their physicochemical properties.

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CALCULATION OF ELECTRONIC PROPERTY CHANGES IN Zn-DOPED α-SiO_2 USING DENSITY FUNCTIONAL THEORY

Annotation. *In this study the Vienna Ab-initio Simulation Package (VASP 6. 5) with the Heyd–Scuseria–Ernzerhof 2006 (HSE06) hybrid functional was used to calculate the variation in the electronic density of states and band gap of α-SiO_2 upon Zn doping using density functional theory (DFT). For undoped silicon dioxide calculations showed a band gap of 9. 06 eV. The band gap dropped to 0. 839 eV when Zn was added at a concentration of 8. 33 percent in relation to silicon atoms. According to an analysis of the electronic density of states the hybridization between the O p-valence orbitals and the Zn d-valence orbitals was responsible for this band gap narrowing. This led to a shift in the valence band and the formation of new electronic states within the forbidden gap. According to the obtained results Zn incorporation into α-SiO_2 increases the materials sensitivity to light in the infrared spectrum and induces semiconductor-like characteristics in terms of band gap energy. The theoretical basis for the possible use of Zn-doped SiO_2 in semiconductor materials sensors photocatalysts and optoelectronic device technologies is provided by these findings.*

Key words:*VASP, HSE06, Silicon dioxide, PBE, TDOS, PDOS*

ZICHLIK FUNKSIONAL NAZARIYASI ASOSIDA Zn KIRITILGAN α -SiO_2 NING ELEKTRON XOSSASIDAGI O‘ZGARISHLARNI HISOBLASH

Annotatsiya.*Ushbu tadqiqotda zichlik funksional nazariyasi (DFT) asosida rux (Zn) kiritilgan α-SiO_2 materialining elektron holatlar zichligi va taqiqlangan zona kengligidagi o‘zgarishlarni hisoblash uchun Heyd–Scuseria–Ernzerhof 2006 (HSE06) gibrid funksionali bilan Vienna Ab-initio Simulation Package (VASP 6.5) dasturidan foydalanildi. Doplanmagan kremniy dioksid uchun hisoblashlar natijasida ta-*