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ANALYSIS OF THE DEFORMATION VIBRATION FREQUENCIES OF CHLOROBENZENE MOLECULES USING RAMAN SPECTROSCOPY

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Abstract
In this article, the vibrational spectra of chlorobenzene, a liquid aromatic hydrocarbon, were studied over a wide frequency range using Raman spectroscopy. The modes of vibration of atoms at different frequencies are determined from the information obtained from the spectra. The feasibility of using a semi-empirical method to calculate potential barriers for chlorobenzene is demonstrated. Analysis using quantum chemistry methods revealed that the low-frequency part of the vibrational spectra primarily consists of stretching vibrations of the molecules.

Keywords: Vibrational spectroscopy, chlorobenzene, deformation vibrations, potential barrier.

Introduction

Vibrational spectra of molecules are characterized by the positions of the lines, their intensities, and their shapes. Studying how these parameters change due to molecular interactions provides insights into the structure of liquids [1-3] and molecular dynamics. Intermolecular interactions in liquids affect the force constants of interatomic bonds within the molecules.

Non-covalent interactions play a crucial role in many chemical and biological processes. The most common of these interactions is hydrogen bonding. Although hydrogen bonds are generally weaker than covalent bonds, they are essential for the formation of molecular clusters that are vital for the functioning of living organisms, such as DNA and proteins [4,5] T he dynamic nature of these interactions causes line broadening in the vibrational spectra of liquids. The presence of relatively long-term local order, associated with the formation of various complexes and associations in the liquid, is reflected in changes in the frequencies of intramolecular vibrations. These changes are clearly observed in the lines corresponding to the vibrations of the atoms involved in the molecular interactions within the associations [6].

In the presented work, we study intermolecular interactions in the liquid aromatic hydrocarbon chlorobenzene (C_6H_5Cl) by analyzing Raman spectra. Chlorobenzene consists of a benzene ring with one hydrogen atom replaced by a chlorine (Cl) atom. The different nature of various substituents attached to the benzene ring makes chlorobenzene a useful model for studying the influence of nonpolar hydrocarbon groups on the relaxation processes of molecules in the liquid phase [7-9].

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Raman spectra were recorded using a laser Raman spectrometer with a wavelength of 785 nm. This method features a compact and flexible system with high sensitivity, suitable for recording weak scattering spectra. The experimental setup is illustrated in Fig. 1.

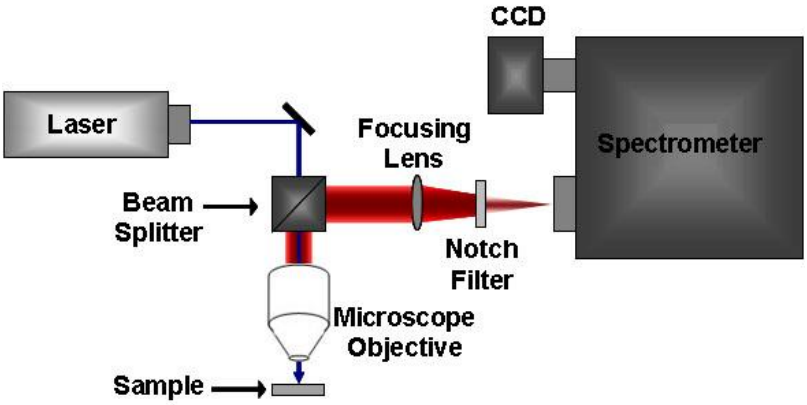

Fig.1 Scheme of the experimental device for recording Raman spectra.

The setup includes a scanning mechanism in the spectral range of 100-5000 cm^{-1} and a 785 nm excitation laser.

It is important to study the torsional vibrations of atomic groups in complex molecules to understand the forces acting on them. Information about the frequencies of rotational movements is crucial for the statistical calculation of thermodynamic functions. Accurate values of these functions are essential for solving various problems. Clarifying frequency values or detecting new lines in the low-frequency range is vital for the reliable interpretation of the entire vibrational spectrum, as low frequencies are highly sensitive to small changes in force constants

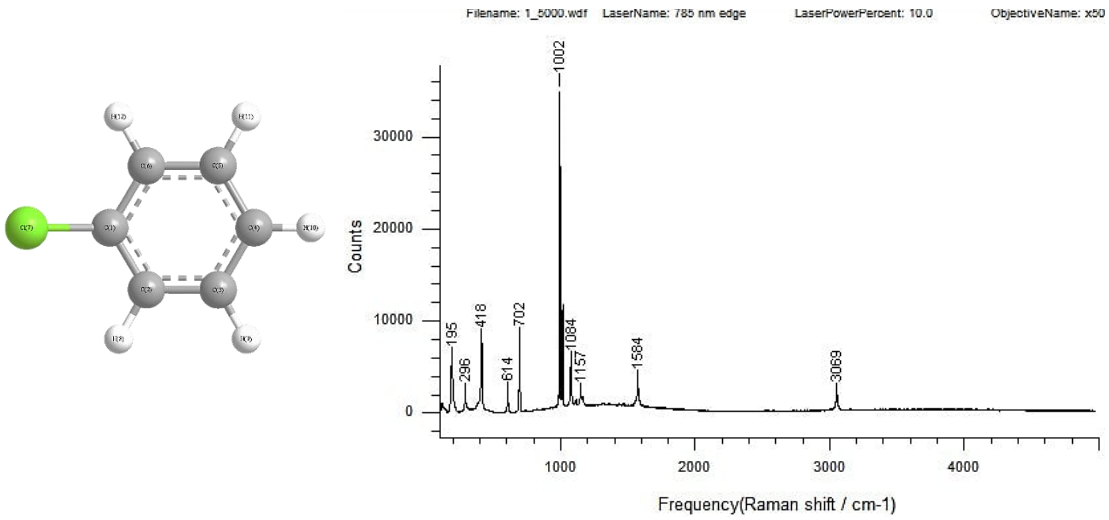

Fig.2 Structural composition of liquid chlorobenzene and its Raman spectrum

An overview of the recorded Raman spectra of pure liquid chlorobenzene in the spectral range of 100–5000 cm^{-1} is presented in Fig. 2. The values of the maxima for the observed lines and their intensities are provided in Table 1.

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Table 1. Maximum frequency and intensity of the Raman spectrum range of chlorobenzene

Chlorobenzene - C_6H_5Cl					
ν, cm^{-1}	**ℑ, (a.u.)**	**ν, cm^{-1}**	**ℑ, (a.u.)**	**ν, cm^{-1}**	**ℑ, (a.u.)**
195.39	5613.43	418.22	7725.73	1084.89	4950.11
298.92	1531.54	614.47	1932.97	1156.69	1836.90
297.63	1755.63	702.32	7711.50	1584.92	3142.47
296.35	1808.00	1001.94	35125.69	3069.90	1848.04

A key difference between polyatomic and monoatomic molecules in molecular spectroscopy is that molecules with at least three atoms exhibit more complex behavior than single atoms. In other words, in addition to the movement of electrons, vibrational (periodic changes in the positions of the nuclei) and rotational (periodic changes in orientation) motions of the molecule also play an important role.

Vibrational relaxation of molecules in liquids is mainly determined by intermolecular interactions. There are three mechanisms of relaxation in molecular vibrations:

- **Energy relaxation:** This refers to the distribution of the energy of intramolecular vibrations to other degrees of freedom, including translational and rotational motions of molecules, as well as other vibrational modes.
- **Phase relaxation:** This involves phase modulation of intramolecular vibrations due to collisions with surrounding molecules, or, in other words, local field fluctuations.
- **Resonance energy exchange:** This is the exchange of energy quanta of intramolecular vibrations between oscillators of the same type.

According to our experimental data, the Raman lines for C–Cl in chlorobenzene are complex. For chlorobenzene, four main bands can be distinguished at approximately 195 cm^{-1}, 418 cm^{-1}, 1001 cm^{-1}, and 3069 cm^{-1}. The most prominent line is at 1002 cm^{-1}, with a relatively low-intensity line at 1010 cm^{-1} in its background. This indicates that, although these lines are associated with the same C–H vibrations, their depolarization coefficients are different. When comparing the spectra of compounds with similar structural features, it was found that, in some cases, along with frequencies, other parameters—such as intensity, width, and degree of depolarization—retain their values when transitioning from one molecule to another.

A key aspect of characteristic structural elements is that they serve as fundamental units within molecules, and their presence is reflected in Raman spectra through their vibrations. When a molecule contains multiple structural elements with the same characteristics, the frequencies of the corresponding Raman lines generally match. Consequently, the intensity of these lines is proportional to the number of such structural elements. This phenomenon is well illustrated in [10] with examples of lines corresponding to the stretching vibrations of the CH_3 group in toluene, which has two C=C bonds. In the spectrum of toluene, the intensity of the 1210 cm^{-1} line is 508 relative units, while in the spectrum of dioxane, which has one C=C bond, the intensity of the corresponding line is 152 (ref. [10]).

If the vibrations of a key structural element change with modifications to the molecule, the lines corresponding to other characteristic elements become more distinct in the spectrum. Identifying these structural elements and their associated Raman lines is the first step toward

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establishing a relationship between Raman spectra and molecular structure. The second step involves studying the behavior of torsional vibrations in individual atomic groups within complex molecules. Torsional vibrations of these atomic groups typically appear in the low-frequency region of the vibrational spectra, ranging from 50 to 500 cm^{-1}. As shown in Fig. 2, a significant number of lines were recorded in the low-frequency region (100–710 cm^{-1}) of the Raman spectra for the object under study. According to the structural formula, in addition to the stretching vibrations of Cl (298 cm^{-1}, 614 cm^{-1}, 702 cm^{-1}), deformation vibrations are also observed in the spectra. The analysis indicates that interpreting the observed regions, particularly identifying the deformation vibrations of the Raman bands, is challenging without specialized theoretical analysis, due to the complexity of the vibrational spectra of these liquids. Therefore, the deformation frequencies of Cl in the studied liquids were calculated using a semi-empirical method.

Table 2. The final experimental frequencies with calculated deformation vibrations

ν, cm^{-1}			
Literature value	Experiment	Quantum chemical calculation	Band
	418	415	ω (C-Cl)
609	614	614	ω (C-C)
1001	1001	1012	ω (C-C)
1156	1156	1188	δ (C-H)
1580	1584	1615	ω (C-C)
3068	3069	3176	ν (C-H)

If the height of the potential barrier for vibrations is known, it is straightforward to find the corresponding frequency and determine the vibrational frequencies by comparing the calculated values with the experimentally observed ones.

Semi-empirical calculation methods are based on the assumption that the height of the potential barrier is equal to the difference in repulsive energies between the two rotating parts of the molecule in the states with the minimum and maximum repulsion. Several semi-empirical methods for calculating barriers are available.

We used a semi-empirical method to calculate the potential barriers, which we significantly modified through quantum chemical calculations to apply it to more complex molecules. The potential barriers for the studied molecules were calculated using the potential repulsion method proposed in [12]. Additionally, barrier values reliably determined from microwave data and precise structural data (such as bond lengths and angles) obtained from quantum chemical calculations can also be utilized.

The second issue is the sudden change in potential values due to variations in interatomic distances. Our calculations indicated that the repulsion function between hydrogen atoms, as used for the studied molecules in [13], is applied.

$$U = 950{,}5 \exp(-1{,}98r) - 1995 \exp(-3{,}7r), \quad (1)$$

where r – is the distance between hydrogen atoms in angstroms. This approach generally provides a satisfactory fit with experimental data without considering interactions between

other atoms. The calculated frequencies of deformation vibrations for the studied substances and the corresponding experimental values are presented in Table 2.

As shown in Table 2, the calculated and experimental frequency values agree satisfactorily. The relationship between the height of the potential barrier U and the frequency of torsional vibrations ν is as follows:

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

For calculations, it is also necessary to know the reduced moment of inertia I_r for torsional vibrations. For a molecule of a higher symmetry type, the expression for the moment of inertia simplifies [10]

$$I_r = \Im_\varphi \left(1 - I_\varphi \sum_i \frac{K_i^2}{I_i}\right) \qquad (3)$$

where i –1, 2, 3; I_i represents the principal moments of inertia of the molecule; K_i – are the direction cosines of the angles formed by the principal axes of inertia and the top axis; and I_φ – is the moment of inertia of the top about the axis of rotation.

Since the low-frequency region of the Raman spectra for the studied aromatic hydrocarbons contains a large number of lines, it is challenging to define the observed ranges and interpret the spectra without specialized theoretical analysis. Deformation oscillations of various modes are present in such complex spectral regions. While lines in the lowest frequency region of the spectrum for molecules containing heavier groups are generally associated with torsional vibrations, the lines corresponding to torsional vibrations in chlorinated benzenes can appear in the relatively broad spectral range around 710 cm^{-1}. This variability can be attributed to differences in the moment of inertia. Considering the experimental data, it is evident that distinguishing a specific group of substances with unique characteristics can be difficult.

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