



## METHODOLOGY FOR PROCESSING RAMAN SPECTRAL RESULTS: QUANTUM-CHEMICAL CALCULATION

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### ABSTRACT

Aromatic hydrocarbons - benzene and bromobenzene liquids were studied using Raman spectroscopy in the frequency range 0-5000  $\text{cm}^{-1}$ . Vibrational modes of molecules in different frequency ranges and their contribution to the shape of the spectral contour were analyzed using the semi-empirical method of quantum chemistry. The capabilities of the ORCA software for quantum-chemical calculations were demonstrated. The possibility of using a semi-empirical method to calculate the potential barriers of benzene and bromobenzene is shown.

**Keywords:** Raman spectroscopy, ab initio, benzene, bromobenzene, vibrational modes, potential barrier.

### INTRODUCTION

Vibrational motion spectroscopy is one of the effective experimental methods for studying the liquid state of matter. The study of light scattering in liquids allows obtaining very important information about the processes occurring in the environment. The shape of the contours in the vibration spectra of substances in the liquid phase is determined both by the orientational movement of molecules and by the dynamics of energy relaxation of intramolecular vibrations [1-3].

Raman spectra in a liquid medium show a shift in the frequencies of intramolecular vibrations due to the presence of intermolecular interactions, a change in the shape of the spectral lines (in addition, they differ depending on the polarization of the scattered light), some and the same vibrations of the atoms in the molecule are spectral division of lines, contour lines occur with a change in the depolarization coefficient, etc.

The dynamic nature of these interactions causes line broadening in the vibrational spectra of liquids. The existence of a relatively long-term local order associated with





the formation of various complexes and associations in the liquid is manifested in the change of frequencies of intramolecular vibrations [4-5].

All these changes are related to molecular processes in the liquid medium. The question of the mechanisms of the manifestation of these molecular processes in the light scattering spectra is as important as the question of the structure of liquids and molecular processes in them.

## METHODOLOGY

Solving this problem, on the one hand, in understanding the details of the interaction of light with matter, the mechanisms of changes in the parameters of electromagnetic waves during the interaction of light with matter, and on the other hand, the structure and properties of the liquid, as well as provides additional information about intermolecular interactions [6-9].

It is very difficult to interpret the obtained results without a special theoretical analysis, using the methods of quantum chemistry, it is possible to describe the electronic structure of atoms of molecules, the mechanisms of formation of spectra and other properties [10].

Quantum chemistry is a branch of theoretical chemistry that examines the structure and properties of chemical compounds, their interactions, and changes in chemical reactions based on the concepts and methods of quantum mechanics. Using the methods of quantum chemistry, it is possible to describe the electronic structure, spectra and other properties of atoms of molecules. To solve these problems, the Schrödinger equation for a polyatomic system is considered. The Hamiltonian of a multi-electron atom with  $n$  electrons and nuclear charge  $Z$  has the following form:

$$H = \sum_{i=1}^n T_i + \sum_{i=1}^n V_{zi} + \sum_i^n \sum_{<j}^n V_{ij}, \quad (1)$$

where  $T_i$  is the kinetic energy of electrons,  $V_{zi}$  is the potential energy of electron interaction with the nucleus,  $V_{ij}$  is the potential energy of electron interaction.

The total energy of an atom is determined from the following expression:

$$E = 2 \sum_{i=1}^n H_i + \sum_{i=1}^n \sum_{j=1}^n (2J_{ij} - K_{ij}), \quad (2)$$

where  $H_i = \int \Psi_i [T_i + V_{zi}] d\tau$  is the main integral,  $i$  is the sum of the kinetic energy of the electron in the orbital and its potential energy of interaction with the nucleus;

$J_{ij} = \iint \Psi_i^2 V_{ij} \Psi_j^2 d\tau_i d\tau_j$  is the Coulomb integral, that is, the average energy of electrostatic repulsion of electrons located in orbitals  $i$  and  $j$ ,

$K_{ij} = \int \Psi_i(1) \Psi_j(1) V_{ij} \Psi_i(2) \Psi_j(2) d\tau_i d\tau_j$  is the exchange integral.

The variational principle is used to find the  $\Psi_i$  orbital position. Determining the functional minimum,



$$\Phi = E - \sum_i \sum_j \varepsilon_{ij} \int \Psi_i \Psi_j d\tau \quad (3)$$

We get the Hartree-Fock equations

$$H_i(1) + \sum_{j=1}^n (2\Psi_i(1) \int \Psi_j^2(2) V_{12} d\tau_2 - \Psi_j(1) \int \Psi_j(2) \Psi_i(2) d\tau_2) = \varepsilon_i \Psi_i(1) \quad (4)$$

The simplest type of electronic structure calculation is the ab initio Hartree-Fock (HF) scheme, which does not take into account electron-electron Coulomb repulsion. Only its average effect (average area) is included in the calculation. This is a variational procedure; therefore, the resulting approximate energies represented by the wave function of the system are always equal to or greater than the exact energy and tend to a limiting value called the Hartree-Fock limit as the size of the basis increases [12-14]. Many calculations begin with the Hartree-Fock calculation and are later adapted to account for electron-electron repulsion, also known as electron correlation.

The Hartree-Fock method can be implemented in different ways depending on how the electrons are placed in the orbits. Since the Hartree-Fock method cannot obtain atomic orbitals analytically, analytical approximations are proposed. The set of properties used to represent molecular orbitals is called a "Basis Set".

$$\Psi_i = c_{i1}\varphi_1 + c_{i2}\varphi_2 + \dots + c_{in}\varphi_n, \quad (5)$$

$\Psi_i$ - molecular orbital,  $\varphi_j$  - functions of some basis set (basis).  $c_{ij}$  are the variational parameters found by solving the corresponding field equations for expansion coefficients  $i = 1, 2, \dots, n$  ( $n$  is the number of basis set functions). In the simplest case, in the expansion,  $\varphi_j$  are the wave functions of atomic orbitals occupied by electrons in the ground state. Such a basis set is called a minimal basis. There are various methods for determining the basis set function [15-18].

## EXPERIENCE

Raman spectra were recorded with a confocal microscope using a STR250 laser Raman spectrometer. It is a very compact flexible system with high sensitivity that can be used to record weak Raman scattering spectra. The installation consists of a spectrometer (07) with a scanning mechanism in the spectral range of 50-7000  $\text{cm}^{-1}$ , a focal length of 250 mm, three types of automatically changing diffraction gratings (600; 1200; 1800 lines per 1 mm), size 1  $\text{cm}^{-1}$  and CCD (08) camera cools down to -600 C. It also includes an optical microscope (03) for a small sample with <1 mm spatial resolution and an excitation laser (01) for the visible region (532 nm). The scheme of the experimental setup is presented in Fig. 1.

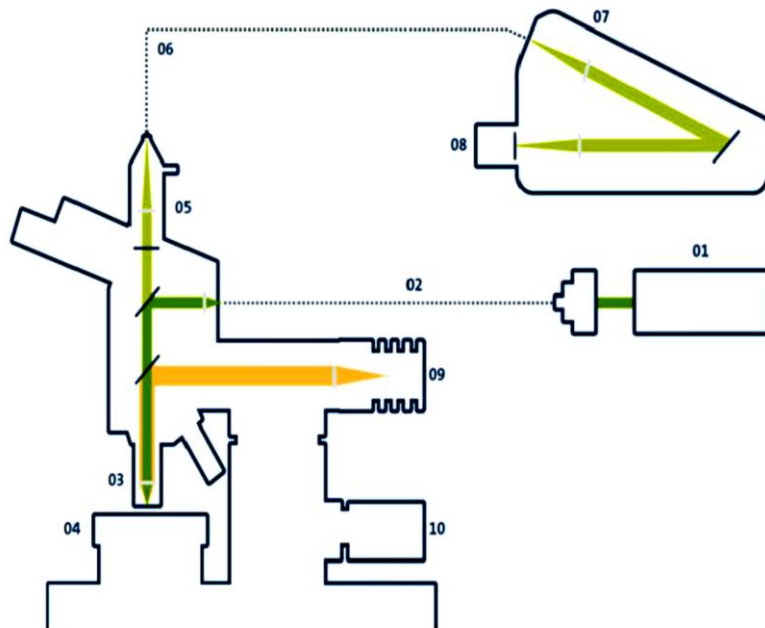


Figure 1. Scheme of the experimental device for recording Raman spectra: 01 - laser; 02, 06 – optical fiber cable with capacity up to 90%; 03 - adjusted lens; 04 – microscope table; 05 - set of filters; 07 – STR250 spectrometer; 08 - piezoelectric detector; 09 - white light; 10 - screw focus

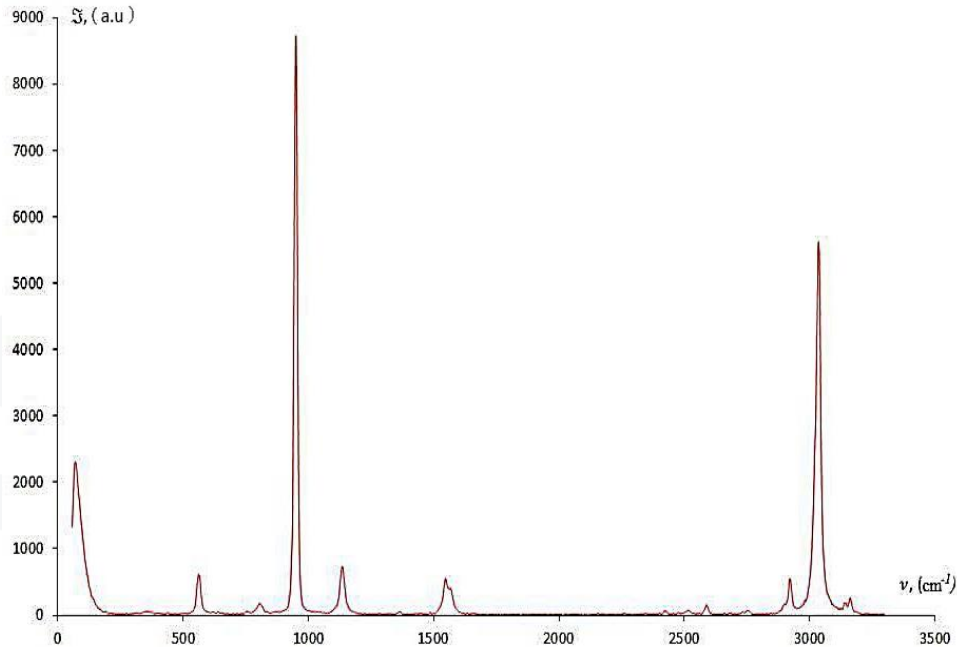


Figure 2. Raman spectrum of liquid benzene

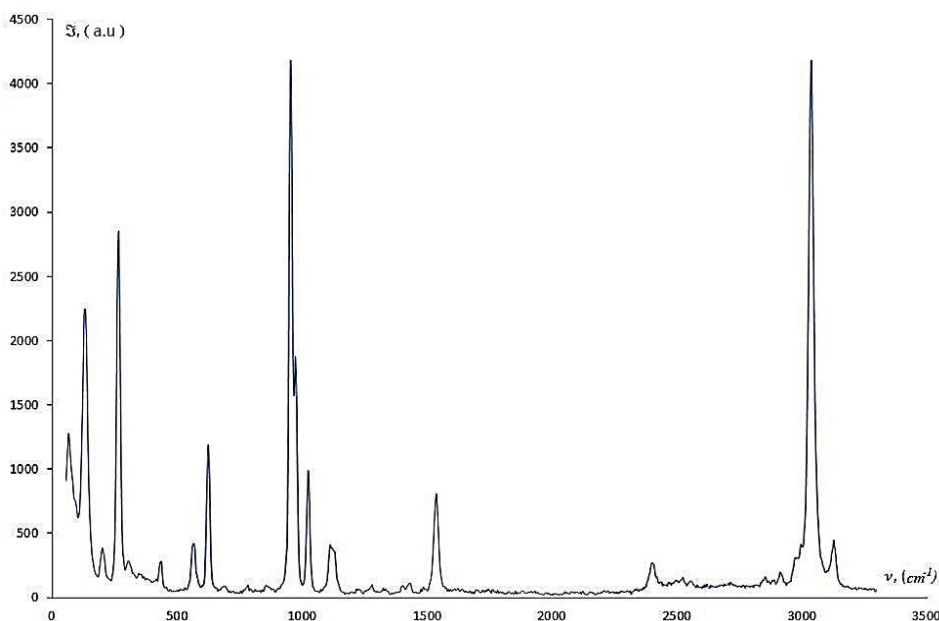


Figure 3. Raman spectrum of liquid bromobenzene

Raman spectra were recorded at an angle of 180° to the incident light. Study objects were thoroughly cleaned according to the procedures described in [24].

## RESULTS AND DISCUSSION

In order to compare the obtained results, quantum-chemical calculations of the molecular structure, electronic structure and spectroscopic parameters of all studied objects were carried out in two GAUSSIAN and ORCA quantum-chemical software packages.

GAUSSIAN and ORCA quantum-chemical software packages are designed to calculate the structure and properties of molecular systems both in the gas phase and in the condensed state [15]. The GAUSSIAN program consists of a series of links, each of which is a separate computer program. In terms of capabilities, the GAUSSIAN suite is one of the most powerful and allows solving a wide range of problems related to chemistry, condensed matter physics, and quantum mechanics.

A Gaussian program can be executed in serial or parallel mode. A task file is compiled to include the initial data. An assignment file mainly consists of an assignment specification and a molecule specification. The assignment file consists of sections:

- Preprocessor Instructions - The instructions in this section include configuring dynamic memory and specifying the number of processors to use for parallel execution.
- Task specification - The task specification includes the computational method and atomic basis set, the type of problem to be solved, the setting of parameters for various



application procedures (convergence criteria of SCF and optimization procedures, selection of specific algorithms, etc.). You can choose one of the built-in packages or install your own, or a combination of the two.

- Task name - contains information to identify the task
- Molecule specification - the specification of a molecule includes the molecular charge and its multiplet and the initial geometry of the molecule.
- Additional sections - Various additional tasks can be included.

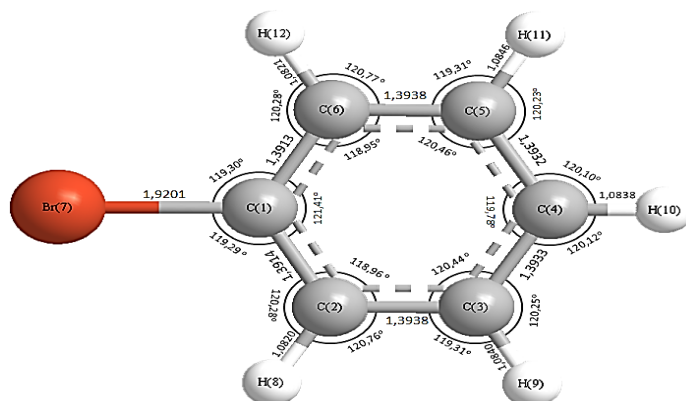


Figure 3. Distances and angles between bonds of atoms of bromobenzene molecule. Quantum-chemical calculations in the GAUSSIAN program are usually performed according to the algorithm shown in Figure 4.

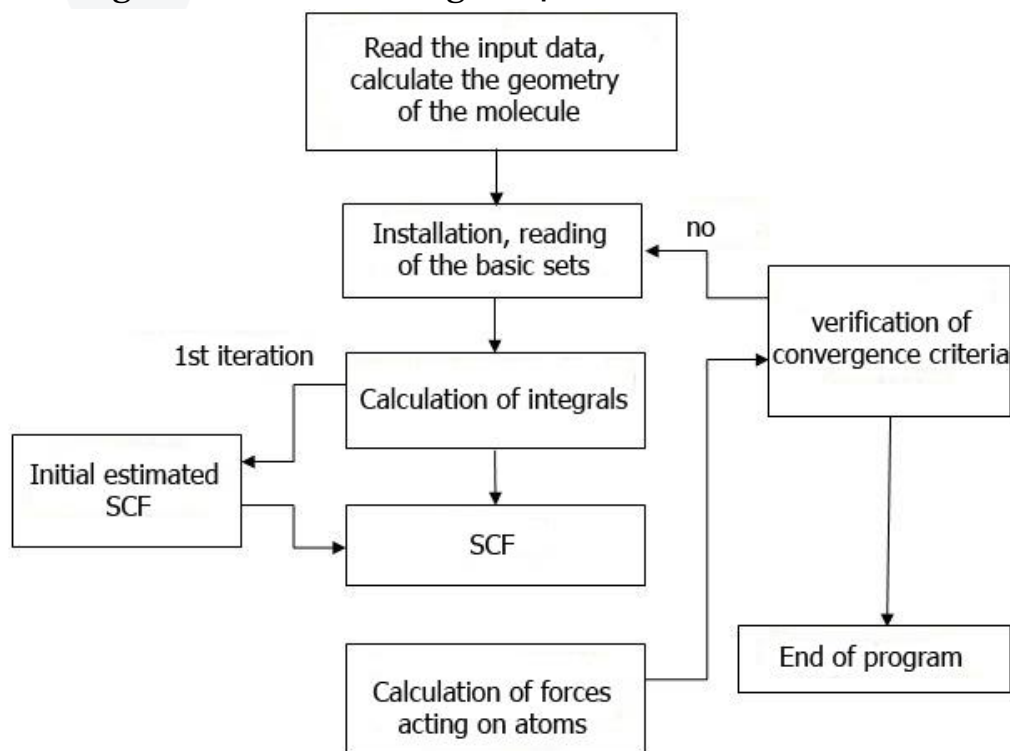


Figure 4. Algorithm for solving quantum-chemical calculations in the GAUSSIAN program.



This program is based on the Hartree-Fock (HF) method to determine the intermolecular interaction parameters. We used HF/6-31G\*\* in our calculations, which is based on the Hartree-Fock approximation and performs much better than other models such as HF/STO-3G [19–22].

Fig. 5 shows the spectral dependence of the intensity of the Raman spectral contours on the frequency of the studied liquids obtained in the spectra taken with a confocal microscope on the STR250 laser Raman spectrometer and calculated by ab initio quantum-chemical methods based on the HF/6-31G\*\* semi-empirical ORCA software package. shown. The dependence of the Raman scattering intensity and the frequency of the excitation light can be calculated with more or less restrictions using classical, semi-classical or quantum theories.

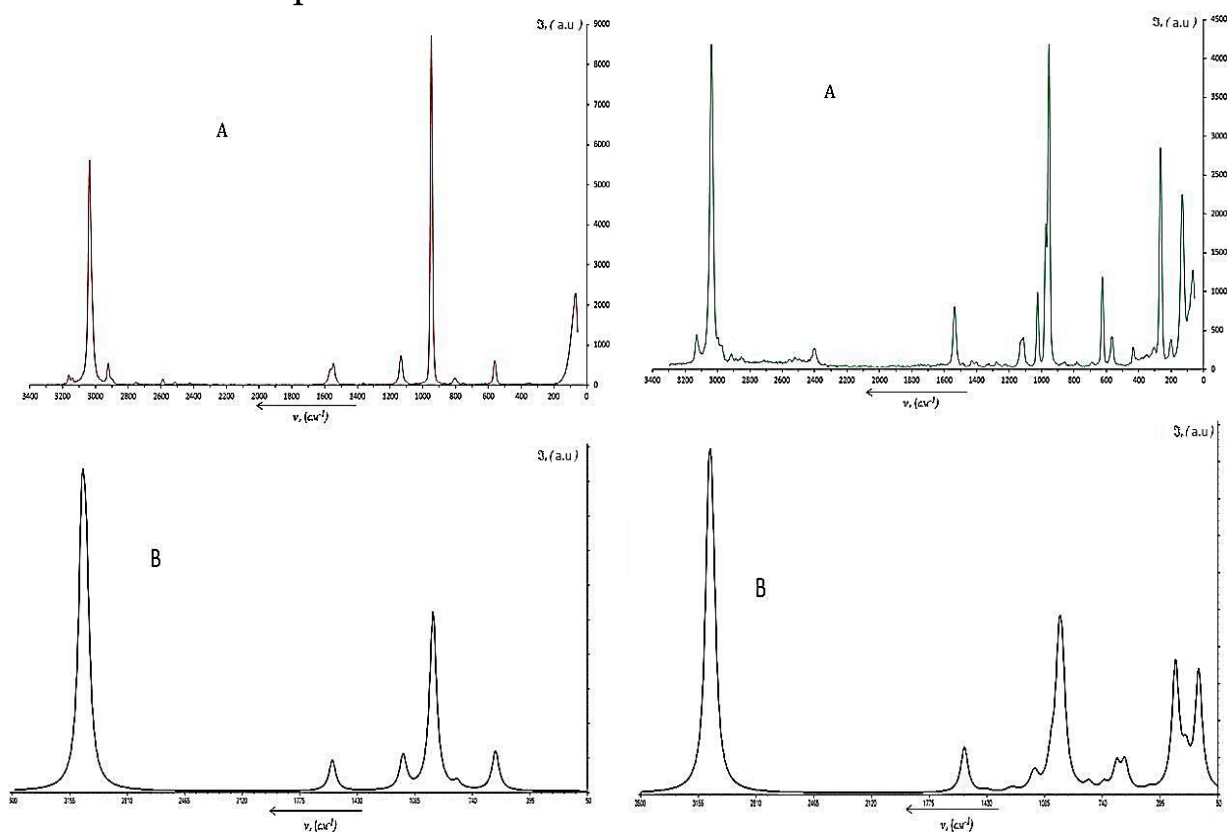


Figure 5. a) Benzene b) in bromobenzene molecules Dependence of the combined light scattering spectral intensity on frequency A - experiment, B - quantum-chemical calculation.

For bromobenzene, four intense lines with frequencies of approximately  $177\text{ cm}^{-1}$ ,  $310\text{ cm}^{-1}$ ,  $998\text{ cm}^{-1}$  and  $3077\text{ cm}^{-1}$  can be distinguished. The most intense line is at  $3077\text{ cm}^{-1}$ , and its background is a line of relatively low intensity at  $3142\text{ cm}^{-1}$ . This shows that despite the fact that all these lines belong to the same vibration  $C = H$ , their depolarization coefficients are different. Table 1 presents the results obtained using the experiment and the quantum chemical calculation method.



Table 1

Benzene $C_6H_6$				
Experience		Quantum chemical calculation		
$\nu$ , ( $cm^{-1}$ )	$\Im$ , (a.u.)	$\nu$ , ( $cm^{-1}$ )	$\Im$ , (a.u.)	$\rho$ , (%)
608	302	601,94	570	0,7499
		602,18	738	0,7498
851	76	830,10	98	0,7499
		833,00	121	0,7498
993	5461	978	5872	0,0893
1179	311	1156,4	595	0,7499
		1156,8	535	0,7498
1589	207	1581,3	515	0,7499
		1581,5	482	0,7498
1607	154	-	-	-
2629	85	-	-	-
2960	290	-	-	-
		3054,0	2764	0,7411
3073	2409	3055,1	2624	0,7499
		3079,6	7728	0,1283
3178	82	-	-	-
3197	109	-	-	-

Bromobenzene - $C_6H_5Br$				
Experience		Quantum chemical calculation		
$\nu$ , ( $cm^{-1}$ )	$\Im$ , (a.u.)	$\nu$ , ( $cm^{-1}$ )	$\Im$ , (a.u.)	$\rho$ , (%)
177	980	163,93	3024	0,7499
244	231	241,14	738	0,7499
310	1745	301,98	3223	0,3378
481	187	457,19	69	0,7492
613	389	605,76	727	0,7499
668	696	657,14	659	0,1994
998	2530	978,17	2276	0,1255
1018	1592	1002,10	2858	0,0874
1068	826	1045,45	624	0,1007
1156	175	1143,08	321	0,7499
1165	344	1159,60	185	0,4487
1580	261	1563,87	812	0,6875
3077	1710	3059,87	2304	0,3472
3142	196	-	-	-





When comparing the spectra of compounds with common structural features, it was found that in a number of cases, along with frequencies, other line parameters - intensity, width and degree of depolarization - retain their value when passing from one molecule to another. In addition to works that attempt to find the height of potential barriers from general physical considerations, there are works that propose simple semi-empirical methods for calculating potential barriers.

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 molecules in the positions with the smallest and largest repulsion. There are several methods of semi-empirical calculation of obstacles [23,24]. The authors of [23] proposed the following general formula for the potential interaction:

$$U = \sum_{i,j} \left( \frac{k_{ji}}{r_{ij}^p} + \frac{h_{ij}}{r_{ij}^s} \right) \quad (6)$$

In this expression, the first term describes repulsive forces, and the second term describes other interactions. Here,  $r_{ij}$  are the distances in angstroms between the hydrogen atoms of both rotating groups ( $i$  is the index of the atoms of the first group,  $j$  is the index of the atoms of the second group). It is very important due to the sudden change in the potential values with the change of the interatomic distance. It should be noted that, because the calculated value of the barrier is the difference between two large numbers: repulsive energies at positions with the smallest and largest repulsion between groups.

## CONCLUSION

If it is possible to determine the origin of molecular spectroscopy, including the spectral lines, and relate them to the characteristics of the studied compounds, it is possible to achieve a sufficiently full use of the capabilities of Raman spectroscopy. Useful information about the origin of lines and the structure of molecules can be obtained only on the basis of empirical correlations. The calculated interatomic distances in very large bases, which give results close to the Hartree-Fock limit, turn out to be significantly smaller than the experimental values. Taking electron correlation into account increases valence bond lengths and reduces calculation errors. From these data, it becomes clear why ab initio calculations in valence-divided basis sets agree well with experiment. This is due to the incompleteness of the basis used and the mutual compensation of errors associated with the neglect of electron correlation.





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