TORSIONAL IR SPECTRA OF THREE CONFORMERS OF THE RESORCINOL MOLECULE

G. Pitsevich[a], A. Malevich[b]

[a]Department of Physical Optics and Applied Informatics, Faculty of Physics, Belarusian State University, Nezavisimosti Ave., 4, 220030, Minsk, Belarus
[b]Department of Differential Equations and System Analysis, Faculty of Mechanics and Mathematics, Belarusian State University, Nezavisimosti Ave., 4, 220030, Minsk, Belarus

*Corresponding author email: pitsevich@bsu.by (G.A. Pitsevich)

ABSTRACT

Conformational states, barriers to internal rotation, 2D potential energy surfaces, kinetic coefficients and dipole moment components of the resorcinol molecule are calculated at the MP2/CBS(T,Q), MP2/Aug-cc-pVTZ, MP2/dAug-cc-pVTZ and B3LYP/Aug-cc-pVTZ levels of theory. After symmetrization of the calculated data, they were approximated by the symmetry-adapted sets of basis functions. Using the calculated data sets, the energies and wave functions of stationary torsional states were determined for the first time using a numerical solution of the vibrational Schrödinger equation of limited dimensionality. This made it possible to establish the values of the tunneling splitting of the ground vibrational and a number of excited torsional states of the energetically most preferred conformer of the molecule, belonging to the point symmetry group C_S. The 100 lowest torsional states of the resorcinol molecule are classified according to the symmetry species of the molecular symmetry group $C_{2V}(M)$, which unites all three conformers of the molecule. The calculations of the matrix elements of the dipole moment operator and the partition functions made it possible to simulate the torsional IR spectra of three conformers of the molecule at different temperatures. The calculated values of the frequency of the most intense torsional vibration in the most stable conformer of the molecule (316 and 320 cm^{-1}), obtained at the MP2/dAug-cc-pVTZ and MP2/CBS(T,Q) levels of theory are in good agreement with the experimental value of the frequency of this vibrations (318 cm^{-1}), obtained in [W.G. Fateley, J.Phys.Chem., 79 (1975) 199 – 204.].

KEYWORDS: torsional vibrations, potential barriers, resorcinol, PES, internal rotation, conformers, 1,3-dihydroxybenzene, vibrational Schrödinger equation, Fourier series, $C_{2V}(M)$ molecular symmetry group

1. INTRODUCTION

Dihydroxybenzenes are a very interesting group of molecules, characterized by a variety of conformers, some of which can be realized in the form of two equivalent configurations, resulting in the splitting of a number of energy levels due to tunneling. The resorcinol (RES) molecule, which belongs to this group and is characterized by a meta - arrangement of hydroxyl groups in the benzene ring, is no exception. Interest in this molecule is also due to its numerous practical applications. Thus, in the works [1,2] the effectiveness of using RES-formaldehyde resin for cleaning tank waste is shown. Phenolic resins based on RES were also intensively studied in works [3-5]. The antibacterial properties of resins based on RES, p-nitrophenol and

formaldehyde were studied in [6]. A copolymer of RES and acetone was synthesized and analyzed in [7]. The possibility of its use for the development of plastic and biomaterials is noted. Microwave-assisted methylation of dihydroxybenzenes with dimethyl carbonate is presented in [8]. Cu-doped organic RES-based aerogels, widely used as thermal insulators, light guides, and particle detectors, are studied in [9]. The properties of RES-based adhesives for joining wood are analyzed in [10].

The widespread practical application of RES has led to intensive research into the structure and spectral characteristics of this molecule. Bacon [11,12] using neutron diffraction established that in the crystalline phase the RES molecule is flat and contains 4 molecules connected by hydrogen bonds in the crystal cell. The structural parameters of the molecule were also determined for the first time. Later, Kudchadker [13], using the semi-empirical CNDO/2 method, for the first time predicted the existence of three stable planar configurations for the RES molecule in the gas phase. The minimum energy according to the calculations of this work corresponded to a configuration with C_S symmetry (hereinafter conformer A), and the other two configurations (conformers B and C) belonged to the point symmetry group C_{2V} (see Fig. 1). These predictions, obtained using a very primitive calculation method, turned out to be correct. However, the relative energies of conformers calculated using this method were incorrect: E_A , E_B , E_C − 0, 64 and 3 cm^{-1} , respectively. The potential barriers to rotation for all conformers were postulated to be approximately the same and equal to 1459 cm^{-1}. Konschin [14,15], with the help of STO-3G molecular orbital research and complete optimization of molecular parameters in work [15], obtained the correct order of growth of the internal energy of conformers: E_A , E_B , E_C − 0, 83 and 171 cm^{-1}. The values of the permanent dipole moments of the three conformers calculated in [15] turned out to be 1.22, 2.39 and 1.77 D, respectively. In the work of Poebla [16], calculations were also carried out with full optimization of geometric parameters, but at higher levels of theory - SCF/4-31G and SCF/4-31G*. This made it possible to clarify the energy ratio of the conformers E_A , E_B , E_C − 0, 84 and 377 cm^{-1}. In addition, the barriers to rotation were calculated more accurately. Along the path from A to C, the barrier value turned out to be 1122.7 cm^{-1} , along the path from A to B − 1154.2 cm^{-1} , along the path from B to A − 989.8 cm^{-1} and along the path from C to A − 811.4 cm^{-1} . It became obvious that such high potential barriers to transitions from one conformer to another can ensure the existence of not only conformer B, but also conformer C in a wide temperature range. In the same work, the harmonic vibrational frequencies of the RES molecule were first calculated, but there was confusion with the frequencies of torsional vibrations. The first *Ab initio* calculation (HF/6-31G(d,p) and & HF/6-311++G(d,p)) of the structure and spectra of three conformers of the RES molecule was performed in the work of Gerhards [17]. Taking into account the vibrational zero

point energy (VZPE), the energy ratio of the three conformers turned out to be equal: E_A, E_B, E_C - 0, 80 and 235 cm^{-1}. Taking this into account and the configurational degeneracy for conformer A, the population ratio of conformers at a temperature of 70^0 C was estimated: A:B:C – 1:0.36:0.19. The harmonic values of torsion vibration frequencies calculated in this work for conformers A and B turned out to be 306, 318 and 304, 304 cm^{-1}. In the article they are compared with the experimental frequencies of 387 and 460 cm^{-1} obtained in [18]. Geppert studied RES complexes with H_2O [19] and CO [20], but there is no information about torsional vibrations in these works. The harmonic frequencies of torsional vibrations in conformers A and B were also calculated at the B3LYP/6-311G(d,p) and MP2/6-311G(d,p) levels of theory in [21]. For conformer A they turned out to be 337, 358 and 247, 271 cm^{-1}, respectively, and for conformer B – 336, 342 and 249, 260 cm^{-1} for similar levels of theory. It is obvious that the *Ab initio* MP2 method predicts significantly lower values of torsional frequencies in comparison with the DFT method. Note that, as in the case of [21], for comparison, the experimental frequencies were taken from [18] too. Calculations of the torsional states of the RES molecule, taking into account the force interaction of two hydroxyl tops within the framework of perturbation theory, were undertaken in [22,23], but the results obtained should rather be considered unsatisfactory. A recent article by Manojkumar [24] on the spectral and energetic properties of the RES molecule is not based on the available literature data and contains a number of elementary errors.

Experimental spectral studies of RES began in the work of Wilson [25], in which the IR spectrum of molecular vapor was recorded. The limited spectral range (4000 – 625 cm^{-1}) did not allow, however, to identify absorption IR bands caused by torsional vibrations of hydroxyl groups. Later, Fateley [26] performed extensive studies of torsional IR spectra of substituted phenol in cyclohexane solution. The absorption band at 318 cm^{-1} was associated with the torsional vibration of the O-H groups in the RES molecule. The article does not indicate which conformer this absorption band belongs to. Tripathi [27] recorded and interpreted the IR and Raman spectra of RES in the crystalline phase, but the IR bands or Raman lines were not assigned to torsional vibrations. Free-Jet spectra were recorded in the work of Dunn [28]. The presence of all three conformers in the sample was confirmed. REMPI and hole–burning spectra were recorded in [17]. For conformers A and B, the following low-frequency absorption bands were recorded: 225, 325, 448, 458 cm^{-1} and 243, 326, 443, 455 cm^{-1}, respectively, but none of them were assigned to torsional vibrations. The IR and Raman spectra of the RES molecule were recorded by Mironenko [18]. The absorption bands at 387 and 460 cm^{-1} were assigned to torsional vibrations of hydroxyl groups. The millimeter absorption spectrum of the RES molecule in the range of 60 – 78 GHz was recorded in the work of Melandri [29]. The authors

also were able to register all three conformers and experimentally estimate the ratio of the internal energies of the conformers: E_A, E_B, E_C – 0, 20 and 450 cm^{-1}. It was also noted that it was not possible to detect the splitting of spectral lines due to tunneling in the A conformer. In the work [30] using infrared photoinduced Rydberg ionization spectroscopy, the spectra of the cation RES were obtained. Bands 540 and 577 cm^{-1} in the cation of conformer A were assigned to torsional vibrations. Jet-cooled and Dispersed Fluorescence Spectroscopy of RES spectra were recorded in [21]. The observed bands were assigned to conformers A and B. None of the low-frequency bands were assigned to torsional vibrations. In the work of Myszkiewicz [31], high-resolution UV spectra of the conformers of RES and some of its deuterated derivatives were obtained. The authors note the presence of only A and B conformers in the samples, and also that torsional splitting of lines remained unresolved for all nondeuterated RES conformers. Infrared (IR) photodissociation spectra RES+Ar and RES+2Ar were registered in the works of Patzer [32] and Miyazaki [33], however, the authors analyzed only the region of O-H stretching vibrations. The work of Schneider [34], although it concerns mainly 1,3 dimethoxybenzenes, however, provides important arguments explaining why in some cases, when recording RES spectra, only two and not three conformers of the molecule are observed.

As follows from the analysis of literature data, there are currently no experimental data on the splitting of bands in RES spectra due to tunneling in the A conformer. The frequencies of torsional vibrations of the RES molecule are theoretically analyzed only in the harmonic approximation, and there is a complete lack of data on the overtones of torsional vibrations and on theoretical estimates of the values of tunneling splittings of torsional states. Reliable experimental data on the frequencies of fundamental torsional vibrations in the gas phase are also absent today. At the same time, as shown by the results of Bruckhuisen's work [35], although band splitting due to tunneling of the ground state of the 1,2 dihydroxybenzene (catechone - CTL) molecule could not be resolved, band splitting due to tunneling in the first excited torsional state was successfully resolved: $1.041*10^{-5}$ cm^{-1}. At the same time, our somewhat later calculations of the splitting of torsional states of the CTL molecule (from $1.1*10^{-5}$ to $2.7*10^{-6}$ cm^{-1} for different levels of theory) in conformer A [36] showed good agreement with experimental value. At the same time, the calculated value of the splitting of the ground state of the conformer A of the CTL molecule turned out to be in the range from $1.9*10^{-8}$ to $9.1*10^{-8}$ cm^{-1}, which may be the reason for the lack of experimental detection of this splitting. Let us recall that the RES molecule belongs to the same molecular symmetry group ($C_{2V}(M)$) as the CTL molecule. Previously, we calculated the torsional IR spectra of a number of molecules ($HO(CH_2)OH$, $HOOOH$, $HOSOH$, $HSOSH$, $HSSSH$) belonging to this molecular symmetry group [37-41]. Based on an analysis of literature data and relying on the experience gained from

analyzing torsional vibrations of similar molecules, we performed calculations of the torsional states of the RES molecule. The 2D potential energy surface (PES) of the molecule was calculated at several levels of theory. The calculated data were approximated by basis functions adapted to molecular symmetry. The vibrational Schrödinger equation of restricted dimensionality was solved numerically using complex Fourier series. Torsional IR spectra of three molecular conformers were simulated for several temperatures, taking into account the dependence of the dipole moment of the molecule on torsional coordinates and the calculated partition functions.

2. SYMMETRY PROPERTIES

As was noted in Section 1, the RES molecule is realized in the form of three stable conformers, one of which (conformer A) can exist in two equivalent configurations. All of them are presented in Fig. 1
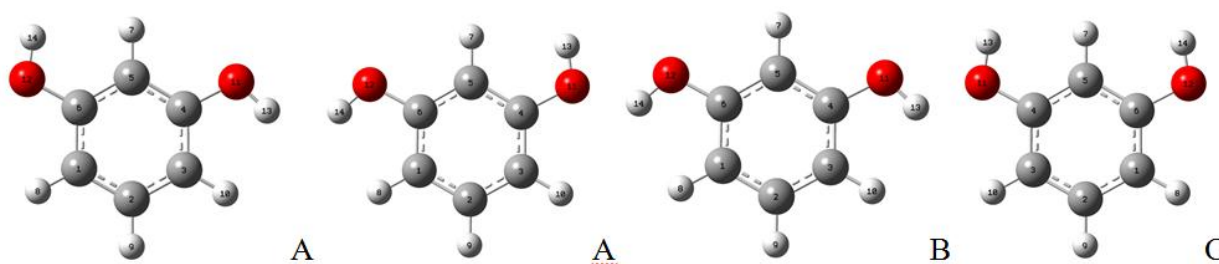

Figure 1 Equilibrium configurations of three conformers (A, B and C) of the RES molecule calculated at the MP2/Aug-cc-pVTZ level of theory.

Since it is generally accepted that the internal energy of conformers increases from left to right in Fig. 1, we decided on their following designation: A, B and C. Thus, the increase in the energy of conformers corresponds to the sequence of letters denoting them in the alphabet. It is obvious that tunneling between equivalent configurations is possible only for conformer A belonging to the point symmetry group C_S. Conformers B and C belong to the point symmetry group C_{2V}. However, since the RES molecule is non-rigid, molecular symmetry groups [42-44] are much better suited for its description. Indeed, all three conformers are united by the molecular symmetry group $C_{2V}(M)$ [45], which includes the identical operation E (we will also denote it P_1), the permutation operation (1,3)(4,6)(8,10)(11, 12)(13,14) – (hereinafter operation P_2) inversion operation E* (hereinafter operation P_3), and the product of the 2nd and 3rd symmetry operations (1,3)(4,6)(8,10)(11,12)(13,14)* - (hereinafter operation P_4). Table 1 presents the characters of irreducible representations of the group $C_{2V}(M)$.

Table 1 The characters of the irreducible representations of the $C_{2V}(M)$, C_{2V} and C_S symmetry groups, as well as the transformations of torsional coordinates under the symmetry

operations. The last row presents symmetry operations on the torsional coordinate plane of γ_1 and γ_2.

	1	2	3	4	5	6	7
1	C_{2v}(M)	P_1	P_2	P_3	P_4		
		Conformers B and C				Conformer A	
2	C_{2v}	E	C_2	$\sigma(XZ)$	$\sigma(YZ)$	C_S	
3	A_1	1	1	1	1	A'	Z, p_z, U, $F_{\gamma_1\gamma_2}$, $F_{\gamma_1\gamma_1} + F_{\gamma_2\gamma_2}$
4	A_2	1	1	-1	-1	A''	
5	B_1	1	-1	1	-1	A'	X, p_x
6	B_2	1	-1	-1	1	A''	Y, p_y
7		γ_1, γ_2	γ_2, γ_1	$-\gamma_1, -\gamma_2$	$-\gamma_2, -\gamma_1$		
8	Symmetry elements of the 2D surfaces	E	Reflection in plane 1	Rotation around C_2	Reflection in plane 2		

To make it clear why Cartesian coordinates are transformed according to the corresponding symmetry species, Fig. 2 shows how the Cartesian coordinate system is positioned in relation to the molecular skeleton. The values of torsional angles in this configuration are assumed to be zero.
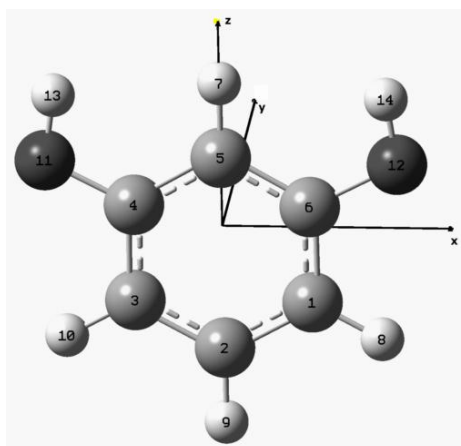

Figure 2 Configuration of the RES molecule, in which the values of the torsional coordinates γ_1 and γ_2 are taken equal to zero. The figure also shows the location of the Cartesian coordinate system with the origin at the center of mass. All atoms of the molecule lie in the X0Z plane.

The last row of Table 1 presents an important correspondence between the symmetry operations of the molecular symmetry group C_{2v}(M) and the symmetry operations applicable to the description of 2D potential energy, kinetic coefficients, dipole moment components, and wave functions surfaces on the coordinate plane (γ_1, γ_2). The corresponding symmetry elements are presented in Fig. 3.
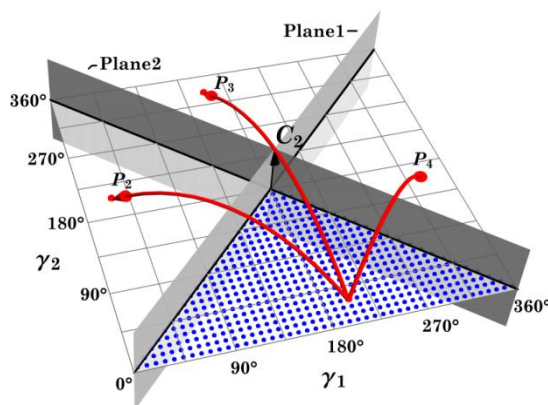
Figure 3 The symmetry elements of 2D surfaces of physical characteristics on the 2D plane of torsional coordinates γ_1, γ_2 of the RES molecule. The blue triangle is the area where it is enough to calculate the values of physical characteristics.

Using the indicated correspondence, it can be shown that the components of the dipole moment (p_x, p_y, p_z) are transformed according to the symmetry species in column 7 of Table 1. Then, in the dipole approximation (and under the assumption of a linear dependence of the components of the dipole moment on the Cartesian coordinates), transitions between the following states are forbidden: $A_1 \Leftrightarrow A_2$; $B_1 \Leftrightarrow B_2$; . In addition, Fig. 2 also shows that torsional vibrations of any hydroxyl groups in any conformer with small amplitude lead to a change in the dipole moment of the molecule along the Y axis. It is easy to see that this coordinate and, therefore, the corresponding component of the dipole moment are transformed according to the B_2 symmetry specie. Thus, for the matrix elements of the dipole moment operator to be nonzero, the direct product of the symmetry species of the initial and final torsional states during transitions in the conformer A must be B_2 specie. Consequently, only transitions $A_1 \Leftrightarrow B_2$ and $A_2 \Leftrightarrow B_1$ can appear in the IR spectrum of conformer A with a non-zero intensity in this case. In conformers B and C, as will be shown below, the fundamental torsional vibrations belong to the symmetry species A_2 and B_2. The torsional vibration of the A_2 specie leads to a change in the dipole moment of the molecule only along the Z axis. Thus, for the matrix elements of the dipole moment operator to be nonzero, the symmetry species of the initial and final torsional states during transitions in the conformer B and C must the same species, which is impossible in this case. The torsional vibration of the B_2 specie changes the dipole moment along the Y and Z axis. This means that *1)* the fundamental torsional vibration of the A_2 specie is not active in the IR spectrum of conformers B and C, *2)* with a non-zero intensity only following transitions can appear in the IR spectrum of conformers B and C: $A_1 \Leftrightarrow B_2$ and $A_2 \Leftrightarrow B_1$.

Despite the fact that the RES molecule belongs to the same molecular symmetry group as the molecules of methanediol $HO(CH_2)OH$, hydrogen trioxide HOOOH, and a number of other

analogous molecules [46,47], the classification of the torsional vibrations of the RES molecule differs from previously proposed for studied molecules. In the case of conformer A of the RES molecule, which belongs to the C_S point group, the X0Z is the symmetry plane (see Fig.2). Obviously, the torsional vibrations of both hydroxyl groups in conformer A cannot be totally symmetrical. Therefore, in the C_S point group they must be antisymmetric with respect to the X0Z plane. As follows from the 4th column of Table 1 of this work, due to tunneling, these torsional vibrations split in the $C_{2V}(M)$ molecular symmetry group into A_2 and B_2 species. In conformers B and C, which belong to the C_{2V} point symmetry group, the torsional vibrations of the two hydroxyl groups, which are equivalent in this case, can be classified using the projection operator. As follows from the data in row 7 of Table 1, symmetry of torsional coordinates can only be of A_2 specie - $\gamma_1 + \gamma_2$ or B_2 specie - $\gamma_1 - \gamma_2$. However, it should be kept in mind that other symmetry species (A_1 and B_1) are also possible for overtones and combination torsional vibrations of the molecule.

The Hamiltonian, describing the internal rotation of hydroxyl tops, must be invariant with respect to the following transformations of two torsional coordinates γ_1, γ_2:

$$P_1 H(\gamma_1, \gamma_2) = H(\gamma_1, \gamma_2); \quad P_2 H(\gamma_1, \gamma_2) = H(\gamma_2, \gamma_1); \quad P_3 H(\gamma_1, \gamma_2) = H(-\gamma_1, -\gamma_2); \quad P_4 H(\gamma_1, \gamma_2) = H(-\gamma_2, -\gamma_1); \quad (1)$$

That is:
$$H(\gamma_1, \gamma_2) = H(\gamma_2, \gamma_1) = H(-\gamma_1, -\gamma_2) = H(-\gamma_2, -\gamma_1); \quad (2)$$

As noted above, the potential energy and kinetic coefficient for the mixed derivative are transformed according to the fully symmetric representation A_1. However, the diagonal kinetic coefficients are not fully symmetric and are transformed as follows under the action of the symmetry operations of the $C_{2V}(M)$ group:

$$P_1 F_{\gamma_1\gamma_1}(\gamma_1, \gamma_2) = F_{\gamma_1\gamma_1}(\gamma_1, \gamma_2); \quad\quad P_2 F_{\gamma_1\gamma_1}(\gamma_1, \gamma_2) = F_{\gamma_1\gamma_1}(\gamma_2, \gamma_1) = F_{\gamma_2\gamma_2}(\gamma_1, \gamma_2);$$
$$P_3 F_{\gamma_1\gamma_1}(\gamma_1, \gamma_2) = F_{\gamma_1\gamma_1}(-\gamma_1, -\gamma_2); \quad P_4 F_{\gamma_1\gamma_1}(\gamma_1, \gamma_2) = F_{\gamma_1\gamma_1}(-\gamma_2, -\gamma_1) = F_{\gamma_2\gamma_2}(\gamma_1, \gamma_2); \quad (3)$$

This means that the symmetrized basis functions used to approximate the calculated data sets must be different for the potential energy and off-diagonal kinetic coefficient (formulas (4) and (5)) on the one hand, and the diagonal kinetic coefficients (formulas (6) and (7)) – on the other hand:

$$U(\gamma_1, \gamma_2) = U_0 + \sum_{k=1,K,1} U_k \left(\cos(k\gamma_1) + \cos(k\gamma_2) \right) + \sum_{k=1,K,1} U_{k,\pm k}^{\gamma_1\gamma_2} \cos(k\gamma_1 \pm k\gamma_2) +$$
$$+ \sum_{\substack{k,l=1,K,1 \\ k \prec l}} U_{k,\pm l}^{\gamma_1\gamma_2} \left(\cos(k\gamma_1 \pm l\gamma_2) + \cos(l\gamma_1 \pm k\gamma_2) \right); \quad\quad (4)$$

$$F_{\gamma_1\gamma_2}(\gamma_1, \gamma_2) = F_{\gamma_1\gamma_2 0} + \sum_{k=1,K,1} F_{\gamma_1\gamma_2 k} \left(\cos(k\gamma_1) + \cos(k\gamma_2) \right) + \sum_{k=1,K,1} F_{\gamma_1\gamma_2 k,\pm k}^{\gamma_1\gamma_2} \cos(k\gamma_1 \pm k\gamma_2) +$$
$$+ \sum_{\substack{k,l=1,K,1 \\ k \prec l}} F_{\gamma_1\gamma_2 k,\pm l}^{\gamma_1\gamma_2} \left(\cos(k\gamma_1 \pm l\gamma_2) + \cos(l\gamma_1 \pm k\gamma_2) \right); \quad\quad (5)$$

$$F_{\gamma_1\gamma_1}(\gamma_1,\gamma_2) = F_{\gamma_1\gamma_1 0} + \sum_{k=1,K,1} F_{\gamma_1\gamma_1 k}^{\gamma_1} cos(k\gamma_1) + \sum_{k=1,K,1} F_{\gamma_1\gamma_1 k}^{\gamma_2} cos(k\gamma_2) + \sum_{k,l=1,K,1} F_{\gamma_1\gamma_1 k,+l}^{\gamma_1\gamma_2} cos(k\gamma_1 + l\gamma_2) + \sum_{k,l=1,K,1} F_{\gamma_1\gamma_1 k,-l}^{\gamma_1\gamma_2} cos(k\gamma_1 - l\gamma_2) \ (6)$$

$$F_{\gamma_2\gamma_2}(\gamma_1,\gamma_2) = F_{\gamma_1\gamma_1 0} + \sum_{k=1,K,1} F_{\gamma_1\gamma_1 k}^{\gamma_2} cos(k\gamma_1) + \sum_{k=1,K,1} F_{\gamma_1\gamma_1 k}^{\gamma_1} cos(k\gamma_2) + \sum_{k,l=1,K,1} F_{\gamma_1\gamma_1 l,+k}^{\gamma_2\gamma_1} cos(k\gamma_1 + l\gamma_2) + \sum_{k,l=1,K,1} F_{\gamma_1\gamma_1 l,-k}^{\gamma_2\gamma_1} cos(k\gamma_1 - l\gamma_2); \ (7)$$

3. CALCULATION DETAILS

The molecular characteristics were calculated at the nodes of a two-dimensional equidistant grid. The value of the torsional coordinates γ_1 and γ_2 changed from 4^0 to 356^0 with a step of 8^0. During the increasing of the torsional coordinates, the O-H groups rotate counterclockwise when observing along the O-C bonds starting from the position shown in Fig. 2. In this case, the values of physical quantities were calculated at 45*45=2025 points. For each fixed pair of torsional coordinates, the geometry of the molecule was optimized for all remaining 3N-8 natural coordinates. This type of calculation on the entire coordinate plane was performed at the following levels of theory: B3LYP/Aug-cc-pVDZ [48-52], MP2/cc-pVTZ [53-55]. In both cases, the calculated physical quantities were averaged over equivalent points on the coordinate plane (see Fig. 3). Based on the symmetry analysis, presented in Section 2, the calculation of the physical characteristics of the RES molecule can be carried out only within the triangle, indicated in Fig.3. The value of the torsional coordinate γ_1 changed from 4^0 to 356^0 with a step of 8^0. The coordinate γ_2 value changed from 4^0 to γ_1, if $\gamma_1 \leq 180^0$, and from 4^0 to $2\pi - \gamma_1$, if $\gamma_1 \succ 180^0$. At each calculated point, the geometry of the molecule was also optimized on the remaining 3N-8 vibrational coordinates. This type of calculation on a quarter coordinate plane was performed at the following levels of theory: B3LYP/dAug-cc-pVDZ [56] and MP2/dAug-cc-pVDZ [52,56]. Thus, in this case, calculations were performed at 529 points. Then the calculated values of physical quantities were assigned to equivalent points on the coordinate plane. The optimized molecular geometries obtained by the first and second methods were subsequently used to calculate 2D PES without geometry optimization at higher levels of theory (MP2/Aug-cc-pVTZ [51,52], MP2/cc-pVQZ [55] and MP2/dAug- cc-pVTZ [52,56]). Using the results of calculations at the MP2/cc-pVTZ and MP2/cc-pVQZ levels of theory, the results were extrapolated to the CBS limit (MP2/CBS(T,Q)) using the well-known formulas [57,58]. All calculations were carried out using quantum – chemical package ORCA 5.0.3 [59].

The vibrational Schrödinger equation of restricted dimensionality for two torsional coordinates has the form (8) [60-63]:

$$\left[-F_{\gamma_1\gamma_1}(\gamma_1,\gamma_2)\frac{\partial^2}{\partial\gamma_1^2} - F_{\gamma_2\gamma_2}(\gamma_1,\gamma_2)\frac{\partial^2}{\partial\gamma_2^2} - F_{\gamma_1\gamma_2}(\gamma_1,\gamma_2)\frac{\partial^2}{\partial\gamma_1\partial\gamma_2} + U(\gamma_1,\gamma_2) \right]\Psi(\gamma_1,\gamma_2) = E\Psi(\gamma_1,\gamma_2); \ (8)$$

As can be seen, the kinetic coefficients $F_{\gamma_1\gamma_1}$, $F_{\gamma_2\gamma_2}$, $F_{\gamma_1\gamma_2}$, the potential energy U, and the wave functions Ψ are functions of the coordinates γ_1 and γ_2. The 2D surfaces of the kinetic coefficients for the torsional coordinates were calculated using the Wilson $\vec{s}$ vectors [64] as it was done in [37,38]. Equation (8) was solved numerically using the Fourier method [65-67]. The elements of the Hamiltonian matrix were calculated by the formula:

$$H_{(m,n)(m',n')} = -m^2 F_{m-m',n-n'}^{\gamma_1\gamma_1} - n^2 F_{m-m',n-n'}^{\gamma_2\gamma_2} - mn F_{m-m',n-n'}^{\gamma_1\gamma_2} + U_{m-m',n-n'} \quad (9)$$

where $F_{m,n}^{\gamma_1\gamma_1}, F_{m,n}^{\gamma_2\gamma_2}, F_{m,n}^{\gamma_1\gamma_2}, U_{m,n}$ were found by fitting calculated data using symmetry adopted basis functions (4-7). Using Euler's formulas, cosine polynomials were transformed into complex exponential polynomials (10). All transformations were carried out using the Mathematica package [68]:

$$F_{\gamma_1\gamma_1}(\gamma_1,\gamma_2) = \sum_{m,n=-M}^{M} F_{m,n}^{\gamma_1\gamma_1} e^{i(m\gamma_1+n\gamma_2)}, \qquad F_{\gamma_2\gamma_2}(\gamma_1,\gamma_2) = \sum_{m,n=-M}^{M} F_{m,n}^{\gamma_2\gamma_2} e^{i(m\gamma_1+n\gamma_2)},$$

$$\quad (10)$$

$$F_{\gamma_1\gamma_2}(\gamma_1,\gamma_2) = \sum_{m,n=-M}^{M} F_{m,n}^{\gamma_1\gamma_2} e^{i(m\gamma_1+n\gamma_2)}, \qquad U(\gamma_1,\gamma_2) = \sum_{m,n=-M}^{M} U_{m,n} e^{i(m\gamma_1+n\gamma_2)}$$

The wave function is described by a complex two-dimensional Fourier series of the form [65-67]:

$$\Psi(\gamma_1,\gamma_2) = \sum_{m,n=-N}^{N} \Psi_{m,n} e^{i(m\gamma_1+n\gamma_2)}, \quad N \succ M; \quad (11)$$

The intensities of the torsional transitions were calculated using formula (12) [45,69-74]:

$$I_{i\to f} = \frac{Const \cdot \tilde{v}_{if} \cdot \left(e^{-\frac{E_i-E_1}{kT}} - e^{-\frac{E_f-E_1}{kT}} \right)}{Q(T)} p_{if}^2; \quad Q(T) = \sum_i e^{-\frac{E_i-E_1}{kT}}; \quad (12)$$

Here $Q(T)$ - partition function over torsional states, i, f - denote initial and final states, $\tilde{v}_{if}$ - wave number for a transition from initial to a final state, p_{if}^2 - square of the matrix element of the dipole moment operator, which was calculated by the formula (13) using the package [68].

$$p_{if}^2 = \sum_{k=x,y,z} \left(\int_{\gamma_1=0}^{2\pi} \int_{\gamma_2=0}^{2\pi} \Psi_i(\gamma_1,\gamma_2) p_k(\gamma_1,\gamma_2) \Psi_f(\gamma_1,\gamma_2) d\gamma_1 d\gamma_2 \right)^2 \quad (13)$$

The absorption bands in the IR spectrum were modeled using Lorentz spectral contours with a half-width on half-height of 1 cm^{-1}.

4. DISCUSSION

Figure 4 shows the potential surface map and 2D PES of the RES molecule calculated at the MP2/dAug-cc-pVTZ level of theory.
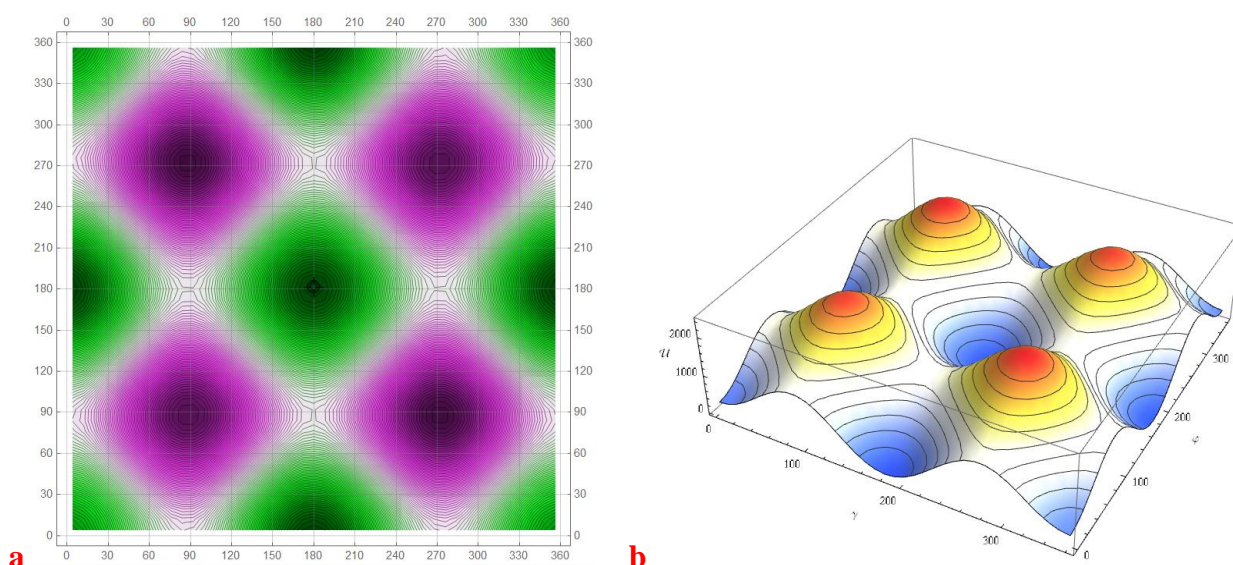
Figure 4 PES map (a) with isoenergy contours and 2D PES (b) of the RES molecule calculated at the MP2/dAug-cc-pVTZ level of theory. An increase in pink color corresponds to an increase in energy, and an increase in green color corresponds to a decrease in energy.

In accordance with Fig. 1 and the definition of zero values of torsional coordinates in section 2, as well as the description of the rotation of hydroxyl groups with increasing torsional coordinates (see section 3), conformer B corresponds to the minimum in Fig. 4a with coordinates $(180^0, 180^0)$. Conformer C corresponds to minima in the corners of the square in Fig. 4a with coordinates $(0^0, 0^0)$, $(0^0, 360^0)$, $(360^0, 0^0)$ and $(360^0, 360^0)$. Two equivalent configurations of conformer A correspond to pairs of minima $(0^0, 180^0)$; $(360^0, 180^0)$ and $(180^0, 0^0)$; $(180^0, 360^0)$. Also from Fig. 4a and 4b it is quite obvious that tunneling between equivalent configurations of conformer A is possible 1) along a short path with simultaneous in-phase or antiphase rotation of hydroxyl groups. In this case, the height of the potential barrier turns is equal to 2450 cm^{-1}. The second, longer path is associated with the initial rotation of one hydroxyl group with a transition to the B or C conformation and subsequent rotation of the second hydroxyl group. In this case, it is necessary to overcome a barrier with a height of about 1240 cm^{-1} twice. It is also obvious that conformers B and C are separated from each other and from conformer A by potential barriers with a minimum height of 1240 cm^{-1}. These results confirm the conclusions of [16,34] about the potentially high stability of conformer C. Indeed, according to the calculations performed, the energies of conformers A and B are very close, while the energy of conformer C is more than 200 cm^{-1} higher than the energy of conformers A and B (see Table 2).

Table 2 Energies A, B and C of conformers of the RES molecule with and without taking into account the energy of zero-point vibrations, values of rotational constants and frequencies of fundamental torsion vibrations in the harmonic approximation, calculated at various levels of theory.

Level of theory	Physical properties	Conformers		
		A	B	C
MP2/dAug-cc-pVDZ	Energy of conformers	-381.6881468008 [Ha] 0 [cm^{-1}]	-381.68810316442 [Ha] 9.6 [cm^{-1}]	-381.68703975422 [Ha] 243.0 [cm^{-1}]
	ZPVE(harm)	23770.51	23765.26	23749.07
	E+ZPVE [cm^{-1}]	0	4.4	221.6
	v_1 [cm^{-1}](I[a.u])	322(1.9) A"	335(0.0) A$_2$	310(0.0) A$_2$
	v_2 [cm^{-1}](I[a.u])	339(185) A"	326(181) B$_1$	302(174) B$_1$
	Rotational constants	3.6985731 GHz 1.8018722 GHz 1.2116030 GHz	3.6847049 GHz 1.8095590 GHz 1.2135731 GHz	3.7189314 GHz 1.7918890 GHz 1.2092414 GHz
MP2/cc-pVTZ	Energy of conformers	-381.97884517427 [Ha] 0 [cm^{-1}]	-381.97870357545 [Ha] 31.08 [cm^{-1}]	-381.97772153456 [Ha] 246.6 [cm^{-1}]
	ZPVE(harm)	23970.53	23953.20	23945.58
	E+ZPVE [cm^{-1}]	0	13.8	221.7
	v_1 [cm^{-1}](I[a.u])	325(8.8) A"	333(0.0) A$_2$	306(0.0) A$_2$
	v_2 [cm^{-1}](I[a.u])	339(186) A"	324(184) B$_1$	305(186) B$_1$
	Rotational constants	3.7733521 GHz 1.8340050 GHz 1.2341548 GHz	3.7668369 GHz 1.8386827 GHz 1.2355711 GHz	3.7850442 GHz 1.8263761 GHz 1.2319366 GHz
MP2/Aug-cc-pVTZ	Energy of conformers	-382.0085318851 [Ha] 0 [cm^{-1}]	-382.00849115726 [Ha] 8.9 [cm^{-1}]	-382.00740780262 [Ha] 246.7 [cm^{-1}]
	ZPVE(harm)	23839.49	23832.83	23810.97
	E+ZPVE [cm^{-1}]	0	2.2	218.2
	v_1 [cm^{-1}](I[a.u])	322(8.8) A"	334(0.0) A$_2$	307(0.0) A$_2$
	v_2 [cm^{-1}](I[a.u])	337(181) A"	327(180) B$_1$	304(179) B$_1$
	Rotational constants	3.7685120 GHz 1.8328363 GHz 1.2331077 GHz	3.7586908 GHz 1.8383782 GHz 1.2345560 GHz	3.7829662 GHz 1.8242550 GHz 1.2307514 GHz
MP2/cc-pVQZ	Energy of conformers	-382.10244653612 [Ha] 0 [cm^{-1}]	-382.10236475997 [Ha] 17.9 [cm^{-1}]	-382.10131948220[Ha] 247.4 [cm^{-1}]
	ZPVE(harm)	23973.91	23958.88	23952.28
	E+ZPVE [cm^{-1}]	0	2.9	225.8
	v_1 [cm^{-1}](I[a.u])	330(8.3)A"	337(0.0)A$_2$	310(0.0) A$_2$
	v_2 [cm^{-1}](I[a.u])	342(184)A"	329(183)B$_1$	310(185) B$_1$
	Rotational constants	3.7843168 GHz 1.8400781 GHz 1.2380778 GHz	3.7778320 GHz 1.8450124 GHz 1.2396123 GHz	3.7964765 GHz 1.8323477 GHz 1.2358647 GHz
MP2/CBS(T,Q)	Energy of conformers	-382.1926421245 [Ha] 0[cm^{-1}]	-382.19260400272 [Ha] 8.3[cm^{-1}]	-382.19151257910[Ha] 247.9[cm^{-1}]
	ZPVE(harm)	23976.38	23963.02	23957.17
	E+ZPVE [cm^{-1}]	4.7	0	233.4
	v_1 [cm^{-1}](I[a.u])	334(8.0) A"	340(0.0)A$_2$	313(0.0) A$_2$
	v_2 [cm^{-1}](I[a.u])	344(181)A"	330(187) B$_1$	314(184) B$_1$
	Rotational constants	3.79231807GHz 1.84450982GHz 1.24094053GHz	3.791799903GHz 1.849853573GHz 1.243302032GHz	3.8063353676GHz 1.8382531838GHz 1.2395602703GHz
MP2/dAUG-cc-pVTZ	Energy of conformers	-382.01191270886 [Ha] 0 [cm^{-1}]	-382.01184946919 [Ha] 13.9 [cm^{-1}]	-382.01075692423 [Ha] 253.7 [cm^{-1}]
	ZPVE(harm)	23922.25	23911.40	23897.66
	E+ZPVE [cm^{-1}]	0	3.1	229.1
	v_1 [cm^{-1}](I[a.u])	331(5.1) A"	340(0.0) A$_2$	310(0.0) A$_2$
	v_2 [cm^{-1}](I[a.u])	341(184) A"	334(181) B$_1$	311(183) B$_1$
	Rotational constants	3.7676738 GHz 1.8327500 GHz 1.2329788 GHz	3.7586906 GHz 1.8383783 GHz 1.2345561 GHz	3.7821794 GHz 1.8240950 GHz 1.2305952 GHz

As follows from the data in Table. 2, the energy of conformer B, taking into account the VZPE, is only slightly higher than the energy of conformer A. Depending on the level of theory, the excess of energy B over A is in the range of 41.4- 2.2 cm^{-1}. Moreover, the higher the level of theory, the closer the energies of these two conformers. The energy of conformer C is 211 – 229 cm^{-1} higher than the energy of conformer A, depending on the level of theory. And in this case, the higher the level of theory, the greater the difference in the energies of C and A conformers. Also according to the data in Tabl.2 rotational constants of all three conformers are very close, and their ratio indicates that all conformers are close to prolate symmetric tops. Calculations of

normal vibrations of conformers of the RES molecule predict that in conformer B the torsional in-phase vibration of O-H groups of A_2 specie, which keeps symmetry with respect to the C_2 axis and is inactive in the IR spectrum, has a 5-8 cm^{-1} higher frequency than the antiphase torsional vibration of B_1 specie, active in the IR spectrum. In conformer C, these vibrations, according to harmonic calculations, have almost the same frequencies, while their frequencies are 20- 30 cm^{-1} lower than the frequencies of the corresponding vibrations in conformer B. For conformer A, the calculation of normal vibrations predicts the preservation of in-phase and anti-phase torsional vibrations of O-H groups, but the vibrational amplitudes of hydroxyl groups are no longer the same. Due to this, both vibrations are active in the IR spectrum. The antiphase torsional vibration is more intense than in-phase torsional vibration. Note that all fundamental torsional vibrations in all three conformers of the RES molecule are active in the Raman spectra.

As noted above, the energies of stationary torsional states were calculated using a numerical solution of the vibrational Schrödinger equation of restricted dimensionality at several levels of theory. Table 3 shows the energies of the 100 lowest torsional states, torsional quantum numbers, symmetry species and values of tunneling splittings of torsional states of conformer A of the RES molecule, calculated at the MP2/dAug-cc-pVTZ level of theory (optimization of geometric parameters was carried out at the MP2/dAug-cc-pVDZ level of theory).

Table 3 Calculated at the MP2/dAug-cc-pVTZ level of theory 1) values of the energies of stationary torsional states of the RES molecule (columns 3 and 10), 2) the splittings of torsional states due to tunneling (columns 4 and 11), 3) the symmetry species of torsional states in molecular symmetry group $C_{2V}(M)$ (columns 7 and 14), 4) classification of torsional states using vibrational quantum numbers n_1, n_2 for conformer A and n_s, n_{as} for conformers B and C (columns 5,6 and 12,13), 5) types of conformations of a molecule (columns 2 and 9).

1	2	3	4	5	6	7	8	9	10	11	12	13	14
Energy level number N	Confor-mation	Energy [cm^{-1}]	Energy splitting [cm^{-1}]	n_s n_1	n_{as} n_2	Symmetry species	Energy level number N	Confor-mation	Energy [cm^{-1}]	Energy splitting [cm^{-1}]	n_s n_1	n_{as} n_2	Symmetry species
GS	A C_S	312.45											
1	A	0	7.84*10^{-7}	0	0	A_1	51	A	1145.93	9.15*10^{-3}			B_2
2	A	0		0	0	B_1	52	A	1145.94				A_2
3	B	2.09	0	0	0	A_1	53	B	1147.11	0			A_1
4	C	237.75	0	0	0	A_1	54	A	1149.67	7.35*10^{-1}			B_1
5	A	295.17	1.81*10^{-6}	1	0	A_2	55	A	1150.40				A_1
6	A	295.17		1	0	B_2	56	A	1170.11	6.42*10^{-2}			B_1
7	B	300.06	0	1	0	A_2	57	A	1170.17				A_1
8	B	303.09	0	0	1	B_2	58	C	1174.87	0			B_1
9	A	316.23	2.22*10^{-5}	0	1	A_2	59	C	1175.02	0			A_1
10	A	316.23		0	1	B_2	60	A	1179.42	1.10*10^{-1}			A_2
11	C	521.68	0	1	0	A_2	61	A	1179.53				B_2
12	C	530.73	0	0	1	B_2	62	C	1290.63	0			B_1
13	A	566.81	9.14*10^{-5}	2	0	B_1	63	C	1294.03	0			A_1
14	A	566.81		2	0	A_1	64	A	1296.01	1.97*10^{-1}			B_2
15	B	575.09	0	2	0	A_1	65	A	1296.20				A_2
16	B	575.56	0	1	1	B_1	66	A	1322.62	5.11*10^{-2}			B_2
17	B	600.84	0	0	2	A_1	67	A	1322.68				A_2
18	A	602.38	4.65*10^{-3}	0	2	B_1	68	A	1329.94	4.36*10^{-3}			B_2
19	A	602.38		0	2	A_1	69	A	1329.95				A_2
20	A	612.48	3.73*10^{-4}	1	1	B_1	70	A	1342.84	1.05*10^{-2}			B_1
21	A	612.48		1	1	A_1	71	A	1342.85				A_1
22	C	781.11	0	1	1	B_1	72	C	1346.33	0			A_1

N	Conf	Energy [cm⁻¹]	Energy splitting [cm⁻¹]	n_1	n_2	Symmetry	N	Conf	Energy [cm⁻¹]	Energy splitting [cm⁻¹]			Symmetry
23	C	782.43	0	2	0	A_1	73	B	1378.13	0			A_2
24	A	809.29	$4.26*10^{-4}$	3	0	B_2	74	A+B	1379.68	0			B_2
25	A	809.29		3	0	A_2	75	B+A	1382.51	0			A_2
26	B	816.45	0	2	1	B_2	76	B	1392.88	0			B_2
27	B	816.54	0	1	2	A_2	77	A+C	1398.68	$8.63*10^{-2}$			A_2
28	C	820.06	0	0	2	A_1	78	A+C	1398.76				B_2
29	A	853.72	$9.53*10^{-6}$	0	3	B_2	79	A+C	1399.32	$1.81*10^{-1}$			B_1
30	A	853.72		0	3	A_2	80	A+C	1399.50				A_1
31	B	870.24	0	3	0	A_1	81	A	1409.36	$1.48*10^{-2}$			A_2
32	B	877.62	0	0	3	B_2	82	A	1409.38				B_2
33	A	883.21	$6.69*10^{-6}$	2	1	A_2	83	A	1421.47	$8.22*10^{-1}$			A_2
34	A	883.21		2	1	B_2	84	A	1422.29				B_2
35	A	899.14	$7.63*10^{-3}$	1	2	A_2	85	A+B	1442.52	$8.27*10^{-3}$			A_1
36	A	899.14		1	2	B_2	86	A+B	1442.53				B_1
37	C	994.46	0	2	1	B_2	87	C+A	1477.22	0			B_2
38	C	995.00	0	1	2	A_2	88	C+A	1479.27	0			A_2
39	A	999.31	$2.04*10^{-3}$	2	2	B_1	89	A+C	1489.23	$7.52*10^{-1}$			B_1
40	A	999.31		2	2	A_1	90	A+C	1489.98				A_1
41	A	1009.1	$2.74*10^{-2}$	4	0	B_1	91	C	1550.06	0			A_2
42	A	1009.13		4	0	A_1	92	B+A	1566.04	1.39			A_1
43	C	1068.56	0			A_2	93	B+A	1567.43				B_1
44	A	1083.71	$1.13*10^{-2}$			B_1	94	C	1578.72	0			B_2
45	A	1083.72				A_1	95	A+C	1604.89	0			B_1
46	C	1088.03	0			B_2	96	A+C	1606.52	0			A_1
47	B	1113.16	0			A_1	97	A	1614.39	$1.33*10^{-2}$			B_1
48	B	1114.34	0			B_1	98	A	1614.40				A_1
49	A	1124.76	$2.68*10^{-2}$			B_1	99	A	1616.30	$3.93*10^{-3}$			B_2
50	A	1124.79				A_1	100	A	1616.30				A_2

Tabl. 4 shows the energies of the 25 lowest torsional states, torsional quantum numbers, symmetry species and values of tunneling splittings of conformer A of the RES molecule, calculated at the MP2/CBS(T,Q) level of theory (optimization of geometric parameters was carried out at the MP2/cc-pVTZ level of theory).

Table 4 Calculated at the MP2/CBS(T,Q) level of theory 1) values of the energies of stationary torsional states of the RES molecule (columns 3), 2) the splittings of torsional states due to tunneling (columns 4), 3) the symmetry species of torsional states in molecular symmetry group $C_{2V}(M)$ (columns 7), 4) classification of torsional states using vibrational quantum numbers n_1, n_2 for conformer A and n_s, n_{as} for conformers B and C (columns 5,6), 5) types of conformations of a molecule (columns 2).

1	2	3	4	5	6	7
Energy level number N	Conformation	Energy [cm⁻¹]	Energy splitting [cm⁻¹]	n_s n_1	n_{as} n_2	Symmetry species
GS	B	313.94				
1	B	0	0	0	0	A_1
2	A	1.35	$5.99*10^{-7}$	0	0	B_1
3	A	1.35		0	0	A_1
4	C	235.55	0	0	0	A_1
5	B	299.97	0	1	0	A_2
6	A	310.34	$1.97*10^{-6}$	1	0	B_2
7	A	310.34		1	0	A_2
8	B	302.80	0	0	1	B_2
9	A	321.37	$5.60*10^{-6}$	0	1	A_2
10	A	321.37		0	1	B_2
11	C	525.50	0	1	0	A_2
12	C	535.70	0	0	1	B_2
13	A	578.20	$4.79*10^{-5}$	2	0	B_1
14	A	578.20		2	0	A_1
15	B	578.98	0	1	1	B_1
16	B	579.04	0	2	0	A_1
17	B	603/26	0	0	2	A_1
18	A	611.98	$5.26*10^{-4}$	0	2	B_1
19	A	611.98		0	2	A_1
20	A	621.32	$1.12*10^{-4}$	1	1	B_1
21	A	621.32		1	1	A_1
22	C	792.67	0	1	1	B_1
23	C	793.00	0	2	0	A_1
24	B	826.56	0			B_2
25	B	856.56	0			A_2

Note that according to the data in Table 4, calculations at the MP2/CBS(T,Q) level of theory, conformer B is energetically preferable to conformer A by 1.35 cm^{-1}. As follows from the data in Table. 3,4 and results of calculations at other levels of theory the value of the tunneling splitting of the ground vibrational state of conformer A is sensitive to the level of theory. Its value varies in the range from $1.4*10^{-6}$ to $6*10^{-7}$ cm^{-1}. This is more than an order of magnitude greater than the calculated value of tunneling splitting in a similar conformer of the CTL [34] molecule (from $9.1*10^{-8}$ to $1.9*10^{-8}$ cm^{-1}). This is quite consistent with the fact that in the case of the CTL molecule, tunneling between equivalent configurations is associated with the breaking of a hydrogen bond. According to calculations, the first excited torsional state of conformer A of the RES molecule is split due to tunneling by $2*10^{-6}$ cm^{-1}. This is comparable to the calculated value of the tunneling splitting of the first excited torsional state of the CTL molecule [34] (from $1.1*10^{-5}$ to $6.1*10^{-6}$ cm^{-1}, experimental value $1.04*10^{-5}$ cm^{-1} [33]). It can be assumed that the tunneling splitting of the first excited torsion state of conformer A of the RES molecule can also be resolved experimentally. However, it must be borne in mind that, according to calculations, in the CTL molecule the first excited torsional energy level lies approximately 100 cm^{-1} lower than the similar level in the RES molecule. This should lead to the fact that the part of conformers A of the RES molecule in this state will be significantly less than in the case of the CTL molecule, which will complicate their experimental detection.

Let us now consider the torsional vibrations of O-H groups in the RES molecule. Table 5 contains the values of the frequencies of fundamental vibrations, overtones and combinations of the three conformers of the RES molecule, calculated at the two highest levels of theory.

Table 5. Values of frequencies and intensities of fundamental torsional vibrations, their overtones and combinations of three conformers of the RES molecule, calculated at the MP2/dAug-cc-pVTZ and MP2/CBS(T,Q) levels of theory.

	MP2/dAug-cc-pVTZ (T=300 K)					
	Conformer A		Conformer B		Conformer C	
	Symmetry species	Frequency [cm^{-1}]	Symmetry species	Frequency [cm^{-1}]	Symmetry species	Frequency [cm^{-1}]
ν_1	A_2, B_2 I($1A_1 \rightarrow 5A_2$) I($1A_1 \rightarrow 6B_2$) I($2B_1 \rightarrow 5A_2$) I($2B_1 \rightarrow 6B_2$)	295.17 0 3.25 3.25 0	A_2 I($3A_1 \rightarrow 7A_2$)	299.97 0	A_2 I($4A_1 \rightarrow 11A_2$)	283.93 0
ν_2	A_2, B_2 I($1A_1 \rightarrow 9A_2$) I($1A_1 \rightarrow 10B_2$) I($2B_1 \rightarrow 9A_2$) I($2B_1 \rightarrow 10B_2$)	316.23 0 4.87 4.87 0	B_2 I($3A_1 \rightarrow 8B_2$)	301.00 8.04	B_2 I($4A_1 \rightarrow 12B_2$)	292.98 3.18
$2\nu_1$	A_1, B_1 I($1A_1 \rightarrow 13B_1$) I($1A_1 \rightarrow 14A_1$) I($2B_1 \rightarrow 13B_1$) I($2B_1 \rightarrow 14A_1$)	566.81 0.29 0.11 0.11 0.29	A_1 I($3A_1 \rightarrow 15A_1$)	573.00 0.21	A_1 I($4A_1 \rightarrow 23A_1$)	544.68 0.35
$2\nu_2$	A_1, B_1 I($1A_1 \rightarrow 18B_1$) I($1A_1 \rightarrow 19A_1$) I($2B_1 \rightarrow 18B_1$) I($2B_1 \rightarrow 19A_1$)	602.38 0.01 0.54 0.54 0.01	A_1 I($3A_1 \rightarrow 17A_1$)	598.75 0.006	A_1 I($4A_1 \rightarrow 28A_1$)	582.31 0.023

	A₁, B₁	612.48	B₁	578.98	B₁	543.36
$\nu_1+\nu_2$	$I(1A_1{\rightarrow}20B_1)$	0.001	$I(3A_1{\rightarrow}15B_1)$	0.52	$I(4A_1{\rightarrow}22B_1)$	0.005
	$I(1A_1{\rightarrow}21A_1)$	0.01				
	$I(2B_1{\rightarrow}20B_1)$	0.01				
	$I(2B_1{\rightarrow}21A_1)$	0.001				
	MP2/CBS(T,Q) (T=300 K)					
	Conformer A		Conformer B		Conformer C	
	Symmetry species	Frequency [cm⁻¹]	Symmetry species	Frequency [cm⁻¹]	Symmetry species	Frequency [cm⁻¹]
ν_1	B_2, A_2	308.99	A_2	297.97	A_2	289.95
	$I(2B_1{\rightarrow}6B_2)$	0	$I(1A_1{\rightarrow}5A_2)$	0	$I(4A_1{\rightarrow}11A_2)$	0
	$I(2B_1{\rightarrow}7A_2)$	3.99				
	$I(3A_1{\rightarrow}6B_2)$	3.99				
	$I(3B_1{\rightarrow}7A_2)$	0				
ν_2	A_2, B_2	320.02	B_2	302.80	B_2	300.15
	$I(2B_1{\rightarrow}9A_2)$	5.84	$I(1A_1{\rightarrow}8B_2)$	10.36	$I(4A_1{\rightarrow}12B_2)$	3.85
	$I(2B_1{\rightarrow}10B_2)$	0				
	$I(3A_1{\rightarrow}9A_2)$	0				
	$I(3B_1{\rightarrow}10B_2)$	5.84				
$2\nu_1$	B_1, A_1	576.85	A_1	579.04	A_1	557.45
	$I(2B_1{\rightarrow}13B_1)$	0.17	$I(1A_1{\rightarrow}16A_1)$	0.37	$I(4A_1{\rightarrow}23A_1)$	0.34
	$I(2B_1{\rightarrow}14A_1)$	0.21				
	$I(3A_1{\rightarrow}13B_1)$	0.21				
	$I(3B_1{\rightarrow}14A_1)$	0.17				
$2\nu_2$	B_1, A_1	610.63	A_1	603.26	A_1	595.41
	$I(2B_1{\rightarrow}18B_1)$	0.53	$I(1A_1{\rightarrow}17A_1)$	0.011	$I(4A_1{\rightarrow}28A_1)$	0.023
	$I(2B_1{\rightarrow}19A_1)$	0				
	$I(3A_1{\rightarrow}18B_1)$	0				
	$I(3B_1{\rightarrow}19A_1)$	0.53				
$\nu_1+\nu_2$	B_1, A_1	619.97	B_1	573.47	B_1	557.12
	$I(2B_1{\rightarrow}20B_1)$	0.005	$I(1A_1{\rightarrow}16B_1)$	0.65	$I(4A_1{\rightarrow}22B_1)$	0.001
	$I(2B_1{\rightarrow}21A_1)$	0				
	$I(3A_1{\rightarrow}20B_1)$	0				
	$I(3B_1{\rightarrow}21A_1)$	0.005				

Fig. 5a-5d show the torsional IR spectra of three conformers of the RES molecule calculated using formulas (12) and (13) at temperatures of 300 and 30 K.
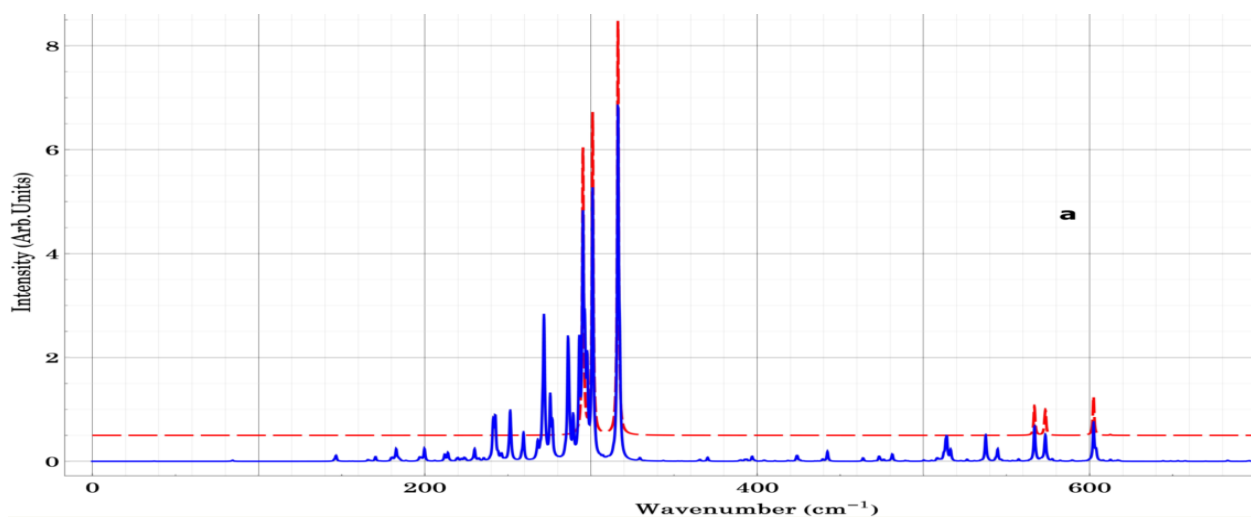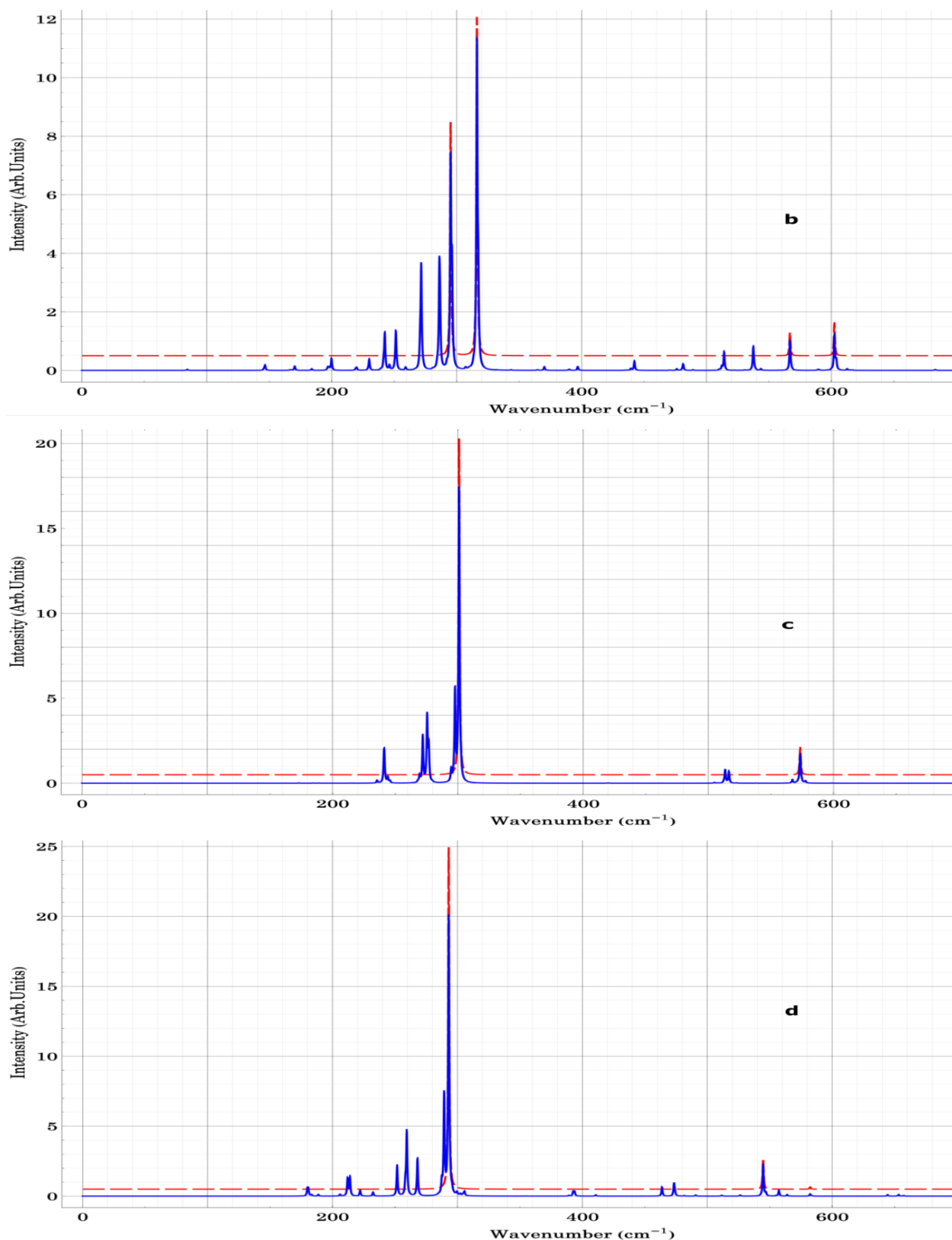
Figure 5 Torsional IR spectra of the RES molecule, calculated at the MP2/dAug-cc-pVTZ level of theory at temperatures of 300 (blue) and 30 K (red) for a mixture of conformers at thermodynamic equilibrium (5a), for conformer A (5b), for conformer B (5c) and for conformer C (5d).

As follows from the data in Table 5, the fundamental torsional vibration with a calculated frequency in the range of 316 – 320 cm^{-1} should appear with the highest intensity in the IR spectrum of conformer A (see Fig. 5b). The second fundamental torsional vibration with a frequency in the range of 295 – 309 cm^{-1} should appear with less intensity. The antiphase torsional vibration of B$_2$ specie in conformer B with a calculated frequency in the range of 301 – 303 cm^{-1} should be even more intense (see Fig. 5c). It is also expected that at room temperature, an antiphase torsional vibration of B$_2$ specie in conformer C can appear with average intensity with a calculated frequency in the range of 293 – 300 cm^{-1} (see Fig. 5d). Analyzing the experimental data presented in the literature on the IR and microwave spectra of the RES molecule, we note that the spectral range of interest to us and, accordingly, torsional vibrations of O-H groups were studied only in [18,26]. In [17,21] the results of work [18] are presented as experimental data. The authors [18] indicate that to record the low-frequency IR spectrum (40 – 400 cm^{-1}), the sample was placed in vaseline oil, and to record the range of 400 – 4000 cm^{-1}, the sample was prepared in the form of a KBr tablet. Obviously, both options are not very well suited for comparison with theoretical data from the calculation of torsional vibrations of a free RES molecule. The authors of [17,21] assigned the IR absorption bands at 460 and 387 cm^{-1} to the torsional vibrations of O-H groups. Today, these assignments for the free RES molecule look very doubtful. Indeed, according to [33,34,75], the torsional vibration of the hydrogen-bonded O-H group in the free CTL molecule appears at a frequency of 415 cm^{-1}. Since, in addition to the barrier to overcoming planarity, an additional contribution that prevents exit from the plane is made by the hydrogen bond, these two effects provide a significant increase in the frequency of torsional vibration in comparison with H-bond free the phenol molecule - 309.2 cm^{-1} [76]. Therefore, the bands 460 and 387 cm^{-1} have unreasonably high frequencies in order to correspond to torsional vibrations of O-H groups in a free RES molecule in which there are no hydrogen bonds. At the same time, in the absence of more modern studies of the gas phase of RES, attention should be paid to the results of systematic studies of torsional vibrations of substituted phenols in work [26]. The author recorded the low-frequency range by preparing RES and CTL samples in a cyclohexane solution. The possibility of the formation of associates of the molecules under study was carefully analyzed and the appropriate solution concentration was selected to ensure the presence of only monomers. A comparison of the experimental frequencies of torsional vibrations of a number of para- and meta-substituted phenols in cyclohexane with the corresponding frequencies in the gas phase showed very good agreement [26], which indicates a very weak influence of cyclohexane on the values of the frequencies of torsional vibrations in para- and meta-substituted phenols. In addition, the assignment of the band at 411 cm^{-1} to the torsional vibration of the O-H bond in the CTL molecule [26] is in good

agreement with the results of [33,75] (415 cm^{-1}). Therefore, we think the assignment in [26] of the band at 318 cm^{-1} to the torsional vibration of O-H bonds in the RES molecule to be very reliable.

Returning to the calculations performed in this work, we note that the frequencies of the most intense torsional vibration in the A conformer of the RES molecule, calculated at the highest levels of theory, turned out to be equal to 316 and 320 cm^{-1}. Obviously, this is in very good agreement with the experimental value of 318 cm^{-1} [26]. At the same time, the authors of [26] do not report that any bands near 300 cm^{-1} are assigned to torsional vibrations of the RES molecule. But it is near this frequency calculations predict an intense band caused by torsional vibrations of the B$_2$ specie in the B conformer of the RES molecule. It is difficult to make any assumptions here. Indeed, on the one hand, the author of [26] do not report the assignment of any absorption band near 222 cm^{-1} to the torsional vibration of the free hydroxyl group in the CTL molecule, although it is reliably observed in the works of [33,75]. On the other hand, it is possible that cyclohexane stabilizes only the A conformer of the RES molecule. But even in this case, calculations predict in the IR spectrum of conformer A second, less intense absorption band with frequencies for the two highest levels of theory 295 and 309 cm^{-1}, although in [26] only one is attributed to the torsional vibrations of the O-H groups. A possible assumption to explain this could be the situation when the real value of the frequency of the second torsional vibration in the A conformer is greater than 309 cm^{-1} but, of course, less than 318 cm^{-1}. Then, taking into account the spectral resolution of 4 cm^{-1} in [26], these two bands could not be resolved. In any case, an experimental study of the RES molecule, similar to the studies performed in [33,75] for the CTL molecule, seems necessary.

Concluding our consideration of torsional vibrations of the RES molecule, we note that the form of the wave functions of the excited torsional states of conformers B and C confirms the in-phase and anti-phase vibrations of A$_2$ and B$_2$ species, respectively. Fundamental vibrations in conformer A are of a more complex quantum nature. The shape of the wave functions indicates the simultaneous involvement in torsional modes of two equivalent configurations that form the common vibration. In each of the equivalent configurations, only one of the two hydroxyl groups vibrates, while in the second equivalent configuration, the second hydroxyl group vibrates. Depending on whether the hydroxyl hydrogen atoms appear in two equivalent configurations on the same side relative to the plane of the benzene ring during vibration or on different sides, the intensity of the vibration turns out to be different from zero or equal to it.

5. CONCLUSIONS

For the first time, the energies of stationary torsional states of the RES molecule were calculated using a numerical solution of the vibrational Schrödinger equation, based on the 2D

surfaces of 1) potential energy, 2) kinetic coefficients and 3) dipole moments calculated quantum chemically at several levels of theory. The calculations confirmed the existing literature data on the closeness of the energies of conformers A and B of the RES molecule (see Fig.1), while the energy of conformer C is approximately 240 cm^{-1} higher than the energy of conformers A and B, which also agrees well with a number of literature sources (see Section 1). According to calculations, all three conformers are separated from each other by potential barriers with a height of at least 1240 cm^{-1}. This confirms the conclusions of [16,34] about the stability of conformer C, even at room temperatures.

The frequency values of the most intense torsional vibration of hydroxyl groups in conformer A of the RES molecule, calculated at the MP2/dAug-cc-pVTZ and MP2/CBS(T,Q) levels of theory are 316 and 320 cm^{-1}, which is in good agreement with the experimental value of the frequency of this vibrations (318 cm^{-1}) obtained in [26]. The second, less intense torsional vibration in this conformer, according to calculations at the above levels of theory, should appear near 295 or 309 cm^{-1}, respectively. In conformer B, the only fundamental torsional vibration active in the IR spectrum should appear in the form of an intense absorption band near 300 cm^{-1} according to both levels of theory. A similar vibration in conformer C, according to calculations at the two mentioned levels of theory, can appear as band of average intensity in the range 292 – 300 cm^{-1} (see Table 5 and Fig. 5).

The calculated values of the tunneling splitting of the ground vibrational state of conformer A are in the range from $1.4*10^{-6}$ to $6*10^{-7}$ cm^{-1}, depending on the level of theory used. This is an order of magnitude larger than the corresponding value for the CTL molecule (from $9.1*10^{-8}$ to $1.9*10^{-1}$ cm^{-1}) [34], which could be expected due to the absence of intramolecular hydrogen in the case of the RES molecule. The calculated tunneling splittings of the first excited torsional state in the RES (from $1.59*10^{-6}$ to $3.06*10^{-6}$ cm^{-1}) and CTL (from $1.1*10^{-5}$ to $6.1*10^{-6}$ cm^{-1}) molecules are comparable, which allows to hope that this splitting can be experimentally resolved, as was the case with the CTL molecule [33].

The calculated wave functions of the stationary torsional states of conformers A, B and C made it possible, based on the provisions set out in Section 2, to classify the 100 lowest torsional states of the molecule by symmetry species of the molecular symmetry group $C_{2V}(M)$. At the same time, the classification of torsional states, based on the use of quantum numbers, which essentially characterize the normal modes of the corresponding vibrations, turned out to be possible only for several of the lowest excited torsional states (see Table 3). We attribute this to the limitations of using the normal vibrations model to analyze large-amplitude vibrations. Indeed, analysis of the wave functions shows that with increasing energy of torsional states, pairs of conformers are involved in common vibrational modes. In addition, at sufficient energies, the

wave functions describe the inhibited rotation of hydroxyl groups over potential barriers rather than the classical vibrations with the small amplitudes of atomic displacements. This, of course, does not fit into the standard framework of normal molecular vibrations. However, we see that even such complex vibrations with large amplitudes are completely subject to the requirements of molecular symmetry.

Torsional IR spectra of three conformers of the RES molecule separately, as well as their mixtures in the case of thermodynamic equilibrium at room and low temperatures, are modeled based on the calculated values of the energies of stationary torsional states, matrix elements of the dipole moment and partition functions. This can serve as a basis for interpreting the low frequency IR and microwave spectra of the RES molecule.

6. ACKNOWLEDGMENTS

REFERENCES

[1] Hubler, T.L., Franz, J.A., Shaw, W.J., Bryan, S.A., Hallen, R.T., Brown, G.N., Bray, L.A., & Linehan, J.C. (1995). Synthesis, structural characterization, and performance evaluation of resorcinol-formaldehyde (R-F) ion-exchange resin (PNL--10744). United States.

[2] M.A. Ksenofontov, E.Yu. Bobkova, M.B. Shundalau, L.E. Ostrovskaya, V.S. Vasil'eva, Quantum Chemical Simulation of the Interaction of Functional Groups in Polyurethanes with 3d – Metal Ions During Their Extraction from Aqueous Solutions,   J.Appl.Spectr., 84 (2017) 816 – 823.

[3] G. Konishi, Precision polymerization of designed phenol: new aspects of phenolic resin chemistry. J. Syn. Org. Chem. Jpn. 66 (2008) 705-713.

[4] P. Timmerman, W. Verboom, D. N. Reinhoudt, Resorcinarenes. Tetrahedron 52 (1996) 2663-2704.

[5] V. Bohmer. Calixarenes, macrocycles with (almost) unlimited possibilities. Angew. Chem. Inr. Ed. Engl, 34 (1995) 713-745.

[6] A.D. Kushwaha, A.B. Kalambe, V.V. Hiwase, D.N. Urade, Structural and Antibacterial Study of Resin-II Derived from p-Nitrophenol, Resorcinol and Formaldehyde, J.Chem.Pharm.Res., 4 (2012) 1111-1116.

[7] A. Kobayashi, G. Konishi, Synthesis and Analysis of Resorcinol-Acetone Copolymer, Molecules, 14 (2009) 364-377.

[8] M.Y. Lui, K.S. Lokare, E. Hemming, J.N.G. Stanley, A. Perosa, M. Selva, A.F. masters, T. Maschmeyer, Microwave-assisted Methylation of Dihydroxybenzene Derivatives with Dimethyl Carbonate, RSC Adv., 6 (2016) 58443-58451.

[9] S.M. Attia, W.I.A. Ismail, M.M. Mossad, Characterization of Pure and Composite Resorcinol Formaldehyde Aerogels Doped with Copper, Egypt.J.Phys., 45 (2017) 11-22.

[10] M.Özparpucu, E. Windeisen-Holzhauser, G. Wegener, K. Richter, Wood Science and Technology, 56 (2022) 349-365.

[11] G.E. Bacon, N.A. Curry, A Study of α – Resorcinol by Neutron Diffraction, Proc. R. Soc. Lond. Ser. A, 235 (1956) 552-559.

[12] G.E. Bacon, R.J. Jude, Neutron – Diffraction Studies of Salicyclic Acid and α – Resorcinol, Z. Kristallogr.-Crystalline Materials, 138 (1973) 19-40.

[13] S.A. Kudchadker, B.J. Zwolinski, Conformational Analysis of Benzenediols: Pyrocatechol, Resorcinol and Hydroquinone, J.Mol.Struct., 48 (1978) 271 – 277.

[14] H. Konschin, An STO-3G Molecular Orbital Investigation of Planar Anisole, cis – Guaiacol and trance – Veratrole, J.Mol.Struct., 105 (1983) 213 – 224.

[15] H. Konschin, An STO-3G Molecular Orbital Investigation of Planar m – and p – Dihydroxybenzene: Fully Optimized Molecular Structures, J.Mol.Struct. (Theochem), 110 (1984) 267 – 276.

[16] C. Puebla, T.-K. Ha, A Theoretical Study of Conformations and Rotational Barriers in Dihydroxybenzenes, J.Mol.Struct. (Theochem), 204 (1990) 337 – 351.

[17] M. Gerhards, W. Perl, K. Kleinermanns, Rotamers and Vibrations of Resorcinol by Spectral Hole Burning, Chem.Phys.Lett., 240 (1995) 506 – 512.

[18] V.A. Mironenko, N.I. Rogalevich, M.A. Ksenofontov, Calculating and Interpreting the Vibrational Spectra of Phenols, J.Appl.Spectr., 44 (1986) 53-56.

[19] W.D. Geppert, C.E.H. Dessent, S. Ullrich, K. Müller-Dethlefs, Observation of Hydrogen – Bonded Rotational Isomers of the Resorcinol – Water Complex, J.Phys.Chem. A, 103 (1999) 7186 – 7191.

[20] W.D. Geppert, C.E.H. Dessent, K. Müller-Dethlefs, ZEKE and Hole – Burning Spectroscopy of the Rotational Isomers of Resorcinol – CO, J.Phys.Chem. A, 103 (1999) 9687 – 9692.

[21] P. Imhof, R. Brause, K. Kleinermanns, Determination of Ground State Vibrational Frequencies of Jet – Cooled Resorcinol by Mean of Dispersed Fluorescence Spectroscopy and Ab Initio Calculations, J.Mol.Spectr., 211 (2002) 65 – 70.

[22] M.B. Shundalov, G.A. Pitsevich, M.A. Ksenofontov, D.S. Umreiko, Calculation of the Energies of Torsional States for Dihydroxybenzenes, J.Appl.Spectr., 74 (2007) 199 – 206.

[23] M.B. Shundalov, G.A. Pitsevich, M.A. Ksenofontov, D.S. Umreiko, Calculation of Transition Intensities for Torsional Vibrations in IR and Raman Spectra of Dihydroxybenzenes, J.Appl.Spectr., 74 (2007) 659 – 665.

[24] M. Manojkumar, M. Manjula, C. Sudhakar, Vibrational Analysis, NMR, Homo – Lumo and MEP Analysis of Resorcinol Based on Density Functional Theory Calculations, Int.J.Mult.Ed.Res., 11 (2022) 146 – 156.

[25] H.W. Wilson, The Vapor Phase Infrared Spetra of Hydroquinone, Pyrocatechol, and Resorcinol, Spectrochim.Acta, 30A (1974) 2141 – 2152.

[26] W.G. Fateley, G.L. Carlson, F. Bentley, Phenolic – O-H Torsional Frequency as a Probe for Studying π – Electron Distortions in Aromatic Systems, J.Phys.Chem., 79 (1975) 199 – 204.

[27] G.N.P. Tripathi, Crystal Spectra and Vibrational Assignments in α – Resorcinol, J.Chem.Phys., 74 (1981) 250 – 255.

[28] T.M. Dunn, R. Tembreull, D.M. Lubman, Free – Jet Spectra and Sructure of o - , m - , and p – Dihydroxybenzenes, Chem.Phys.Lett., 121 (1985) 453 – 457.

[29] S. Melandri, G. Maccaferri, W. Caminati, P.G. Favero, Conformational Equilibrium in Resorcinol by Means of the Free – Jet Absorption Millimeter Wave Spectrum, Chem.Phys.Lett., 256 (1996) 513 – 517.

[30] M. Gerhards, C. Unterberg, S. Schumm, Structure and Vibrations of Dihydroxybezene Cations and Ionization Potentials of Dihydroxybezenes Studied by Mass Analyzed Threshold Ionization and Infrared Photoinduced Rydberg Ionization Spectroscopy as well as Ab Initio Theory, J.Chem.Phys., 111 (1999) 7966 – 7975.

[31] G. Myszkiewicz, W.L. Meerts, C. Ratzer, M. Schmitt, Structure Determination of Resorcinol Rotamers by High – Resolution UV Spectroscopy, ChemPhysChem, 6 (2005) 2129 – 2136.

[32] A. Patzer, J. Langer, H. Knorke, H. Neitsch, O. Dopfer, M. Miyazaki, K. Hattori, A. Takeda, S.-I. Ishiuchi, M. Fujii, IR Spectra of Resorcinol$^+$ - Ar$_n$ Cluster Cations (n=1,2): Evidence for Photoionization – Induced π → H Isomerization, Chem.Phys.Lett., 474 (2009) 7 – 12.

[33] M. Miyazaki, K. Chatterjee, K. hattori, R. Otsuka, S.-I. Ishiuchi, O. Dopfer, M. Fujii, Ionization – Induced π → H Site Switching in Resorcinol – Ar$_n$ (n=1 and 2) Clusters Probed by Infrared Spectroscopy, J.Phys.Chem. A, 123 (2019) 6828 – 6839.

[34] M. Schneider, M. Wilke, M.-L. Hebestreit, J.A. Ruiz – Santoyo, L. Álvarez – Valtierra, J.T. Yi, W.L. Meerts, D.W. Pratt, M. Schmitt, Rotationally Resolved Electronic Spectroscopy of the Rotamers of 1,3 – Dimethoxybenzene, Phys.Chem.Chem.Phys., 19 (2017) 21364.

[35]] J. Bruckhuisen, G. Dhont, A. Roucou, A. Jabri, H. Bayoudh, T.T. Tran, M. Goubet, M.-A. Martin-Drumel, A. Cuisset, Intramolecular H – Bond Dynamics of Catechol Investigated by THz High – Resolution Spectroscopy of its Low – Frequency Modes, Molecules, 26 (2021) 3645.

[36] G. Pitsevich, A. Malevich, Torsional Motions of the Free and H − Bonded Hydroxyl Groups of the Catechol Molecule, J.Mol.Spectr., 387 (2022) 111664.

[37] G.A. Pitsevich, A.E. Malevich, V.V. Sapeshko, The Hydroxyl Groups Internal Rotations in a Methanediol Molecule, J.Mol.Spectr., 360 (2019) 31-38

[38] G.A. Pitsevich, A.E. Malevich, U.U. Sapeshka, The Torsional Spectrum of the Hydrogen Troxide Molecule, Chem.Phys., 530 (2020) 110633

[39] G.A. Pitsevich, A.E. Malevich, D.G. Kisuryna, A.A. Ostyakov, U.U. Sapeshka, Torsional States and Tunneling Probability in HOSOH, DOSOD, and DOSOH Molecules Analyzed at the CBS Limit, J.Phys.Chem. A, 124 (2020) 8733-8743

[40] G. Pitsevich, A. Malevich, V. Zheutok, A. Khrapunova, U. Sapeshka, Torsional Vibrations of Two Thiol Groups in the HSOSH, DSOSH, and DSOSD Molecules: 2D PES Study in CBS Limit, Vibr.Spectr., 113 (2021) 103208

[41] G.A. Pitsevich, A.E. Malevich, U.U. Sapeshka, D. Kisuryna, I.Yu. Doroshenko, Modelling of the Torsional IR Spectrum of the HSSSH, DSSSH, and DSSSD Molecules, Comp.Theor.Chem., 1222 (2023) 114080.

[42] H.C. Longuet-Higgins, The Symmetry Groups of Non − Rigid Molecules, Mol. Phys. 6 (1962) 445-460.

[43] J.T. Hougen, Classification of Rotational Energy Levels for Symmetric − Top Molecules, J. Chem. Phys. 37 (1962) 1433-1441.

[44] P. R. Bunker (1975). Practically Everything You Ought to Know About The Molecular Symmetry Group, in, "Vibrational Spectra and Structure," vol. 3 (J. R. Durig, Ed.), chapter 1, Dekker, New York, 1.

[45] P. R. Bunker and P. Jensen, Molecular Symmetry and Spectroscopy, NRC Research Press, Ottawa (1998).

[46] G.A. Pitsevich, A.E. Malevich, F.V. Markovich, U.U. Sapeshka, Barriers to Internal Rotation and Tunnelling Splittings of the Torsional States in the $HO(CH_2)OH$, $DO(CH_2)OH$, and $DO(CH_2)OD$ Molecules, Mol.Phys., 118 (2020) e1746425

[47] G.A. Pitsevich, A.E. Malevich, D.G. Kisuryna, A.U. Vasilevsky, A.S. Vasilevich, U.U. Sapeshka, A.A. Kamnev, Quantum Aspects of Torsional Vibrations in the HO_3H, DO_3H, and DO_3D Molecules, Spectrochim.Acta Part A, 239 (2020) 118209.

[48] A.D. Becke, Density − Functional Thermochemistry. III The Role of Exect Exchange, J.Chem.Phys., 98 (1993) 5648 - 5652

[49] C. Lee, W. Yang, R.G. Parr, Development of the Colle − Salvetti Correlation − Energy into a Functional of the Electron Density, Phys.Rev. B, 37 (1988) 785 - 789

[50] P.J. Stephens, F.J. Devlin, C.F. Chabalowski, M.J. Frisch, Ab Initio Calculation of Vibrational Absorption and Circular Dichroism Spectra Using Density Functional Force Fields, J.Phys.Chem. 98 (1994) 11623 – 11627

[51] R.A. Kendall, T.H. Dunning, Jr., R.J. Harrison, Electron Affinities of the First – Row Atons Revisited. Systematic Basis Sets and Wave Functions, J.Chem.Phys., 96 (1992) 6796 - 6806

[52] D.E. Woon, T.H. Dunning, Jr., Gaussian Basis Sets for Use in Correlated Molecular Calculations. IV. Calculation of Static Electrical Response Properties, J.Chem.Phys., 100 (1994) 2975 – 2988.

[53] G. Hertzer, P. Pulay, H.J. Werner, Multipole Approximation of Distant Pair Energies in Local MP2 Calculations, Chem.Phys.Lett., 290 (1998) 143 – 149.

[54] M. Schutz, G. Hetzer, H.J. Werner, Low – Order Scaling Local Electron Correlation Methods. I. Linear Scaling Local MP2, J.Chem.Phys., 111 (1999) 5691-5705.

[55] T.H. Dunning, Jr., Gaussian Basis Sets for Use in Correlated Molecular Calculations. I. The Atoms Boron through Neon and Hydrogen, J.Chem.Phys., 90 (1989) 1007 – 1023.

[56] B.P. Pritchard, D. Altarawy, B. Didier, T. D. Gibson, T.L. Windus, A New Basis Set Exchange: An Open, Up-to-date Resource for the Molecular Sciences Community. J. Chem. Inf. Model., 59 (2019) 4814-4820.

[57] A. Halkier, T. Helgaker, P. Jørgensen, W. Klopper, H. Koch, J. Olsen, A.K. Wilson, Basis – Set Convergence in Correlated Calculations on Ne, N_2, and H_2O, Chem.Phys.Lett., 286 (1998) 243-252

[58] M. Okoshi, T. Atsumi, H. Nakai, Revisiting the Extrapolation of Correlation Energies to Complete Basis Set Limit, J.Comp.Chem., 36 (2015) 1075 – 1082.

[59] F. Neese, F. Wennmohs, U. Becker, C. Riplinger, The ORCA quantum chemistry program pockage, J.Chem.Phys., 152 (2020) 224108

[60] T.J. Lukka, A Simple Method for the Derivation of Exact Quantum – Mechanical Vibration – Rotation Hamiltonian in Terms of Internal Coordinates, J.Chem.Phys., 102 (1995) 3945-3955.

[61] G.A. Pitsevich, A.E. Malevich, Features of the Interaction of Hydroxyl and Methyl Tops in the Ethanol Molecule: 2D – Calculation of the Torsion Energy Levels, J.Appl.Spectr., 82 (2015) 540 – 553.

[62] G.A. Pitsevich, A.E. Malevich, U.V. Lazicki, U.U. Sapeshka, Journal of the Belarusian State University. Physics, 2 (2021) 15-24.

[63] G. Pitsevich, A. Malevich, I. Doroshenko, Explicitly Correlated Study of the Torsional Vibrations of HSOSH Molecule. Comparison with MP2/CBS(T,Q) Level of Theory, Mol.Cryst.Liq.Cryst., 749 (2022) 9 – 17.

[64] E.B. Wilson, J.J.C. Decius, P.C. Cross, Molecular Vibration. Dover Publications, Inc., New York, 1955

[65] C. Lanczos, Discourse on Fourier Series, Oliver and Boyd Ltd, Edinburgh and London, 1966

[66] G.A. Pitsevich, A.E. Malevich, Simple Method of the Formation of the Hamiltonian Matrix for Some Schrödinger Equations Describing the Molecules with Large Amplitude Motions, Optics and Photonic Journal, 2 (2012) 332-337

[67] G. Pitsevich, V. Balevicius, Hydrogen Bonded Pyridine N − Oxide/Trichloroacetic Acid Complex in Polar Media: 2D Potential Energy Surface and O − H …O Vibration Analysis Using Exact Vibrational Hamiltonian, J.Mol.Struct., 1072 (2014) 38 − 44.

[68] Mathematica, Wolfram Research, Inc., http://www.wolfram.com/mathematica

[69] W. Gordy, R.L. Cook, Microwave Molecular Spectra, Interscience Publishers, 1970

[70] J.M. Flaud, C. Camy-Peyret, Vibration − Rotation Intensities in H_2O − Type Molecules Application to the $2\nu_2$, ν_1 and ν_3 Bands of $H_2{}^{16}O$, J.Mol.Spectr., 55 (1975) 278

[71] G. Duxbury, Infrared Vibration-Rotation Spectroscopy, John Wiley & Sons LTD, 2000

[72] Carlo Di Lauro, Rotational Structure in Molecular Infrared Spectra, Elsevier, 2013

[73] G. Pitsevich, I. Doroshenko, A. Malevich, E. Shalamberidze, V. Sapeshko, V. Pogorelov, L.G.M. Pettersson, Temperature Dependence of the Intensity of the Vibration − Rotational Absorption Band ν_2 of H_2O Trapped in an Argon Matrix, Spectrochim.Acta Part A, 172 (2017) 83 − 90.

[74] G. Pitsevich, E. Shalamberidze, A. Malevich, V. Sablinskas, V. Balevicius, L.G.M. Pettersson, Calculation of the Vibration − Rotational Transition Intensities of Water Molecules Trapped in an Argon Matrix: Stretching O − H Vibrations Spectral Region, Mol.Phys., 115 (2017) 2605 − 2613.

[75] D.J. Bakker, Q. Ong, A. Dey, J. Mahé, M.-P. Gaigeot, A.M. Rijs, Anharmonic, Dynamic and Functional Level Effects in Far − Infrared Spectroscopy: Phenol Derivatives, J.Mol.Spectr., 342 (2017) 4 − 16.

[76] S. Albart, P. Lerch, R. Prentner, M. Quack, Tunneling Switching Dynamics in Phenol and Its Isotopomers from High − Resolution FTIR Spectroscopy with Synchrotron Radiation, Angew.Chem., 125 (2013) 364 − 367.