POTENTIAL AND KINETIC INTERACTION OF TWO INTERNAL TOPS IN MOLECULES BELONGING TO C_{2V}(M) MOLECULAR SYMMETRY GROUP.

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Abstract

Fourier analysis of the kinetic and potential interactions of non-coaxial internal tops in the molecules $C_6H_4(OH)_2$*,* $HO(CH_2)OH$*, HOOOH, HOSOH, HSSSH, and HSOSH was carried out. It was found that for the all six molecules, in which both tops are characterized by a period* 2π*, the harmonics with a period of* π *are dominate, with its contribution to the Fourier representation of potential surfaces increasing in the sequence mentioned above. Contributions of internal tops interactions to the kinetic and potential energies were determined for analyzed molecules. The influence of potential and kinetic interactions of internal tops on 1) the features of tunneling splitting of the ground and excited torsional states of molecules, 2) the landscape of 2D potential energy surfaces, 3) frequencies of fundamental torsional vibrations of hydroxyl and thiol groups, 4) the ratio of trans- and cis-conformer energies is also analyzed.*

1. Introduction

Internal rotation in molecules (one of the types of large amplitude motion (LAM)) continues to attract the attention of researchers today [1-7]. This is due to the important role that internal rotation plays in determining the thermodynamic properties of molecules [1], as well as in the formation of the fine structure of rotational and vibrational-rotational absorption bands [8-10]. Although early works addressed only molecules with a single internal top [11-15], research soon expanded to molecules with two or more internal tops. In the initial studies on the internal rotation of multiple tops within a single molecule, the consideration of their kinetic and potential interactions was either neglected [16-19] or only the first one was taken into account [20]. However, with time, the full account of both interactions gradually emerged as a compelling and attainable research objective [21-24]. Of course, determining the heights of barriers to internal rotation for each of the tops remained critically important. However, only 1) determining the contributions of the kinetic and potential interactions of internal tops to the total kinetic and potential energy, 2) establishing the influence of these interactions on the position of torsional energy levels and on the magnitude of their tunneling splitting, allowed answering the question: how important is the consideration of these interactions for the correct solution to the problem of internal rotation or torsional vibrations of several tops in one molecule. In pioneering works [21-24], molecules with two equivalent methyl tops were analyzed, the diagonal kinetic coefficients for which are equal and are usually denoted as $F_1=F_2=F$, and the off-diagonal kinetic coefficient, describing the kinetic interaction – F_{12}. The two-dimensional potential energy function in these works can be written as follows:

$$\begin{gathered}U(\gamma_1,\gamma_2)=U_{0,0}+U_{3,0}cos(3\gamma_1)+U_{0,3}cos(3\gamma_2)+U_{6,0}cos(6\gamma_1)+U_{0,6}cos(6\gamma_2)+\\+U_{3,3}cos(3\gamma_1)cos(3\gamma_2)+U'_{3,3}sin(3\gamma_1)sin(3\gamma_2)\end{gathered} \quad (1)$$

Here γ_1 and γ_2 are the torsional coordinates of the two tops. Due to the high symmetry of molecules, $U_{3,0}=U_{0,3}=U_3;\quad U_{6,0}=U_{0,6}=U_6;$, is valid, however $U_{3,3}\neq U'_{3,3}$. Coefficients U_3 and U_6 describe the inherent potential energy of the tops and interaction with the molecular frame, and coefficients $U_{3,3}$ and $U'_{3,3}$ describe their potential interaction. The results of the works [21-24] showed that the kinetic interaction of two methyl tops in the studied molecules is insignificant (F_{12}/F does not exceed 4%). However, the potential interaction is quite significant ($U_{3,3}/U_3$ is about 40% [22,24], and $U'_{3,3}/U_3$ can be over 40% [24]) and, therefore, this interaction cannot be neglected. Several studies noted that accounting for $U_{3,3}$ leads to a shift in the torsional energy levels, and accounting for $U'_{3,3}$ and F_{12} leads to a splitting of torsional states. However, Dreizler [8] noted that accounting for $U_{3,3}$ also leads to an increase in the splitting of torsional energy levels, but this becomes noticeable only for sufficiently large values of torsional quantum numbers. The development of quantum-chemical methods for calculating multi-dimensional potential energy surfaces (PES) of molecules and computational technology capabilities have allowed calculating multi-dimensional potential functions, not relying on empirical data, and increasing the number of harmonics in their representation [25-28]. However, it should be noted that most works analyzing the interactions of internal tops concern methyl groups. There are also works where the interactions of methyl and hydroxyl tops [29,30], as well as methyl and aldehyde tops [26], are analyzed. However, a consistent analysis of the potential and kinetic interaction of several hydroxyl or thiol groups is virtually absent in the literature.

We have previously calculated the two-dimensional PES and torsional spectra of several molecules containing two hydroxyl groups ($HO(CH_2)OH$ (II) [31,32], HOOOH (III) [33,34], HOSOH (IV) [35] and $C_6H_4(OH)_{2\text{-ortho}}$ (I) [36]), as well as two molecules containing two thiol internal tops (HSOSH (V) [37] and HSSSH (VI) [7]). All calculations for the molecules listed above were performed at the MP2/CBS(T,Q) [38-42] level of theory. To assess the influence of the level of theory on the values of the analyzed characteristics, we additionally used CCSD(T)/Aug-cc-pVTZ [43,44] (in the case of relatively small molecules) and MP2/Aug-cc-pVTZ [45-47] (in case of the $C_6H_4(OH)_{2\text{-ortho}}$ molecule) levels of theory. The datasets generated from these prior investigations facilitate an examination of the kinetic and potential interactions between these tops.

The experimental study of analyzed molecules in the gas phase is a very difficult task; therefore, there are only a small number of relevant publications in the literature. Among them, noteworthy works [48-51] in which the structure, conformational composition and spectroscopic constants of the molecules HSSSH [48,49], HOSOH [50], and HOOOH [51] are analyzed. The experimentally determined values of rotational constants, potential barriers and relative energies of molecular conformers are in good agreement with the calculated values in the above-mentioned works [7,35,33,34]. However, in the experimental works noted above, it was not possible to detect the splitting of spectral lines due to tunneling between equivalent configurations of molecular conformers. This is also consistent with the results of works [7,35,33,34] according to which the tunneling splittings of the ground vibrational states in the trans and cis conformers of the HSSSH, HOSOH and HOOOH molecules are very small (the maximum calculated value of the tunneling splitting was found in the cis conformer of the molecule HOOOH and ranged from $3*10^{-7}$ [34] to $1*10^{-6}$ [33] cm^{-1}). As far as we know, only in [4] the tunneling splitting of the first excited torsional state of the $C_6H_4(OH)_{2\text{-ortho}}$ molecule was experimentally recorded, the value of which was $1.041*10^{-5}$ cm^{-1}. This is in reasonable agreement with the tunneling splittings of the corresponding torsional state calculated at various levels of theory (from $0.27*10^{-5}$ to $0.61*10^{-5}$ cm^{-1}) [36].

However, the main research aims of present investigation to understand how potential and kinetic interactions affect 1) the energy ratio of the trans - and cis - conformers, 2) the degree of splitting within torsional states, 3) the magnitude of rotational barriers for corresponding tops, and other molecular features. This study's central objective revolves around these key areas.

2. Calculation details

The Schrödinger torsional equation for the molecules analyzed in this work, which contain two internal tops, can be written as follows [7, 31]:

$$-F_{\gamma\gamma}(\gamma,\varphi)\frac{\partial^2\Psi(\gamma,\varphi)}{\partial\gamma^2}-F_{\varphi\varphi}(\gamma,\varphi)\frac{\partial^2\Psi(\gamma,\varphi)}{\partial\varphi^2}-F_{\gamma\varphi}(\gamma,\varphi)\frac{\partial^2\Psi(\gamma,\varphi)}{\partial\gamma\partial\varphi}+U(\gamma,\varphi)\Psi(\gamma,\varphi)=E\Psi(\gamma,\varphi) \quad (1)$$

Here γ and φ describe the torsional coordinate of two hydroxyl or thiol tops. The kinetic coefficients and potential energy in equation (1) were approximated by trigonometric series:

$$A_0+\sum_{k=1,K,1}A_k^{\gamma}cos(k\gamma)+\sum_{k=1,K,1}A_k^{\varphi}cos(k\varphi)+\sum_{k,l=1,K,1}A_{k,+l}^{\gamma\varphi}cos(k\gamma+l\varphi)+\sum_{k,l=1,K,1}A_{k,-l}^{\gamma\varphi}cos(k\gamma-l\varphi) \quad (2)$$

Below, as an example, the approximations of potential energy and the kinetic coefficient at one of the second derivatives are provided:

$$U(\gamma,\varphi)=U_0+\sum_{k=1,K,1}U_k^{\gamma}cos(k\gamma)+\sum_{k=1,K,1}U_k^{\varphi}cos(k\varphi)+\sum_{k,l=1,K,1}U_{k,+l}^{\gamma\varphi}cos(k\gamma+l\varphi)+\sum_{k,l=1,K,1}U_{k,-l}^{\gamma\varphi}cos(k\gamma-l\varphi); \quad (3)$$

$$F_{\gamma\gamma}(\gamma,\varphi)=F_0+\sum_{k=0,K,1}F^{\gamma}_{\gamma\gamma k}cos\left(k\gamma\right)+\sum_{k=1,K,1}F^{\varphi}_{\gamma\gamma k}cos\left(k\varphi\right)+\sum_{k,l=1,K,1}F^{\gamma\varphi}_{\gamma\gamma k,+l}cos\left(k\gamma+l\varphi\right)+\sum_{k,l=1,K,1}F^{\gamma\varphi}_{\gamma\gamma k,-l}cos\left(k\gamma-l\varphi\right);\quad(4)$$

In expressions (2-4), the last two terms on the right describe either the potential or one type of kinetic interaction between the tops. Thus, the contribution of a certain harmonic of a particular type of interaction to the total potential or kinetic energy of the molecular torsional motion, compared to the inherent characteristics of each top, can be estimated as the ratio of the following coefficients $A^{\gamma\varphi}_{k,+k}/A^{\gamma}_{k}$, $A^{\gamma\varphi}_{k,-k}/A^{\gamma}_{k}$, or $(A^{\gamma\varphi}_{k,+k}+A^{\gamma\varphi}_{k,-k})/A^{\gamma}_{k}$. To compare these ratios with similar results presented in the literature (see Section 1), the third and fourth terms in expressions (2-4) can be represented as follows:

$$\begin{aligned}A^{\gamma\varphi}_{k,+l}cos\left(k\gamma+l\varphi\right)&=A^{\gamma\varphi}_{k,+l}cos\left(k\gamma\right)cos\left(l\varphi\right)-A^{\gamma\varphi}_{k,+l}sin\left(k\gamma\right)sin\left(l\varphi\right);\\A^{\gamma\varphi}_{k,-l}cos\left(k\gamma-l\varphi\right)&=A^{\gamma\varphi}_{k,-l}cos\left(k\gamma\right)cos\left(l\varphi\right)+A^{\gamma\varphi}_{k,-l}sin\left(k\gamma\right)sin\left(l\varphi\right);\end{aligned}\quad(5)$$

Adding these two equations, we get:

$$A^{\gamma\varphi}_{k,+l}cos\left(k\gamma+l\varphi\right)+A^{\gamma\varphi}_{k,-l}cos\left(k\gamma-l\varphi\right)=\left(A^{\gamma\varphi}_{k,+l}+A^{\gamma\varphi}_{k,-l}\right)cos\left(k\gamma\right)cos\left(l\varphi\right)-\left(A^{\gamma\varphi}_{k,+l}-A^{\gamma\varphi}_{k,-l}\right)sin\left(k\gamma\right)sin\left(l\varphi\right);$$

Therefore, expression (2) can be rewritten:

$$\begin{aligned}&A_0+\sum_{k=1,K,1}A^{\gamma}_{k}cos\left(k\gamma\right)+\sum_{k=1,K,1}A^{\varphi}_{k}cos\left(k\varphi\right)+\sum_{k,l=1,K,1}A^{\gamma\varphi}_{k,+l}cos\left(k\gamma+l\varphi\right)+\sum_{k,l=1,K,1}A^{\gamma\varphi}_{k,-l}cos\left(k\gamma-l\varphi\right)=A_0+\sum_{k=1,K,1}A^{\gamma}_{k}cos\left(k\gamma\right)+\\&+\sum_{k=1,K,1}A^{\varphi}_{k}cos\left(k\varphi\right)+\sum_{k,l=1,K,1}\left(A^{\gamma\varphi}_{k,+l}+A^{\gamma\varphi}_{k,-l}\right)cos\left(k\gamma\right)cos\left(l\varphi\right)-\sum_{k,l=1,K,1}\left(A^{\gamma\varphi}_{k,+l}-A^{\gamma\varphi}_{k,-l}\right)sin\left(k\gamma\right)sin\left(l\varphi\right)\equiv\qquad(6)\\&\equiv A_0+\sum_{k=1,K,1}A^{\gamma}_{k}cos\left(k\gamma\right)+\sum_{k=1,K,1}A^{\varphi}_{k}cos\left(k\varphi\right)+\sum_{k,l=1,K,1}A^{\gamma\varphi}_{cc\,kl}\,cos\left(k\gamma\right)cos\left(l\varphi\right)-\sum_{k,l=1,K,1}A^{\gamma\varphi}_{ss\,kl}\,sin\left(k\gamma\right)sin\left(l\varphi\right);\end{aligned}$$

where $A^{\gamma\varphi}_{cc\,kl}=A^{\gamma\varphi}_{k,+l}+A^{\gamma\varphi}_{k,-l}$; и $A^{\gamma\varphi}_{ss\,kl}=A^{\gamma\varphi}_{k,+l}-A^{\gamma\varphi}_{k,-l}$;

Thus, the ratios of the type $U_{3,3}/U_3$ and $U'_{3,3}/U_3$ described in Section 1 for equivalent tops with a period of $2\pi/3$ can now be directly compared with ratios of the type $A^{\gamma\varphi}_{cc11}/A^{\gamma}_{1}$ and $A^{\gamma\varphi}_{ss11}/A^{\gamma}_{1}$ for equivalent tops with a period of 2π, respectively. In addition to this kind of estimation of top interaction contributions to the potential and kinetic energy of molecular torsional motion, the following quantities were also determined:

$$A(\gamma,\varphi)=A_0+\sum_{k=1,K,1}A^{\gamma}_{k}cos\left(k\gamma\right)+\sum_{k=1,K,1}A^{\varphi}_{k}cos\left(k\varphi\right)+\sum_{k,l=1,K,1}A^{\gamma\varphi}_{cc\,kl}\,cos\left(k\gamma\right)cos\left(l\varphi\right)-\sum_{k,l=1,K,1}A^{\gamma\varphi}_{ss\,kl}\,sin\left(k\gamma\right)sin\left(l\varphi\right);$$

$$A_{free}(\gamma,\varphi)=A_0+\sum_{k=0,K,1}A^{\gamma}_{k}cos\left(k\gamma\right)+\sum_{k=0,K,1}A^{\varphi}_{k}cos\left(k\varphi\right);$$

$$A_{int}(\gamma,\varphi)=\sum_{k,l=1,K,1}A^{\gamma\varphi}_{cc\,kl}\,cos\left(k\gamma\right)cos\left(l\varphi\right)-\sum_{k,l=1,K,1}A^{\gamma\varphi}_{ss\,kl}\,sin\left(k\gamma\right)sin\left(l\varphi\right);$$

$$A_{cc}(\gamma,\varphi)=\sum_{k,l=1,K,1}A^{\gamma\varphi}_{cc\,kl}\,cos\left(k\gamma\right)cos\left(l\varphi\right);$$

$$A_{-cc}(\gamma,\varphi)=A_0+\sum_{k=1,K,1}A^{\gamma}_{k}cos\left(k\gamma\right)+\sum_{k=1,K,1}A^{\varphi}_{k}cos\left(k\varphi\right)-\sum_{k,l=1,K,1}A^{\gamma\varphi}_{ss\,kl}\,sin\left(k\gamma\right)sin\left(l\varphi\right);$$

$$A_{ss}(\gamma,\varphi)=-\sum_{k,l=1,K,1}A^{\gamma\varphi}_{ss\,kl}\,sin\left(k\gamma\right)sin\left(l\varphi\right);$$

$$A_{-ss}(\gamma,\varphi)=A_0+\sum_{k=1,K,1}A_k^{\gamma}cos\left(k\gamma\right)+\sum_{k=1,K,1}A_k^{\varphi}cos\left(k\varphi\right)+\sum_{k,l=1,K,1}A_{cckl}^{\gamma\varphi}\,cos\left(k\gamma\right)cos\left(l\varphi\right);$$

It is clear that the following is true:

$$A_{int}(\gamma,\varphi)=A_{cc}(\gamma,\varphi)+A_{ss}(\gamma,\varphi);$$

$$A(\gamma,\varphi)=A_{free}(\gamma,\varphi)+A_{int}(\gamma,\varphi);$$

Quantities $A(\gamma,\varphi),\ A_{free}(\gamma,\varphi),\ A_{-cc}(\gamma,\varphi),\ A_{-ss}(\gamma,\varphi)$ can be utilized, for instance, to compute the magnitudes of the splittings in torsional states resulting from tunneling, whether certain tops interactions are taken into account, ignored, or partially considered. In addition, for each of the analyzed molecules, the path of minimum energy when moving from one potential minimum to its equivalent counterpart on the 2D potential energy surface $U(\gamma,\varphi)$ was calculated. This path was preserved in the form of a sequential set of points, each of which was matched with two torsional coordinates, a one-dimensional path coordinate, and the energy value at this point. Then, the corresponding energy values were determined on the same path for $U_{free}(\gamma,\varphi),\ U_{int}(\gamma,\varphi),$ and so on, which allowed us to construct corresponding graphs of potential barriers and visually assess various types of contributions to the potential energy.

3. DISCUSSION OF RESULTS

3.1 Fourier Analysis of the Potential and Kinetic Energy of Molecules

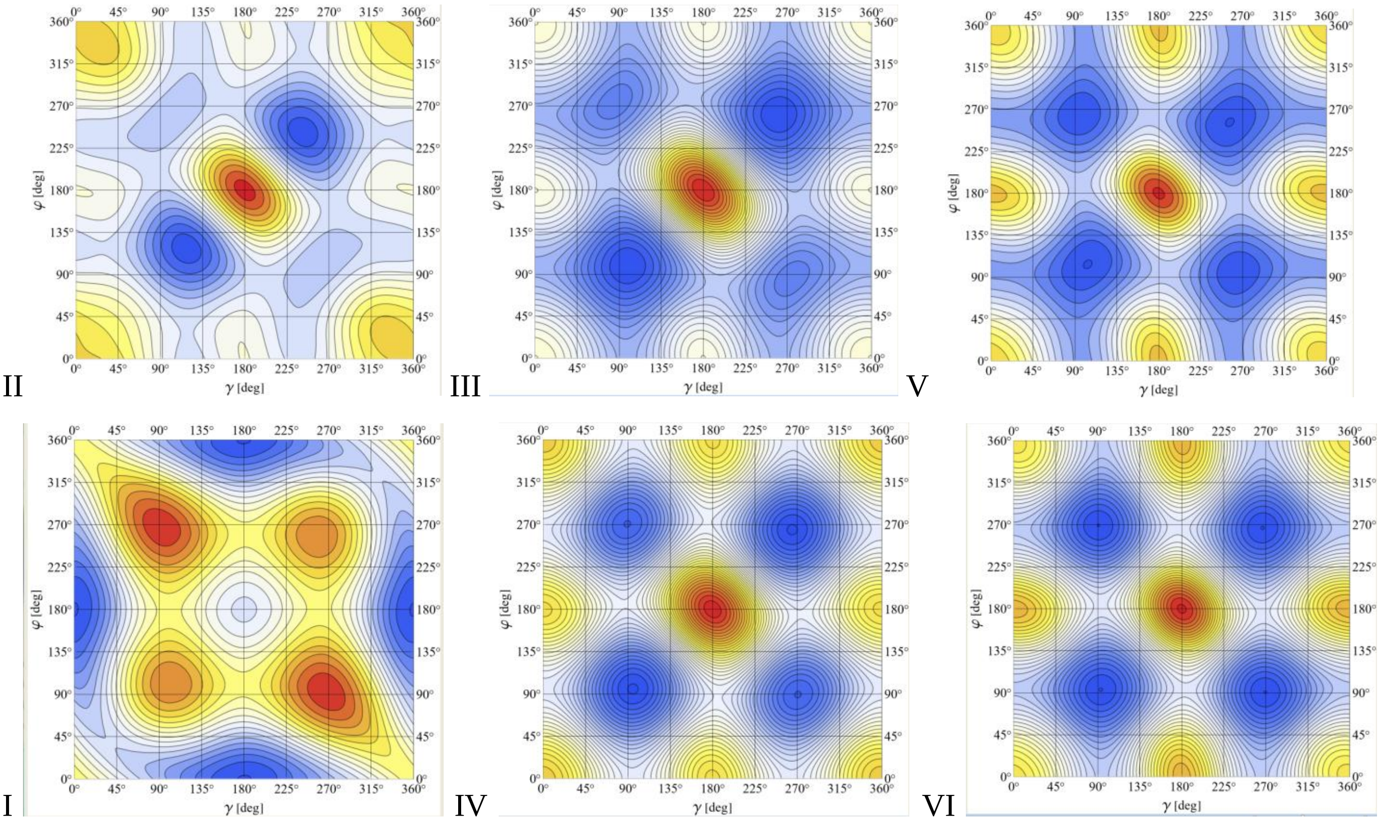
The potential and kinetic energy of the analyzed molecules was approximated using a set of basis functions, described by equations (2) and (3). Then it was transformed to a set of basis functions described by equation (6). In this case, the value of *K* in (6) was chosen to be 8. Tabl. 1 collects coefficients obtained as a result of approximating potential energy using the Mathematica software package [52], for certain basis functions (harmonics).

Table 1The amplitudes of the most significant harmonics in Fourier approximations of the potential energy of the I-VII molecules. In first four rows are represented 1) energy difference of molecular conformers, 2) and 3) equilibrium values of torsional coordinates for cis – and trans – conformers of the I-VI molecules, 4) potential energy difference in point $(0,180^0)$ and $(180^0,180^0)$ for I-VI molecules, respectively.

Molecular characteristics	Molecules						
	$C_6H_4(OH)_{2-o}$	$HO(CH_2)OH$	HOOOH	HOSOH	HSOSH	HSSSH	
E_{cis}-E_{trans} or E_{gosh}-E_{cis} $[cm^{-1}]$	1321.2	951.9	872.1	423.8	35.1	20.5	
γ_0 cis [deg]	0^0	77.6^0	94.1^0	90.6^0	84.9^0	90^0	
γ_0 trans [deg]	-	61.1^0	80.4^0	84.2^0	76.9^0	86.7^0	
U(0,180)-U(180,180) $[cm^{-1}]$	1321.2	1587.7	3385.5	2070.8	762.1	1321.9	
	Amplitudes of harmonics $[cm^{-1}]$						
Harmonics							
Cos(g)	-192.84	208.53	-320.61	-118.62	-9.88	-155.15	
Cos(2g)	-641.54	360.31	981.79	1548.31	717.02	1441.02	
Cos(3g)	-34.48	-186.45	-123.46	-112.68	-167.00	-195.69	
Cos(4g)	-12.35	2.16	-9.15	8.48	-0.6110	-10.83	
Cos(nf)	-192.84	208.53	-320.61	-118.62	-9.88	-155.15	
Cos(2nf)	-641.54	360.31	981.79	1548.31	717.02	1441.02	

Cos(3nf)	-34.48	-186.45	-123.46	-112.68	-167.00	-195.69	
Cos(4nf)	-12.35	2.16	-9.15	8.48	-0.6110	-10.83	
Cos(g)Cos(nf)	777.81	538.46	786.21	493.77	80.94	80.72	
Cos(2g)Cos(2nf)	265.77	136.94	301.81	86.01	296.91	242.14	
Cos(3g)Cos(3nf)	10.95	4.73	5.72	2.80	-1.75	2.16	
Cos(4g)Cos(4nf)	2.39	0.0061	-2.97	-0.92	2.89	6.42	
Sin(g)Sin(nf)	-313.19	-275.62	-499.85	-249.76	-47.61	-53.50	
Sin(2g)Sin(2nf)	-168.40	-257.57	-288.90	-193.93	-199.79	-121.66	
Sin(3g)Sin(3nf)	-5.35	-2.94	-6.29	-3.29	-3.67	-1.11	
Sin(4g)Sin(4nf)	-3.06	0.5257	2.55	0.53	-3.12	-8.16	
Cos(2g)Cos(nf)	386.70	-179.72	-268.15	-162.27	19.77	-16.86	
Cos(3g)Cos(nf)	60.57	37.60	56.43	43.75	36.66	39.44	
Cos(4g)Cos(nf)	13.39	-11.53	-17.06	-8.14	-3.69	-6.81	
Cos(g)Cos(2nf)	386.70	-179.72	-268.15	-162.27	19.77	-16.86	
Cos(g)Cos(3nf)	60.57	37.60	56.43	43.75	36.66	39.44	
Cos(g)Cos(4nf)	13.39	-11.53	-17.06	-8.14	-3.69	-6.81	
Sin(2g)Sin(nf)	-194.64	174.07	292.96	193.02	54.65	75.10	
Sin(3g)Sin(nf)	-43.58	-52.82	-55.79	-37.58	-38.83	-36.53	
Sin(4g)Sin(nf)	-13.56	9.98	14.90	10.79	7.27	7.10	
Sin(g)Sin(2nf)	-194.64	174.07	292.96	193.02	54.65	75.10	
Sin(g)Sin(3nf)	-43.58	-52.82	-55.79	-37.58	-38.83	-36.53	
Sin(g)Sin(4nf)	-13.56	9.98	14.90	10.79	7.27	7.10	

According to the data in Tabl. 1, for all molecules, a harmonic with π period dominates in the decomposition of potential energy. It is evident that the period for each of the hydroxyl and thiol tops in molecules I-VI equals 2π. The fact that the amplitudes of the harmonics $cos(2\gamma)$ and $cos(2\varphi)$ turn out to be at least twice, and in some cases more than ten times greater than the amplitudes of the seemingly main harmonics $cos(\gamma)$ and $cos(\varphi)$ suggests (according to [53]) the existence of a hidden period π for potential energy surfaces of the I-VI molecules. Comparing this data with some structural parameters and energetic characteristics of equilibrium configurations of cis - and trans - conformers allows us to understand in which cases a period π can be a dominant period for the potential energy of these molecules. It is quite obvious that 1) when torsional angles X-Y-X-H (here X,Y=O,S) in the equilibrium configurations of cis- and trans- conformers are close to 90^0 (which corresponds to the case when the planes X-Y-X and Y-X-H are orthogonal), a 180^0 rotation of both tops leads to equivalent conformer configurations with the same energy. If 2) the energies of cis- and trans- conformers turn out to be close enough, then if the first condition is met, even the rotation of one of the tops, say in the trans – conformer, by 180^0 leads to transformation into a cis- conformer, but with almost the same energy. As can be seen from the data presented in Tabl. 1, a strong increase in the amplitudes of harmonics with a period of π is characteristic of molecules IV-VI, which either have torsional top angles in equilibrium configurations close to 90^0, or the energies of cis- and trans- conformers almost coincide, or both conditions are met (see first three rows in Tabl.1). Of course, the period π should be present not only for equilibrium configurations, but for the entire potential energy surface. And if you look at the 2D potential energy surfaces (PES) of some molecules (see Fig. 1), the condition 3) for the dominance of the period π becomes clear - this corresponds to this period when moving parallel to the coordinate axes along the lines (0,180) – (360,180) and (180,0) – (180,360).



II III V I IV VI

Figure 1 2D PES of the I-VI molecules (upper row): HO(CH$_2$)OH (II) – on the left, HOOOH (III) – in the middle and HSOSH (V) – on the right, (lower row): C$_6$H$_4$(OH)$_{2\text{-orth}}$ (I) – on the left, HOSOH (IV) – in the middle and HSSSH (VI) – on the right

From Fig. 1, it is evident that a feature common to all molecules at point (180,180) disrupts this periodicity when moving along the aforementioned lines on the PES, and primarily provides a sufficiently high amplitude for the lowest frequency harmonics ($cos(\gamma)$ and $cos(\varphi)$). It is clear that deviations from the period π and correspondingly the contribution of $cos(\gamma)$ and $cos(\varphi)$ harmonics should be less the smaller the energy difference $\Delta U = U(180,180) - U(0,180)$. Recall that the following holds:

$$U(0,180) = U(180,0) = U(360,180) = U(180,360).$$

Indeed, we see from fourth row of Tabl. 1 that the molecule HSOSH, for which ΔU is minimal, has extremely low amplitudes of $cos(\gamma)$ and $cos(\varphi)$ harmonics. It is also evident from the presented data that in case 2) the amplitude of $cos(2\gamma)cos(2\varphi)$ harmonics dramatically increases and becomes three times larger than the amplitude of $cos(\gamma)cos(\varphi)$ harmonics (see the results for molecules V and VI in Tabl. 1).

To compare the potential energies of the interactions between the tops and the energy of their interaction with the molecular framework, let's find the following relationships: $(|U^{\gamma\varphi}_{cc11}| + |U^{\gamma\varphi}_{cc22}|)/(|U^{\gamma}_{1}| + |U^{\gamma}_{2}|)$ and $(|U^{\gamma\varphi}_{ss11}| + |U^{\gamma\varphi}_{ss22}|)/(|U^{\gamma}_{1}| + |U^{\gamma}_{2}|)$. These values reach their maximum for molecules I and II (125% and 94% respectively). It is clear that accounting for the potential energy of tops interactions in the studied molecules is very important.

The situation is different in the case of kinetic energy. Tabl. 1 SM in the Supplementary Materials 1 presents coefficients obtained as a result of approximating kinetic energy using the Mathematica software package [52], for certain harmonics. Fig. 2 presents 2D surfaces of non-diagonal kinetic coefficients for the three molecules with the most distinct PES, which show that they do not contain any structures characterized by periods less than 2π.

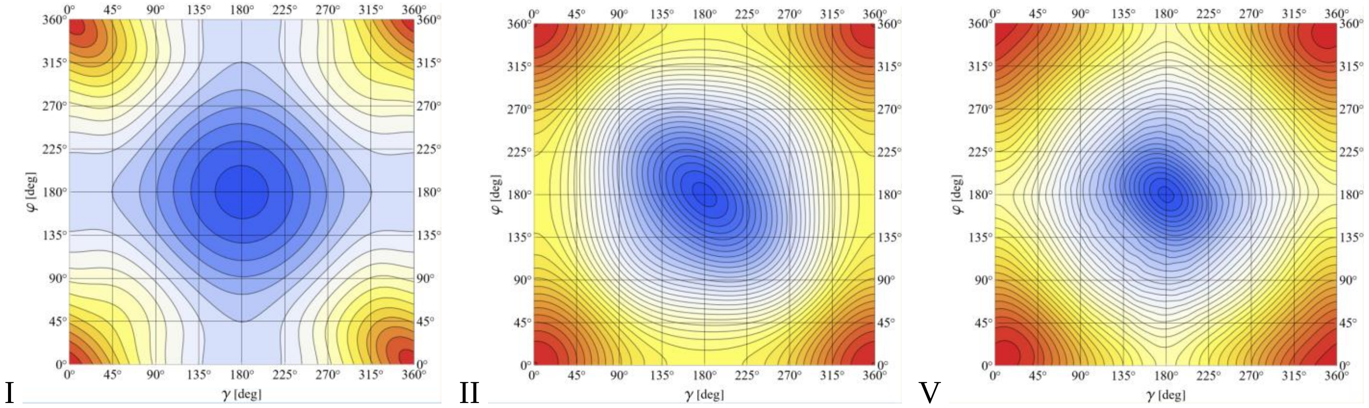


Figure 2 2D surfaces of the non-diagonal kinetic coefficient $F_{\gamma\varphi}(\gamma,\varphi)$ for molecules $C_6H_4(OH)_{2\text{-orth}}$ (I) - left, $HO(CH_2)OH$ (II) – middle and HSOSH (V) – right.

Therefore, as follows from the data in Tabl. 1 SM – 3 SM, the amplitudes of the lowest frequency harmonics, which have a period 2π, are maximal in the case of kinetic coefficients, while the amplitudes of multiple harmonics monotonically decrease. The share of the kinetic interaction energy in the non-diagonal kinetic coefficient can be estimated from the ratios $F^{\gamma\varphi}_{\gamma\varphi cc11} / F^{\gamma}_{\gamma 1}$ and $F^{\gamma\varphi}_{\gamma\varphi ss11} / F^{\gamma}_{\gamma 1}$ which are minimal for the molecule CH_3OOH (5.6% and 2.1% respectively) and maximal for the molecule $HO(CH_2)OH$ (79.6% and 35.2% respectively). The variations in the diagonal kinetic coefficients $F_{\gamma\gamma}(\gamma,\varphi)$ and $F_{\varphi\varphi}(\gamma,\varphi)$ over the entire range of torsional coordinates are minimal. Thus, in essence, these coefficients can be considered as constant.

3.2 Potential Barriers and Splitting of Torsional Energy Levels

If the torsional coordinate is the only one for the molecule under analysis, the potential barrier to internal rotation is unambiguously defined and characterized by the energy at the maximum, half-width, and shape of the contour. In the case of two or more torsional coordinates and the presence of multiple minima on the multidimensional potential energy surface, there are many possible paths of movement from one energy minimum to another equivalent one. Each of such paths is characterized by a certain probability of realization and contributes to the tunneling process. In this case, tunneling along the path of minimum energy is the most probable. If one constructs the corresponding path and determine the potential energy value at each point of this path, then one can construct a one-dimensional graph of the potential barrier on the path from one equivalent minimum to another, as was the case for a single torsional coordinate.

In order to visualize the influence of the internal tops interactions in the analyzed molecules on the heights and shapes of the potential barriers, the paths of minimum energy on the potential surface that included all types of interactions were calculated. Information about these paths was stored as a set of pairs of values of the two torsional coordinates at each point of the path and the length of the arc from the original minimum to this point. Then the energy values along these paths were determined on the 2D potential energy surface from which either all interactions were excluded or those that, for example, were described by harmonics of the form $sin(k\gamma)sin(l\varphi)$ or $cos(k\gamma)cos(l\varphi)$, where k and l are both greater than zero. In these cases, it was possible to visualize the potential barrier to rotation in the case of absence of certain potential interactions. Fig. 3 presents the potential barrier for movement along the path of minimum energy for the HO(CH$_2$)OH molecule.

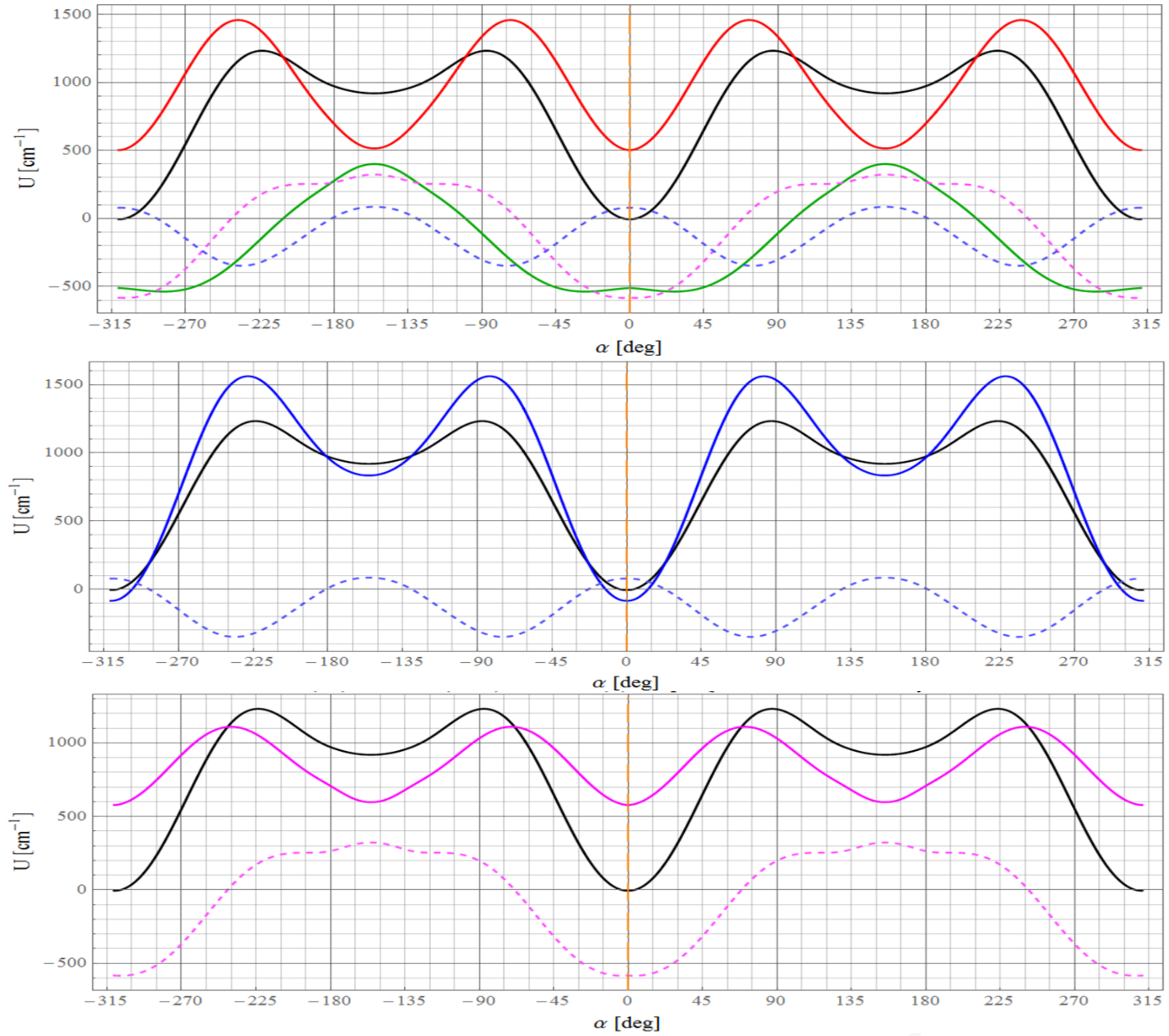
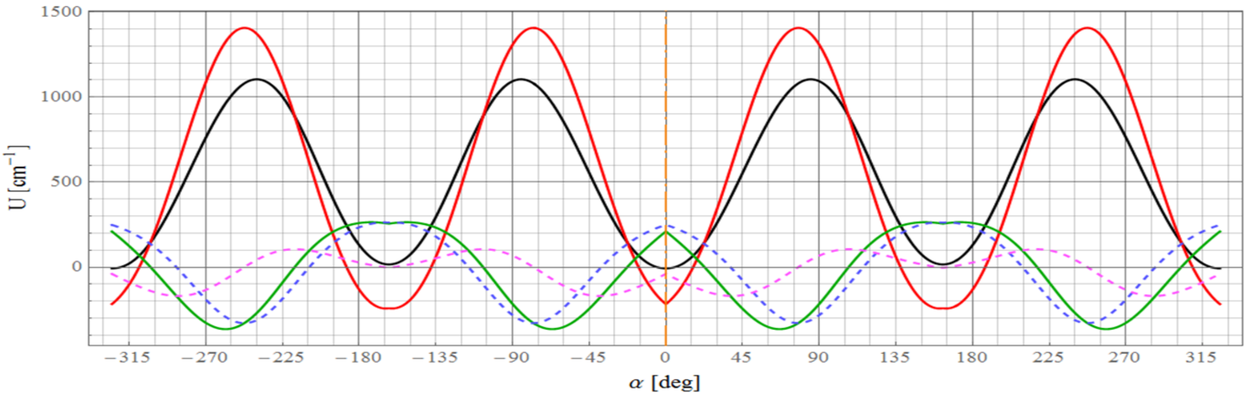


Figure 3 The potential barriers along the path of minimum energy for the HO(CH$_2$)OH molecule. In the top figure (3a) the following are depicted: $U(\gamma,\varphi)$ - black, $U_{free}(\gamma,\varphi)$ - red, $U_{int}(\gamma,\varphi)$ - green, $U_{cc}(\gamma,\varphi)$ -

blue, $U_{ss}(\gamma,\varphi)$ - pink. In the middle figure (3b), the following are depicted: $U(\gamma,\varphi)$ - black, $U_{-cc}(\gamma,\varphi)$ - blue, $U_{cc}(\gamma,\varphi)$ - blue dotted line. In the bottom figure (3c), the following are depicted: $U(\gamma,\varphi)$ - black, $U_{-ss}(\gamma,\varphi)$ - pink, $U_{ss}(\gamma,\varphi)$ - pink dotted line. The angle α describes the path length in degrees along the minimum energy path.

In Fig. 3 $\alpha = 0^0$ is the starting point of the path, located in one of two global minima (trans-conformer). Positive α values correspond to movement along the path of minimum energy towards the equivalent global minimum clockwise, while negative α values correspond to similar movement counter-clockwise. The values of α equal to $\pm 155^0$ correspond to equivalent local minima (cis-conformers). As can be seen from Fig. 3a, the potential interaction of hydroxyl tops in the HO(CH$_2$)OH molecule contributes to the increasing of the potential barrier when tunneling along the path of minimum energy for the trans-conformer. However, for the cis-conformer the situation is the opposite (compare the black and red curves in Fig.3a). It is also evident that the significant difference in the energies of the trans- and cis-conformers is entirely due to the potential interaction of the internal tops. Fig. 3b and 3c show that the contribution of interaction harmonics of the form $cos\left(k\gamma\right)cos\left(l\varphi\right)$ leads to an increase in potential barriers for both conformers, while the contribution of interaction harmonics of the form $sin\left(k\gamma\right)sin\left(l\varphi\right)$ on the contrary helps to reduce rotation barriers for both conformers. The latter circumstance should contribute to the increase in the splitting of stationary torsional states of the HO(CH$_2$)OH molecule. A similar picture is realized in the case of other molecules, however, the scale of influence on the heights of potential barriers of both conformers is not as significant as in the case of the HO(CH$_2$)OH molecule (see Fig. 4 for HSOSH molecule).



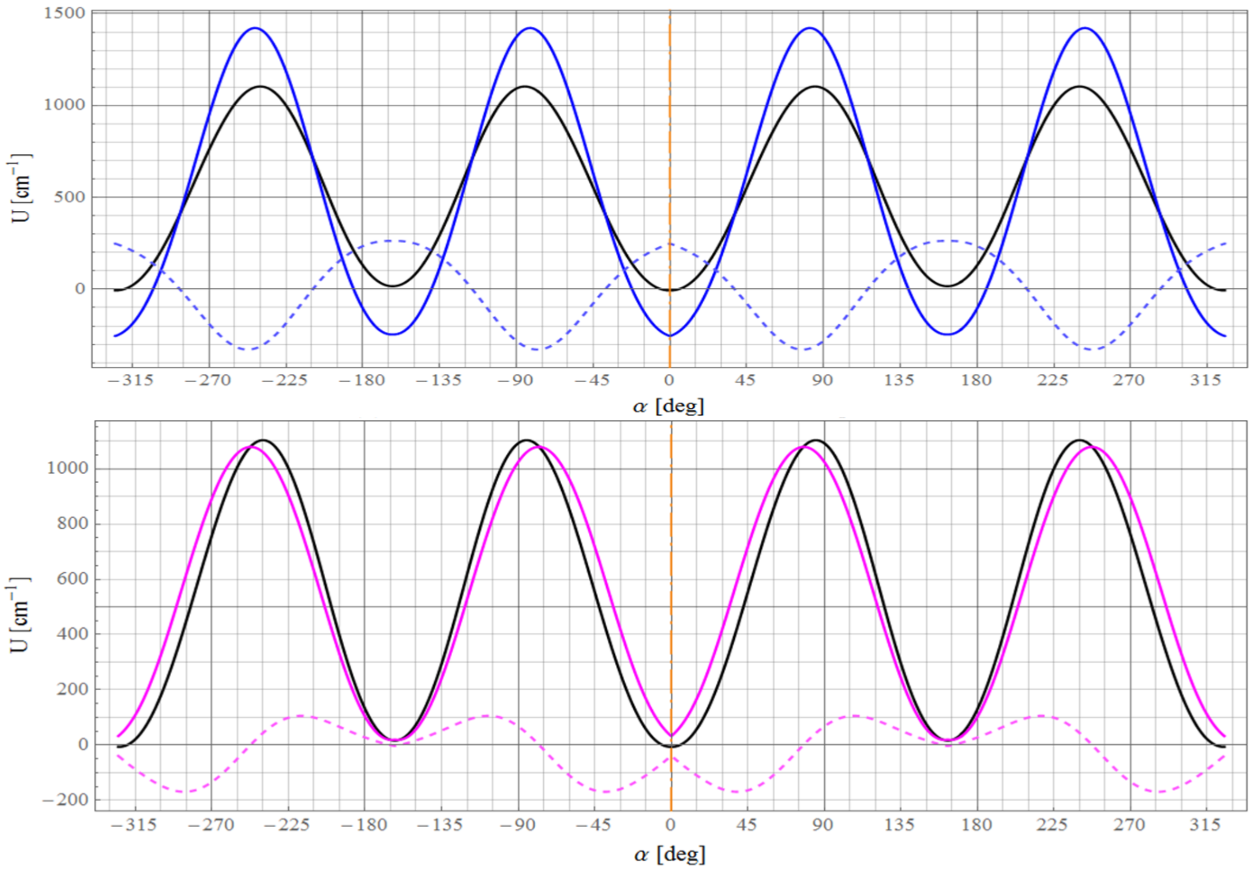


Figure 4 The potential barriers along the path of minimum energy for the HSOSH molecule. On the top figure (4a), the following are depicted: $U(\gamma,\varphi)$ - black, $U_{free}(\gamma,\varphi)$ - red, $U_{int}(\gamma,\varphi)$ - green, $U_{cc}(\gamma,\varphi)$ - blue, $U_{ss}(\gamma,\varphi)$ - pink. On the middle figure (4b), the following are depicted: $U(\gamma,\varphi)$ - black, $U_{-cc}(\gamma,\varphi)$ - blue, $U_{cc}(\gamma,\varphi)$ - blue dotted line. On the bottom figure (4c) the following are depicted: $U(\gamma,\varphi)$ - black, $U_{-ss}(\gamma,\varphi)$ - pink, $U_{ss}(\gamma,\varphi)$ - pink dotted line.

Similar figures for the remaining molecules are presented in the Supplementary Materials (see Fig. 1SM – 5 SM).

Calculations were also performed for the torsional states of the studied molecules, which include or exclude the potential and/or kinetic interactions. This data is presented in Tabl. 4 SM for molecules I-VI in the Supplementary Materials 1. Analyzing relative conformers energies, energies of stationary torsional states and their splitting due to tunneling for molecules II-VI, which are close in terms of energy and structural characteristics (see Tabl. 4 SM), we note that the energy difference between trans- and cis-conformers decreases if kinetic or potential interactions of the internal tops are excluded when compiling the Hamiltonian matrix. If both types of interactions are not taken into account, the energies of both conformers in molecules II-VI become very close. Additionally, it is noticeable that taking into account the contributions of potential interaction harmonics of the type $sin(k\gamma)sin(l\varphi)$ leads to an increase in the relative energy of the cis-conformer in molecules II-VI, while the inclusion of corresponding harmonics of the type $cos(k\gamma)cos(l\varphi)$ lowers the relative energy of the cis-conformer in the case of the HO(CH$_2$)OH molecule, and raises it in the case of the HSOSH molecule. Also, the pattern of tunneling splittings of the ground states of trans- and cis-conformers of the molecules HO(CH_2)OH and HSOSH overall correlates with changes in the shape of potential barriers in these molecules when moving along the path of minimum energy. In particular, as mentioned above, potential interaction leads to an increase in the height of the potential barrier between equivalent trans-configurations and, simultaneously, to a decrease in the height of the potential barrier between equivalent cis-configurations in the HO(CH_2)OH molecule (see Fig. 3a). This is consistent with the data presented in columns 2 and 4 of Tabl. 4 SM, according to which in the absence of potential interaction between the tops in the trans-conformer, the tunneling splitting of the ground state is greater ($3.37 \cdot 10^{-2}$ cm^{-1}), than when it is taken into account ($2.44 \cdot 10^{-6}$ cm^{-1}), whereas for the cis-conformer the opposite situation is realized ($3.34 \cdot 10^{-2}$ and 0.33 cm^{-1}respectively). In the case of the HSOSH molecule, the potential interaction of the tops reduces the heights of the potential barriers between the equivalent configurations of both conformers (see Fig. 4a). This is consistent with the results presented in columns 2 and 4 of Tabl. 4 SM, where in the absence of potential interaction the tunneling splittings in both conformers are smaller ($11.81 \cdot 10^{-12}$ and $1.92 \cdot 10^{-12}$ cm^{-1} for trans - and cis -conformers, respectively) than when it is taken into account ($2.32 \cdot 10^{-11}$ and $3.71 \cdot 10^{-11}$ cm^{-1} respectively). Similar parallels can be drawn from various other scenarios where certain interactions are either considered or not considered. Undoubtedly, taking into account the kinetic and potential interactions of the tops also affects the values of the fundamental torsional vibration frequencies of the analyzed molecules. In particular, in the case of neglecting all interactions, the frequencies of these vibrations become very similar, as in the case of the HO(CH_2)OH molecule, or these vibrations become essentially eight-fold degenerate, as in the case of the HSOSH molecule.

4 CONCLUSION

In this study, an analysis of the potential kinetic interaction of two equivalent hydroxyl and thiol tops in the $C_6H_4(OH)_{2\text{-}o}$, HO(CH_2)OH, HOOOH, HOSOH, HSOSH, and HSSSH molecules was performed. A Fourier analysis of the potential and kinetic energy of the analyzed molecules was carried out. It was established that in all molecules, in which the asymmetric O-H and S-H internal tops have a period of 2π, the harmonics with a period of π dominate in the 2D Fourier representation of potential energy. It has been shown that the contribution of these harmonics becomes more significant the closer 1) the values of torsional coordinates in equilibrium configurations of trans- and cis-conformers to 90^0, 2) the energy values of two conformers in equilibrium configurations, 3) the potential energy values at points with coordinates (0^0, 180^0) and (180^0, 180^0). At the same time, in the Fourier representation of kinetic energy of all molecules, harmonics with a period of 2π dominate.

The proportion of the energy of the potential and kinetic interaction of equivalent tops in molecules I - VI, in comparison with the corresponding energies of the interaction of the tops with the molecular backbone, is quite large. Specifically, for molecules I and II, the kinetic interaction of the first type is comparable to the interaction of the second type, and the potential interaction of the first type even predominates over the corresponding interaction of the second type.

It has been demonstrated that the potential interaction of the tops in molecules I-VI is primarily determined by the difference in energies between the trans - and cis - conformers, as well as by the magnitude of splitting in the symmetric and antisymmetric torsional vibrations in both conformers.

At the same time, direct calculations showed that there are no general trends in the behavior of tunneling splittings of the ground and excited torsional states of the trans - and cis - conformers, depending on whether the potential interactions of the tops are taken into account in the form of harmonics of the type $cos\left(k\gamma\right)cos\left(l\varphi\right)$ or in the form of harmonics $sin\left(k\gamma\right)sin\left(l\varphi\right)$ as was the case, for example, in the molecule of acetone [24], where it was shown that accounting for the former leads to a shift in torsional levels, and accounting for the latter leads to their significant splitting. We attribute this situation to the fact that, unlike the acetone molecule where the methyl tops exhibit high symmetry, smoothing their interaction with the molecular frame and among themselves, the hydroxyl and thiol tops are asymmetrical. This asymmetry significantly complicates their interaction with the molecular skeleton and each other. Additional complications arise due to existence of few conformers for analyzed molecules.

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