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ТОРСИОННЫЕ СОСТОЯНИЯ МОЛЕКУЛЫ ГИДРОПЕРОКСИДА МЕТИЛА, РАССЧИТАННЫЕ С УЧЕТОМ АНГАРМОНИЧЕСКОЙ ЭНЕРГИИ НУЛЕВЫХ КОЛЕБАНИЙ

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2D-поверхности потенциальной энергии, кинематических коэффициентов и компонент дипольного момента, а также высоты потенциальных барьеров, энергии стационарных торсионных состояний и частоты туннелирования гидроксильной и метильной групп в молекуле гидропероксида метила были рассчитаны на уровнях теории MP2/CBS и CCSD(T)/Aug-cc-pVTZ. Дополнительно выполнены расчеты 2D-поверхности энергии нулевых колебаний молекулы в гармоническом и ангармоническом приближениях на уровне теории MP2/Aug-cc-pVTZ. Энергия нулевых колебаний, вычисленная в двух приближениях, просуммирована с потенциальной энергией молекулы гидропероксида метила, рассчитанной на двух уровнях теории. Четыре варианта уточненной потенциальной энергии использованы для вычислений энергий стационарных торсионных состояний и частот туннелирования. Полученные результаты сопоставлены с представленными в литературе экспериментальными и теоретическими данными в целях оценки эффективности учета энергии нулевых колебаний при анализе внутреннего вращения в молекулах.

Ключевые слова: энергия нулевых колебаний; внутреннее вращение; торсионные колебания; частота туннелирования; молекула гидропероксида метила.

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THE TORSIONAL STATES OF METHYL HYDROPEROXIDE MOLECULE CALCULATED USING ANHARMONIC ZERO POINT VIBRATIONAL ENERGY

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The 2D surfaces of potential energy, kinematic coefficients, components of the dipole moment, the heights of potential barriers, the energies of stationary torsional states, and the tunneling frequencies of hydroxyl and methyl groups in the methyl hydroperoxide molecule were calculated at MP2/CBS and CCSD(T)/Aug-cc-pVTZ levels of theory. Additionally, calculations of the 2D surface of zero point vibrational energy of the molecule in the harmonic and anharmonic approximations were performed at MP2/Aug-cc-pVTZ level of theory. The zero point vibrational energy calculated in two approximations is summed up with the potential energy of the methyl hydroperoxide molecule, calculated at two levels of theory, and the resulting four outcomes of the refined potential energy are used to calculate the energies of stationary torsional states and tunneling frequencies. The results obtained are compared with the experimental and theoretical data presented in the literature to evaluate the efficiency of taking into account the zero point vibrational energy when examining the internal rotation in molecules.

Keywords: zero point vibrational energy; internal rotation; torsional vibrations; tunneling frequency; methyl hydroperoxide molecule.

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Introduction

The molecule of methyl hydroperoxide (CH_3OOH) is the smallest and simplest among organic peroxides and one of the simplest peroxide molecules, second only to hydrogen peroxide (HOOH) in the latter case. The main characteristic feature of peroxides is the presence of the (O — O) bond, which is rather weak and is often unstable even at room temperatures. Wherein the dissociation energy of the peroxide bond in the methyl hydroperoxide (MHP) molecule – 42.6 kcal/mol [1] is comparable to the dissociation energy of complexes with the strongest hydrogen bonds – 30 kcal/mol [2]. The methyl hydroxide molecule also attracts the attention of researchers due to its active participation in atmospheric, tropospheric, and stratospheric processes [3–5], as well as because it is one of the probable candidates for detection in interstellar space. Studies of the processes of formation and thermal decomposition of the MHP molecule were initiated a long ago [6–9]. Later, the attention of researchers was focused on the interaction of MHP molecules with surface water and ice [10; 11], as well as on the investigation of the properties of MHP molecules in water and in water clusters [12]. Unfortunately, we were unable to find literature data on experimental IR and Raman spectra in the low-frequency spectral range (10–500 cm^{-1}). At the same time, the spectral region, in which the overtones of the stretching vibrations of the hydroxyl group (6000–19 500 cm^{-1}) appear, has been studied experimentally and theoretically in great detail [13–17]. These studies showed the existence of a significant interaction of stretching and torsional vibrations of the hydroxyl group. These results once again emphasise the importance of analysing the torsional vibrations of O — H and CH_3 groups in the MHP molecule. For the ground state of a molecule, such an analysis was first performed in [18]. In this work, rotational microwave and millimeter spectra of the molecule were obtained and analysed for the first time. It was found that the tunneling of the hydroxyl group in the ground state occurs at a frequency of 14.97 cm^{-1}, while the corresponding tunneling frequency of the methyl group was $7.64 \cdot 10^{-5}$ cm^{-1}. Recently [19], a more deep and detailed theoretical study of torsional vibrations in the MHP molecule was carried out. 2D potential energy surface (PES) for two torsional coordinates was calculated at a high level of theory (CCSD(T)/Aug-cc-pVTZ). In this case, the computed value of the tunneling frequency of the hydroxyl group in the ground vibrational state (14.805 cm^{-1}) turned out to be very close to the experimental value. Besides, at the MP2/Aug-cc-pVTZ level of theory, the zero point vibrational energy ZPVE) of the remaining 13 bending and stretching modes was additionally taken into account in the harmonic approximation. Although it could be expected that this should improve the representation of the potential energy of torsional vibrations, the calculated value of the tunneling frequency, in this case, turned out to be underestimated (10.978 cm^{-1}) compared to the experimental result.

In this work, an attempt has been made to calculate more accurately the 2D surface of the ZPVE of the MHP molecule. It is well known that the values of vibrational frequencies calculated in the anharmonic approximation turn out to be much closer to the experimental values than in the case of using the harmonic approximation. Due to anharmonic calculations requiring considerably more time they were carried out at the MP2/Aug-cc-pVTZ level of theory. Calculations of the 2D PES due to the variation of the torsional coordinates were performed at two levels of theory (CCSD(T)/Aug-cc-pVTZ and MP2/CBS). Besides, we paid special attention to determining the values of the torsional coordinate of the methyl group when constructing the 2D PES.

Calculation details

Determination of the values of the torsional coordinates of the methyl group. We will denote the torsional coordinates of the hydroxyl group α, and the methyl group – θ. The geometry of the molecule corresponding to zero values of these coordinates is presented in fig. 1.

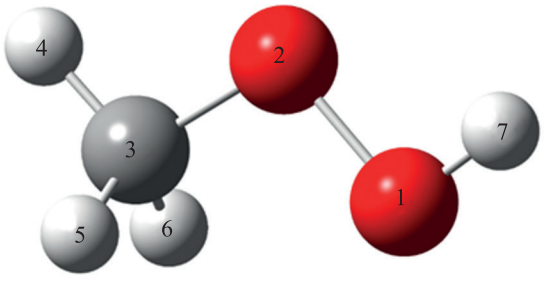


Fig. 1. Configuration of the MHP molecule,
in which the values of the torsional coordinates α
of the hydroxyl group and θ methyl group are considered to be zero

In fig. 1, atoms H_4, C_3, O_2, O_1, and H_7 lie in the same plane, while H_5 and H_6 are located symmetrically relative to this plane. The value of the torsional coordinate α is equal to the value of the dihedral angle $\angle C_3O_2O_1H_7$ which is 180° in the configuration presented in fig. 1. Therefore, the coordinate α can always be calculated by the formula $\alpha = \angle C_3O_2O_1H_7 - 180°$. The coordinate θ determines the rotation of the methyl group around the C_3O_2 bond. If the values of the dihedral angles $\angle H_4C_3O_2H_5$, $\angle H_4C_3O_2H_6$ and $\angle H_5C_3O_2H_6$ are fixed and are not optimised in the process of calculating the potential energy at the given nodes on a two-dimensional grid, then the value of the angle is uniquely determined by the formula:

$$\theta = \left(\angle H_4C_3O_2O_1 + \angle H_5C_3O_2O_1 + \angle H_6C_3O_2O_1\right) : 3. \quad (1)$$

However, it is clear that in those cases when the values of the torsional coordinate $\alpha \neq 0°$, $\alpha \neq 180°$, i. e. H_7 appear outside the atomic plane $C_3O_2O_1$, the local symmetry of the methyl group decreases to C_1. Consequently, only one of the three angles in formula (1) can be left fixed, and the other two are optimised while minimising energy. In this case, it is clear that the value of the coordinate ceases to be uniquely determined. Therefore, the method for specifying the coordinate should be described in more detail. In this work, we used two approaches. In the first case (I), the angle value θ is considered equal to the value of the dihedral angle $\angle H_4C_3O_2O_1$ taking the values: 4°, 12°, 20°, 28°, 36°, 44°, 52°, 60°, 68°, 76°, 84°, 92°, 100°, 108°, 116°, and when calculating the energy, these values are fixed, while the values of the other two angles are optimised ($\angle H_5C_3O_2O_1$, $\angle H_6C_3O_2O_1$). The α coordinate takes the following values: 12°, 36°, 60°, 84°, 108°, 132°, 156°, 180°. Thus, the potential energy ($U(\alpha, \theta)$) is calculated at 120 points and then expands to the full potential surface using the relation $U(\alpha, \theta) = U(-\alpha, -\theta) = U\left(\frac{2\pi}{3} - \alpha, 2\pi - \theta\right)$. It should be taken into account here that despite the absence of local symmetry, the potential function still has a period of 120° along the coordinate α. Indeed, for any relative arrangement of the H_4, H_5, and H_6 atoms and an arbitrary arrangement of the H_7 atom, if we rotate the methyl group so that in place of H_4 there is H_5, in place of H_5 there is H_6 and in place of H_6 – H_4, then the internal energy of the molecule is certainly will not change, and the value of the angle θ determined by the formula (1) will increase exactly by 120°. In the second case (II), already performed calculations are used, but the value of the angle θ at each of the 120 points is determined by the formula (1). In this case, the values θ are somewhat different from those values in which the potential energy has to be found ($\theta_j \rightarrow$ 4°, 12°, 20°, 28°, 36°, 44°, 52°, 60°, 68°, 76°, 84°, 92°, 100°, 108°, 116°). The differences are not comprehensive, but at some points, the deviations exceed 2°. For example, in the case when the value of the torsional coordinate is $\alpha = 84°$, the true values of the torsional coordinate of the methyl group, which we will denote θ_j^r for distinction, were: $\theta_j^r \rightarrow 3.986°$,

11.408°, 18.914°, 26.577°, 34.459°, 42.595°, 51.0°, 59.644°, 68.442°, 77.25°, 85.843°, 94.269°, 102.315°, 110.087°, 117.674°. To find the values of the potential energy at the required points, by analogy with [20], we introduced an analytical function in the form: $V(\alpha, \theta) = \sum_{m, n = 0} \left(V^c_{m, n} \cos m\alpha \cdot \cos 3n\theta + V^s_{m, n} \sin m\alpha \cdot \sin 3n\theta\right)$. Then, using the *Mathematica* package[1], the function $V(\alpha, \theta)$ was fitted to find the coefficients $V^c_{m, n}$ and $V^s_{m, n}$ which satisfy the following condition $V\left(\alpha_i, \theta^r_{ij}\right) = U\left(\alpha_i, \theta^r_{ij}\right)$, where $\alpha_i \in 12°–180°$ in steps of 24°, $i \in 1–15$ while θ^r_{ij} – true values of the torsional coordinate of the methyl group for a fixed torsional coordinate of the hydroxyl group α_i, $j \in 1–8$. Then, using the described $V(\alpha, \theta)$ the potential energy at the nodes with the required values: $U\left(\alpha_i, \theta_j\right) = V\left(\alpha_i, \theta_j\right)$ of the torsional coordinates was determined. It turned out that the deviations in the values of the potential energy at some points exceeded 100 cm^{-1}. A similar adjustment was made for the 2D ZPVE surface calculated in harmonic and anharmonic approximations.

Determination of the energies of stationary torsional states of the MHP molecule. The vibrational Schrödinger equation with reduced dimensionality has the form (2). It was solved numerically and the values of the energies of the stationary torsional levels were calculated [21–26]:

$$\left[-F_{\alpha\alpha}(\alpha, \theta)\frac{\partial^2}{\partial\alpha^2} - F_{\theta\theta}(\alpha, \theta)\frac{\partial^2}{\partial\theta^2} - F_{\alpha\theta}(\alpha, \theta)\frac{\partial^2}{\partial\alpha\partial\theta} + U(\alpha, \theta)\right]\Psi(\alpha, \theta) = E\Psi(\alpha, \theta). \quad (2)$$

The kinematic parameters $F_{\alpha\alpha}$, $F_{\theta\theta}$, $F_{\alpha\theta}$ were calculated using the formalism of the Wilson vectors [27; 28] using formulas [29–31]

$$F_{\alpha\alpha} = B_{\mathrm{O}}\left[\left(\vec{s}^{\,\alpha}_1\right)^2 + \left(\vec{s}^{\,\alpha}_2\right)^2\right] + B_{\mathrm{C}}\left(\vec{s}^{\,\alpha}_3\right)^2 + B_{\mathrm{H}}\left(\vec{s}^{\,\alpha}_7\right)^2,$$

$$F_{\theta\theta} = B_{\mathrm{O}}\left[\left(\vec{s}^{\,\theta}_1\right)^2 + \left(\vec{s}^{\,\theta}_2\right)^2\right] + B_{\mathrm{C}}\left(\vec{s}^{\,\theta}_3\right)^2 + B_{\mathrm{H}}\left[\left(\vec{s}^{\,\theta}_5\right)^2 + \left(\vec{s}^{\,\theta}_6\right)^2 + \left(\vec{s}^{\,\theta}_7\right)^2\right],$$

$$F_{\gamma_1\gamma_2} = 2B_{\mathrm{O}}\left[\vec{s}^{\,\alpha}_2 \cdot \vec{s}^{\,\theta}_2 + \vec{s}^{\,\alpha}_1 \cdot \vec{s}^{\,\theta}_1\right] + 2B_{\mathrm{C}}\left(\vec{s}^{\,\alpha}_3 \cdot \vec{s}^{\,\theta}_3\right).$$

Here, $\vec{s}^{\,x}_N$ is the Wilson vector for the coordinate $x = \{\alpha, \theta\}$, and for the atom with the number N (the numeration of atoms corresponds to fig. 1, $B_Y = \frac{\hbar^2}{2M_Y l_0^2}$, $Y \in \{\mathrm{H, C, O}\}$, $\hbar$ is the Planck's constant, $l_0 = 1$ Å, M_{H}, M_{C}, M_{O} are the corresponding masses of the hydrogen, carbon, and oxygen atoms).

Equation (2) was solved using the Fourier method [32–34]. Elements of the Hamiltonian matrix were calculated by the formula [23]

$$H_{(m, n)(m', n')} = -m^2 F^{\alpha\alpha}_{m-m', n-n'} - 9n^2 F^{\theta\theta}_{m-m', n-n'} - 3mn F^{\alpha\theta}_{m-m', n-n'} + U_{m-m', n-n'},$$

where $F^{\alpha\alpha}_{m, n}$, $F^{\theta\theta}_{m, n}$, $F^{\alpha\theta}_{m, n}$, $U_{m, n}$ were found by fitting coefficients in equation (2) and employing 2D complex Fourier series using the *Mathematica* package:

$$F_{\alpha\alpha}(\alpha, \theta) = \sum_{m, n = -M}^{M} F^{\alpha\alpha}_{m, n} e^{i(m\alpha + 3n\theta)},\ F_{\theta\theta}(\alpha, \theta) = \sum_{m, n = -M}^{M} F^{\theta\theta}_{m, n} e^{i(m\alpha + 3n\theta)},$$

$$F_{\alpha\theta}(\alpha, \theta) = \sum_{m, n = -M}^{M} F^{\alpha\theta}_{m, n} e^{i(m\alpha + 3n\theta)},\ U(\alpha, \theta) = \sum_{m, \boldsymbol{n} = -M}^{M} U_{m, n} e^{i(m\alpha + 3n\theta)}.$$

The wave function is described by a complex two-dimensional Fourier series of the form [34]

$$\Psi(\alpha, \theta) = \sum_{m, n = -N}^{N} \Psi_{m, n} e^{i(m\alpha + 3n\theta)},\ N \succ M.$$

2D PES for two torsional coordinates of the MHP molecule calculated at MP2/Aug-cc-pVTZ [35–37] and MP2/Aug-cc-pVQZ [35; 36; 38] levels of theory at 120 nodes of the above-described grid using quantum-chemical package Gaussian 09 [39]. Then, using the formulas presented in [40; 41], the values of the kinetic parameters and energies were extrapolated to the complete basis set limit. Besides, 2D PES calculations were performed at 120 nodes of a similar grid at the CCSD(T)/Aug-cc-pVTZ [37; 42; 43] level of theory.

[1]Wolfram Mathematica [Electronic resource]. URL: http://www.wolfram.com/mathematica (date of access: 12.11.2020).

2D ZPVE computations were performed in harmonic and anharmonic approximations at 120 nodes of a similar grid using the [39] package at the MP2/Aug-cc-pVTZ [35; 36; 43] level of theory. When calculating the energies of stationary torsional states of the MHP molecule, which takes into account the ZPVE for the potential energy, calculated at one of the two levels of theory, the ZPVE was added at each of 120 points.

Discussion of the results

It is known, the MHP molecule is realised in two equivalent equilibrium gauche configurations, one of which is shown in fig. 2.

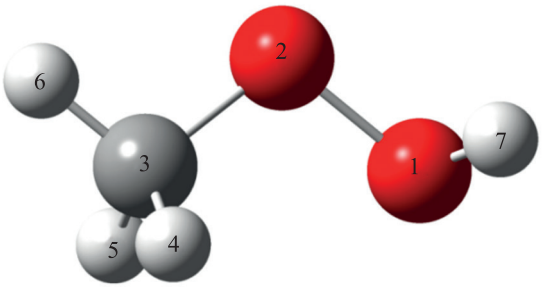


Fig. 2. Equilibrium configuration of the MHP molecule, calculated at the CCSD(T)/Aug-cc-pVTZ level of theory

The 2D PES of the molecule calculated at the CCSD(T)/Aug-cc-pVTZ level of the theory is shown in fig. 3.

As can be seen from fig. 3, the cis-barrier (θ = 180°) is significantly higher than the trans-barrier (θ = 0°). On the 2D PES, six equivalent energy minima are formed, which leads to the splitting of each torsional state of the molecule into six sublevels. Figure 4 shows a 2D surface of the ZPVE calculated at the MP2/Aug-cc-pVTZ level of the theory.

Figure 5 presents 2D surfaces of the kinetic parameters of the MHP molecule, calculated at the CCSD(T)/Aug-cc-pVTZ level of the theory.

To classify torsional states, we used the notation: $(n_{CH_3}, n_{OH}^{\pm}, X)$, where n_{CH_3} and n_{OH} are vibrational quantum numbers of the torsional vibrations of methyl and hydroxyl groups, respectively; sign + and sign – determine the symmetry or antisymmetry of the torsion state for the plane containing the atoms C_3, O_2, O_1 (plane normal to the coordinate plane (α, θ) and intersecting it along the coordinate $\alpha = 0°$); X is one of the symmetry species (A_1, A_2, E) of the group G_6 [44]. The computation results are collected in tables 1 and 2, where the following designations for various calculation options will be used: for the CCSD(T)/Aug-cc-pVTZ and MP2/CBS levels of theory, at which the potential energy was calculated – CCSD(T) and MP2, respectively, the first and second methods for determining the torsional coordinate θ will be denoted by adding (I) or (II), respectively. Since the energy of zero point vibrations was calculated only at one level of theory (MP2/Aug-cc-pVTZ), its accounting is denoted as +ZPVE.

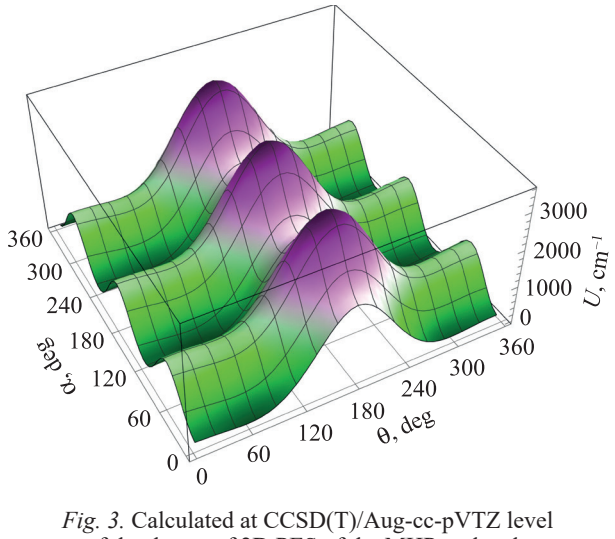


Fig. 3. Calculated at CCSD(T)/Aug-cc-pVTZ level of the theory of 2D PES of the MHP molecule

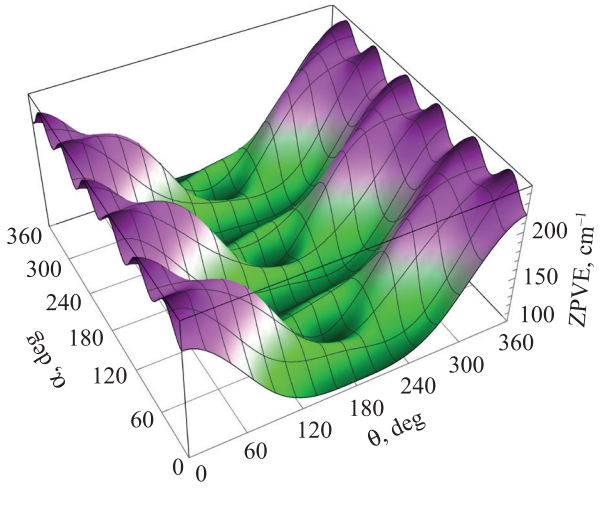


Fig. 4. 2D surface of the ZPVE of the MHP molecule calculated at the MP2/Aug-cc-pVTZ level of theory

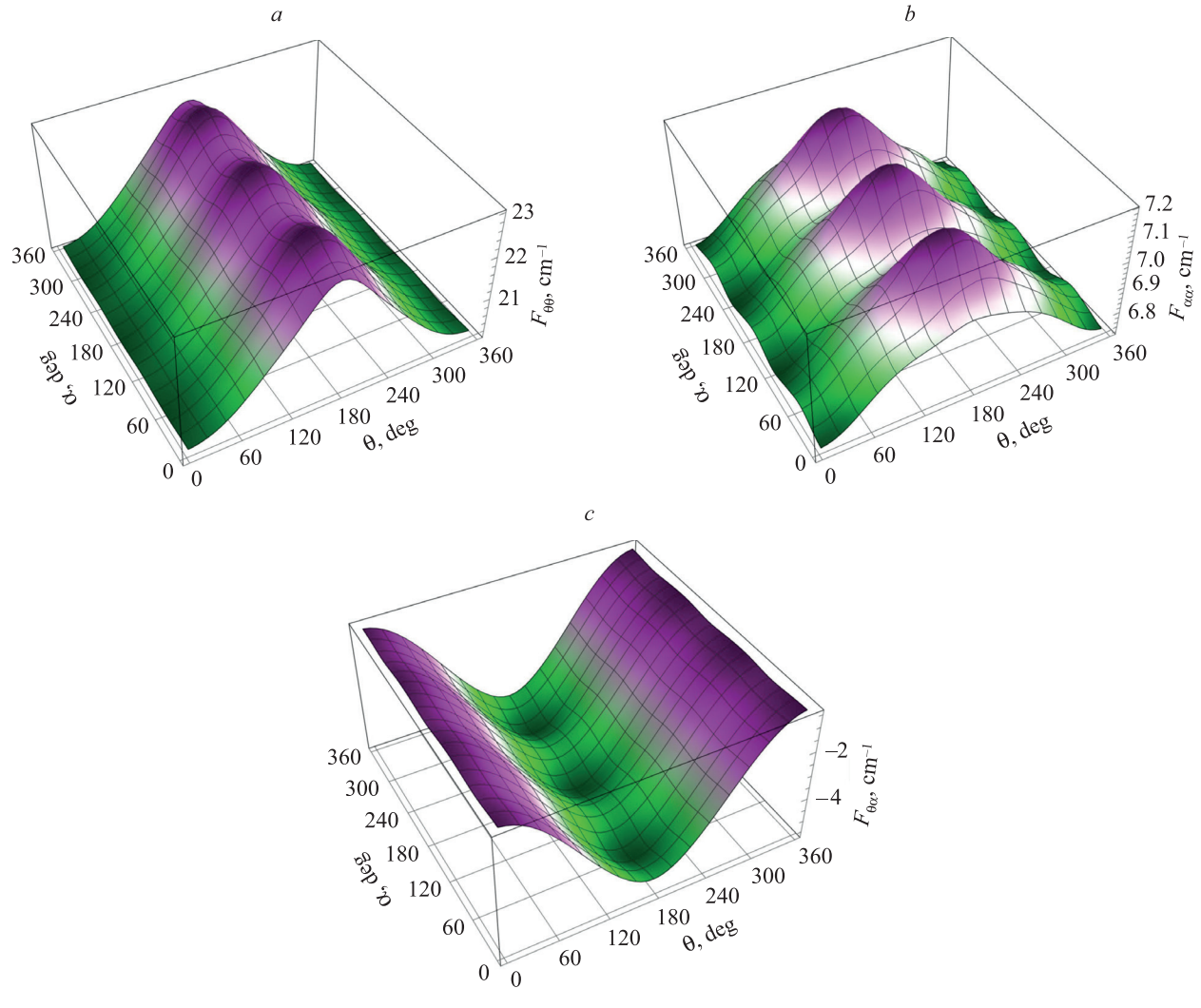


Fig. 5. 2D surfaces of the kinetic coefficients $F_{\theta\theta}$ (*a*), $F_{\alpha\alpha}$ (*b*), and $F_{\theta\alpha}$ (*c*), calculated at the CCSD(T)/Aug-cc-pVTZ level of theory

Also, the symbols *h* or *a* will be used to denote the harmonic or anharmonic approximation when calculating ZPVE.

Table 1

Calculated at the CCSD(T)/Aug-cc-pVTZ and MP2/CBS levels of theory and using two methods for determining the value of the torsional coordinate of the energy of stationary torsional states of the MHP molecule without taking into account the zero point vibration energy

n_{CH_3}, $n^{\pm}_{OH}$, X	Case (I)		Case (II)		CCSD(T), cm^{-1} [19]	Experiment, cm^{-1} [18; 19]
	CCSD(T), cm^{-1}	MP2, cm^{-1}	CCSD(T), cm^{-1}	MP2, cm^{-1}		
1	*2*	*3*	*4*	*5*	*6*	*7*
0 0^+ A_1	0.000	0.000	0.000	0.000	0.000	0.000
0 0^+ E	0.000 17	0.000 091	0.000 122	0.000 064	0.001	0.000 074 5 [18]
0 0^- A_2	14.62	22.17	14.47	22.01	14.81	14.97 [18]
0 0^- E	14.62	22.17	14.47	22.01	14.80	14.97 [18]
0 1^+ A_1	119.19	115.88	118.70	115.25	119.05	130.00 [19]
0 1^+ E	119.19	115.88	118.70	115.25	119.05	130.00 [19]
0 1^- A_2	202.48	209.11	202.24	208.42	203.52	191.00 [19]
0 1^- E	202.48	209.11	202.24	208.42	203.52	191.00 [19]

Ending table 1

n_{CH_3}, $n^{\pm}_{OH}$, X	Case (I)		Case (II)		CCSD(T), cm^{-1} [19]	Experiment, cm^{-1} [18; 19]
	CCSD(T), cm^{-1}	MP2, cm^{-1}	CCSD(T), cm^{-1}	MP2, cm^{-1}		
1	*2*	*3*	*4*	*5*	*6*	*7*
$1\,0^{-}\,A_2$	230.43	239.88	248.06	259.21	243.21	–
$1\,0^{-}\,E$	230.42	239.87	248.06	259.20	243.21	–
$1\,0^{+}\,A_1$	244.41	262.88	262.51	282.25	257.48	–
$1\,0^{+}\,E$	244.40	262.73	262.50	282.25	257.47	–
$0\,2^{+}\,A_1$	314.85	322.51	314.11	321.49	316.26	–
$0\,2^{+}\,E$	314.85	322.51	314.11	321.49	316.85	–
$1\,1^{-}\,A_2$	347.71	356.09	365.67	375.26	361.84	–
$1\,1^{-}\,E$	347.71	356.09	365.67	375.26	361.84	–
$0\,2^{-}\,A_2$	430.16	447.54	435.43	445.85	438.80	–
$0\,2^{-}\,E$	430.21	447.54	435.43	445.85	438.82	–
$1\,1^{+}\,A_1$	436.98	449.93	449.03	469.36	445.58	–
$1\,1^{+}\,E$	436.98	449.94	449.06	469.37	445.60	–
$2\,0^{+}\,A_1$	451.85	469.87	476.02	497.06	467.75	–
$2\,0^{+}\,E$	451.98	469.96	476.19	497.17	467.76	–
$2\,0^{-}\,A_2$	463.07	492.53	488.45	520.28	467.76	–
$2\,0^{-}\,E$	463.24	492.62	488.63	520.39	479.91	–

Table 2

Calculated at the CCSD(T)/Aug-cc-pVTZ and MP2/CBS levels of the theory, using two methods for determining the value of the torsional coordinate of the energy of stationary torsional states of the MHP molecule while taking into account the ZPVE

n_{CH_3}, $n^{\pm}_{OH}$, X	Case (I)			Case (II)		CCSD(T) +ZPVE(h), cm^{-1} [19]	Experiment, cm^{-1} [18; 19]
	CCSD(T) +ZPVE(hI), cm^{-1}	CCSD(T) +ZPVE(aI), cm^{-1}	MP2 +ZPVE(aI), cm^{-1}	CCSD(T) +ZPVE(aII), cm^{-1}	MP2 +ZPVE(aII), cm^{-1}		
1	*2*	*3*	*4*	*5*	*6*	*7*	*8*
$0\,0^{+}\,A_1$	0.000	0.000	0.000	0.000	0.000	0.000	0.000
$0\,0^{+}\,E$	0.000 18	0.000 14	0.000 084	0.000 085	0.000 089	0.001	0.000 074 5 [18]
$0\,0^{-}\,A_2$	11.24	8.70	15.97	7.21	13.91	10.98	14.97 [18]
$0\,0^{-}\,E$	11.24	8.70	15.97	7.21	13.91	10.98	14.97 [18]
$0\,1^{+}\,A_1$	121.24	120.75	111.88	129.99	110.54	121.11	130.00 [19]
$0\,1^{+}\,E$	121.24	120.75	111.88	129.99	110.54	121.11	130.00 [19]
$0\,1^{-}\,A_2$	198.73	190.35	193.27	198.42	191.60	199.36	191.00 [19]
$0\,1^{-}\,E$	198.73	190.35	193.27	198.42	191.60	199.36	191.00 [19]
$1\,0^{-}\,A_2$	233.22	241.29	249.30	256.06	269.12	245.58	–
$1\,0^{-}\,E$	233.21	241.29	249.30	256.06	269.12	245.58	–
$1\,0^{+}\,A_1$	243.86	248.07	263.30	262.29	282.46	255.85	–
$1\,0^{+}\,E$	243.85	248.06	263.30	262.29	282.46	255.85	–
$0\,2^{+}\,A_1$	309.33	303.85	306.74	308.89	310.00	310.24	–
$0\,2^{+}\,E$	309.33	303.85	306.74	308.89	310.00	310.24	–
$1\,1^{-}\,A_2$	352.14	353.36	357.36	384.39	376.79	365.75	–
$1\,1^{-}\,E$	352.13	353.36	357.36	384.38	376.79	365.95	–

Ending table 2

n_{CH_3}, $n^{\pm}_{OH}$, X	Case (I)			Case (II)		CCSD(T) +ZPVE(h), cm^{-1} [19]	Experiment, cm^{-1} [18; 19]
	CCSD(T) +ZPVE(hI), cm^{-1}	CCSD(T) +ZPVE(aI), cm^{-1}	MP2 +ZPVE(aI), cm^{-1}	CCSD(T) +ZPVE(aII), cm^{-1}	MP2 +ZPVE(aII), cm^{-1}		
1	*2*	*3*	*4*	*5*	*6*	*7*	*8*
$0\ 2^{-}\ A_2$	429.24	419.73	425.64	425.82	424.17	430.40	–
$0\ 2^{-}\ E$	429.30	419.73	425.64	425.82	424.17	430.40	–
$1\ 1^{+}\ A_1$	439.80	421.06	436.63	452.94	454.53	443.93	–
$1\ 1^{+}\ E$	439.80	421.08	436.64	452.95	454.54	443.95	–
$2\ 0^{+}\ A_1$	456.93	472.26	488.92	490.63	517.06	472.33	–
$2\ 0^{+}\ E$	456.94	472.40	489.01	490.77	571.17	472.45	–
$2\ 0^{-}\ A_2$	465.42	475.49	501.28	495.21	529.86	480.61	–
$2\ 0^{-}\ E$	465.53	475.64	501.36	495.35	529.95	480.75	–

Analysis of the data given in columns *2* and *4* of table 1 indicates excellent agreement in the values of the calculated energies of torsional states of the hydroxyl group obtained in this work and in [19], despite the different approaches to compiling the vibrational Schrödinger equation and a different number of points, in which the calculations of the potential energy were carried out. Comparable inferences can be made by analysing the data in columns *2* and *7* of table 2, where the calculations took into account the ZPVE in the harmonic approximation at the MP2/Aug-cc-pVTZ level of theory.

If we now compare the results discussed above with experimental data, it is clear that taking into account ZPVE in the harmonic approximation lowers the accuracy of the calculated tunneling frequency in the ground vibrational state (10.978 [19] and 11.239 cm^{-1}) in comparison with the experimental value (14.97 cm^{-1}). It should be noted that in the case of neglecting the ZPVE, the calculated value of the tunneling frequency of the hydroxyl group in the ground state (14.805 [19] and 14.621 cm^{-1}) is in excellent agreement with the experimental value. The work [19] also gives the experimental values of the first excited torsional states of the hydroxyl group $0\ 1^{+}$ – 130.0 and $0\ 1^{-}$ – 191.0 cm^{-1}, but it is not clear from which work these data were taken since the work [18] does not present the torsion-rotational transitions between states $0\ 0^{+}$, $0\ 0^{-}$ on one hand and $0\ 1^{+}$, $0\ 1^{-}$ on the other hand. The work [18] also provides the experimentally obtained value of the tunneling frequency of the methyl group in the ground state ($7.45 \cdot 10^{-5}$ cm^{-1}). As can be seen from tables 1 and 2, the corresponding calculated values of the tunneling frequencies of the methyl group, presented in the second columns with and without ZPVE, are respectively equal to $1.8 \cdot 10^{-4}$ and $1.7 \cdot 10^{-4}$ cm^{-1}. These values are much closer to the experimental in comparison with the result obtained in [19] ($1 \cdot 10^{-3}$ cm^{-1}). Note also that the computed value of the tunneling frequency of the hydroxyl group in the ground state, obtained at the MP2/CBS level of theory without taking into account the ZPVE, turns out to be overvalued (22.01 cm^{-1}) in comparison with the experimental one.

Now we turn to the analysis of the results, which take into account the ZPVE in the anharmonic approximation (see table 2). As can be seen from the data in columns *2*, *3*, and *5* of table 2, the transition to the anharmonic approximation of the ZPVE in combination with the CCSD(T)/Aug-cc-pVTZ level of the theory leads to a further decrease in the calculated tunneling frequency of the hydroxyl group in the ground state to 8.7 cm^{-1} and up to 7.21 cm^{-1} in the case of determining the value of the torsional coordinate by the second method. This leads to a further discrepancy with the experimental data. In this case, the calculated value of the energy of the $0\ 1^{+}$ torsional state (129.99 cm^{-1}) fully matches with the experimental value (130.0 cm^{-1}). Also, the computed value of the tunneling frequency of the methyl group ($8.5 \cdot 10^{-5}$ cm^{-1}) turns out to be very close to the experimental one. In calculations at the MP2/CBS theory level of theory, the situation is different. As in the previous case, taking into account ZPVE in the anharmonic approximation and determining the values of the torsion angle θ by the second method reduces the tunneling frequency of the hydroxyl group to 15.97 and 13.91 cm^{-1}, which suggests that taking the ZPVE into account improves the predictive ability of the approach at this level theory. Also, according to the data in column *6* of table 2, it can be argued that in the latter case, excellent agreement is achieved in the calculated value of the $0\ 1^{-}$ energy of the excited torsional state of the hydroxyl group (191.60 cm^{-1}) with the experimental value (191.00 cm^{-1}). However, there is a big deviation in the calculated energy of the torsional state $0\ 1^{+}$ (110.54 cm^{-1}) from the experimental value (130.00 cm^{-1}).

The computed value of the tunneling frequency of the methyl group ($8.9 \cdot 10^{-5}$ cm^{-1}) is also in good agreement with the experimental one ($7.45 \cdot 10^{-5}$ cm^{-1}). In summary, relying on the most assuredly established value of the tunneling frequency of the hydroxyl group in the ground vibrational state of the MHP molecule, it can be argued that taking into account the ZPVE, both in the harmonic and, to a greater extent, in the anharmonic approximation in combination with the CCSD(T)/Aug-cc-pVTZ level of theory worsens the agreement with the experimental result. However, in the case of taking into account the ZPVE, both in the harmonic and in the anharmonic approximation in combination with the MP2/CBS level of theory, the opposite is true.

Conclusions

The energies of the torsional states of the hydroxyl and methyl groups in the MHP molecule were calculated at two levels of theory (CCSD(T)/Aug-cc-pVTZ and MP2/CBS) with and without taking into account the ZPVE, calculated in both harmonic and anharmonic approximations. Additionally, the values of the torsional coordinate of the methyl group were determined in two ways. For several variants of the calculation, good agreement was obtained with the previously performed calculations presented in [19] as well as with the experimentally established values of the tunneling frequencies of hydroxyl and methyl groups in the ground vibrational state.

It is shown that taking into account the ZPVE in the harmonic and, to a greater extent, in the anharmonic approximation leads to a decrease in the calculated frequency of O—H group tunneling in the ground vibrational state of the MHP molecule in calculations at MP2/CBS level of the theory that significantly improves the agreement with the experimental value.

It was found that in the second method for determining the value of the torsional coordinate of the methyl group, the calculated values of the energies of the torsional states of the hydroxyl group, as expected, change insignificantly.

More accurate conclusions in regards to the efficiency of taking into account ZPVE when calculating the energies of torsional states can be made after registering low-temperature, low-frequency (10–500 cm^{-1}) torsion-rotational IR spectra of the MHP molecule in the gas phase.

References

1. Matthews J, Sinha A, Francisco JS. Unimolecular dissociation and thermochemistry of CH_3OOH. *Journal of Chemical Physics.* 2005;122(22):221101. DOI: 10.1063/1.1928228.

2. Pitsevich GA, Kozlovskaya EN, Malevich AE, Doroshenko IYu, Satsunkevich VS, Pettersson LGM. Some useful correlations for H-bonded systems. *Molecular Crystals and Liquid Crystals.* 2020;696(1):15–28. DOI: 10.1080/15421406.2020.1731090.

3. Morgan RB, Jackson AV. Measurements of gas-phase hydrogen peroxide and methyl hydroperoxide in the coastal environment during the PARFORCE project. *Journal of Geophysical Research*. 2002;107(D19):8109. DOI: 10.1029/2000JD000257.

4. Snow JA, Heikes BG, Shen H, O'Sullivan DW, Fried A, Walega J. Hydrogen peroxide, methyl hydroperoxide and formaldehyde over North America and the North Atlantic. *Journal of Geophysical Research.* 2007;112(D12):D12S07. DOI: 10.1029/2006JD007746.

5. Zhang X, He SZ, Chen ZM, Zhao Y, Hua W. Methyl hydroperoxide (CH_3OOH) in urban, suburban and rural atmosphere: ambient concentration, budget, and contribution to the atmospheric oxidizing capacity. *Atmospheric Chemistry and Physics*. 2012;12:8951–8962. DOI: 10.5194/acp-12-8951-2012.

6. Subbaratnam NR, Calvert JG. The mechanism of methyl hydroperoxide formation in the photoöxidation of azomethane at 25°. *Journal of the American Chemical Society*. 1961;84(7):1113–1118. DOI: 10.1021/ja00866a010.

7. Kirk AD. The thermal decomposition of methyl hydroperoxide. 1965;43(8):2236–2242. *Canadian Journal of Chemistry.* DOI: 10.1139/v65-301.

8. DeCorpo JJ, McDowell MV, Sheinson RS, Wyatt JR. Quantitative measurement of methyl hydroperoxide in the acetaldehyde cool flame. *Journal of the Chemical Society, Chemical Communications*. 1974;14:533–534. DOI: 10.1039/C39740000533.

9. Davies DM, Deary ME. A convenient preparation of aqueous methyl hydroperoxide and a comparison of its reactivity towards triacetylethylenediamine with that of other nucleophiles: the mechanism of peroxide bleach activation. *Journal of the Chemical Society. Perkin Transactions 2.* 1992;2:559–562.

10. Kamboures MA, Nizkorodov SA, Gerber RB. Ultrafast photochemistry of methyl hydroperoxide on ice particles. *Proceedings of the National Academy of Sciences of the United States of America*. 2010;107(15):6600–6604. DOI: 10.1073/pnas.0907922106.

11. Ignatov SK, Gadzhiev OB, Kulikov MYu, Pitrov AI, Razuvaev AG, Gand M, et al. Adsorption of methyl hydroperoxide (CH_3OOH) on water ice. Theoretical study with systematic assessment of coordination modes. *Journal of Physical Chemistry C.* 2011; 115(18):9081–9089. DOI: 10.1021/jp112177x.

12. Epstein SA, Shemesh D, Tran VT, Nizkorodov SA, Gerber RB. Absorption spectra and photolysis of methyl peroxide in liquid and frozen water. *Journal of Physical Chemistry A*. 2012;116(24):6068–6077. DOI: 10.1021/jp211304v.

13. Homitsky SC, Dragulin SM, Haynes LM, Hsieh S. O—H stretch overtone excitation in methyl and ethyl hydroperoxides. *Journal of Physical Chemistry A*. 2004;108(44):9492–9499. DOI: 10.1021/jp047455l.

14. Haynes LM, Vogelhuber KM, Pippen JL, Hsieh S. Effects of torsion on O—H stretch overtone spectra and direct overtone photolysis of methyl hydroperoxide. *Journal of Chemical Physics*. 2005;123(23):234306. DOI: 10.1063/1.2139673.

15. Matthews J, Sinha A, Francisco JS. The importance of weak absorption features in promoting tropospheric radical production. *Proceedings of the National Academy of Sciences of the United States of America*. 2005;102(21):7449–7452. DOI: 10.1073/pnas.0502687102.

16. Matthews J, Martinez-Avilés M, Francisco JS, Sinha A. Probing OH stretching overtones of CH_3OOH through action spectroscopy: influence of dipole moment dependence on HOOC torsion. *Journal of Chemical Physics.* 2008;129(7):074316. DOI: 10.1063/1.2967185.

17. Matthews J, Sinha A. Rotational contour analysis of jet-cooled methyl hydroperoxide action spectra in the region of the 2ν(OH) and 3ν(OH) bands. *Journal of Physical Chemistry A*. 2009;113(47):13100–13112. DOI: 10.1021/jp902146z.

18. Tyblewski M, Ha T-K, Meyer R, Bauder A, Blom CE. Microwave and millimeter-wave spectra, electric dipole moment, and internal rotation effects of methyl hydroperoxide. *Journal of Chemical Physics*. 1992;97(9):6168–6180. DOI: 10.1063/1.463725.

19. Dalbouha S, Senent ML, Komiha N. Theoretical spectroscopic characterisation at low temperatures of methyl hydroperoxide and three S-analogs. *Journal of Chemical Physics*. 2015;142(7):074304. DOI: 10.1063/1.4907941.

20. Senent ML, Puzzarini C, Hochlaf M, Domínguez-Gómez R, Carvajal M. Theoretical spectroscopic characterisation at low temperatures of S-methyl thioformate and O-methyl thioformate. *Journal of Chemical Physics*. 2014;141(10):104303. DOI: 10.1063/1.4894487.

21. Lukka TJ. A simple method for the derivation of exact quantum-mechanical vibration – rotation Hamiltonians in terms of internal coordinates. *Journal of Chemical Physics*. 1995;102(10):3945–3955. DOI: 10.1063/1.468571.

22. Makarewicz J, Skalozub A. Exact quantum mechanical kinetic energy operator in valence coordinates for internal motions of a polyatomic molecule. *Chemical Physics Letters.* 1999;306(5–6):352–356. DOI: 10.1016/S0009-2614(99)00466-2.

23. Pitsevich GA, Malevich AE. Features of the interaction of hydroxyl and methyl tops in the ethanol molecule: 2D-calculation of the torsion energy levels. *Journal of Applied Spectroscopy*. 2015;82(4):540–553. DOI: 10.1007/s10812-015-0143-7.

24. Pitsevich G, Malevich A, Zheutok V, Khrapunova A, Sapeshka U. Torsional vibrations of two thiol groups in the HSOSH, DSOSH, and DSOSD molecules: 2D PES study in CBS limit. *Vibrational Spectroscopy*. 2021;113:103208. DOI: 10.1016/j.vibspec.2021.103208.

25. Pitsevich GA, Malevich AE, Kisuryna DG, Ostyakov AA, Sapeshka UU. Torsional states and tunneling probability in HOSOH, DOSOD and DOSOH molecules analyzed at the CBS limit. *Journal of Physical Chemistry A.* 2020;124(42):8733–8743. DOI: 10.1021/acs.jpca.0c06411.

26. Pitsevich GA, Malevich AY, Sapeshko VV. The hydroxyl groups internal rotations in a methanediol molecule. *Journal of Molecular Spectroscopy*. 2019;360:31–38. DOI: 10.1016/j.jms.2019.04.013.

27. Wilson EBJr, Decius JJC, Cross PC. *Molecular vibrations: the theory of infrared and Raman vibrational spectra.* New York: McGraw-Hill; 1955. 388 p.

28. Wilson EBJr. Some mathematical methods for the study of molecular vibrations. *Journal of Chemical Physics*. 1941;9(1):76–84. DOI: 10.1063/1.1750829.

29. Pitsevich GA, Malevich AE, Sapeshka UU. The torsional spectrum of the hydrogen trioxide molecule. *Chemical Physics*. 2020;530:110633. DOI: 10.1016/j.chemphys.2019.110633.

30. Pitsevich GA, Malevich AE, Markovich FV, Sapeshka UU. 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. *Molecular Physics.* 2020;118(17):e1746425. DOI: 10.1080/00268976.2020.1746425.

31. Pitsevich GA, Malevich AE, Kisuryna DG, Vasilevsky AU, Vasilevich AS, Sapeshka UU, et al. Quantum aspects of torsional vibrations in the HO_3H, DO_3H and DO_3D molecules. *Spectrochimica Acta. Part A: Molecular and Biomolecular Spectroscopy.* 2020;239:118209. DOI: 10.1016/j.saa.2020.118209.

32. Lanczos C. Discourse on Fourier series. Edinburgh: Oliver and Boyd; 1966. 255 p.

33. Pitsevich GA, Malevich AE. Simple method of the formation of the Hamiltonian matrix for some Schrödinger equations describing the molecules with large amplitude motions. *Optics and Photonic Journal.* 2012;2(4):332–337. DOI: 10.4236/opj.2012.24041.

34. Pitsevich GA, Malevich AE. Comparison of the Fourier and discrete-variable-representation methods in the numerical solution of multidimensional Schrödinger equations. *Journal of Applied Spectroscopy.* 2016;82(6):893–900. DOI: 10.1007/s10812-016-0200-x.

35. Hetzer G, Pulay P, Werner H-J. Multipole approximation of distant pair energies in local MP2 calculations. *Chemical Physics Letters.* 1998;290(1):143–149. DOI: 10.1016/S0009-2614(98)00491-6.

36. Schütz M, Hetzer G, Werner H-J. Low-order scaling local electron correlation methods. I. Linear scaling local MP2. *Journal of Chemical Physics.* 1999;111(13):5691–5705. DOI: 10.1063/1.479957.

37. Kendall RA, Dunning TH, Harrison RJ. Electron affinities of the first-row atoms revisited. Systematic basis sets and wave functions. *Journal of Chemical Physics.* 1992;96(9):6796–6806. DOI: 10.1063/1.462569.

38. Woon DE, Dunning TH. Gaussian basis sets for use in correlated molecular calculations. III. The atoms aluminum through argon. *Journal of Chemical Physics.* 1993;98(2):1358–1371. DOI: 10.1063/1.464303.

39. Frisch MJ, Trucks GW, Schlegel HB, Scuseria GE, Robb MA, Cheeseman JR, et al. *Gaussian 09, revision A.1.* Wallingford: Gaussian Inc.; 2009.

40. Halkier A, Helgaker T, Jørgensen P, Klopper W, Koch H, Olsen J, et al. Basis-set convergence in correlated calculations on Ne, N_2, and H_2O. *Chemical Physics Letters.* 1998;286(3):243–252. DOI: 10.1016/S0009-2614(98)00111-0.

41. Okoshi M, Atsumi T, Nakai H. Revisiting the extrapolation of correlation energies to complete basis set limit. *Journal of Computational Chemistry.* 2015;36(14):1075–1082. DOI: 10.1002/jcc.23896.

42. Raghavachari K, Trucks GW, Pople JA, Head-Gordon M. A fifth-order perturbation comparison of electron correlation theories. *Chemical Physics Letters.* 1989;157(6):479–483. DOI: 10.1016/S0009-2614(89)87395-6.

43. Scuseria GE. Analytic evaluation of energy gradients for the singles and doubles coupled cluster method including perturbative triple excitations: theory and applications to FOOF and Cr_2. *Journal of Chemical Physics.* 1991;94(1):442–447. DOI: 10.1063/1.460359.

44. Bunker PR, Jensen P. *Molecular symmetry and spectroscopy.* Ottawa: NRC Research Press; 1998. [771 p.].

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