Conformational Structure and Torsional Spectrum of the HSOSH Molecule

G.A. Pitsevich[1], A.M. Malevich[2], U.U. Sapeshka[1]

[1]Department of the Physical Optics and Applied Informatics, Belarusian State University, Minsk, Belarus
[2]Department of Physical Optics and System Analysis, Belarusian State University, Minsk, Belarus

БЕЛОРУССКИЙ ГОСУДАРСТВЕННЫЙ УНИВЕРСИТЕТ

ФИЗИЧЕСКИЙ ФАКУЛЬТЕТ БГУ

HOSOH belongs to an interesting group of molecules that can be specified by following formulae HXYXH, where Y and X can be the same. Recently we analyzed symmetry properties and the torsional spectra of the $HOCH_2OH$ [1] and HOOOH [2] molecules that belong to above mention group. Calculations technics of the data preparation and numerical solution of the vibrational Schrödinger equation using DVR and Fourier methods in the case of very small splitting of the lowest torsional states due to tunneling was discuss [2].

It was found that tunneling frequencies in the ground state of the $HOCH_2OH$ and HOOOH are in order of 10^{-6} and 10^{-10} cm^{-1} respectively. As in the case of hydrogen peroxide molecule, it is very interesting how the substitution of the oxygen atoms on sulfur one in the HOOOH molecule affects the height of potential barriers and torsional states splittings taking into account, for example, the possibility to detect the parity violation effect in HSSSH molecule [3]. 2D PES of the HSOSH molecule was calculated at the B3LYP/cc–pV5Z, MP2/acc–pVQZ, and CCSD(T)/acc–pVTZ levels of theory. It was found the HSOSH molecule has two stable configurations: trans– and cis– conformers. The internal energy of the cis– conformer only 28, 26, and 41 cm^{-1} higher than the internal energy of the trance conformer for B3LYP/cc–pV5Z, MP2/acc–pVQZ, and CCSD(T)/acc–pVTZ levels of theory. The 2D surfaces of the kinetic coefficients were calculated at the three above mention levels of theory. The energies of the stationary torsional states were found too by numerical solution of the vibrational Schrödinger equation. It was found that tunneling frequency in the ground state of the HSOSH molecule is in order of 10^{-10} cm^{-1}. Classification of the stationary torsional energy levels was proposed. The difference in the potential barriers of the $HOCH_2OH$, HOOOH, and HOSOH molecules was discussed.

References
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[2] G. Pitsevich, A. Malevich, V. Sapeshko. The Torsional Spectrum of the Hydrogen Trioxide Molecule // Chemical Physics. – 2020. – V. 530. – 110633.
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Discussion of the results

Tables 1 and 2 represent the values of the geometric parameters, rotational constants, and kinetic parameters of the two conformers of the HSOSH molecule obtained at the MP2/CBS level of theory. As follows from the data in **Tables 1 and 2**, the values of the geometrical and kinetic parameters, as well as the rotational constants of the trans– and cis– conformers of the HSOSH molecule are very close. Both conformers are asymmetric tops close to prolate symmetric tops.

Table 1. Calculated at the MP2/CBS level of theory equilibrium geometrical parameters of the trans– and cis–conformers of the HSOSH molecule (see the numbering of atoms in Fig. 1)

Conformer	l_{OH} [Å]	l_{SO} [Å]	φ_{HOS} [deg]	θ_{OSO} [deg]	τ_{H1OSO} [deg]	τ_{HSOSO} [deg]
Trance	1.3392	1.6727	97.009	116.614	76.400	76.400
Cis	1.3396	1.6723	97.446	116.538	84.564	− 84.564

Table 2. Calculated at the MP2/CBS level of theory rotational constants and kinetic parameters of the equilibrium configurations of the trans– and cis–conformers of the HSOSH molecule

Conformer	A_e [MHz]	B_e [MHz]	C_e [MHz]	$F_{\gamma1\gamma1}$ [cm^{-1}]	$F_{\gamma2\gamma2}$ [cm^{-1}]	$F_{\gamma1\gamma2}$ [cm^{-1}]
Trance	35983.96	3632.91	3447.65	10.982	10.982	− 1.956
Cis	36259.66	3623.82	3444.29	11.073	11.073	− 2.215

Fig. 1. The equilibrium geometries of trans– (two upper molecules) and cis– (two lower molecules) conformers of the HSOSH molecule in two structurally equivalent configurations
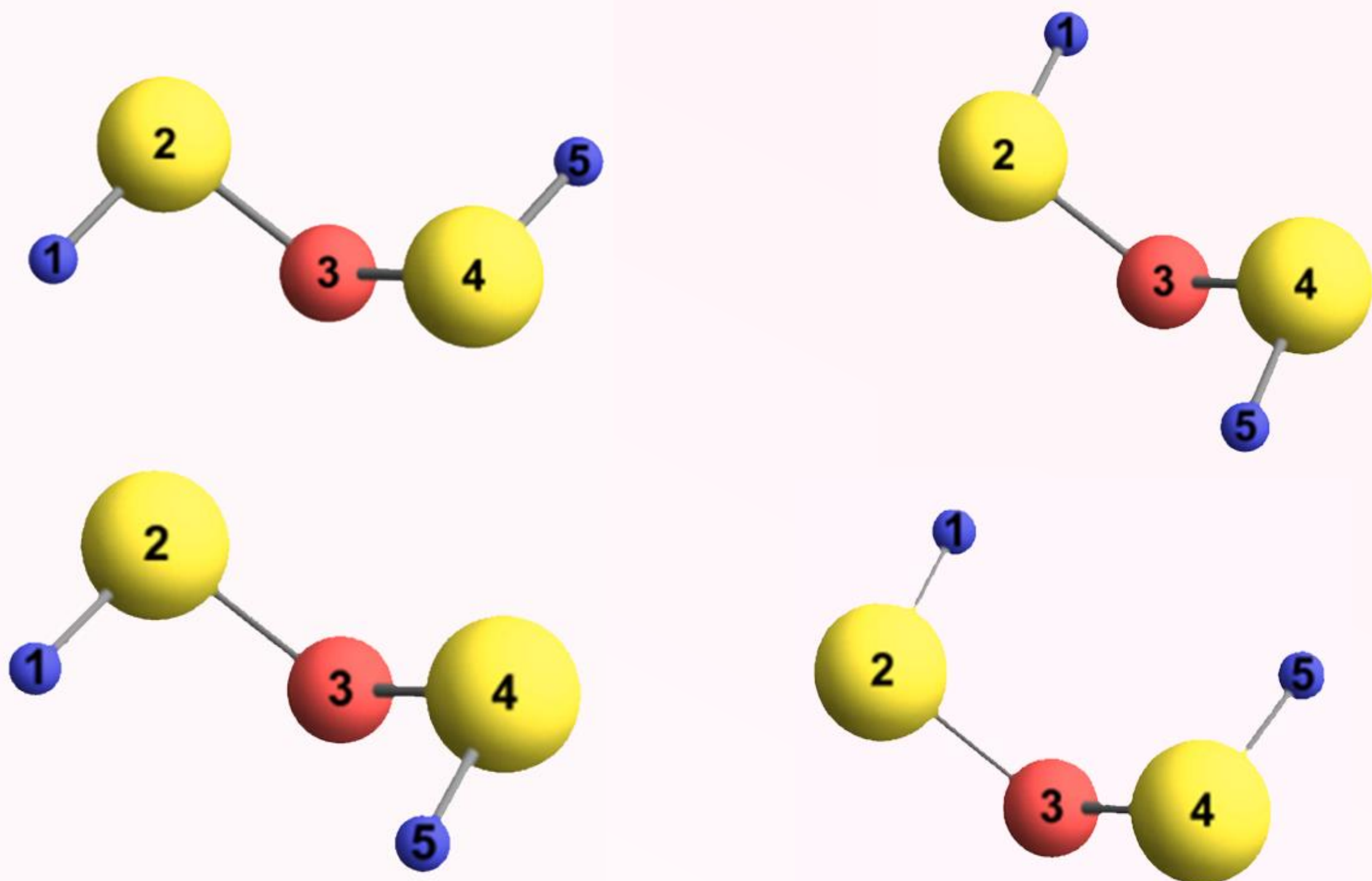

Fig. 2 presents 2D surfaces of the kinetic coefficients and the components of the dipole moment of the HSOSH molecule calculated at the MP2/CBS level of theory.
The construction of 2D surfaces of the three Cartesian components of the dipole moment of the HSOSH molecule made it feasible, without being limited to the linear approximation, to calculate the matrix elements of the dipole moment operator for all pairs of torsional states. Subsequently, the torsional IR absorption spectra of the trans– and cis– conformers of the three analyzed molecules were calculated at temperatures of 300 and 30 K. It was found that for the calculated torsional states interconformational transitions are not realized due to the different spacious localization of the wave functions of the trans– and cis– conformers.
Fig. 3 shows the 2D PES of MD, HT, and HSOSH molecules with isoenergy contours. It is clear from Fig. 3 that the energy of the cis– conformer is continuously decreased in relation to the trans– conformer in the set of MD, HT, and HSOSH molecules.
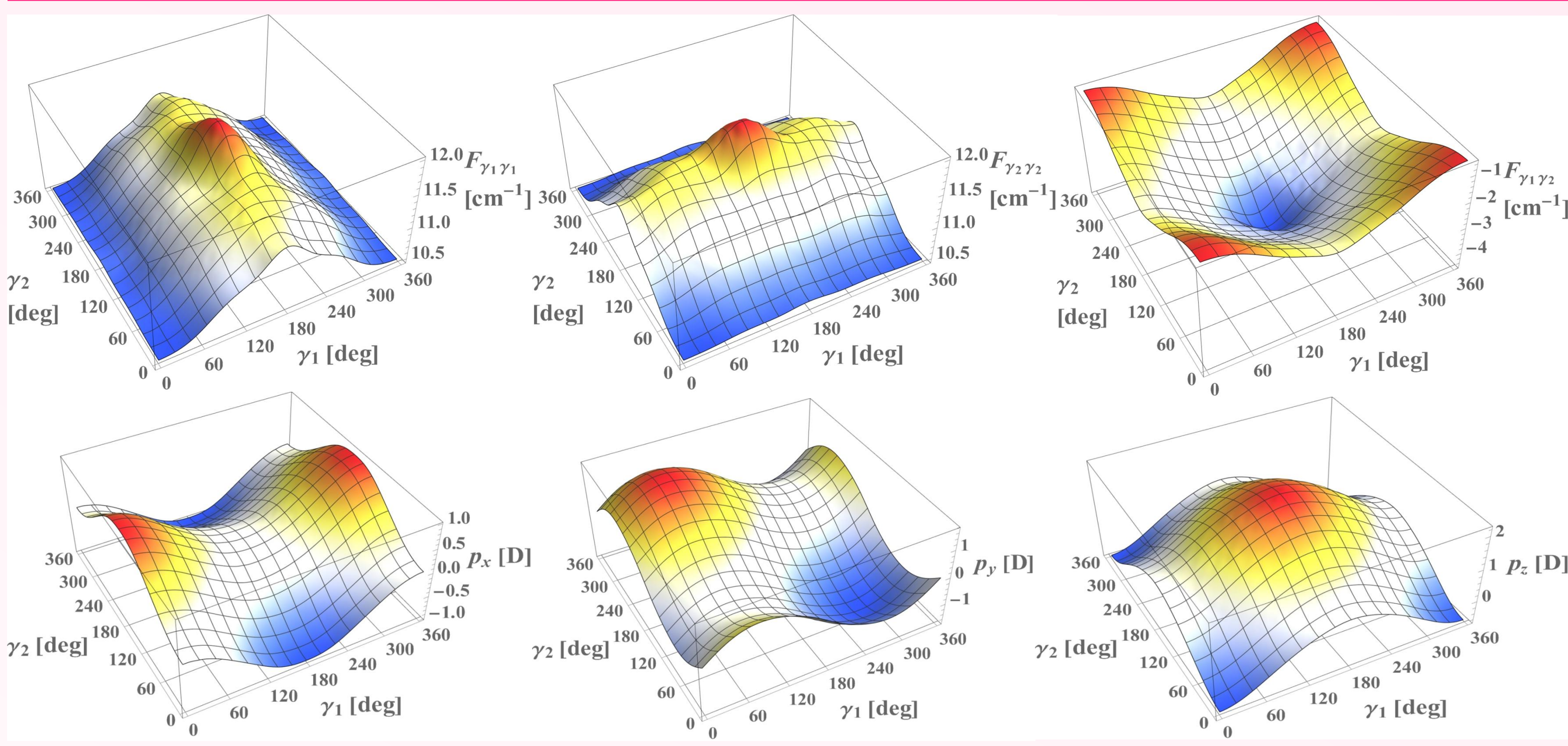
Fig. 3. Isoenergy contours of the potential energy surfaces of MD (left), HT (center), and HSOSH (right) molecules. The potential energy increases from the minima (dark green) to the maxima (dark purple). The dark curves represent the paths of the minimum energy corresponding to the transition between the equilibrium configurations of the conformers
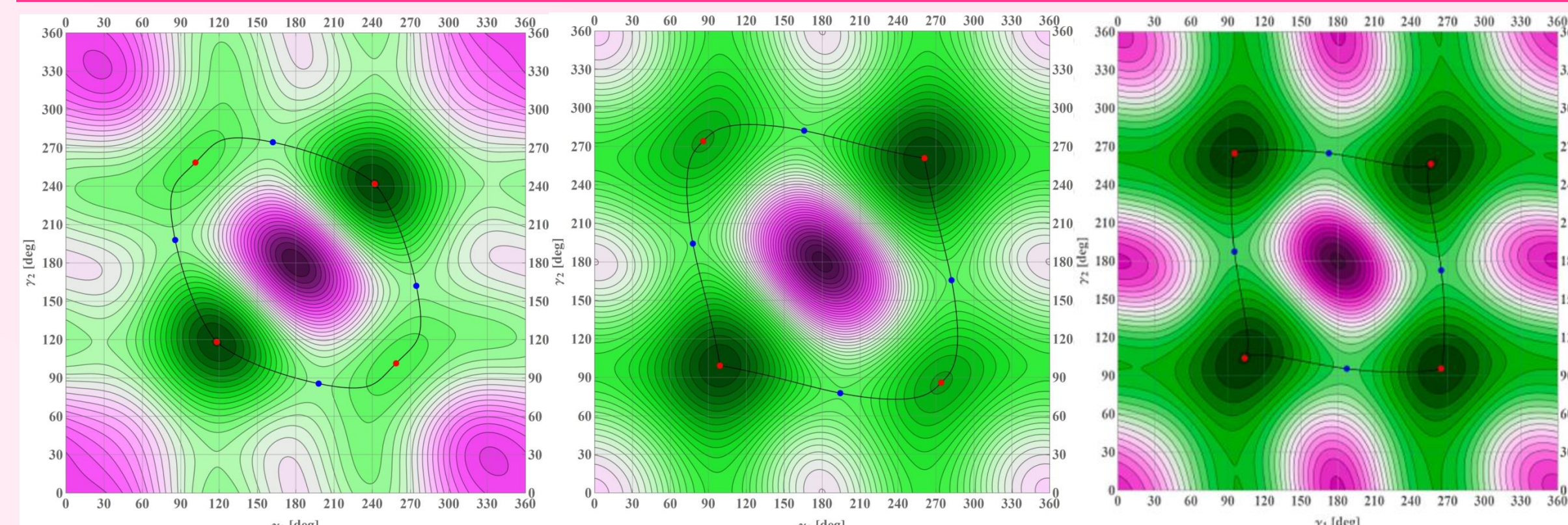

Fig. 4. Calculated at the MP2/CBS level of theory torsional IR spectra of the HSOSH molecule at temperatures of 300 K (black color) and 30 K (red color) for the case when trans– and cis–conformers are in thermodynamic equilibrium
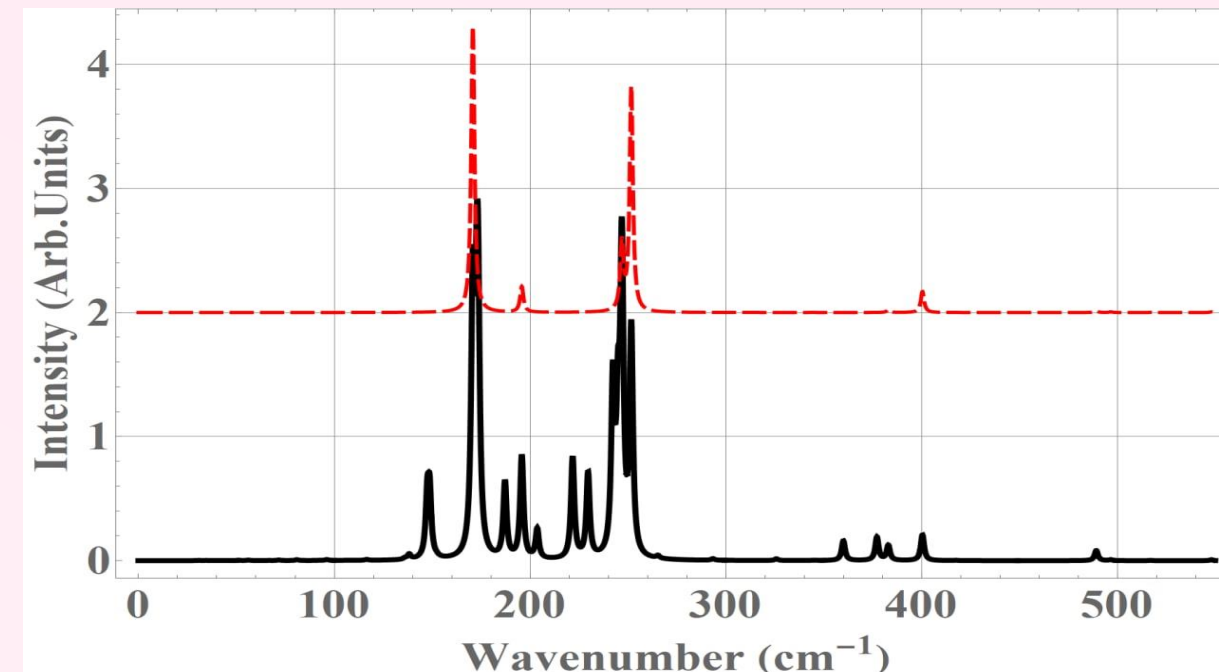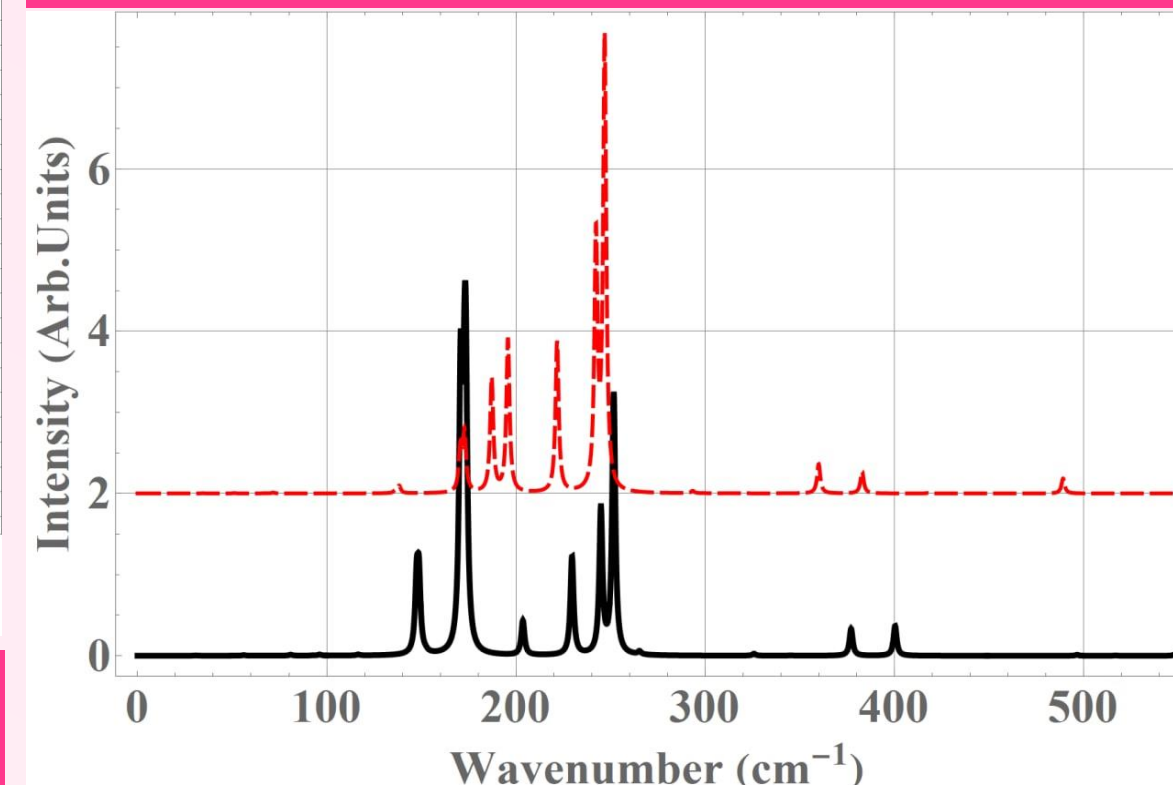

Fig. 5. Calculated at the MP2/CBS level of theory torsional IR spectra of the HSOSH molecule at temperatures of 300 K formed by only trans – trans (black color) or by only cis – cis transitions

Fig. 2. 1) 2D surfaces of the kinetic coefficients (top row): $F_{\gamma1\gamma1}$ ($\gamma1$, $\gamma2$) – left, $F_{\gamma2\gamma2}$ ($\gamma1$, $\gamma2$) – middle, $F_{\gamma1\gamma2}$ ($\gamma1$, $\gamma2$) – right, 2) 2D surfaces of the three components of the dipole moment (bottom row): $p_x(\gamma1, \gamma2)$ – left, $p_y(\gamma1, \gamma2)$ – middle, $p_z(\gamma1, \gamma2)$ – right

Conclusion

The performed calculations show that in the ground torsional states of both trans– and cis– conformers, tunneling is unlikely due to the relatively small values of the kinetic coefficients and rather high barriers for internal rotation of thiol groups. However, while raising the energy of torsional states, the splitting of torsional states develops up to 10^{-2} cm^{-1}, which indicates a significant increase in the tunneling probability for excited torsional states of both conformers of the HSOSH molecule.