CONFORMATIONAL STRUCTURE AND IR SPECTRUM OF THE METHYL HYDROPEROXIDE

Darya Kisurina[1], Vladimir Sapeshko[2], Ekaterina Kozlovskaya[1], George Pitsevich[1], Vytautas Balevicius[3]

[1] Belarusian State University, Minsk, Belarus
[2]University of Illinois at Chicago, Chicago, USA
[3]Vilnius University, Vilnius, Lithuania
kisurinadasha@gmail.com

Methyl hydroperoxid (CH_3OOH) belongs to the class of non-rigid molecules. During the rotation of the hydroxyl group in relation to the peroxide bond, two equivalent configurations of the molecule are formed. Plane, that is formed by the three heavy atoms (COO), is occurs to be the symmetry plane for the trans- (Fig.1) and cis- configurations, which are the transition states of the molecule.

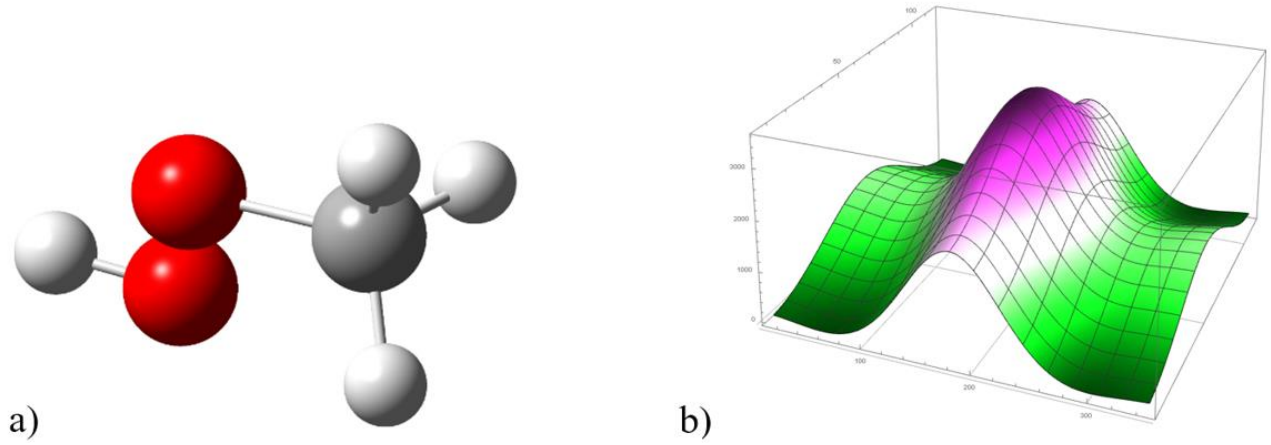

Fig.1. Trans-conformation of the methyl hydroperoxide molecule (a) and 2D PES, constructed during the variation of two torsion angles (b).

Two equivalent equilibrium configurations of the molecule are gosh-conformers. The molecule is characterized by the internal rotation of hydroxyl and methyl groups. Equilibrium configuration of CH_3OOH was calculated at the MP2/acc-pVTZ level of theory. Value of C-O-O-H dihedral angle occurred to be close to 120°, and length of the peroxide O-O bond occurred to be equal to 1.456 Å. With this, methyl group loses the C_{3V} symmetry. In particular, values of three O-C-H angles occur to be equal to 110, 109 и 104°, and the difference between the C-H bonds – approximately 0.001 Å. These lead to vanishing of degeneracy of the antisymmetric stretching C-H bonds vibrations, which frequencies occur to be equal to 3151 and 3178 cm^{-1}. Calculated in the harmonic approximation frequency values of the torsion vibrations are 170 and 261 cm^{-1} for hydroxyl and methyl groups correspondingly. For more accurate evaluation of the torsion vibrations frequencies of methyl hydroperoxide molecule, calculations of 2D potential energy surface, caused by variation of two torsion coordinates, were performed (see Fig. 1b). As can be seen from Fig. 1b, trans-barrier is significantly lower than cis-barrier. Their values, according to calculations, are 102 and 2001 cm^{-1}. Height of the potential barrier of methyl group rotation is around 1000 cm^{-1}. Calculations of the torsion vibrations frequencies were performed.