TORSIONAL SPECTRUM OF THE METHYL HYDROPEROXIDE MOLECULE CALCULATED AT MP2/cc-pVQZ

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Methyl hydroperoxide ($HOOCH_3$) is a one of the simplest molecules that have two internal tops: the hydroxyl group (OH) which can rotate around the O-O bond and the methyl group (CH_3) which can rotate around the C-O bond. This molecule was detected in the cosmic space therefore it is of interest to astrophysics. It also takes part in the Earth atmospheric phenomena as an intermediate product of the chemical reactions. $HOOCH_3$ is a non-rigit molecule. It can exist in two configurationally - equivalent states which are separated by relatively low potential barrier. To analyze the torsional spectrum of the methyl hydroperoxide (MHP) the 2D PES and 2D kinematic coefficients surface were calculated at MP2/cc-pVQZ level of theory. Two torsional angles (γ and φ) were used to specify the positions of the hydroxyl and methyl groups relative the C-O-O plane during internal rotation. When choosing the appropriate points for potential energy calculations one has to keep in mind that the C-O-O plane is a symmetry plane for any distorted configuration of the molecule. We varied the value of the γ in the range 4^0 – 356^0 with a step of 8^0. Due to φ has $2\pi/3$ period we varied the value of the φ in the range 4^0 – 56^0 with a step of 8^0. At every point of the 2D equidistant grid we performed energy optimization on all the rest internal coordinates to take into account geometry changing during internal rotation. Then the stationary vibrational Schrödinger of the following form

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

was solved using Fourier method. Here $F_{\gamma\gamma}(\gamma,\varphi)$, $F_{\varphi\varphi}(\gamma,\varphi)$, $F_{\gamma\varphi}(\gamma,\varphi)$ are the kinematics coefficients and $U(\gamma,\varphi)$ - potential energy. Calculated value of the tunneling frequency in the ground state is equal to 19.23 cm^{-1}. Torsional spectrum of the MHP molecule, represented on Fig.1, was calculated at 300^0 K.

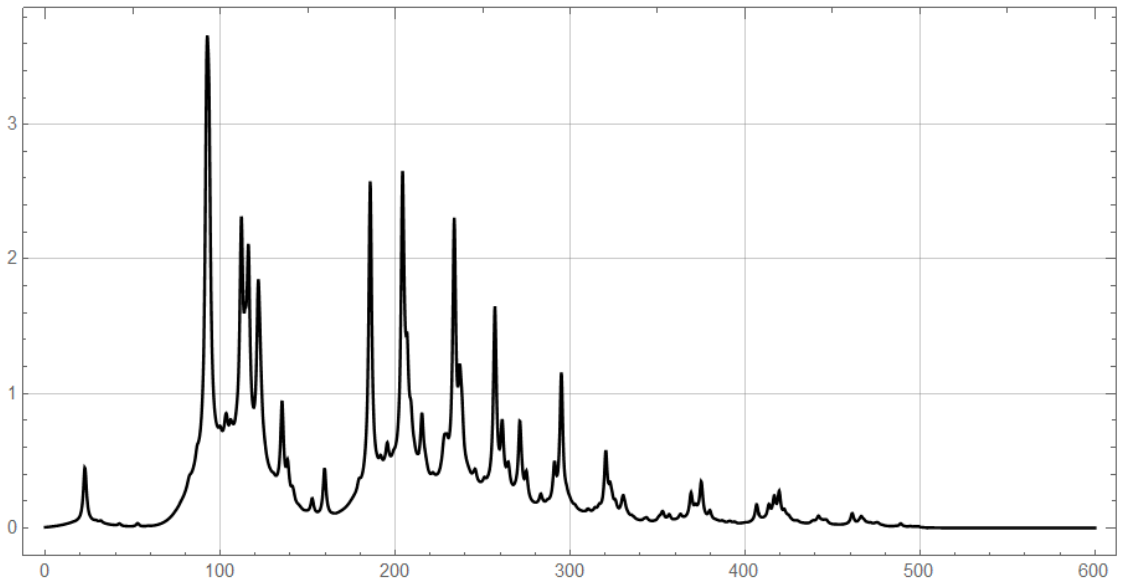

Fig. 1. Calculated at the MP2/cc-pVQZ level of theory torsional spectrum of MHP molecule at 300^0 K.

As one can see the torsional IR spectrum of the MHP molecule is rich on intensive IR bands which appears in wide spectral region. This information will be useful for the more successful search of this molecule in the cosmic space and the Earth atmosphere.