NUMERICAL SIMULATION OF QUANTUM EFFECTS DUE TO INTERNAL ROTATION IN A HYDROGEN PEROXIDE MOLECULE

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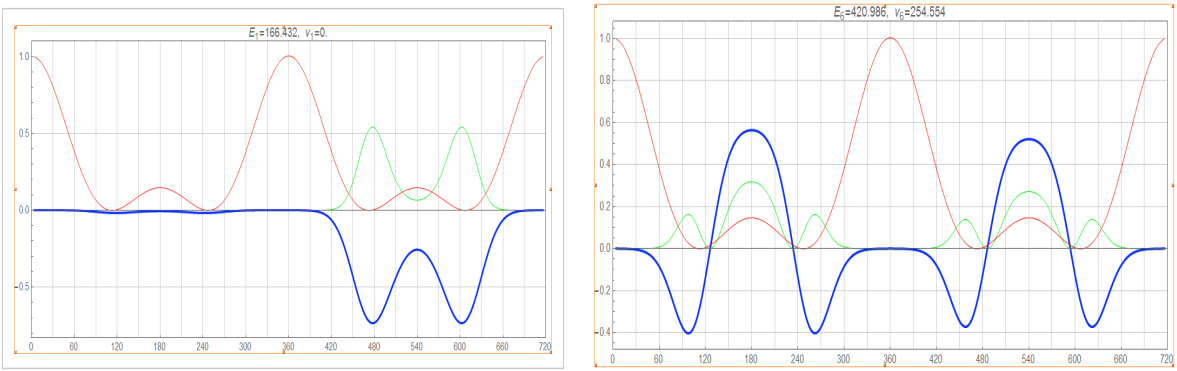
Hydrogen peroxide molecule (HOOH) is a simplest object with internal rotation around O-O bond. It plays an important role in the Earth atmospheric phenomena, was found in cosmic space and has an application in a number of industrial processes. In the equilibrium configuration H_2O_2 molecule exists in the gosh- conformation. During internal rotation molecule goes through the low trans-barrier and the high cis-barrier. Splitting of the torsional levels of energy due to the tunneling through trans- barrier was experimentally confirmed, while tunneling through the cis-barrier is still not experimentally detected. We have calculated 1D potential energy curve and kinematic coefficients as functions of the torsional angle γ at the MP2/acc-pVQZ level of theory. To estimate the energies splitting through cis-barrier the torsional coordinate range was doubly increased ($0° \le \gamma \le 720°$). Then the stationary Schrödinger equation of the following form

$$F(\gamma)\frac{\partial^2\Psi}{\partial\gamma^2}+U(\gamma)\Psi=E\Psi,$$

where F(γ) is kinematic coefficient and U(γ) is potential function, was numerically solved using DVR method. It was found that the calculated splitting of the ground state due to tunneling through the cis- barrier is close to zero ($3.21\cdot10^{-12}$ cm^{-1}), while the calculated splitting through the trans-barrier (12.51 cm^{-1}) is very close to the experimental value (11.43 cm^{-1}). As one can see from Fig.1a in the ground state the wave function is localized in one half of the full region of γ variation.



a) b)

Fig. 1. U(γ) - red curve, Ψ(γ) - blue curve, $\Psi^2(\gamma)$ - green curve calculated at MP2/acc-pVQZ level of theory for different energy levels.

It means tunneling through cis-barrier in this case rather absent. Different situation appears for the sixth torsional energy level (see Fig.1b). The wave function is delocalized in full region of γ variation. And it means the tunneling has place in this case even though the value of the tunneling frequency does not increase significantly ($6.31\cdot10^{-11}$ cm^{-1}).

To analyze some time depended quantum effects due to internal rotation in hydroxyl peroxide molecule the following time-depended Schrödinger equation was solved numerically using DVR method:

$$B_0\frac{\partial\Psi(\gamma,t)}{\partial t}+F(\gamma)\frac{\partial^2\Psi(\gamma,t)}{\partial\gamma^2}+(U(\gamma)+D(\gamma)\cdot\Theta(t)-E)\Psi(\gamma,t)=0$$

where D(γ) is a dipole momentum operator, Θ(t) is oscillating electric field of the incident light, B_0 – constant which value depends on time scale. We have found the energy fluctuations due to Heisenberg uncertainty relation when time-dependent perturbation is absent and wave function time dependence in the opposite case.