Inversion – torsional motion in the ethyl radical

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The ethyl radical is the simplest hydrocarbon radical with a single C-C bond. The CH in β position with respect to the radical centre presents a model compound exhibiting hyperconjugation effects. The ethyl radical was extensively studied both experimentally and theoretically over the past three decades. The ab initio calculation showed that the methylene group is almost planar [1]. Thus the effects of the internal motion has been studied as a one dimensional problem having a 6-fold potential [1,2].

In the later paper [2] a suggestion appears that the large amplitude problem should be studied as a multidimensional problem. Here we present such a study where the inversion and torsional motions are studied as a 2-dimensional problem, both in the ground vibrational state and in excited states of CH stretching vibrations. The 2-dimensional potential function is calculated ab initio using the MP2 method and the Dunning's aug-cc-pVQZ basis set. This was tested against CCSD(T) method is the same basis set and against larger basis set aug-cc-pV5Z and the relative energies of the saddle points did not exceed 1 cm^{-1}. The barrier to the planar configuration is as low as 30 cm^{-1} , which is higher than the barrier obtained with DFT methods [1]. At each geometry determined by the inversion angle and torsional angle the geometry was allowed to relax.

In previous models the changes in molecular parameters such as bond lengths and angles were expressed as functions of torsional coordinate, only. In the present model these parameters are explicit functions of two coordinates describing inversion and torsion. This gives an insight into the geometrical changes of the radical for bending of the methylene group.

The 2-dimensional inversion-torsional potential function has been derived not only for the ground vibrational state but also for selected excited CH stretching motions. The solution of the inversion-torsion-rotation Schrödinger equation has been solved for the calculated potentials and the energies of low lying vibrational states are given.

[1] P.M.Johnson, T.J.Sears, *J.Chem.Phys*. **1999**, *111*, 9222.
[2] T.Häber, A.C.Blair, D.J.Nesbitt, J.Chem.Phys. **2006**, *124*, 054316.