

Theoretical Study on Geometrical Isotope Effect and Rotational Constants of Polyatomic Molecules

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It is of great importance to determine the geometrical structure of an isolated polyatomic molecule. Recently, it has been shown the possibility of the direct comparison in the experimental spectroscopic observations and *ab initio* theoretical calculation due to the achievements of both accurate measurements and calculations.

However, in the usual *ab initio* calculations, the equilibrium structures are obtained, although the determine structures by the experiment mean the averaged structures. This difference becomes larger when the mass of atom becomes smaller, i. e., hydrogen case. In addition, due to the anharmonicity of the potential, it is well known that the X-D distance in D-compounds are shorter than the X-H one in H-compounds. But, it is difficult to discuss the difference of X-H/X-D distances under the conventional *ab initio* calculations.

To take into account the geometrical changes by the H/D isotope effect, we developed the multi-component molecular orbital (MC_MO) approach [1]. The MC_MO method enables one to analyze the quantum effects of a proton (deuteron) because the MC_MO method determines both the electronic and the protonic (deuteronic) wavefunctions simultaneously and directly. We have already found that the MC_MO method can be used to analyze the geometrical isotope effect and kinetic isotope effect induced the difference in quantum behavior between protons and deuterons. Before the analysis of spectroscopic properties, we first optimized the H/D-compounds for polyatomic molecules, such as, acetaldehyde, acetone, benzene, and methoxy radical. The rotational constants based on the optimized structures including H/D geometrical isotope effect showed good agreement with the experimental value. We clearly found that the geometrical changes induced by the H/D isotope effect influence the spectroscopic properties, such as rotational constants [2-4].

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References

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