

Theoretical study of H/D isotope-induced chemical shift in ethylene and benzene derivatives

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The isotope effect induced by deuterium substituted species is observed in molecular properties, such as geometry, kinetics, and electronic state of the molecules thorough nuclear-electron interaction. Theoretical considerations and experimental alignments have been studied by *ab initio* molecular orbital (MO), density functional (DF) theory, and other empirical strategies. The Born-Oppenheimer (BO) approximation with nuclear vibrational wavefunction can treat isotope effect because nuclear mass effect account for the average distance of vibrational motion partially.

Recently, multi-component quantum chemical theory [1–3] has been available to describe nuclear wavefunction and electronic wavefunction simultaneously, even in H/D isotope effect [4–6]. Dios and Jameson have proposed combination nuclear vibrational states with Gauge Independent Atomic Orbital (GIAO) method [9] to determine isotope shifts of nuclear magnetic resonance (NMR) shielding constant [10].

In this study, we focus on NMR shielding constants of the H/D isotopomer and/or isotopologue of small molecules, such as ethylene and benzene derivatives with the average distances obtained by expectation value of Morse vibrational wavefunction. Primary and secondary H/D isotope NMR shifts calculated by using GIAO with CCSD/cc-pVTZ and B3LYP/cc-pVTZ method are discussed with additivities of experimental results. From the difference of the results of ethylene and benzene, we show the influence of double bond in the isotope shift.

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