DIRECT ELUCIDATION OF THE REASON FOR ALMOST THE SAME BOND LENGTHS FOR THE C–H AND C–D BONDS IN C_6H_6 AND C_6D_6: A PATH INTEGRAL MOLECULAR DYNAMICS STUDY

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Recently, Baba group found that ro-vibrationally averaged bond lengths of C–H and C–D are observed as being almost identical ($r_{0,\mathrm{eff}}$(C–H) $\cong r_{0,\mathrm{eff}}$(C–D)) for planar aromatic hydrocarbons from high-resolution laser spectroscopy.[a] Quite recently, the reason of the same $r_{0,\mathrm{eff}}$(C–H) and $r_{0,\mathrm{eff}}$(C–D) bond lengths has been brilliantly unveiled by Hirano et al. by high-level *ab initio* molecular orbital calculations.[b] They revealed that the experimental bond lengths derived from effective rotational constants are "not" the ro-vibrationally averaged bond lengths but their projected lengths on the principle axis.

In this study, we have carried out the path integral molecular dynamics (PIMD) simulations for C_6H_6 and C_6D_6 to directly estimate the distribution of the C–H and C–D bond lengths projected onto the principle axis. Our PIMD simulation strongly supports the previous explanation by Hirano et al.[a] for the experimentally observed fact ($r_{0,\mathrm{eff}}$(C–H) $\cong r_{0,\mathrm{eff}}$(C–D)) in C_6H_6 and C_6D_6.

[a] S. Kunishige, T. Katori, M. Baba, et al., J. Chem. Phys. **143**, 244302 (2015).
[b] T. Hirano, U. Nagashima, M. Baba, J. Mol. Struct. **1243**, 130537 (2021).