RO-VIBRATIONALLY AVERAGED MOLECULAR STRUCTURE OF BENZENE I. ALMOST THE SAME BOND LENGTHS FOR THE C–H AND C–D BONDS.

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Contrary to the common sense that the C–H bond-length is longer than that of the C–D bond due to the anharmonicity of the potential, Baba group found, from high-resolution laser spectroscopy, 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, such as benzene[a], naphthalene[b], and anthracene[c]. The vibrationally averaged bond lengths of benzene deduced from experimental rotational constants and *ab initio* geometry[b] are r_0(C–H) = r_0(C–D) = 1.0831 Å.[a]

In this study, the vibrationally averaged structures of benzene are derived from the DVR (Discrete Variable Representation) wavefunction based on the 3D potential energy surface at the level of valence-CCSD(T)/[aVQZ(H,C)] theory. The zero-point C–H(D) bond-length, $r_{0,\mathrm{eff}}$(C–H(D)), determined from the experimental effective rotational constants, is, in definition, the r_0 bond-length projected onto the a-b principal axis plane, $r_{0,\mathrm{proj}}$(C–H(D)). The DVR wavefunction gives $r_{0,\mathrm{proj}}$(C–H) = 1.0815 Å and $r_{0,\mathrm{proj}}$(C–D) = 1.0819 Å, so that the difference is of a negligibly small value −0.0004 Å. Thus, the seemingly strange experimental finding ($r_{0,\mathrm{eff}}$(C–H) $\cong$ $r_{0,\mathrm{eff}}$(C–D)), which is controversial to the common sense, is resolved. The details will be given in the next presentation (part II.)

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[a] S. Kunishige, M. Baba, et al., J. Chem. Phys. **143**, 244302 (2015).

[b] M. Baba, U. Nagashima, et al., J. Chem. Phys. **135**, 054305 (2011).

[c] M. Baba, U. Nagashima, et al., J. Chem. Phys. **130**, 134315 (2009).