

AB INITIO CALCULATIONS ON ROTATIONAL CONSTANT AND AVERAGED C-H(D) BOND LENGTHS OF BENZENE

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Rotational constants in the ground states of benzene and its deuterated isotopologues were accurately determined by high-resolution spectroscopy [1]. It was demonstrated that the averaged bond length $r_{0,\text{eff}}(\text{C-H})$ is approximately identical to the $r_{0,\text{eff}}(\text{C-D})$. Bearing in mind that the experimentally observed rotational constants correspond to the averaged ro-vibrating structure projected onto each principal axis [2], we discussed this finding in terms of wavefunction for the local modes derived from the CCSD(T)/[aVQZ (C, H)] ab initio potential energy surface. Due to the anharmonicity in the C-H stretching motion, $r_{\text{str},0}(\text{C-H})$ is calculated to be longer than $r_{\text{str},0}(\text{C-D})$ by 0.0024 Å. Since the vibrationally averaged projection-angle of the C-H(D) bond with respect to the principal axis is larger for the C-H bond (having lighter H atom) than the C-D bond, the projected bond-lengths $r_{\text{proj},0}(\text{C-H})$ in the out-of-plane and in-plane bending motions become shorter than $r_{\text{proj},0}(\text{C-D})$ by 0.0017 Å and 0.0011 Å, respectively. Thus, in the sum of $r_{\text{str},0}$ and $r_{\text{proj},0}$, the difference in $r_{0,\text{eff}}(\text{C-H})$ and $r_{0,\text{eff}}(\text{C-D})$ becomes negligibly small value of 0.0004 Å, which explains why we observed $r_{0,\text{eff}}(\text{C-H}) \approx r_{0,\text{eff}}(\text{C-D})$.

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

[2] T. Hirano, U. Nagashima, and M. Baba, *J. Mol. Spectrosc.*, in press.