Temperature driven interchange of the effective size of proton with deuterium.

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Streszczenie

We employ *ab initio* molecular dynamics to study the H/D isotope effect in order to introduce the usually neglected effect of temperature in answering the controversial question: Could deuterium be bigger than protium as suggested from neutron diffraction studies on benzene crystals? Especially that recent neutron powder diffraction study by Fortes and Capelli contradicts previous observations made by Dunitz and Ibberson. Our simulations of the dynamics of isolated benzene and perdeuterated isotopologues have shown surprisingly that, if an environment is not present, the deuterium atom is always larger than the hydrogen atom for temperatures from 100 K up to 1200 K with the rate of change increasing with temperature. Only the inclusion of quantum effects of the nuclei reverses the situation, with hydrogen atoms in isolated benzene becoming larger in volume at low temperatures. In benzene-crystal simulations, we have demonstrated that at some temperatures, above 400 K, deuterium atoms appear bigger than protium atoms. Further studies on the isotope effect and inverse kinetic isotope effect are required from different perspectives; in particular, our results support one of the competing mechanisms of olfaction, in which molecular shape (size) is important in the process. In consequence, the spectral mechanism, which assumes that shape/size of the molecule remains unchanged after deuteration, appears less favorable.

Słowa kluczowe

Ab Initio Molecular Dynamics, Isotope effect, Deuterium, Atom volume, Atom size

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