On the intramolecular hydrogen bond in solution: Car-Parrinello and path integral molecular dynamics perspective.

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Streszczenie

The issue of the symmetry of short, low-barrier hydrogen bonds in solution is addressed here with advanced ab initio simulations of a hydrogen maleate anion in different environments, starting with the isolated anion, going through two crystal structures (sodium and potassium salts), then to an aqueous solution, and finally in the presence of counterions. By Car–Parrinello and path integral molecular dynamics simulations, it is demonstrated that the position of the proton in the intramolecular hydrogen bond of an aqueous hydrogen maleate anion is entirely related to the solvation pattern around the oxygen atoms of the intramolecular hydrogen bond. In particular, this anion has an asymmetric hydrogen bond, with the proton always located on the oxygen atom that is less solvated, owing to the instantaneous solvation environment. Simulations of water solutions of hydrogen maleate ion with two different counterions, K^+ and Na^+, surprisingly show that the intramolecular hydrogen-bond potential in the case of the Na^+ salt is always asymmetric, regardless of the hydrogen bonds to water, whereas for the K^+ salt, the potential for H motion depends on the location of the K^+. It is proposed that repulsion by the larger and more hydrated K^+ is weaker than that by Na^+ and competitive with solvation by water.

Adres publiczny

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https://www.acs.org/content/acs/en.html