

Molecular property investigations of an *ortho*-hydroxy Schiff base type compound with the first-principle molecular dynamics approach.

Autorzy

Aneta Jezierska-Mazzarello

R. Vuilleumier

Jarosław J. Panek

G. Ciccotti

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The structure, proton transfer, and vibrational dynamics under ambient conditions of a selected *ortho*-hydroxy Schiff base type compound, 2-(*N*-methyl- α -iminoethyl)-4-chlorophenol, containing a very short intramolecular hydrogen bond, were investigated computationally in the gas phase and in the crystal by density functional theory (DFT) based first-principle molecular dynamics (FPMD). It is found that the proton is well localized on the nitrogen side of the O...H...N bridge in the crystal phase, in agreement with X-ray diffraction experiments, while a more labile proton is located most of the time on the oxygen side in a vacuum. Environmental effects on this very strong hydrogen bond thus appear crucial and lead to drastic changes of the infrared (IR) spectrum: The computed gas-phase IR spectrum shows a very broad absorption band that covers frequencies from about 1000 to 3000 cm⁻¹ assigned to the labile proton. In mere contrast, a much more localized absorption band around 2600–2700 cm⁻¹ is predicted in the crystal phase. Finally, effects of the quantization of the proton motion on the hydrogen bond structure were estimated in two ways. First, we constructed the one-dimensional (1D) potential energy surface (PES) for the proton along the O...H...N bridge in a vacuum. The 1D Schrödinger equation was then solved. Next, path integral molecular dynamics (PIMD) was performed in the solid state. Inclusion of quantum effects does not affect the observed change of the most probable tautomer, upon going from the gas phase to the crystal.

Adres publiczny

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