

Structure and Dynamics of Hydrated NH_4^+ : An *ab initio* QM/MM Molecular Dynamics Simulation

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Abstract: A combined *ab initio* quantum mechanical/molecular mechanical (QM/MM) molecular dynamics simulation has been performed to investigate solvation structure and dynamics of NH_4^+ in water. The most interesting region, the sphere includes an ammonium ion and its first hydration shell, was treated at the Hartree–Fock level using DZV basis set, while the rest of the system was described by classical pair potentials. On the basis of detailed QM/MM simulation results, the solvation structure of NH_4^+ is rather flexible, in which many water molecules are cooperatively involved in the solvation shell of the ion. Of particular interest, the QM/MM results show fast translation and rotation of NH_4^+ in water. This phenomenon has resulted from multiple coordination, which drives the NH_4^+ to translate and rotate quite freely within its surrounding water molecules. In addition, a “structure-breaking” behavior of the NH_4^+ is well reflected by the detailed analysis on the water exchange process and the mean residence times of water molecules surrounding the ion.

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Key words: NH_4^+ ; QM/MM; water exchange; mean residence time

Introduction

Solvation structure and dynamics of ions in water play an important role in many chemical and biological systems.^{1–4} Besides the simple alkaline and alkaline–earth metal cations, ammonium ion (NH_4^+) is an important chemical species that provides a simple model for solvated amides.^{5,6} In addition, in compactly folded RNAs, coordination or hydrogen bonding of this ion in specific sites is a crucial aspect for its ability to stabilize the RNA fragment structure.⁷ The detailed interpretation on the structure and dynamics of NH_4^+ in aqueous solution has been studied extensively.^{8–20} Of particular interest, recent NMR measurements^{6,8} have shown that NH_4^+ rotates quite fast in aqueous solution, despite the expected strong hydrogen bonding between the NH_4^+ and its surrounding water molecules. To explain such surprising phenomenon, several rotational mechanisms have been proposed based on either *ab initio* geometry optimizations^{11–13} as well as Monte Carlo (MC)¹⁴ and molecular dynamics (MD)^{10,15–20} simulations. Most of the previous studies have provided useful information on the dynamical properties of the hydrated NH_4^+ , such as its fast diffusive rotational motion. However, the agreement on the structure of the first solvation shell of NH_4^+ , which is a necessary prerequisite for understanding its rotational mechanism, is still far from satisfactory. On the structural viewpoint of NH_4^+ in aqueous

solution, the most representative picture of the coordination to emerge is of two groups of water molecules. There is a first group of four, which is strongly oriented so as to create nearly linear N–H···O interactions. This structural aspect is supported by experimental X-ray and neutron diffraction studies.^{9,10} The second group of water molecules is much less strongly oriented than the first, and its structure is a source of major disagreement between the theoretical observations, consisting of 1–8 water molecules.^{10,14–20} Thus, the comprehensive knowledge of how NH_4^+ interacts with water molecules remains incomplete.

Recently, MD simulation with polarizable models¹⁷ has been performed to provide a qualitative prediction on the rotational dynamics of NH_4^+ in water, which is in good agreement with the experimental observations. However, the contributions of the ion's polarizability are not directly obtainable because there is no direct measurement of this quantity in aqueous solution, and the available data are usually extrapolations from ionic crystal and salt solu-

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