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The role of non-additive contributions on the hydration shell structure of Mg^{2+} studied by Born–Oppenheimer ab initio quantum mechanical/molecular mechanical molecular dynamics simulation

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Abstract

An ab initio quantum mechanical/molecular mechanical (QM/MM) molecular dynamics simulation has been performed to investigate the effects of non-additive contributions on the hydration shell structure of Mg^{2+}. The active-site region, the sphere including the second hydration shell of Mg^{2+}, was treated by Born–Oppenheimer ab initio quantum mechanics, while the rest is described by classical pair potentials. A hydration complex with six inner shell waters and 12 second shell waters was observed. It was also found that the effects of non-additive terms play an important role in the preferential orientation of water molecules inside the hydration sphere of Mg^{2+}. © 2001 Published by Elsevier Science B.V.

1. Introduction

Due to the diverse functions of metal ions in chemical and biological systems, understanding of the detailed structure of aqueous metal ions is of considerable interest for chemists and biologists. Among the alkaline-earth metal cations, Mg^{2+} is crucial for the structural integrity and biological activitiy of nucleic acids [1–3]. Mg^{2+} can stabilize RNA in several distinct ways, including diffuse binding and site binding, mostly distinguished by its hydration properties, and hence, has been shown to be important for the specific structure and function of many RNAs [4,5].

Structural information on hydrated Mg^{2+} in aqueous solutions has been reported both from experiments and computer simulations. In experiments, a hexaaquo Mg^{2+} has been established by proton NMR [6], X-ray diffraction [7] and by Raman spectroscopy [8]. Computer simulations, by means of Monte Carlo and molecular dynamics simulations, have been carried out to investigate structural and other properties [9–12]. The results from computer simulations can in principle provide a more detailed interpretation and prediction of experimental observations at molecular level, in particular where the experimental results are prone to large errors [13,14]. In the earlier simulations,

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