Effects of Many-Body Interactions on the Preferential Solvation of Mg^{2+} in Aqueous Ammonia Solution: A Born−Oppenheimer ab Initio QM/MM Dynamics Study

Anan Tongraar,*,† Kritsana Sagarik,† and Bernd Michael Rode‡

School of Chemistry, Institute of Science, Suranaree University of Technology, Nakhon Ratchasima 30000, Thailand, and Department of Theoretical Chemistry, Institute of General, Inorganic and Theoretical Chemistry, University of Innsbruck, Innrain 52a, A-6020 Innsbruck, Austria

Received: June 1, 2001; In Final Form: August 28, 2001

A combined ab initio quantum mechanical/molecular mechanical (QM/MM) molecular dynamics simulation has been performed to describe the solvation shell structure of Mg^{2+} in 18.4% aqueous ammonia solution. The most relevant region, the solvation sphere of Mg^{2+} in which the many-body effects are expected to play an important role, is treated by Born−Oppenheimer ab initio quantum mechanics using LANL2DZ basis sets, while the rest of the system is described on the basis of pairwise additive interactions. The results show a significant role of nonadditive contributions on the geometrical arrangement as well as on the coordination number of the solvated ion. An octahedral arrangement with five water and one ammonia ligand within the first solvation shell of Mg^{2+} is observed, in contrast to a polyhedral structure with six water and three ammonia molecules obtained by classical pair potential simulation. The observed differences in coordination numbers and in the preference for ligands are discussed on the basis of detailed simulation results.