

## Solvation Structure and Dynamics of Ammonium (NH<sub>4</sub><sup>+</sup>) in Liquid Ammonia Studied by HF/MM and B3LYP/MM Molecular Dynamics Simulations

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The characteristics of NH<sub>4</sub><sup>+</sup> solvated in liquid ammonia have been investigated by means of combined HF/MM and B3LYP/MM molecular dynamics simulations, in which the ion and its surrounding ammonia molecules were treated by HF and B3LYP methods, respectively, using the D95\* basis set. For both HF/MM and B3LYP/MM simulations, it is observed that four nearest-neighbor ammonia molecules directly hydrogen-bonded to each of the ammonium hydrogen atoms, forming a well-defined tetrahedral cage structure of the NH<sub>4</sub><sup>+</sup> solvate. Nevertheless, the solvation shell of NH<sub>4</sub><sup>+</sup> is rather flexible, in which several possible species of solvated NH<sub>4</sub><sup>+</sup> exist, ranging from 4- to 7-fold and from 3- to 6-fold coordinated complexes for the HF/MM and B3LYP/MM simulations, respectively. In terms of the dynamical details, i.e., the self-diffusion coefficients and the mean residence times of ammonia molecules surrounding the ion, the B3LYP/MM simulation shows slower dynamics of the solvated NH<sub>4</sub><sup>+</sup> when compared with the HF/MM results. With regard to the reported tendency of density functional theory (DFT) methods to predict overly rigid ion solvations as well as hydrogen bonds that are too short, the ab initio HF formalism has been demonstrated to be more reliable for providing a detailed description of this solvated ion.

### 1. Introduction

Among the hydrogen-bonded liquids, ammonia (NH<sub>3</sub>) is special because it is known as one of the weakest hydrogen-bonded liquids found in nature and is often used as a solvent in a variety of organic reactions. Analogously, its associated ions, in particular ammonium (NH<sub>4</sub><sup>+</sup>), also play an important role in chemical and biological processes.<sup>1–4</sup> According to existing detailed analysis of the structure, thermodynamics, and spectral data for NH<sub>4</sub><sup>+</sup> in liquid ammonia,<sup>5,6</sup> it has been demonstrated that this ion forms a stable solvation shell with a coordination number of 4. In a subsequent study by Liu and Tuckerman,<sup>7</sup> the solvation structure and dynamics of NH<sub>4</sub><sup>+</sup> in liquid ammonia were evaluated on the basis of the Car–Parrinello molecular dynamics (CP-MD) approach.<sup>8</sup> One clear finding is that the NH<sub>4</sub><sup>+</sup> possessed a tight 4-fold solvation shell, comprised almost entirely of hydrogen bonds donated by the ion. However, this approach was applied to a relatively small system, i.e., a replicated cubic box made up of only 31 ammonia molecules plus one ion, and all interactions were evaluated by a simple BLYP functional with limited accuracy. In particular, for the description of hydrogen bonds between bulk ammonia molecules, the CP-MD simulation has reported somewhat different results for the characteristics of liquid ammonia when compared with the corresponding data obtained from an earlier CP-MD study.<sup>9</sup>

By means of quantum-mechanics-based simulations, an alternative approach to obtain detailed knowledge of condensed-phase systems is to apply a so-called combined quantum mechanics/molecular mechanics (QM/MM) method. During the

past decades, the QM/MM MD technique has been proven to be a very reliable simulation scheme to elucidate microscopic details of various ionic solutions.<sup>10–21</sup> For the study of hydrogen-bonded liquids, the QM/MM simulations of HF/MM, B3LYP/MM, and MP2/MM types have been performed for liquid water.<sup>22</sup> Interestingly, it has been demonstrated that the HF- and MP2-based simulations provided detailed descriptions of liquid water that agree well with the most recent experimental data, while the density functional theory (DFT) method, even with the B3LYP functional, has predicted improper dynamics due to overly rigid hydrogen bonds. On the basis of the HF/MM scheme, however, the correct description of liquid water could only be achieved when the second-shell waters were included in the QM region.<sup>22</sup> The failure of the HF method to reproduce the structural and dynamical properties of liquid water has been demonstrated. For example, a recent MD study by Todorova and co-workers<sup>23</sup> showed that the use of HF approximations has led to strongly under-structured liquid water. In light of the previous simulation data for water, the reliability of the HF method for describing other liquids, such as liquid ammonia, might be doubtful. Recently, the HF/MM and B3LYP/MM MD simulations have been carried out for liquid ammonia,<sup>24</sup> supplying information that the hydrogen bonds in liquid ammonia are rather weak. The structural features and related dynamical properties of this liquid are suggested to be determined by the steric packing effects, rather than by the hydrogen-bond interactions. In particular, the HF/MM and B3LYP/MM simulations have predicted properties of liquid ammonia in better agreement with experimental data, especially when compared with previous studies based on either an empirical or CP-MD approach.<sup>9,25</sup> Since the results yielded from the HF/MM and B3LYP/MM simulations<sup>24</sup> (cf. Figure 2) are almost comparable, the HF method, which consumes less time, was chosen for this study. On the other hand, it could be expected that the HF

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