

QUANTUM-MECHANICAL BASED SIMULATION OF AN AMMONIUM ION IN AQUEOUS SOLUTION

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ABSTRACT: A molecular dynamics simulation based on combined *ab initio* QM/MM approach has been performed to investigate the properties of $\text{NH}_4^+\text{-H}_2\text{O}$ complex in aqueous solution. By the QM/MM technique, the NH_4^+ ion and its first hydration sphere were treated at the Hartree-Fock level using DZV basis sets, while the rest of the system was described by classical pair potentials. It was found that the structure of the $\text{NH}_4^+\text{-H}_2\text{O}$ complex was rather flexible and more disordered. The influence of the ion on the vibrational motions of its surrounding water molecules were evaluated by means of Fourier transformation of the velocity autocorrelation functions (VACFs) and the results were compared to those obtained by a QM/MM simulation of pure water.

KEYWORDS: QM/MM, classical pair potentials, *ab initio*, Born-Oppenheimer, molecular dynamics simulation

1. INTRODUCTION

Due to the diverse functions of ions in chemical and biological systems, understanding of the detailed structure and dynamics of hydrated ions is of considerable interest for chemists and biologists. In general, experimental observations can give good insight into the average structural and dynamic properties of the hydrated ions. However, in particular for the interpretation at molecular level, they often lead to ambiguous results due to the limitations of the experimental techniques. As a consequence, computer simulations, such as Molecular Dynamics (MD) and Monte Carlo (MC), in conjunction with X-ray and neutron diffraction experiments have been proven to be useful tools for elucidating such properties.

Among the cations, NH_4^+ ion is crucial for the functional integrity and biological activity of nucleic acids. NH_4^+ ion can stabilize RNA in several distinctive 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. For NH_4^+ ion in aqueous solution (Johnson 2000), 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 \cdots O interactions. The second group of water molecules is much less strongly oriented than the first and its structure is a source of marked disagreement between the theoretical calculations: its predicted membership varies between one and ten water molecules for which, the most probable N-O distance lies in the range of 2.8-3.1 Å. The presence of the first group is supported by experimental X-ray and neutron diffraction studies (Hardman 1981, Pálinkás 1981).

In fact, most of statistical mechanical simulations relied on classical pair potentials, and hence, no consensus results were found, depending on the type and quality of the potential models employed in the simulations. In principle, *ab initio* calculations would be the most accurate methods for describing all interaction types in the system. However, their direct application to a full condensed-phase system consisting of a large number of molecules is too time-consuming. Alternatively, a "Born-Oppenheimer *ab initio* QM/MM MD" technique has been proposed and successfully applied for studying structural and dynamic properties of various ions in solutions. This technique treats the active-site region, e.g. the solvation shell around the ions, at *ab initio* Hartree-Fock level, while the

environment consisting of further solvent molecules is described by molecular mechanical potentials. By the QM/MM method, the complicated many-body contributions which are mostly due to polarization effects within the first solvation sphere of ions can be reliably included. The QM/MM results have already demonstrated a significant role of higher (>3) many-body terms on both structural and dynamic properties of solvated ions. In the present work, therefore, the high-level QM/MM technique was applied in the study of properties of $\text{NH}_4^+ \text{-H}_2\text{O}$ complex in aqueous solution.

2. METHOD

QM/MM MD Methodology: The QM/MM method partitions the whole system into a quantum mechanical (QM) region and a region treated by molecular mechanics (MM). All particles within the QM region, e.g. the ion and its first hydration shell, are treated by means of quantum mechanics. Ion-water interactions within the MM and between QM and MM regions are described by means of classical potentials. Basically, the reliability of the QM/MM results - besides the requirement of adequate simulation time - depends crucially on the selection of QM size as well as the basis sets employed for describing all interactions within the QM region. In this work, the diameter of the QM region was set to 7.6 Å. With respect to the amount of particles involved within the QM region, the DZV basis sets were employed, compromising between the quality of the simulation results and the requirement of CPU time. In each simulation step, an *ab initio* calculation was performed to provide quantum mechanical forces to be incorporated into the total force of the system by the following formula,

$$F_i = S_m(r)F_{QM} + (1 - S_m(r))F_{MM} \quad (1)$$

where F_{QM} and F_{MM} are quantum mechanical and pair potential forces, respectively. $S_m(r)$ is a smoothing function,

$$\begin{aligned} S_m(r) &= 1, & \text{for } r \leq r_1, \\ S_m(r) &= \frac{(r_0^2 - r^2)^2 (r_0^2 + 2r^2 - 3r_1^2)}{(r_0^2 - r_1^2)^3}, & \text{for } r_1 < r \leq r_0, \\ S_m(r) &= 0, & \text{for } r > r_0, \end{aligned} \quad (2)$$

applied to ensure a continuous change of forces at the transition between QM and MM regions.

Potential functions: The pair potential function for describing $\text{NH}_4^+ \text{-H}_2\text{O}$ interactions was newly constructed in the present work using Aug-cc-PVTZ basis set. With respect to a symmetric tetrahedral geometry of the NH_4^+ ion, 878 Hartree-Fock interaction energies for various $\text{NH}_4^+ \text{-H}_2\text{O}$ configurations, computed from Gaussian98, were fitted to an analytical function:

$$\Delta E_{\text{NH}_4^+ \text{-H}_2\text{O}} = \sum_{i=1}^5 \sum_{j=1}^3 \left[\frac{A_{ij}}{r_{ij}^5} + \frac{B_{ij}}{r_{ij}^7} + C_{ij} \exp(-D_{ij} r_{ij}) + \frac{q_i q_j}{r_{ij}} \right] \quad (3)$$

where A , B , C and D are the fitting parameters (see Table 1). r_{ij} denote the distances between the i -th atoms of NH_4^+ ion and the j -th atoms of water and q are atomic net charges. The charges on N and H of NH_4^+ ion and on O and H of water were set to -0.5186 , 0.3796 , -0.6598 and 0.3299 , respectively.

Table 1. Optimized parameters for the analytical pair potential function of $\text{NH}_4^+ \text{-H}_2\text{O}$

Pair	A (kcal mol ⁻¹ Å ⁵)	B (kcal mol ⁻¹ Å ⁷)	C (kcal mol ⁻¹)	D (Å ⁻¹)
N-O	305.5759	3783.8268	-1794.3299	2.1408
N-H	-3508.8159	1388.9633	10361.9735	2.5057
H-O	-349.7620	176.0625	-9493.4261	3.7945
H-H	27.0492	23.9161	-31.5685	1.0399

Simulation conditions: The *ab initio* QM/MM MD simulation was performed in a canonical ensemble containing one NH_4^+ ion and 199 water molecules with periodic boundary conditions. The cubic box, with the box length of 18.17 Å, was chosen to give a pure water density. The temperature was kept constant at 298 K. The temperature had been controlled by the method of temperature-bath coupling. The reaction-field method was employed for the treatment of long-range interactions. This method also implies a compensation of the electrical non-neutrality of the cubic box. The time step was set to 0.2 fs, which allows for explicit movement of hydrogen atoms of water. The MD system was initially equilibrated by performing a QM/MM MD simulation, in which only the NH_4^+ ion was treated quantum mechanically, for 200,000 time steps. Then, the QM/MM simulation with the QM diameter of 7.6 Å was started with the system's re-equilibration for 25,000 time steps, followed by another 80,000 time steps to collect configurations every 10th step.

3. RESULTS AND DISCUSSION

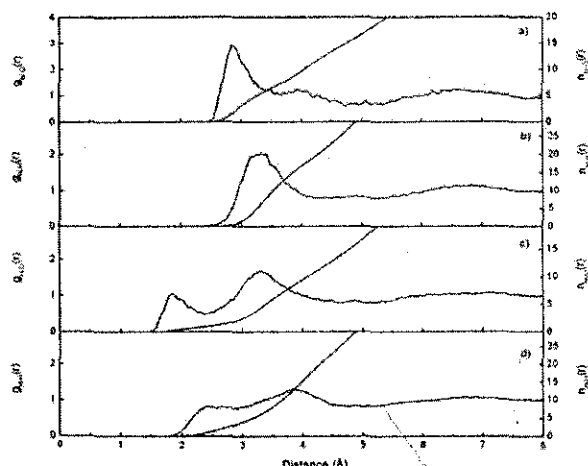


Figure 1. a) N-O, b) N-H, c) H-O, and d) H-H RDFs and their corresponding integration numbers.

Radial distribution functions

The N-O, N-H, H-O and H-H radial distribution functions (RDFs) and their running integration numbers obtained from the QM/MM simulation are displayed in Figure 1. The QM/MM simulation reveals a broad unsymmetrical first N-O RDF peak with maximum at 2.84 Å, together with a shoulder peak between 3.5-4.8 Å. The shape of N-O peak implies rather weak $\text{NH}_4^+ \text{-H}_2\text{O}$ interactions and high mobility of water molecules in the solvation shell of the NH_4^+ ion. In addition to the broad N-O RDF, a broad N-H peak supports well a high flexibility and rather freely oriented arrangements of the first shell water molecules. The integration, calculated up to first N-O minimum, yields an average coordination number of 6.5 ± 0.5 . The H-O

and H-H RDFs, which describe hydrogen bonding between NH_4^+ ion and its first shell water molecules, are depicted in Figures 1c and 1d, respectively. The first H-O peak appears at 1.84 Å, corresponding to the hydrogen bonding between NH_4^+ ion and its neighboring water molecules. Apparently, the first H-O peak is not well separated from the second one, allowing more frequent and easy exchange of water molecules between the first shell and the outer region.

Intramolecular geometry of water

Besides the accurate description on the structure of the hydrated NH_4^+ ion, another advantage of *ab initio* QM/MM MD technique is the ability to reliably investigate the intramolecular geometry of the

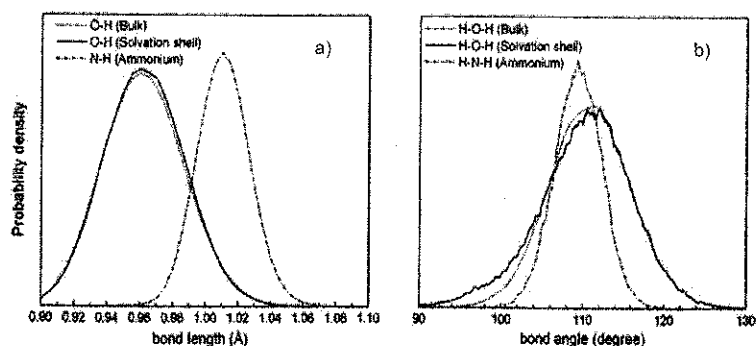


Figure 2. Distributions of: a) bond length and b) angle of water molecules in the first hydration shell of NH_4^+ ion and in the bulk.

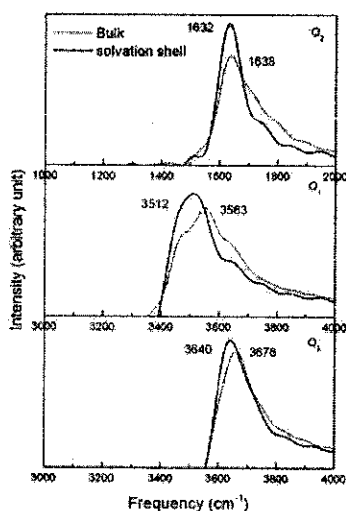


Figure 3. Power spectra of the intramolecular vibrational motions of water molecules in the first hydration shell of NH_4^+ ion and in the bulk.

species inside the QM region. The distributions of N-H and O-H bond lengths as well as H-N-H and H-O-H angles of NH_4^+ ion and water molecules, calculated for only waters located within the first solvation shell, are depicted in Figure 2. For the structure of NH_4^+ ion, the N-H bonds and H-N-H angles are arranged within the range of $1.01 \pm 0.05 \text{ \AA}$ and $109.5 \pm 8^\circ$, respectively. The observed deviations of both N-H bond lengths and H-N-H angles

obviously confirm the necessity of QM/MM treatment, in particular to correctly describe the flexibility of the $\text{NH}_4^+\text{-H}_2\text{O}$ complex. For the intramolecular geometry of water molecules surrounding the NH_4^+ ion, the QM/MM simulation indicates small influence of NH_4^+ ion on the geometrical arrangement of its nearest-neighbor water molecules, compared to the properties of pure water treated at similar QM/MM level of accuracy.

Vibrational ligand motions

The three quantities Q_2 , Q_1 and Q_3 (Bopp 1986), calculated from the VACFs of water's hydrogens for describing systematic stretching and bending and asymmetric stretching vibrations, respectively, are shown in Figure 3. As can be seen, the influence of NH_4^+ ion reflects the red-shifted for both bending and stretching vibrational modes of first shell water molecules. However, this effect is less significance in accordance to the rather weak $\text{NH}_4^+\text{-H}_2\text{O}$ interactions.

4. CONCLUSION

Since experimental treatments on weakly hydrated ion are rather difficult, the QM/MM simulation technique have been proven to be a useful method to provide reliable description on the behavior of the NH_4^+ ion in aqueous solution.

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