General Introduction

Many biologically important compounds such as amino acids and peptides are present in ionic form in vivo. In the study of biological phenomena, it is important to determine the geometries of these essential compounds in ionized form in aqueous solution. However, it is difficult to determine the geometries of those ions in aqueous solution. For that reason, in the fields of Quantitative Structure Activity Relationship (QSAR) and so on, when the geometries and charges on atoms of those ions in aqueous solution are needed, the geometries and charges on atoms in aqueous solution are approximated by the geometries and charges on atoms of those ions in the gas phase. However, for example, the C-C and C-N bond lengths of glycine zwitterion in the gas phase are considerably longer than the standard C-C and C-N bond lenghts [1,2]. Therefore, it is predict that the geometries of amino acids in aqueous solution are essentially different from those geometries in the gas phase. In general, it has been thought that the geometries and charges on atoms of ions (organic compounds) in aqueous solution are different from those in the gas phase. However, to my knowledge, the question remains open: (1) it is important to determine to what extent the geometries and charges on atoms of ions in aqueous solution are different from those in the gas phase. Why do the geometries and charges on atoms of ions in aqueous solution differ from those in the gas phase ? and (2) it is unknown that the geometries and charges on atoms of ions in aqueous solution are really different from those

in the gas phase.

This study clarifies above questions as follow: (1) first I determined the geometries and charges on atoms of the following aqueous clusters of model ions for biologically important compounds using ab initio molecular orbital method and (2) next I predicted the geometries and electronic structures of those ions in aqueous solution based on those geometries and charges of the aqueous clusters.

Chapter 1.

This chapter was performed for analyzing the characteristics of geometries of aqueous clusters of $RCOO^-$ (Chapter 2) and CH_3O^- (Chapter 3). The R-C bond lengths of $R-COO^-$ (R = H, CH_3 and C_2H_5) are longer in the gas phase than those of R-COOH in the gas phase. By way of contrast, in the gas phase, the C-O bond length of CH_3-O^- is shorter than that of CH_3OH. Also, the R-C bond lengths of $R-COO^-$ (R = H and CH_3) in a crystal structure determined experimentally are shorter than those in the gas phase estimated using high level calculation (MP2/6-31++G(d,p)). The cause of these elongations and shortening in the gas phase has not been quantitatively examined. In addition, why the R-C· bond lengths of $R-COO^-$ are longer in the gas phase than in the crystal structure has not been studied.

The purpose of this chapter are (1) to quantitatively find the cause for these elongations in $R-COO^-$ and shortening in CH_3-O^- in the gas phase, and (2) to discuss why the R-C bond lengths of $R-COO^-$ in the gas phase are longer than those in the crystal

structure.

Chapter 2.

The geometry of RCOO⁻ in aqueous solution is interesting because many chemically and biologically important species such as amino acids and peptides have carboxylate groups in aqueous solution. However, at the present stage of experimentation, it is impossible to determine the structure of RCOO⁻ in aqueous solution.

The purpose of this chapter is to predict the geometries of RCOO⁻ in aqueous solution. For this purpose, I determined the geometries and charges on atoms of aqueous clusters of RCOO⁻.

Chapter 3.

Many chemically and biologically important species exist in RO⁻ and RS⁻ in aqueous solution. Many important drugs (for example, alcohols) exist in RO⁻ in aqueous solution. The compounds (for example, thiols) related to the protection of DNA from radiation damage exist in RS⁻ in aqueous solution. However, at the present stage of experimentation, it is impossible to determine the geometries of RO⁻ and RS⁻ in aqueous solution. As the initial step in determining the geometries of RO⁻ and RS⁻ in aqueous solution, the geometries and charges on atoms of CH_3O^- and CH_3S^- in aqueous solution are interesting.

The purpose of this chapter is to predict the geometries and charges on atoms of CH_3O^- and CH_3S^- in aqueous solution. For this purpose, I determined the geometries and charges on atoms of

aqueous clusters of CH_3O^- and CH_3S^-.

Chapter 4.

Since many biologically important species such as amino acids and peptides have $-NH_3^+$ groups, the geometry of RNH_3^+ in aqueous solution is interesting. However, it is difficult to determine the geometry of RNH_3^+ in aqueous solution at the present stage of experimentation and theory.

The purpose of this chapter is to predict the geometry of $CH_3NH_3^+$ in aqueous solution as the initial step in determining the geometry of RNH_3^+ in aqueous solution. For this purpose, I determined the geometries and charges on atoms of aqueous clusters of $CH_3NH_3^+$.

Also, it is predicted that the geometry of $CH_3PH_3^+$ in aqueous solution is almost equal to that in the gas phase.

Chapter 5.

In Chapter 3, I obtained an interesting prediction: (1) the geometry of CH_3O^- in aqueous solution differs from that in the gas phase; the discrepancy stems from a lower contribution of the resonance structure, $H^-...CH_2=O$, in aqueous solution than in the gas phase. (2) by way of contrast, the geometry of CH_3S^- in aqueous solution is almost equal to that in the gas phase. This means that the contribution of the resonance structure, H^- $...CH_2=S$, in aqueous solution is almost equal to that in the gas phase. Therefore, the geometries of $CH_3OH_2^+$ and $Ch_3SH_2^+$ in aqueous solution are interesting.

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The purpose of this chapter is to predict the geometries of $CH_3OH_2^+$ and $CH_3SH_2^+$ in aqueous solution. For this purpose, I determined the geometries and charges on atoms of aqueous clusters of $CH_3OH_2^+$ and $CH_3SH_2^+$.

These studies show that (1) the geometries and charges on atoms of $RCOO^-$ (R = H, CH_3 and F), CH_3O^-, $CH_3NH_3^+$ and $CH_3OH_2^+$ in aqueous solution are considerably different from those in the gase phase and (2) the geometries of CH_3S^-, $CH_3PH_3^+$ and $CH_3SH_2^+$ (except for the S-H bond lengths) in aqueous solution are almost equal to those in the gas phase.

References

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[2] D.Yu, D.A.Armstrong and A.Rauk, Can.J.Chem. 70(1992)1762.