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一、中文摘要

在過去三年裏，我們探討了鹼金屬原子和羰基化合物，小肽分子以及三-(乙胺基)胺所形成之分子錯合物的物理和化學性質。我們也研究一系列 $H_nXCH_2YH_m$ ($XH_n, YH_m=OH, NH_2, SH, PH_2$) 分子的大域構型位能面，以瞭解其分子內氫鍵和 Anomeric 作用力的本質。

關鍵詞：鹼金屬，凡得瓦爾錯合物，分子軌域計算，游離能。

Abstract :

In the past three years, the molecular complexes between the alkali metal atoms and carbonyl compounds, dipeptides, and tris(2-aminoethyl)amine were studied. Their physical and chemical properties were reported. In another research line, through global conformational energy analysis, relative contributing weight of the intramolecular hydrogen bonding and anomeric interactions to the conformation energies in the molecules $H_nXCH_2YH_m$ ($XH_n, YH_m = OH, NH_2, SH, PH_2$) was obtained. Their implications in the related experimental observations were discussed.

Keywords: Alkali metals, van der Waals complexes, ab initio molecular orbital calculations, ionization energies.

二、緣由與目的

The molecular complexes formed between the alkali metal atoms and multi-functional Lewis bases, such as ethylenediamine, 1,2-ethanediol, and 1,2-dimethoxyethane, 12-crown-4 have been studied in this laboratory for some times now. The conformation-dependent bond dissociation energies and photoionization threshold energies of these complexes were specifically investigated. In the past three years, we have extended this line of study to another multifunctional Lewis base molecule, tris(2-aminoethyl)amine. This line of complexes could be regarded as an intermediate during the solvation process of the sodium. Through this study, we could have a better understanding of the details of the electron and/or sodium solvation processes.

Another direction we pursued is the alkali metal complexes formed with the carbonyl compounds and dipeptides. These alkali metal complexes are interesting because there are two possible electronic states that are close to each other for these complexes. Depending on the geometry of the complexes, the ground electronic states could switch from one of the two possible electronic states to the other. They possess completely different chemical and physical properties. For the carbonyl compounds, these alkali complexes open some new reaction pathways for organic chemistry. In the case of the peptide complexes, it would be interesting to look into the possible implications in the protein chemistry and also

protein dynamics in the presence of the sodium cations, especially when there is electron transfer process going through it.

三、結果與討論

The results are discussed in the following six subsections:

(1) "Intramolecular Hydrogen Bonding and Anomeric Interactions in $H_nXCH_2YH_m$ ($XH_n, YH_m = OH, NH_2, SH, PH_2$): A Global Conformational Analysis" (*J. Phys. Chem. A*, **1999**, *103*, 8706).

In this study, the global internal rotation potentials of the title compounds were obtained at the MP2/6-311+g(2d,p) level by scanning through the dihedral angles of the XH_n and YH_m functional groups with the remaining nuclear coordinates being energy-minimized at the MP2/6-31G** level. The intramolecular hydrogen bonding between the XH_n and YH_m functional groups is represented by the general functional forms of the electric dipole-dipole, dipole-quadrupole, and quadrupole-quadrupole interactions. The through-direct-bond potentials between the functional group and its adjacent $-CH_2X$ or $-CH_2Y$ molecular fragment were represented by the conventional three Fourier terms. The general functional forms of these two types of potentials could adequately represent the global conformational potentials of these molecules. The present energy decomposition analysis suggests that both the electrostatic interactions and the charge-delocalization interaction of the lone-pair electrons of the X or Y atom to its adjacent molecular fragment are equally important in determining the global conformational potentials, and the origin of the anomeric effect of these compounds could be quantitatively explained in terms of these two types of interactions. Quantitative comparisons of the anomeric interaction strengths and the related orbital interaction energies among the title compounds were

emphasized. Their general implications on the related molecular systems reported in the literature were also discussed.

(2) "Molecular Complexes between Sodium and Carbonyl Compounds: Photoionization and ab Initio Molecular Orbital Studies" (*J. Phys. Chem. A* **2000**, *104*, 10825).

In this work, the molecular complexes formed between sodium and three carbonyl compounds, formaldehyde (fd), acetaldehyde (ad), and acetone (ac), were studied by the ab initio molecular orbital method and photoionization mass spectrometry. In the case of the monosodium complexes, searching over the global electronic ground state at the MP2/6-31+G(d,p) level, three locally stable minima were located for each of the three complex systems. One of them is van der Waals interaction in nature and is designated as complexation-pair state (*cp* state). The other two are in ion-pair form and are denoted as *ip1* and *ip2* states. The nature of the sodium *cp* bonding with a carbonyl group was compared to the traditional alkali metal atom bonding with a simple Lewis-base molecule. At the CCSD(T)/6-311+G(2d,p) level, except for the formaldehyde complex, whose most stable *ip* state has a small bonding energy, the energies of the other ion-pair states are all found to be slightly higher than those of the dissociation limit of the neutral dissociation channel. The energies of these three locally stable isomers are actually quite close to each other with the largest energy separation being only 0.617 eV in Na(ac). For the disodium complexes, only the *cp* states were considered. The photoionization threshold energies of Na(ad) (*cp*), Na(ac) (*cp*) and Na₂(ac) were determined to be 4.23 ± 0.04 , 4.12 ± 0.05 , and 4.34 ± 0.04 eV, respectively. The photoionization threshold energy of Na₂(ad) was estimated to be 4.5 eV. These experimental values are in good agreement with those calculated at the B3PW91/6-311+G(2d,p) level. From the photoionization efficiency spectra of the Na(ac) and Na₂(ac), it is suggested that the autoionization process originated from the

$f^* \leftarrow n$ electronic transition of acetone could contribute to the ionization signal around and beyond the threshold region. The related cationic complexes were also studied theoretically. A unified view of the chemical and physical properties of these three systems were emphasized and discussed.

(3) "Conformational Analysis of the Alanine Dipeptide Anion as Stabilized by the Sodium Ion" (Paper in preparation).

In this study, the stable conformers of the sodium/alanine dipeptide complex were searched by the ab initio molecular orbital calculation methods. Two types of the molecular complex were found. One is in the form of the conventional sodium atom/Lewis base molecule interaction. The other is in the ion pair form dominated by the electrostatic interaction.

In the stable ion pair complex, the geometry of the alanine dipeptide anion is drastically different from that of its neutral counterpart. The details of the energetics and the conformations of the sodium/alanine dipeptide complex were reported. The physical and chemical properties of the anionic dipeptide as being stabilized by the sodium ion were emphasized. It would be interesting to look into the possible implications in the protein chemistry and dynamics, especially when there is electron transfer process involved.

(4) "Conformational Analysis of the Sodium/Tris(2-aminoethyl)amine Complexes: Photoionization and ab Initio Molecular Orbital Studies" (Paper in preparation).

(5) "Energetics and Structures of $Na_n(12\text{-Crown-4})$ ($n=1-9$) : an ab Initio Molecular Orbital Study" (Paper in preparation).

This is a study of the solvation of the small sodium metal clusters by single crown ether molecule. This type of complexes could be regarded as the intermediate systems toward the adsorption of a molecule on the bulk metal surfaces. There are interesting periodic changes in the interaction bonding energies

in these systems.

(6) "Energetics and Structures of $Na_n^+(12\text{-Crown-4})$ ($n=1-10$) : an ab Initio Molecular Orbital Study" (Paper in preparation).

This is a study of the solvation of the small sodium metal cationic clusters by single crown ether molecule. They are the cationic counterparts of the neutral sodium clusters. These cationic complexes could be regarded as the intermediate systems toward the adsorption of a cation on the bulk metal surfaces under electrolysis or electric potentials. Compared with those of the neutral counterparts, there are interesting changes in the interaction energies in these systems.