Chiral Effects in Collisions of Protonated Amino Acids and Amino Acid Inclusive Diastereomeric Complexes with Chiral and Achiral Molecules

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Synopsis Applying mass spectrometry based techniques, we have investigated interactions between protonated amino acids and tryptophan containing diastereomeric complexes with chiral (2-butanol) and achiral (argon) targets in high-energy (1 keV in the center-of-mass) and low-energy collisions. The processes of collision induced dissociation, projectile-target complex formation and dissociation have been observed. The reactions were studied for enantioselectivity. Theoretical calculations were performed for proton-bound diastereomeric complexes of tryptophan and 2-butanol. Determination of the mechanism of chiral differentiation in molecular reactions is crucial for understanding the basic principles of sterically dependent interactions.

The chirality phenomenon attracts a special attention from different research areas and plays a crucial role in living nature. The influence of molecular symmetry on human life cannot be underestimated. The origin of biological homochirality is still an open question that must be answered. No scenario for the origin of life can be constructed without solving the question of the mechanism for chiral purity. The question of chiral purity is most probably linked to the question of chiral recognition at the molecular level.

In our work, we conduct an experimental study of chiral ions in the gas-phase. Using the advantages of mass spectrometry based techniques, we have studied collisions of amino acid enantiomers (namely methionine, phenylalanine and tryptophan) with chiral (2-butanol, phenylethanol) and achiral targets. We have achieved interactions in single, monoenergetic conditions utilizing ion beams and thin targets. In the first series of experiments the high-energy collisions of 1 keV in the center-of-mass frame have been studied [1].

The subsequent experiments of low-energy collisions have been performed [2, 3]. The processes of fragmentation, proton-bound projectile-target complex formation and dissociation were investigated. The chirally dependent collision induced dissociation of proton bound complexes of tryptophan and 2-butanol has been observed. Additional collision gas pressure dependence measurement of complex dissociation was performed. The homo-chiral complex was found to be less stable than the heterochiral one in the collision-induced dissociation reactions.

Theoretical calculations have been performed in order to understand the process of chiral discrimination in the complex dissociation reaction. Using the Gaussian09 we calculated the energy of the proton bound complex of Trp and 2-butanol in different chiral combinations.

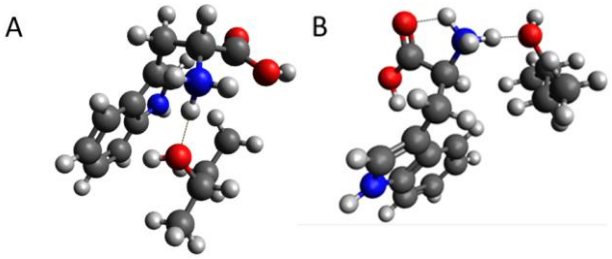

Figure 1. Structures of proton-bound complex of (A) (R)-Trp and (R)-2-butanol; (B) (S)-Trp and (R)-2-butanol calculated with Gaussian09 at the B3LYP/6-31+G(d,p) level of theory.

In this work we have achieved chiral differentiation of simple molecules in the gas phase by applying single collisions with the target. Our experimental results in combination with theoretical calculations provide so far the most simple and direct instance of chiral recognition by means of mass spectrometry.

References

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