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酪氨酸与色氨酸间电子转移——氧化还原活性及电子跃迁能的从头算研究

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摘要 在HF/6-31G和GASSCF/6-31G水平上对色氨酸和酪氨酸间的电子转移进行了理论研究。用类导体屏蔽模型考察体系的溶剂效应。通过对给、受体几何构型的优化， 计算了孤立的给、受体之间电子转移反应的内重组能和反应能差。分别用 Koopmans定理和CASSCF/6-31G方法计算了色氨酸和酪氨酸的电离能。计算了此两种氨基酸从基态到最低激发态的跃迁能。理论计算结果很好地解释了N_3~·高选择性 地氧化色氨酸残基，并诱发电子从酪氨酸残基向色氨酸残基转移的实验现象。

关键词 电子转移反应 氧化还原反应 色氨酸 酪氨酸 构型 跃迁

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Electron Transfer between Tryptophan and Tyrosine— ~~ab~~ initio Study on Redox Reactivity and Electronic Transition Energy

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Abstract Theoretical investigation on the electron transfer between tryptophan and tyrosine has been performed at the level of HF/6-31G and GASSCF/6-31G. The solvent effect has been considered by means of the conductorlike screening model. After geometric optimizations of the isolated donor and acceptor, inner reorganization energy and reaction energy difference of the electron transfer have been obtained. For comparison, the ionization potentials are calculated for tryptophan and tyrosine employing Koopmans' theorem and CASSCF/6-31G method respectively. The transition energy from the ground state to the lowest excited state of these two amino acids is also calculated. Theoretical results give good explanations on the experimental phenomena that N_3~· can preferably oxide the side chain of tryptophan residue and then the electron transfer from tyrosine residue to tryptophan residue follows in peptides involving tryptophan and tyrosine.

Key words CHARGE TRANSFER REACTION OXIDATION REDUCTION REACTION TRYPTOPHAN TYROSINE CONFIGURATION TRANSITION

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