

## 水溶液中四种脱氧核苷酸与水合铀酰离子相互作用的理论计算

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**摘要:** 运用密度泛函理论(DFT)方法 M06-2X,在相对论有效势基组水平下研究水溶液中水合铀酰脱氧核苷酸配合物 $[\text{UO}_2(\text{dNMP})(\text{H}_2\text{O})_3]^{2+}$ (dNMP=单磷酸脱氧核苷酸)的几何结构、能量和电子结构等性质,采用极化连续介质模型考虑水溶剂环境。结果表明,除了脱氧胸苷酸,其它脱氧核苷酸均以磷酸基团 P=O 键与铀原子形成的配位结构最稳定,4 类配离子 U=O 键长值较接近,但配位键键长有所不同。脱氧腺苷酸配离子的总结合能最大,但脱氧腺苷酸变形能最小。振动光谱分析发现 U=O 键和 P=O 键伸缩振动频率均发生红移,脱氧腺苷酸配离子的变化程度最大。电子密度拓扑分析表明 U-dNMP 键和 U-OH<sub>2</sub> 键具有离子键性质。电荷转移分析显示配体片段向铀酰离子发生了电子转移,脱氧腺苷酸配离子中配体转移的电荷数最多。轨道成分分析表明,高占据轨道贡献主要来自脱氧核苷酸配体  $\pi$  轨道,而低阶空轨道基本是 U 的 5f 轨道组成,脱氧鸟苷酸配离子的 HOMO-LUMO 能级差最小。

**关键词:** 铀酰离子; 脱氧核苷酸; 密度泛函理论; 结合能; 电子结构

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### Theoretical Calculations of Interaction between Four Deoxyribonucleotides and Hydrated Uranyl Ion in Aqueous Solution

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**Abstract:** The geometric structures, energetics and electronic structures of  $[\text{UO}_2(\text{dNMP})(\text{H}_2\text{O})_3]^{2+}$  (dNMP=deoxy-nucleotide monophosphate) in aqueous phase have been studied using density functional theory (DFT) method M06-2X with RLC ECP and ECP60MWB-SEG basis sets. Solvent effects of water was simulated by the polarized continuum model. The results showed that the most stable coordination uranyl ions formed by P=O bond of the phosphate group in dNMP, except the dTMP coordination ion. The bond lengths of U=O in four coordination uranyl ions were almost the same, but the coordination bond lengths were significantly different. The deoxyadenosine monophosphate (dAMP) coordination ion had the maximum binding energy among all the coordination ions, however, the coordinated dAMP possessed the smallest deformation energy. Concerning the differences in the calculation results of the two basis sets, the U=O bond lengths calculated by the ECP60MWB-SEG basis set were slightly longer than those obtained by the RLC ECP basis set, while the lengths of the coordination bonds showed opposite tendency. Additionally, the binding energy values calculated at the ECP60MWB-SEG basis set level were more negative than the RLC ECP basis set. The stretching vibrational frequencies of the U=O and P=O bonds exhibited a general red-shift, and the stretching vibrational frequencies of dAMP coordination ion decreased significantly. The topological analysis of electron density indicated that the coordination bond showed ionic character. It revealed that the charge transfer was from ligands to uranyl ion

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