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ClO/ClO~-耦合体系结构性质及反应通道研究

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摘要 利用从头算法和密度泛函理论对ClO/ClO~-体系进行了研究。首先应用密度泛 函理论的六种方法(B3LYP,BLYP,B3P86,BP86,BHLYP,LSDA)和从头算理论的CCSD方法 在6-3+G~*，6-311+G~*及6-311+G(3df)基组水平上对单体进行了优化，选出最适合 该体系的方法和基组B3LYP/6-311+G(3df)；然后在B3LYP/6-311+G(3df)水平上计算 了沿各种反应通道的离解能，并且进行了校正。找出了存在的中间体及中间体异构化的过渡态，并进行了IRC路径解析。对各稳定体进行了频率分析和成键分析。结 果表明，单体ClO和单体ClO~-结合为稳定的中间体后，其离解方式主要是向着 ClOO+Cl~-和ClOO~-+Cl两种方式进行，两种离解方式的离解能分别为-33.39和82. 88kJ/mol，并且前者是一个离解性电子转移过程，经历一个电子转移过渡态。

关键词 密度泛函数理论 次氯酸 反应机理 过渡态 电子转移反应 从头计算法

分类号 064

Studies on Structural Properties and Reaction Pathways of ClO/ClO~- Coupling System

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Abstract On the basis of ab initio and DFT theory, the ClO/ClO~- coupling system has been studied. The equilibrium geometries and harmonic frequencies of ClO/ClO~- system have been determined at B3LYP, B3P86, BLYP, BP86, BHLYP, LSDA, CCSD levels using different basis sets with diffuse and d, f polarization functions. Comparison with available experimental results is also made. The dissociation energies have been calculated using B3LYP method employing the 6-311+G(3df) basis set, and have also been corrected using the BSSE method. The intermediates and the transition state of the isomerization reaction have been found, and the bonding analysis has also been made. The results show that the main products are ClOO + Cl~- and ClOO~- + Cl for the dissociation of two coupling system. The dissociation energies for the corresponding dissociation channels are -33.39 and 82.88 kJ/mol, respectively. It should be noted that the dissociation to ClOO+Cl~- is essentially a dissociative electron transfer process with an electron transfer transition state.

Key words density functional theory HYPOCHLORIC ACID REACTION MECHANISM TRANSITION STATE CHARGE TRANSFER REACTION AB INITIO CALCULATION

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