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研究论文

气相中Cu^+和Zn^+与CS_2反应的计算研究

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摘要 以Cu^+和Zn^+与CS_2反应作为第一过渡金属离子与CS_2反应的范例体系. 采用密度泛函UB3LYP/6-311+G*方法计算研究了第一过渡金属离子在基态和激发态与CS_2反应的反应机理. 全参数优化了反应势能面上各驻点的几何构型, 用频率分析方法和内禀反应坐标(IRC)方法对过渡态进行了验证. 并用UCCSD(T)/6-311G*方法对各驻点作了单点能量校正. 在Cu^+与CS_2反应中, 计算了单重态初始中间体^{1}IM1到三重态插入型中间体^{3}IM2的反应交叉势能面. 确定了第一过渡金属离子与CS_2的反应为插入-消去反应, 找到了基态和激发态金属离子与CS_2反应的主要通道.

关键词 过渡金属离子 二硫化碳 反应机理 密度泛函理论

分类号

Theoretical Study of the Reaction of Cu^+ and Zn^+ with CS_2 in Gas Phase

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Abstract The reaction of Cu^+ and Zn^+ with CS_2, was selected as a representative system of reactions of first-row transition metal ions with CS_2. The reaction mechanism between first-row transition metal ions in ground state and excited state and CS_2 has been studied using the density functional theory (DFT) at UB3LYP/6-311+G* level. The geometries for reactants, the transition states and the products were completely optimized. All the transition states were verified by the vibrational analysis and the intrinsic reaction coordinate calculations. For each stationary point, single-point UCCSD(T) energy calculations were carried out. A potential energy curve-crossing diagram was investigated for state correlation between singlet ^{1}IM1 and triplet ^{3}IM2 in the reactin of Cu^+ with CS_2. The result showed that the reaction mechanism between first-row transition metal ions and CS_2 was an insertion-elimination mechanism. The main reaction path channel was detected in the reaction of metal ions in ground state and excited state with CS_2.

Key words transition-metal ion carbon bisulfide reaction mechanism density functional theory

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