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研究论文

气相中Y^+, Zr^+, Nb^+与CO_2反应的理论研究

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摘要 以Y^+, Zr^+, Nb^+与CO_2反应作为第二前过渡金属离子与CO_2反应的范例体系. 采用密度泛函UB3LYP方法, 对于Y, Zr, Nb采用Stuttgart赝势基组, 对于CO_2采用6-311＋G(2d)基组, 计算研究了三种金属离子在基态和激发态时与CO_2气相反应的机理. 结果表明三种金属离子与CO_2反应以高自旋进入反应通道, 在反应过程中发生系间窜越, 以低自旋中间体和最终产物离开反应通道. 用内禀坐标单点垂直激发计算的方法找到了势能面交叉点, 并作了相应的讨论. 因为有金属离子的参与, 使单分子CO_2的强吸热分解反应变为生成CO和MO^+的放热过程.

关键词 过渡金属离子 两态反应 势能面交叉现象 放热反应

分类号

Theoretical Study of the Reaction of Y^+, Zr^+, Nb^+ with CO_2 in Gas Phase

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Abstract The reactions of Y^+, Zr^+, $Nb^+$with CO_2, producing the metal oxide ion and CO, are taken as a representative examples to elucidate the overall mechanisms of reactions of second-row early transition metal ions with CO_2. The reactions in both ground and excited states are studied by using the UB3LYP density functional method with the Stuttgart pseudopotentials and corresponding basis sets for the metals and the standard 6-311＋G(2d) basis sets for C and O. The geometries for reactants, the transition states and the products are completely optimized. The result shows that the reaction mechanism between second-row early transition metal ions and CO_2 is an insertion-elimination mechanism. The potential energy curve crossings, which dramatically affect reaction mechanisms, are discussed in detail. The reactions are all exothermic due to the participation of the metal ions, to be compared with the strong endothermic process of the unimolecular CO_2 decomposition.

Key words early transition-metal ion two-state reactivity potential energy surfaces crossing point (CP) exothermic process

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