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研究报告

水与三甲基硅烷醇羟基的氢同位素交换反应的理论研究

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摘要 以$(CH_3)_3SiOH$羟基模拟Li_4SiO_4陶瓷表面羟基，研究了H_2O与$(CH_3)_3SiOH$羟基H的氢交换反应机理。采用HF，MP2方法，在3-21G和6-311G++** 水平上优化了$(CH_3)_3SiOH$，H_2O，$(CH_3)_3SiOH—H_2O$复合物及氢交换反应过渡态的结构。计算了生成$(CH_3)_3SiOH—H_2O$复合物的反应热，探讨了氢交换反应的路径。结果表明，可以形成2种形式的$(CH_3)_3SiOH—H_2O$复合物，一种是H_2O的O原子与$(CH_3)_3SiOH$羟基的H原子作用形成的复合物，另一种是H_2O的H原子与$(CH_3)_3SiOH$羟基的O原子作用形成的复合物。MP2/6-311G++** 水平上，对基组重叠能（BSSE）进行校正后，上述2种复合物的反应热分别为20.046 5 kJ/mol和21.630 7 kJ/mol。有利的氢交换反应路径为：H_2O的H原子与$(CH_3)_3SiOH$羟基的O原子作用形成的复合物，然后H_2O提供1个H原子、1个O原子，$(CH_3)_3SiOH$提供1个O原子、1个Si原子形成由O, H, O, Si 4个原子构成的四元环过渡态，最后H_2O的O原子与$(CH_3)_3SiOH$ 的Si原子成键形成新的$(CH_3)_3SiOH$，而$(CH_3)_3SiOH$的Si－O键断裂，由$(CH_3)_3SiOH$的羟基和H_2O的1个H原子形成新的H_2O分子，MP2/ 6-311G++**水平上，BSSE校正后，此路径的反应活化能为186.898 4 kJ/mol。

关键词 三甲基硅烷醇 水 同位素交换 从头算

分类号

Ab Initio Study on the Mechanism of Hydrogen Exchange Reaction Between H_2O and Hydroxyl of $(CH_3)_3SiOH$

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Abstract The hydrogen exchange reaction mechanism between H2O and －OH of surface of Li_4SiO_4 ceramic has been investigated using hydroxyl of $(CH_3)_3SiOH$ as a simple model of hydroxyl of surface of Li_4SiO_4 ceramic. The structures of $(CH_3)_3SiOH$, H_2O, $(CH_3)_3SiOH—H_2O$ complexes and transition states of hydrogen exchange reaction have been optimized at HF/3-21G, HF/6-311G++**, and MP2/6-311G++**levels. The association energies of $(CH_3)_3SiOH—H_2O$ and the path of hydrogen exchange reaction have also been explored. The results show that two of associate complexes can be formed, the O of H_2O interact with the H of hydroxyl of $(CH_3)_3SiOH$ to form one complex and the another complex is formed by the interaction between the H of H_2O and the O of hydroxyl of $(CH_3)_3SiOH$. At HF/6-311G++** and MP2/6-311G++** levels, the association energies after basis set superposition error correction of two complexes above are 18.016 1, 18.816 6, 20.046 5, 21.630 7 kJ/mol, respectively. The favorable path of hydrogen exchange reaction is as follow: first, the H of H_2O interactes with the O of hydroxyl of $(CH_3)_3SiOH$ to form associate complex, second, 4-membered ring transition state consisted of O, from H_2O, H, from H_2O, O, from $(CH_3)_3SiOH$, Si, from $(CH_3)_3SiOH$ is formed, third, the formation of new O—Si bond and the break old O—H bond lead the new $(CH_3)_3SiOH$ to be formed, a

t the same time, the new H_2O is formed resulting in the rupture of old O-Si bond and the formatio
n of new H-O bond. At HF/6-311G++** and MP2/6-311G++** level， the activation energie
s of this path are 232.905 3 kJ/mol and 186.898 4 kJ/mol with counterpoise correction.

Key words $(CH_3)_3SiOH$ _ H_2O isotope exchange ab initio calculation method

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