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Full Papers

# 复合物HNO···$H_2O_2$内N-H···O蓝移氢键的理论研究

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摘要 利用理论方法研究了复合物HNO···$H_2O_2$内N-H···O蓝移氢键和O-H···O红移氢键。在MP2/6-31G(d)、MP2/6-31+G(d,p)、MP2/6-311++G(d,p)、B3LYP/6-31G(d)、 B3LYP/6-31+G(d,p)和B3LYP/6-311++G(d,p)水平上利用标准方法和均衡校正方法计算得到单体和复合物的几何构型和振动频率。计算结果表明：N-H···O氢键内N-H键伸缩频率蓝移达到120 $cm^{-1}$。利用自然键轨道分析发现O-H···O红移氢键主要来自于体系内的超共轭效应。对于N-H···O蓝移氢键，由于体系内存在显著的电子密度重排效应导致超共轭效应削弱，N-H键伸缩频率蓝移主要来自于N-H键轨道再杂化效应。

关键词 红移氢键,蓝移氢键,分子内原子拓扑分析,自然键轨道分析

分类号

# Theoretical Study on N—H…O Blue-shifted H-Bond for HNO…$H_2O_2$ Complex

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**Abstract** A theoretical study on the blue-shifted H-bond N—H…O and red-shifted H-bond O—H…O in the complex HNO…$H_2O_2$ was conducted by employment of both standard and counterpoise-corrected methods to calculate the geometric structures and vibrational frequencies at the MP2/6-31G(d), MP2/6-31＋G(d,p), MP2/6-311＋＋G(d,p), B3LYP/6-31G(d), B3LYP/6-31＋G(d,p) and B3LYP/6-311＋＋G(d,p) levels. In the H-bond N—H…O, the calculated blue shift of N—H stretching frequency is in the vicinity of 120 $cm^{-1}$ and this is indeed the largest theoretical estimate of a blue shift in the X—H…Y H-bond ever reported in the literature. From the natural bond orbital analysis, the red-shifted H-bond O—H…O can be explained on the basis of the dominant role of the hyperconjugation. For the blue-shifted H-bond N—H…O, the hyperconjugation was inhibited due to the existence of significant electron density redistribution effect, and the large blue shift of the N—H stretching frequency was prominently due to the rehybridization of $sp^n$ N—H hybrid orbital.

**Key words** red-shifted H-bond blue-shifted H-bond atoms in molecules topological analysis natural bond orbital analysis

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