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研究论文

Au(II)化合物$[Au(CH_2)_2PH_2]_2X_2$ (X＝F, Cl, Br, I)的量子化学理论研究

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摘要 采用从头计算HF, MP2方法和密度泛函理论, 对Au(II)系列化合物$[Au(CH_2)_2PH_2]_2X_2$ (X＝F, Cl, Br, I)的几何结构、电子结构和振动频率进行了研究. 研究表明Au的5d和6s电子参与Au—Au以及Au—X之间的成键. Au—Au, Au—X键强烈的电子相关作用使HF方法不适于该体系的研究, BP86和B3LYP两种泛函给出较大的Au—Au和Au—X键长, 而MP2方法和局域的密度泛函方法则给出了合理的结构参数.
局域密度泛函方法计算得到的Au—Au键和

Au—X键振动频率也与实验数据符合较好. 还运用含时密度泛函理论计算了$[Au(CH_2)_2PH_2]_2X_2$的电子激发能, 对分子在紫外-可见光谱范围内的电子跃迁进行了分析, 考察了卤素配体对激发能的影响, 并结合分子轨道能级的变化对此给予了解释.

关键词 双核金化合物 从头计算 密度泛函 振动频率 电子光谱

分类号

Quantum Chemical Theoretical Studies on Au(II) Complexes $[Au(CH_2)_2PH_2]_2X_2$ (X＝F, Cl, Br, I)

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Abstract The molecular structures, electronic structures, and vibrational frequencies of dinuclear gold(II) complexes $[Au(CH_2)_2PH_2]_2X_2$ (X＝F, Cl, Br, I) have been investigated by *ab initio* HF, MP2 and density functional theory methods. The obtained results from the different methods were compared to the experimental values. HF method was found to be not suitable for the Au-Au system due to the strong correlation effect. The non-local exchange-correlation functional BP86 and hybrid functional B3LYP afforded long Au—Au and Au—X distances. The MP2 and local density functional theory methods provided good geo-metric features. Local density functional vibrational frequencies are in good agreement with available ex-perimental data. The studies of the electronic structure of the complexes have shown that the 5d and 6s electrons of Au atoms can make great contribution to the bonding of Au—Au and Au—X. The time-dependent density functional theory has been employed to calculate the electronic absorption spectra of the dinuclear gold(II) complexes. These calculations and the molecular orbital analysis have explained the behaviors of the complexes possibly.

Key words dinuclear gold complex *ab initio* density functional theory vibrational frequency electronic spectra

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