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研究论文

一类五核平面开口型过渡金属原子簇电子吸收光谱和二阶非线性光学性质的**TDDFT**研究

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摘要 运用TDDFT B3LYP/LanL2DZ方法,
研究了一类具有非中心对称的五核平面开口构型过渡金属原子簇化合物[$MoS_4Cu_4(py)_6X_2$] (X＝Br, I)
的电子吸收光谱和静态二阶非线性极化率, 估算了晶体的宏观二阶非线性光学系数.
电子吸收光谱的计算结果与实验测量结果比较符合; 碘系簇合物的静态二阶非线性极化率大于溴系.
详细讨论了该类金属簇合物电子吸收光谱的归属及其相关联的电子跃迁方式;
在微观水平上阐述了其二阶非线性光学性质的起源. 研究结果表明外围无机卤素配体4p/5p轨道到簇芯[MoS_4]
杂化轨道的电子转移对静态二阶非线性极化率的贡献大于有机配体的贡献;
而过渡金属簇芯内的电子转移也有较大的贡献.
这对于理解过渡金属原子簇化合物内的电子转移对光学激发的作用以及用来设计新的无机-
有机杂化二阶非线性光学材料有较大的帮助.

关键词 含时密度泛函理论 过渡金属簇合物 电子吸收光谱 二阶非线性光学性质

分类号

TDDFT Study on Electronic Absorption Spectra and Second-order NLO Properties of Penta-nuclear Planar “Open” Transition Metal Cluster Complexes

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Abstract The electronic absorption spectra, the molecular static first hyperpolarizabilities and the macroscopic nonlinear optical coefficients of the pentanuclear planar “open” transition metal clusters, $MoS_4Cu_4(py)_6X_2$ (X＝Br, I), have been studied by using the time-dependent density functional theory (TDDFT) at B3LYP/LanL2DZ level. The absorption peaks are red shifted to the experimental data and the first hyperpolarizabilities are enhanced by the substitu-tion of Br by I. The analyses of the low-lying excited states reveal that the charge transfer from 4p/5p orbi-tals of halide center to hybrid orbitals of MoS_4 can contribute most the NLO responses. The charge transfer inside MoS_4 can make contribution as well. The results are helpful to under-stand the relationships between charge transfer and optical excitation, and to the design of novel or-ganic-inorganic hybrid nonlinear optical materials.

Key words time-dependent density functional theory transition metal cluster electronic absorption spectra second-order nonlinear optical property

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