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研究论文

用密度泛函理论研究一种新型有机硅化合物异构体的振动光谱

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摘要 在B3LYP/6-31＋G(d)的水平上, 对两种含有手性Si原子的新型有机硅单体$Si_2(CH_3)_2H_2N_2(C_2H_5)_4$和$Si_4(CH_3)_4H_4N_2(C_6H_5)_2$的几种异构体进行了研究, 在全参量几何构型优化的基础上, 进行了简谐振动频率计算, 同时对所研究的体系进行了热力学性质和低能激发态的含时密度泛函理论(TDDFT)计算. 理论计算表明, 构象异构体之间的红外光谱差异不大, 热力学和低能激发态性质也相似; 顺/反结构相似的异构体之间红外光谱差异不大, 但热力学和低能激发态性质却呈现差异; 旋光异构体或顺/反结构相差较大的异构体之间, 红外光谱和热力学及低能激发态性质有明显的差异. 从理论上解释了实验红外光谱中Si—H振动峰的裂分是由异构体的存在所致, 并找到裂分峰所对应的异构结构. Si—H键振动频率与其键长相关.

关键词 密度泛函理论(DFT) 几何异构体 红外振动光谱

分类号

DFT Investigation of Vibrational Spectra on a New Kind of Silane Compound Isomers

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Abstract The full-parameter geometry optimization and harmonic vibrational frequency calculations were performed on isomers of diamidodisilanes $Si_2(CH_3)_2H_2N_2(C_2H_5)_4$ and azocyclosilane $Si_4(CH_3)_4H_4N_2(C_6H_5)_2$ by means of density functional theory (DFT) at the B3LYP/6-31＋G(d) level. Some of thermodynamic properties and relatively low excitation energies were also calculated. From the theoretical investigation, it is showed that there are no large differences of their IR spectra and other thermodynamic properties between conformational isomers. The differences were observable of IR spectra and other thermodynamic properties between stereo isomers. It was found that the two split peaks of experimental vibrational spectra of Si-H bonds were due to the different stereo isomers. DFT results agree well with the experimental IR spectra from mixed isomers.

Key words density functional theory stereo isomer IR vibrational spectrum

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