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研究论文

端基取代的长链硅烷二阶超极化率的量子化学研究

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摘要 对端基取代的一维无限长反位硅烷H_2N-(SiH_2-SiH_2)$_n$-NO_2的二阶超极化率进行了系统的量子化学研究. 通过仔细检验和选择外场强度, 采用9个外场强度(0.0000, ±0.0008, ±0.0012, ±0.0016, ±0.0020 a.u.) 计算的体系能量来确定4阶场强展开式中的5个系数, 从而得到可靠的二阶超极化率. 建议数据拟合时用二阶超极化率单元值的平均值形式$\gamma(n)/n$作为拟合对象, 同时用$1/n$的2阶多项式作为拟合函数, 以得到无限长链的二阶超极化率极限值. 拟合数据范围的选择应该使该数据范围得到的极限值与其临近数据范围得到的极限值的均方偏差最小. 分子构型的优化使计算的二阶超极化率增加大约20%, 在基组中增加极化函数使二阶超极化率在无限长链时的极限值减少大约15%. 相关效应的影响最大, MP2 的结果比RHF的结果增加近一倍. 根据本文最高水平MP2/6-31G(d)//RHF/6-31G的计算, 端基取代的一维无限长反位硅烷H_2N-(SiH_2-SiH_2)$_n$-NO_2的二阶超极化率的每单元极限值为0.8364×10^6 a.u.

关键词 长链硅烷 超极化率 拟合函数 渐近极限 从头算

分类号

Quantum Chemical Study on Static Longitudinal Second Hyperpolarizability of Terminal Group Substituted Polysilane

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Abstract *Ab initio* calculations of the static longitudinal second hyperpolarizability were reported for the *trans*-polysilane $H_2N(SiH_2SiH_2)_nNO_2$ up to $n=30$. The magnitude of the electric fields used in the calculations was 0.0, ±0.0008, ±0.0012, ±0.0016 and ±0.0020 a.u. These fields were found suitable for the range of values to characterize the second hyperpolarizabilities of *trans*-polysilane. For the definition of the electrical property value per unit cell it was suggested to use average value $\gamma(n)/n$, instead of the difference value $\gamma(n)-\gamma(n-1)$. These asymptotic values were obtained by extrapolating the expression of $\gamma(n)/n=a+b/n+c/n^2$ to infinite length, of which the parameters have been obtained by fitting the molecular results. The most stable region in data set range ($n1$, $n2$) was selected to those least squares fit to asquire a subunit value for the infinite polymer property. The molecular geometry optimization increased Dγ(¥) value by about 20%, and the calculated D$\gamma(\infty)$ value with 6-31G(d) was approximate 15% lower than that obtained with 6-31G basis set. Electron correlation increased the magnitude of D$\gamma(\infty)$ strongly, and the MP2 values were nealy 100% higher in magnitude than the self-consistent-field values calculated by 6-31G and 6-31G(d) basis sets. Our best value for D$\gamma(\infty)$ of $H_2N(SiH_2SiH_2)_nNO_2$ reached 0.8364×10^6 a.u. with MP2/6-31G(d)//RHF/6-31G level.

Key words polysilane chain hyperpolarizability fitting function asymptotic limit *ab initio*

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