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系列化合物**C-H**伸缩频率的自然杂化轨道研究

胡振明,湛昌国

华中师范大学化学系

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摘要 在计算C-H核自旋-自旋偶合常数的新公式及其与C-H伸缩频率之间的关系的基础上, 得出了计算C-H伸缩频率的新的一般关系式。并利用CNDO/2分子轨道和自然杂化轨道方法, 具体计算了三种不同系列化合物的原子净电荷和自然杂化轨道。给出了计算不同系列化合物C-H伸缩频率的良好线性关系式。结果表明, 碳氢化合物中的C-H伸缩频率主要由原子的轨道杂化作用所决定, 而对于含杂原子的取代碳氢化合物, C-H键的极性成为影响伸缩频率的重要因素。

关键词 微分重叠全忽略近似 化学键 分子轨道理论 杂化轨道 碳氢化合物 自旋偶合常数

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Natural hybrid orbital study of the C-H stretching frequencies in hydrocarbons and heterosubstituted hydrocarbons

HU ZHENMING,ZHAN CHANGGUO

Abstract As a result of earlier interest in the calculation of the C-H nuclear spin-spin coupling constants and its correlation with the C-H stretching frequencies in hydrocarbons and heterosubstituted hydrocarbons, a novel general relationship for the calculation of the C-H stretching frequencies is proposed in this paper. The proposed relationship has been employed to calculate the C-H stretching frequencies (nCH) for a series of hydrocarbons, fluorosubstituted hydrocarbons and substituted aldehydes by use of the CNDO/2 MO approximation and the natural hybrid orbital scheme. It is shown that the C-H stretching frequencies are directly proportional to the s-character of the corresponding C atom in hydrocarbons. But for heterosubstituted hydrocarbons, the net charges of atoms C and H, or the polarity of the C-H bond, become a significant factor. The calculated results may also be utilized to account for other factors affecting nCH, such as steric effect, cis-trans geometry and substituted effects etc. Some discussions concerning the calculated results are also reported.

Key words CNDO APPROXIMATION CHEMICAL BONDS MOLECULAR ORBITAL THEORY HYBRID ORBITAL HYDROCARBAN

DOI:

通讯作者