化学学报 1995 53 (7): 637-644 ISSN: 0567-7351 CN: 31-1320/06

γ-吡啶甲酸及其同位素衍生物的谐性力场和振动光谱的从头计算研究

范康年,王文宁,夏琳,潘石麟

复旦大学化学系

收稿日期 修回日期 网络版发布日期 接受日期

摘要 本文采用TEXAS分析梯度法从头计算程序, 以STO-4-21G基组计算了γ-吡啶甲酸的谐性力场和振动光谱。直接理论计算的谐性力场经由相关分子转移来的校正因子校正后, 得到的振动基频的预测值和固体样品红外光谱实验值之间的平均偏差为20cm^-^1(面内振动23cm^-^1, 面外振动11cm^-^1)。用这组校正因子得到的力场预测了γ-吡啶甲酸的两个同位素衍生物(-C^1^8O~2H和-C^1^6O~2D)的振动光谱, 所得同位素位移值与实验数据符合良好。对平面内振动的个别校正因子依据实验光谱进行了优化, 平面内振动的平均偏差降为15cm^-^1, 总的偏差为14cm^-^1。对预测中的偏差和某些基频的指认进行了讨论。

关键词 从头计算法 振动谱 吡啶甲酸 谐性力场

分类号 0641

Studies on the harmonic force field and vibrational spectra of γ-piconilic acid and its isotopic derivatives with ab initio calculations

FAN KANGNIAN,WANG WENNING,XIA LIN,PAN SHILIN

Abstract The harmonic vibrational force field and the vibrational spectrum of γ-picolinic acid have been calculated by the ab initio gradient program TEXAS using a STO-4-21G basis set. The directly computed theoretical harmonic force field was scaled with a set of scaling factors transferred from related molecules to obtain a prediction of fundamental frequencies. The mean deviation between prediction and experimental IR spectrum of γ-picolinic acid in solid phase was 20cm^-^1(23cm^-^1 for in-plane modes, 11cm^-^1 for out-of-plane ones). The vibrational spectra of two isotopic derivatives of γ-picolinic acid (-C^1^6O~2D, -C^1^8O~2H) have been predicted with the SQM force field resulting from the transferred scaling factors. The calculated isotopic shifts are in good agreement with experimental data. A few scaling factors of in-plane modes were optimized to fit theoretical predicted frequencies to the experimental spectrum, reducing the mean deviation of in-plane modes to 15cm^-^1, and the total one to 14cm^-^1. The deviations and the assignments of some fundamentals were discussed.

Key words AB INITIO CALCULATION VIBRATIONAL SPECTRA PYRIDINECARBOXYLIC ACID

DOI:

通讯作者