**Chinese Journal of Chemistry** 2005 23 (2): 194-199 ISSN: 0567-7351 CN: 31-1320/06

FULL PAPERS

# G3B3和CBS-QB3在化学键裂解能计算中的相关研究

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收稿日期 2003-2-23 修回日期 2004-10-11 网络版发布日期 接受日期

摘要 选用较为权威的数据库，使用一个庞大而有说服力的样本，经过极其大量的计算工作和分析比较，仔细地检验了最新的两种组合从头算方法，即G3B3和CBS-QB3，在计算化学键均裂裂解能时的精度。发现该两种方法的计算精度约为8.4千焦/摩，可以与通常实验能够达到的精度相媲美，因而在今后研究中可以有把握地应用。由于该两种方法的计算精度与标准的G3和CBS-Q方法相近，表明在计算化学键均裂裂解能时体系的几何可以使用UMP2方法来优化。同时发现密度泛函B3LYP方法显著低估了化学键均裂裂解能，误差平均为-16.7到-20.9 千焦/摩。这表明B3LYP方法不能准确地给出化学键均裂裂解能的绝对值，因而有必要在一些应用领域中引起注意。最后，发现有38种化合物其理论计算裂解能与权威实验值有着明显差别（>83.6千焦/摩）。由于本工作中理论计算的级别较高，而且又有着大量吻合的计算结果，因此理论与实验的不一致有必要引起重视，提示后续的工作加以解决。

关键词 G3B3,CBS-QB3,组合从头算方法,键裂解能,密度泛函理论

分类号

## Assessment of Performance of G3B3 and CBS-QB3 Methods in Calculation of Bond Dissociation Energies

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**Abstract** The performance of the newly developed G3B3 and CBS-QB3 methods in calculating absolute bond dissociation energy (BDE) was assessed. It was found that these two methods could predict the BDE with an accuracy of about 8.4 kJ/mol and therefore, they exhibited similar performance as the standard G3 and CBS-Q methods. On the other hand, it was demonstrated that the B3LYP method significantly underestimated the absolute BDE by 16.7—20.9 kJ/mol. This finding was valuable and timely because many researchers could use this relatively cheap method in studying radical reactions. Finally, 38 compounds were showed for which the theoretical BDE seriously deviated from the experimental data.

**Key words** G3B3 CBS-QB3 composite *ab initio* method bond dissociation energy density functional theory

DOI:

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