Quantum DFT and DF–DFT study of vibrational spectra of sulfuric acid, sulfuric acid monohydrate, formic acid and its cyclic dimer

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Abstract

Rigorous theoretical treatment of vibrational frequencies is critically important for the interpretation of unassigned experimental vibrational spectra and accurate determination of thermodynamic properties of molecular clusters. IR spectra of *trans* monomers of sulfuric and acetic acids, sulfuric acid monohydrate and cyclic dimer of the formic acid have been studied using DFT and DF–DFT methods using BLYP, B3LYP and PW91 with 12 different Pople and Dunning basis sets. New data for above-mentioned structures have been reported, scaling factors have been calculated and a comprehensive analysis of the performance of BLYP, B3LYP and PW91 methods has been performed. Comparison of the obtained results with experiments shows that results of pure PW91 and BLYP are better than predictions of well-established hybrid B3LYP method. Our analysis shows on the existence of the considerable difference in scaling factors weighted to high and low frequencies. In the case of formic acid dimer, the deviation the predicted low frequencies from the experimental data is considerable that leads to quite large ($\sim$6–7 kcal mol^{-1}) uncertainties in the absolute values of the cluster Gibbs free energy. In order to determine an efficient computational strategy that comprises accuracy and reasonable computational costs, the effect of density fitting (DF) and basis set superposition error (BSSE) on the vibration frequencies has been investigated. We found that application of the DF that substantially (2.5–3.5 times) increases the performance of pure PW91 and BLYP methods gives excellent results, which are very close to those of conventional DFT. This suggests that DF–DFT is a viable low-cost alternative to conventional DFT in predicting vibrational spectra. It has been found that while vibrational spectra obtained using the counterpoise correction (CP) for the BSSE do not deviate much from uncorrected ones, the difference in absorption intensities between corrected and uncorrected spectra obtained using small and medium-sized basis sets is considerable. This suggests that application of DF–DFT uncorrected for the BSSE with large basis sets is a more efficient strategy of predicting vibrational spectra than the application of conventional DFT with small basis sets.

1. Introduction

Accurate determination of vibrational frequencies is critically important for a number of application in many areas of physics and chemistry, including identification of experimentally observed reactive intermediates, for which theoretical spectra serve as fingerprints, interpretation of unassigned peaks in experimental vibrational spectra and determination of entropies, enthalpies, Gibbs free energies and reaction constants for interacting molecules and molecular clusters [1–7]. Selection of an appropriate method is an essential problem. An appropriate method has to not only reproduce the experimental spectrum with good overall (weighted to high frequencies) accuracy but also be able to predict, with significant degree of confidence, the low-frequency vibrations, which control thermochemical properties of molecules and molecular clusters. At the same time, the method should be fast enough to be affordable. Vibrational spectra can be studied computationally using semi-empirical (e.g., AM1; PM3; MNDO), ab initio (e.g., HF; MP2; CC) and density functional theory (DFT) methods (e.g., B3LYP, PW91, and BLYP) [8]. Semi-empirical methods, which are cheap in computational costs, are insufficiently accurate. Low level ab initio Hartree-Fock (HF) method significantly over-estimates vibrational frequencies. Higher level post-HF ab initio methods are more accurate than HF; however, they demands of substantial computational resources and do not over-perform more affordable DFT.

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Performance of some DFT (not including PW91) and ab initio methods has been evaluated by Scott and Radom [7]; however, their study was focused on relatively small (not more than four heavies) molecules investigated using small basis sets. However, computed vibrational spectra may be largely affected the quality of the basis set and applicability of scaling factors obtained for small molecules to larger ones is not known. More recently, Lewandowski et al. [1] evaluated vibrational spectra for *trans* and *cis* isomers of acetic acid, cyclic dimer of acetic acid and methyl ester predicted by DFT B3LYP, BLYP and PW91 and they reached a conclusion that BLYP outperforms both PW91 and B3LYP. However, this conclusion was based upon the comparison of the predictivity of the above-mentioned methods in combination with Pople basis sets [9] in the high-frequencies region, while the low-frequencies region was not studied in details and both Dunning and co-workers [10] and largest Pople basis sets were not tested. Application of smaller and thus faster, but less comprehensive, basis set helps to reduce computational costs. However, in this case a reduction in the computational expenses is accompanied by uncertainties related to the BSSE [11,12]. Minimization of the basis set is not the only way to speed up computations. Application of density fitting [13,14], which expands the density in a set of atom-centered functions when computing the Coulomb interaction instead of computing all of the two-electron integrals, substantially reduces the computational time. However, the efficiency of this approach in the case, when vibrational spectra are studied using DFT methods, remains unknown.

In the paper, IR spectra of *trans* monomers of sulfuric and acetic acids, sulfuric acid monohydrate and cyclic dimer of the formic acid were using DFT BLYP [15], B3LYP [16,17] and PW91[18] methods with 12 different Pople and Dunning basis sets. The molecules and clusters studied were chosen in such a way as to represent key substances for the atmospheric aerosol formation (both free and hydrated sulfuric acid) and common atmospheric organics (formic acid). Computations of the vibrational frequencies and scaling factors for these structures were carried and performance of BLYP, B3LYP and PW91 methods was evaluated. The impact of the density fitting and counterpoise correction on the predicivity of different DFT methods was studied and a more efficient computational strategy was suggested.

2. Methods

Computations were carried out using Gaussian03W-Revision D.01 [19]. Structures were optimized and equilibrium geometries with real frequencies have been obtained. Values of 10^{-8} hartrees in the energy, 3.0×10^{-4} and 4.5×10^{-4} hartrees/Å in the root mean square (RMS) and maximum forces, respectively, and RMS and maximum forces displacement steps of 1.2×10^{-3} and 1.8×10^{-3} Å, respectively, were used as the convergence criteria. Vibrational frequencies were determined by computing the second derivatives of the energy with respect to the nuclear coordinates and transforming the obtained results into mass-weighted coordinates. Density fitting was introduced by applying

Auto keyword and energies were corrected for BSSE using the counterpoise correction [11,12].

3. Results and discussion

In the paper, the performance of DFT BLYP, B3LYP and PW91 methods has been studied. Tables 1–5 present a comparison of theoretical and experimental vibrational spectra and scaling factors, respectively. The effect of the density fitting and counterpoise corrections has been studied and the comparison of the results is summarized in Tables 5 and 6. The influence of the vibrational spectra on the thermochemical properties of formic acid dimer has been investigated (see Table 7) and, finally, the efficiency of different computation strategies has been discussed. Vibrational frequencies and intensities are given in cm^{-1} and $km\ mol^{-1}$, respectively.

3.1. Vibration spectra and scaling factors

Tables 1–5 present vibrational spectra of and scaling factors for H_2SO_4, $(H_2SO_4)(H_2O)$, CH_2O_2 and $(CH_2O_2)_2$ calculated using B3LYP, BLYP and PW91 functionals. Comparison of theoretical results with experimental data shows that deviation of commonly used hybrid B3LYP from experimental data remains considerable even if large basis sets such as 6-311++G(3df,3pd) and aug-cc-pvtz are used. The performance of PW91 and BLYP, which are in better agreement with experiments than B3LYP, is nearly identical. Scaling factors λ [7] for theoretical harmonic vibrational frequencies weighted to high and low frequencies were calculated by minimizing residuals

$$\Delta = \sum_i^{all} (\lambda \omega_i - v_i)^2, \tag{1}$$

and

$$\Delta = \sum_i^{all} \left(\frac{1}{\lambda \omega_i} - \frac{1}{v_i} \right)^2, \tag{2}$$

respectively. ω_i and v_i are ith theoretical harmonic and ith experimental fundamental frequencies (in cm^{-1}), respectively. Scaling factors weighted to high frequencies for B3LYP for ($\sim$0.96–0.98) derived from experimental fundamentals and present theoretical results are slightly higher than those given by Scott and Radom [7]. Scaling factors obtained using PW91 and BLYP are typically close to unity and a considerable (1–3%) difference has been observed for some basis sets in the case of formic dimer only. It is important to notice that difference in the scaling factors for weighted to high and low frequencies may be significant. Scaling factors for the low-frequencies region for sulfuric acid monohydrate and formic acid dimer obtained by all the B3LYP, BLYP and PW91 significantly deviate from unity and scaling factors for B3LYP/6-31G(d) and BLYP/6-31G(d) dramatically deviate from those obtained in Ref. [7]. While in the case of sulfuric acid monohydrate this deviation could be attributed to the insufficient density of the