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The study of performance of DFT functional for van der Waals interactions

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ABSTRACT

In the present study, the performance of different exchange–correlation functional of DFT for van der Waals molecules has been studied by optimising the structures with augmented cc-pVTZ basis sets. The structural parameters along with vibrational frequencies and rotational constants were calculated using 15 different exchange–correlations functional for 10 molecules and compared with experimental results. Further the interaction energies (basis set superposition error corrected) were calculated using different DFT exchange–correlation functional and compared with MP2 and CCSD(T) method. The error analysis was carried out using MUE (mean unsigned error) and MAPE (mean absolute percentage error) statistical methods.

1. Introduction

Historically van der Waals interaction was used to explain the non-ideal behaviour of noble gases which arises due to long range correlations, because of R^{-6} term and instantaneous dipole fluctuations. This interaction is electrostatic in nature and is found to play an important role in many chemical systems [1,2]. For example, they control the structure of DNA and protein, the packing of crystals and orientation of molecules on the surface. Several theoretical models [3,4] have been constructed to study such weak interactions. However accurate description of weak interactions still remains elusive. The construction of accurate potential functions for the van der Waals interaction by molecular orbital methods is a difficult task. The Kohn–Sham equation of density functional theory (DFT) is an inexpensive alternative to the ab initio correlated methods. The performance of the above equation for the weak interactions is not so good as electron correlated methods of ab initio theory. Many of the DFT functionals are not designed to treat dispersion interactions more precisely, which are sometimes dominant in chemical systems. Recently many functional have been developed to treat van der Waals interactions in the DFT method. The rigorous dispersion functional derived from the first principles have been used for the empirical corrections or parameterizations. A comprehensive study of such methods have been reported by Johnson et al. [5] Truhlar et al. [6,7] Becke and Kannemann [8].

In this article, we have investigated the performance of the new DFT functionals which were developed recently to study the van der Waals interactions present in 10 complexes and compare with the available results of experiment and electron correlated method. We have considered ten heterogeneous van der Waals molecules comprising of two OCS–CO_2 complex, two N_2O–OCS complex, two N_2O dimer, two OCS dimer and two CO_2–N_2O complex which were studied experimentally. The above mentioned molecules were studied using 15 different hybrid DFT functionals (M05, M05-2x, M06, M06-2x, M06-HF, M06-L, B97D, ωB97, ωB97x, ωB97xD, HSEh1PBE, PBE1PBE, BMK, B3LYP and B3LYP-D) [9,7,10–20]. The structural parameters were compared with experimental values [21–24] and MP2 method. The basis set superposition error [25] (BSSE) corrected interaction energies were calculated and compared with MP2 and CCSD(T) [26] values. The error analysis has been carried out using mean unsigned error (MUE) and mean percentage error (MAPE) for all the functional. We believe, that the results of this study be valuable while choosing DFT functional for performing MO calculations for larger molecules with van der Waals interaction.

2. Computational details

All the selected molecules were optimized to their global minima using fifteen different hybrid DFT functional (M05, M05-2x, M06, M06-2x, M06-HF, M06-L, B97D, ωB97, ωB97x, ωB97xD, HSEh1PBE, PBE1PBE, BMK, B3LYP, and B3LYP-D) [9,7,10–20], along with MP2 method using aug-cc-pVTZ [27,28] basis set and the same has been verified by the frequency calculations. The interaction energies calculated were corrected for basis set superposition error (BSSE). Further, single point calculation were carried out using CCSD(T) method [26] with aug-cc-pVTZ basis set with MP2 geometries. The results of CCSD(T) calculations were used for cal-

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culating interaction energy (with and without BSSE). All the above calculations were carried out using Gaussian 09 [29] programme.

3. Results and discussion

All the optimized van der Waals complexes using DFT and MP2 methods along with labelling are shown in Fig. 1. The optimized van der Waals bond lengths along with bond angles calculated using 15 DFT functional and MP2 method for the ten molecules are given in Table 1. The other bond lengths and bond angles of the complexes are presented in Table S1 (Supplementary material). The value of van der Waals bond lengths calculated by DFT functional indicate a difference in the range of 0.006–0.5 Å from the experimental values whereas the MP2 values range from 0.01 Å to 0.4 Å. Among the DFT functional ωB97x, M05, M06, B3LYP-D gave consistent values closer to the experimental values. B3LYP-D functional which includes empirical correction for dispersion predicts bond length values very close to experimental values. In contrast, B3LYP functional shows larger deviation in bond length values (~1.1 in the case of OCS–CO_2 complex). Similarly in the case of bond angles, the results of the DFT functional deviate from the experimental values in the range of 3–45°. The B3LYP functional was found to produce the largest deviation among the bond angles. The ωB97x, M06-L, B97D, B3LYP-D series of functional were found to be better than B3LYP functional, had a maximum deviation of about 10°. Other DFT functional did not predict consistent values for few systems of molecules making difficult to predict the common trend. MP2 method produced a difference of 7° and 8° providing reliability and consistency in predicting bond angles.

We further compared and investigated the stretching frequencies obtained from the experimental methods with our selected functional and the values are presented in Table S2. The experimental stretching frequencies were observed between 1200 cm^{-1} to 2350 cm^{-1} for the bonds comprising C–O, N–O, N–N atoms. Further to have a precise look on the deviation of frequency values from experimental results an frequency shift table with shift values calculated as difference between experimental and calculated values have been presented in Table 2. From the table it is evident

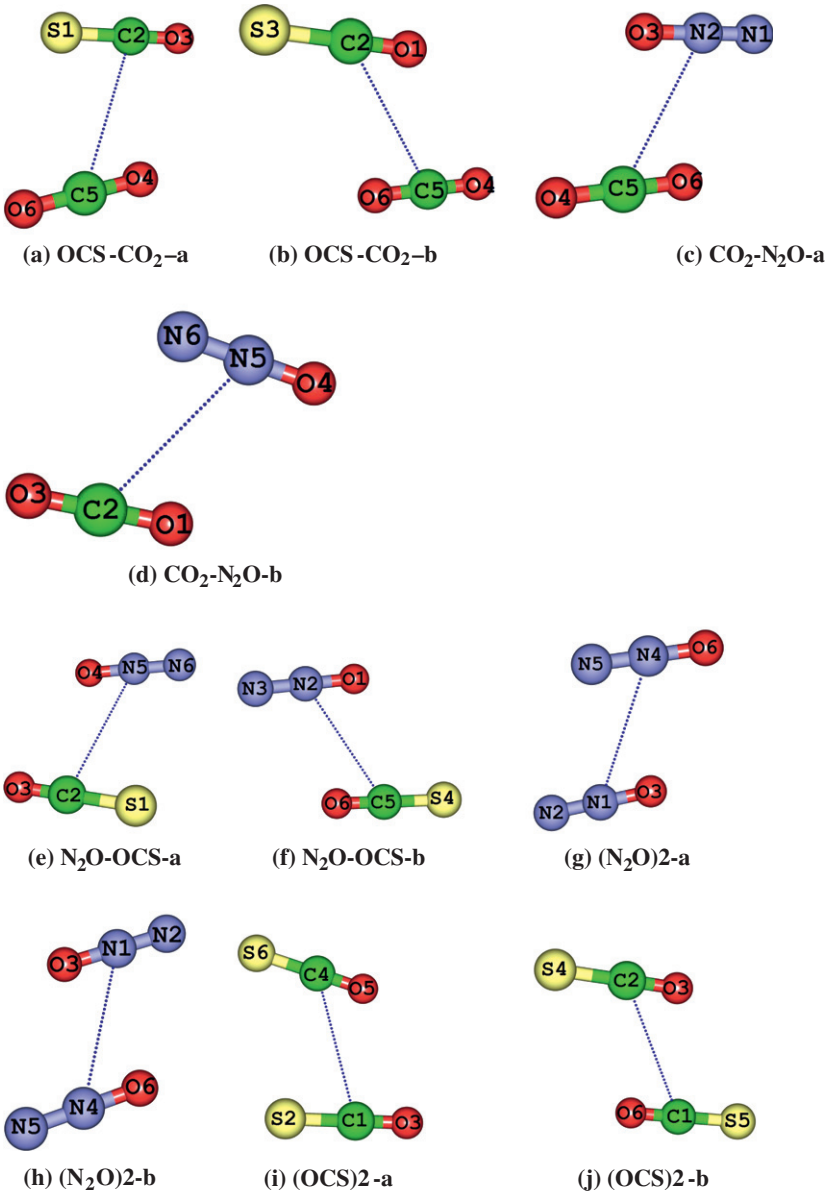

Fig. 1. The optimized structures of (a) OCS–CO_2-a, (b) OCS–CO_2-b, (c) CO_2–N_2O-a, (d) CO_2–N_2O-b, (e) OCS–N_2O-a, (f) OCS–N_2O-b, (g) $(N_2O)2$-a, (h) $(N_2O)2$-b, (i) (OCS)2-a, and (j) (OCS)2-b in MP2/aug-cc-pVTZ level of theory.