Benchmark study of structural and vibrational properties of scandium clusters

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ABSTRACT

Geometries and most stable spin states of Sc_2 and Sc_3 are studied through coupled cluster CCSD(T) calculations. The CCSD(T) calculations at dunning series basis sets (aug-cc-pVDZ, aug-cc-pVTZ and aug-cc-pVQZ) have been performed in order to analyze the stable structure and spin state of the Sc_2 and Sc_3. Then, a series of diverse DFT methods at different basis sets (6-31G (d), LANL2DZ and LANL2MB) are assessed for structural and vibrational properties in order to propose low cost accurate alternative to CCSD(T). Among all the employed DFT methods, BPV86/LANL2MB delivered better results for structural and frequency analysis. On the basis of better agreement, BPV86/LANL2MB is taken for the structural and vibrational analysis of the higher cluster n = 4–14. The vibrational analysis for higher clusters of scandium is reported for the first time.

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1. Introduction

Clusters are aggregates or assemblies of atoms that have intermediate size between bulk and molecule. The study of cluster is said to be "seeing both ends from the middle" [1]. Transition metal clusters are ubiquitous in surface (catalytic, adsorption), optical, magnetic and conductive properties [2]. These intriguing properties of clusters are due to their quantum effects, significant size, huge surface to volume ratio and variety in electronic configurations, geometric representation and spin states [3]. Cluster chemistry has witnessed an exponential growth from experimentalist and theoretician over the last few decades.

Important features of cluster are their surfaces and interfaces, which are characterized by the vibrational responses. The vibrations are important to predict the fundamental physiochemical phenomenon. The distinctive signatures of surfaces then tuned to model molecular electronics, sensing devices, catalysis etc. [4]. Vibrations are the fingerprints of chemical bond, therefore, the investigation of vibrational frequency is necessary and helpful for unravelling the binding sites for adsorption or for the positioning of different groups. For accurate vibrational analysis, a good estimation of bond length is necessary. Bond length is harnessed to many properties like bond energies and other non-bonding interaction of

system [4].

Scandium is the lightest element among transition metals. Due to high strength and melting point, scandium is suitable for technological applications [5]. Besides bulk studies Sc clusters had been the subject of several experimental and theoretical studies [6]. Experimental evidence related to vibrational frequency (239 cm^{-1}) for scandium dimer is already demonstrated by Moskovits, Limm and DiLella by using matrix isolation resonance Raman spectroscopy, however the limitations of bond length and spin states are there [7].

Wang *et al.* demonstrated that quintet is the most stable spin state for Sc_2 followed by triplet. The Sc–Sc bond length is 2.64 Å and vibrational frequency is 261.0 cm^{-1} [8]. However, information about singlet state of dimer, its vibrational frequency and bond length were missing. On contrary, Bhunia *et al.* demonstrated through DFT calculations that singlet is the most stable spin state with bond length 2.24 Å. The quintet spin state is shown as next stable spin state. The energy difference between singlet and quintet spin state is 0.02 eV [9]. But, report of Bhunia *et al.* fails to correlate the vibrational frequency with any of the spin state. In another approach, Akeby *et al.* has shown by using CASSCF and IC-ACPF (internally contracted averaged coupled pair functional) at ANO (atomic natural orbital) basis set that bond length range of Sc_2 is 2.5–2.8 Å [10].

According to Biczysko, conjunction of CCSD(T) (coupled cluster single, double and perturbative inclusion of triple excitations) with ζ inclusive basis set gives results for vibrational frequency in the

range of 10–15 cm^{-1} [11]. Indeed, one of the challenging task is to predict the most stable spin state and vibrational frequency of scandium dimer. The intent of our studies is to relate the experimental frequency results (239.9 cm^{-1}) to the specific spin state. To untangle these lingering shortcomings, we have performed structural and vibrational analysis of Sc$_2$ at CCSD(T) level in combination with at least triple-ζ basis set. Then, different DFT methods were employed for Sc$_2$ and Sc$_3$ cluster to find an accurate and cost effective alternative to CCSD(T). One of the employed method with better agreement at CCSD(T) was carefully chosen to study the larger clusters. DFT methods are better choice for transition metals to anticipate molecular properties. These systems sometimes reveal degenerate or near degenerate electronic states, which is a challenge for methods based on wave function. With the increase use of DFT methods in quantum chemistry, benchmarking also originate as an intrinsically important task.

For the confirmation of ground states, a number of different possible spin states of each cluster were investigated without any symmetry constraint. We first time report the harmonic vibrational frequency of Sc$_n$ (n = 2–14) at most promising and efficient method along with benchmarking studies of scandium dimer.

2. Computational details

All the calculations are performed with GAUSSIAN 09 [12]. The results are analyzed by Gaussview 5 [13]. Ab initio couple cluster CCSD(T) method [14], indicated by iterative inclusion of single and double excitations with perturbative inclusion of triple excitations have been utilized to model the geometric parameters of Sc$_2$ at augmented dunning series basis sets (aug-cc-pVDZ, aug-cc-pVTZ and aug-cc-pVQZ) [15,16]. Furthermore, by taking these values as reference, the optimization and frequency analysis of Sc dimer and trimer at different spin states are carried out at several DFT methods such as local density approximation (LDA) LSDA (SVWN) [17,18], generalized gradient approximation (GGA) methods (G96LYP [19,20], MPW1PW91 [21] and MPWLYP) hybrid GGA functionals (BPV86 [18], B3LYP [20,22], B3PW91 [22], HSEH1PBE [23], PBEPBE [24], B98 [25], X3LYP [26] and B971 [27]) meta GGA methods (TPSSTPSS [28], BB95, BMK [29]) and Global Meta hybrid GGA functionals (M05 [30,31], M05-2X [32] and B1B95). Other functionals such as HCTH [27] (pure GGA functional), CAM-B3LYP [33] (range separated hybrid Meta GGA functional), ωB97XD [34] (range separated hybrid), B-LYP [20,35] (GGA exchange correlation function), THCTHH [36] and TPSSV5LYP [18,20,28] have also been used. All these conventional methods are computed with three different basis sets including 6-31G (d) [37], Los Alamos minimal basis type (LANL2MB [38]) and Los Alamos double-zeta type (LANL2DZ). Standard primitive Gaussian basis set LANL2DZ have been used to reduce computational cost by expanding 3d^1, 4s^2 and other core electrons are represented by effective core potential [39]. Structural optimizations of higher clusters Sc$_n$ (n = 4–14) have been performed by finding local minimum on PES (potential energy surface) and without any symmetry constraints at BPV86, Burke and Perdew's 1986 functional with correlation replaced by Vosko et al. [18] with LANL2MB basis set. Then their optimized geometries are confirmed by frequency calculations.

3. Results and discussion

First, the stable spin state of the Sc dimer is determined by optimization of different spin states of Sc$_2$ at the gold standard method CCSD(T). Second, we assessed performance of diverse DFT methods for Sc$_2$ to propose the accurate alternative to CCSD(T) for structural and frequency calculations. Then, the same procedure is adopted for Sc$_3$. After evaluating the low cost DFT method the

vibrational analysis of Sc$_{4-14}$ is performed at the accurate DFT method.

3.1. Benchmark calculations

The literature is inconsistent regarding the most stable spin states of the scandium dimer. For instance, Jinlan wang et al. demonstrated by using DFT at PBE/DSPP/DND that the quintet spin state is the most stable spin state. Triplet state is shown next stable state for Sc$_2$ which lies 0.027 eV higher than Sc$_2$ quintet [8]. On the other hand Snehasis Bhunia et al. demonstrated through DFT calculations at PBEPBE/LANL2DZ level of theory that singlet spin state is energetically most preferred spin state. Quintet spin state is shown as the next most stable state for Sc$_2$ which lies 0.02 eV higher than Sc$_2$ singlet [9]. This negligible difference of energies between singlet and quintet reveals that both of these spin states can co-exist in quite comparable quantity. To explicit these lingering shortcomings, we use CCSD(T) with different basis sets (aug-cc-pVDZ, aug-cc-pVTZ, aug-cc-pVQZ) for optimization and frequency analysis of Sc dimer at singlet and quintet states.

3.1.1. Optimizations
Optimized energies and bond length are represented in Table 1. Results shows that the energy of the singlet state scandium dimer at CCSD(T)/aug-cc-pVDZ level of theory is −0.076 eV lower than quintet at the same level of theory. Calculations at even higher level indicates that the energy difference between singlet and quintet further increases. At CCSD(T)/aug-cc-pVTZ, the quintet spin state is −0.212 eV higher in energy then singlet spin state. Likewise, the energy of the singlet spin state at CCSD(T)/aug-cc-pVQZ is −0.24 eV lower than the quintet spin state. From these results, we can conclude safely that the energy for the singlet spin state is lower than the quintet spin state. These energy values help us to untangle the puzzle of most stable spin state for Sc dimer. All the energy values, we encountered consequently support the result that singlet spin state for Sc dimer is more stable than quintet spin state.

At CCSD(T)/aug-cc-pVDZ level of theory, optimized bond length of Sc dimer in singlet state is 2.40 Å. Similarly, at CCSD(T)/aug-cc-pVTZ and CCSD(T)/aug-cc-pVQZ level of theory 2.39 Å and 2.38 Å are optimized bond lengths respectively. Computed bond length range 2.38 Å–2.40 Å at CCSD(T) is somewhat different from already reported range (2.56–2.64 Å) [8].

Similarly, for quintet spin state the Sc–Sc bond length at CCSD(T)/aug-cc-pVDZ/aug-cc-pVTZ/aug-cc-pVQZ are 2.575 Å, 2.551 Å and 2.550 Å (the values in three places of decimal are shown just to illustrate the difference at different levels) respectively. These values indicate slight decrease in bond length with increase in the zeta value in the basis set.

3.2. Evaluation of DFT methods for bond lengths (Sc$_2$)

Next intent of our studies is to analyze different DFT methods for their ability to reproduce geometric parameters. All the results related to bond lengths and frequency are depicted in Table 2. A number of DFT methods have been employed to evaluate their performance in properly modelling the geometric parameters such as bond length. These methods include local density approximation (LDA) LSDA (SVWN), generalized gradient approximation (GGA) methods (G96LYP, MPWPW91 and MPWLYP), hybrid GGA functionals (BPV86, B3LYP, B3PW91, MPW1PW91, HSEH1PBE, PBEPBE, B98, X3LYP and B971) meta GGA methods (TPSSTPSS, BB95, BMK) and global meta hybrid GGA functionals (M05, M05-2X and B1B95). Some more functionals such as HCTH (pure GGA functional), CAMB3LYP (rang e separated hybrid meta GGA functional), ωB97XD (range separated hybrid), B-LYP (GGA exchange correlation