



Quantum chemical calculations of Cr₂O₃/SnO₂ using density functional theory method

K RACKESH JAWAHER¹, R INDIRAJITH¹, S KRISHNAN^{2,*}, R ROBERT³ and S JEROME DAS⁴

¹Department of Physics, B.S. Abdhr Rahman Crescent University, Chennai 600 048, India

²Department of Physics, Ramakrishna Mission Vivekananda College (Autonomous), Mylapore, Chennai 600 004, India

³Department of Physics, Government Arts College for Men, Krishnagiri 635 001, India

⁴Department of Physics, Loyola College, Chennai 600 034, India

*Corresponding author. E-mail: skrishnanjp@gmail.com

MS received 7 April 2017; revised 4 October 2017; accepted 10 October 2017; published online 15 February 2018

Abstract. Quantum chemical calculations have been employed to study the molecular effects produced by Cr₂O₃/SnO₂ optimised structure. The theoretical parameters of the transparent conducting metal oxides were calculated using DFT/B3LYP/LANL2DZ method. The optimised bond parameters such as bond lengths, bond angles and dihedral angles were calculated using the same theory. The non-linear optical property of the title compound was calculated using first-order hyperpolarisability calculation. The calculated HOMO–LUMO analysis explains the charge transfer interaction between the molecule. In addition, MEP and Mulliken atomic charges were also calculated and analysed.

Keywords. Cr₂O₃/SnO₂; density functional theory study; nonlinear optics; molecular electrostatic potential.

PACS Nos 81.05.Hd; 81.07.Bc; 81.07.Nb

1. Introduction

Tin oxide (SnO₂) is a very important n-type oxide and wide band gap (3.6 eV) semiconductor [1]. Its good electrical, optical and electrochemical properties are exploited in solar cells [2], high-capacity lithium-storage [3], solid-state chemical sensors [4] and catalytic active materials [5]. Doped SnO₂ nanostructures show strong electrical properties, and they are optically transparent. The coexistence of electrical conductivity and optical transparency is achieved by selecting a wide-gap metal oxide and incorporating native or substitutional dopants.

Cr₂O₃ is a wide band gap ($E_g = 3.4$ eV) p-type semiconductor with corundum structure [6], which can be used in optical and electronic devices and shows high electrical conductivity with reasonable levels of electron transfer. It can be used as heterogeneous catalysts [7–9], coating materials, wear resistant materials [10,11], advanced colorants [12], pigments [13] and solar energy collectors [14].

In previous literature, Singh and Tripathi [15] reported the first principle study of TiO₂ using density functional

theory (DFT). Stashans *et al* [16] reported the DFT study of Cr-doped SnO₂ materials using DFT+U method to find out the DOS of the material. In this paper, we calculate theoretical parameters such as bond parameter, nonlinear optical (NLO) property, electrostatic potential surface (EPS), HOMO–LUMO energy level, Mullikan atomic charges using DFT/B3LYP/LANL2DZ method in solid phase.

2. Synthesis procedure

In a typical synthesis process, 0.24 M of SnCl₂·2H₂O and 0.3 M of C₂H₂O₄·2H₂O were dissolved in 20 ml of ultrapure water under continuous stirring. Subsequently, 0.1 M of CrCl₃·6H₂O and 0.3 M of C₂H₂O₄·2H₂O were dissolved in 20 ml of ultrapure water in a separate beaker. Further, both these solutions were mixed together under continuous stirring for 2 h. After that, 1.8 g of dextrin white solution was gradually added. Finally, the precipitated solution was collected and alternatively rinsed several times with anhydrous ethanol and ultrapure water by centrifugation. The resultant product

Table 1. The bond parameters of Cr₂O₃/SnO₂.

Bond parameters	B3LYP/LANL2DZ
<i>Bond lengths (Å)</i>	
Cr1–Cr2	2.0223
Cr1–O3	1.6498
Cr1–O4	1.5424
Cr1–O5	1.6422
Cr2–O3	2.3316
Cr2–O5	2.3439
O3–O4	1.6375
O3–O8	1.5556
O4–O5	1.6543
O4–Sn6	1.4315
O5–O7	1.5532
Sn6–O7	2.1813
Sn6–O8	2.189
<i>Bond angles (°)</i>	
Cr2–Cr1–O4	120.0466
O3–Cr1–O5	93.1899
O3–Cr2–O5	61.532
Cr1–O3–O8	157.0068
Cr2–O3–O4	101.1354
Cr2–O3–O8	129.5284
O4–O3–O8	101.8917
Cr1–O4–Sn6	144.6367
O3–O4–O5	93.1927
O3–O4–Sn6	96.0235
O5–O4–Sn6	94.4786
Cr1–O5–O7	157.8646
Cr2–O5–O4	100.1133
Cr2–O5–O7	129.9447
O4–O5–O7	102.6914
O4–Sn6–O7	85.1423
O4–Sn6–O8	83.6811
O7–Sn6–O8	123.3739
O5–O7–Sn6	72.7051
O3–O8–Sn6	73.0198
<i>Dihedral angles (°)</i>	
O5–Cr1–O3–O8	–39.0117
Cr2–Cr1–O4–Sn6	–3.5711
O3–Cr1–O5–O7	40.5732
O5–Cr2–O3–O4	–13.6975
O5–Cr2–O3–O8	102.069
O3–Cr2–O5–O4	13.5095
O3–Cr2–O5–O7	–102.6238
Cr2–O3–O4–O5	17.1808
Cr2–O3–O4–Sn6	112.0297
O8–O3–O4–O5	–117.5962
O8–O3–O4–Sn6	–22.7473
Cr1–O3–O8–Sn6	0.7195
Cr2–O3–O8–Sn6	–100.2009
O4–O3–O8–Sn6	15.2442
O3–O4–O5–Cr2	–17.0288
O3–O4–O5–O7	118.099
Sn6–O4–O5–Cr2	–113.3321
Sn6–O4–O5–O7	21.7957
Cr1–O4–Sn6–O7	–59.6724
Cr1–O4–Sn6–O8	64.7208

Table 1. *Continued.*

Bond parameters	B3LYP/LANL2DZ
O3–O4–Sn6–O7	–108.6973
O3–O4–Sn6–O8	15.6959
O5–O4–Sn6–O7	–15.0026
O5–O4–Sn6–O8	109.3906
Cr1–O5–O7–Sn6	–2.09
Cr2–O5–O7–Sn6	100.3072
O4–O5–O7–Sn6	–14.7404
O4–Sn6–O7–O5	16.7316
O8–Sn6–O7–O5	–62.4175

was dried in hot air oven at 80°C for 24 h. Transformation of Sn(OH) and Cr₂(OH)₆ to SnO₂ and Cr₂O₃ nanostructures was carried out in air at 550°C for 4 h.

3. Computational details

Quantum chemical calculations were performed using the Gaussian 03W program package [17]. Geometry optimisations of the complex have been performed using DFT method on the B3LYP/LANL2DZ basis set [18–20]. In this study, the theoretical parameters such as bond parameters, NLO, HOMO–LUMO, MEP and Mulliken atomic charges of transition metal oxide materials are calculated.

4. Results and discussion

4.1 Molecular geometry

The optimised geometrical parameters such as bond lengths, bond angles and dihedral angles are calculated by DFT method using B3LYP/LANL2DZ level and are listed in table 1. The optimised molecular structure of Cr₂O₃/SnO₂ and the atom numbering scheme are shown in figure 1. The title compound consists of 8 atoms. The exact molecule single crystal XRD data are not yet available.

The bond distances of Cr1–O3 and Cr1–O5 are calculated to be 1.6498 and 1.6422 Å, respectively. But, Cr1–O4 length is 1.5424 Å, which is negatively 0.1 Å deviated to the above-mentioned values. Cr1–O3 and Cr1–O5 have these values because they have the same plane. The values of bond angles and dihedral angles were well supported with optimised structure as the title material is planar.

4.2 Non-linear optical properties

Non-linear optical (NLO) properties are at the forefront of current research because of their importance in providing key functions of frequency shifting,

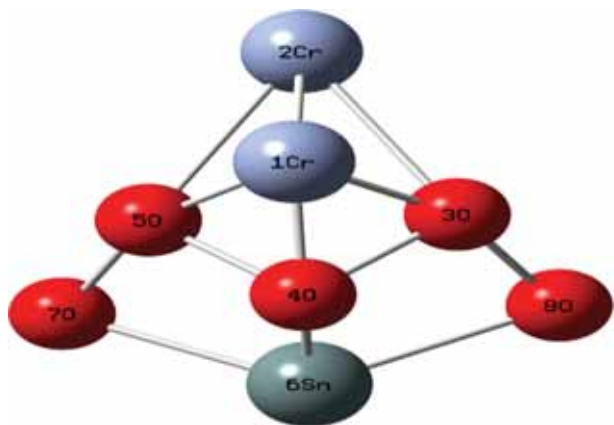


Figure 1. Optimised structure of Cr₂O₃/SnO₂.

Table 2. The NLO measurements of Cr₂O₃/SnO₂.

Parameters	B3LYP/LANL2DZ
Dipole moment (μ) (Debye)	
μ_x	2.3059308
μ_y	0.1829876
μ_z	-1.6462691
μ	2.83919 Debye
Hyperpolarizability (β_0) $\times 10^{-30}$ esu	
β_{xxx}	3662.9184715
β_{xxy}	92.4622612
β_{xyy}	1128.7633873
β_{yyy}	327.8624954
β_{xxz}	-976.5173263
β_{xyz}	-29.8819755
β_{yyz}	-486.5493234
β_{xzz}	1055.5533773
β_{yzz}	57.3969287
β_{zzz}	-1668.6691516
β_0	57.45371×10^{-30} esu

optical modulation, optical switching, optical logic and optical memory for emerging technologies in areas such as telecommunications, signal processing and optical interconnections [21–24]. The first-order hyperpolarisabilities of Cr₂O₃/SnO₂ were calculated using DFT/B3LYP/LANL2DZ level, based on the finite field approach. In the presence of an applied electric field, the energy of a system is a function of the electric field. The first-order hyperpolarisability is a third rank tensor that can be described by a $3 \times 3 \times 3$ matrix. The 27 components of the 3D matrix can be reduced to 10 components due to Kleinman symmetry [25]. The total static dipole moment μ , the polarisability α_0 and first-order hyperpolarisability β_0 , using the x, y, z components are defined as

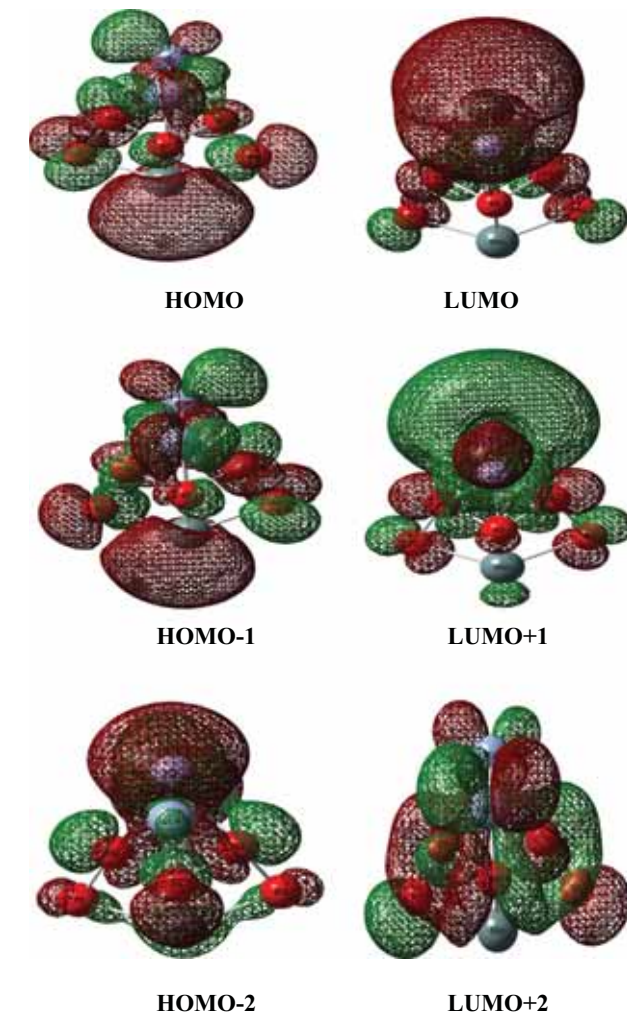


Figure 2. Frontier molecular orbital diagrams of Cr₂O₃/SnO₂.

$$\mu = (\mu_x^2 + \mu_y^2 + \mu_z^2)^{1/2},$$

$$\alpha_0 = \frac{\alpha_{xx} + \alpha_{yy} + \alpha_{zz}}{3},$$

$$\beta_0 = (\beta_x^2 + \beta_y^2 + \beta_z^2)^{1/2}.$$

The NLO properties of Cr₂O₃/SnO₂ have been calculated using B3LYP/LANL2DZ method. The dipole moment (μ) and first-order hyperpolarisability (β_0) are calculated as 2.83919 Debye and 57.45371×10^{-30} esu, respectively. The first-order hyperpolarisability (β_0) of the title molecule is greater than that of ZnO material (1.06371×10^{-30}) and the hyperpolarisability of ZnO is about 56.39×10^{-30} esu [26]. Hence, the molecule might have good NLO activity [27,28]. The dipole moment and first-order hyperpolarisability of Cr₂O₃/SnO₂ are given in table 2.

Table 3. The frontier molecular orbital energies of Cr₂O₃/SnO₂.

Orbitals	Energies (a.u.)	Energies (eV)
HOMO-2	-0.21330	-5.80389
HOMO-1	-0.20029	-5.44989
HOMO	-0.19953	-5.42921
Energy gap	0.06915	1.88157
LUMO	-0.13038	-3.54763
LUMO+1	-0.11978	-3.25921
LUMO+2	-0.11428	-3.10955

4.3 HOMO–LUMO analysis

The HOMO–LUMO and frontier orbital gap help to analyse the chemical reactivity and kinetic stability of the molecules and are important parameters in quantum chemistry [25]. The 3D plots of the frontier molecular orbital energies (FMO) of Cr₂O₃/SnO₂ molecule is shown in figure 2 and their energies are listed in table 3. Gauss-Sum 2.2 Program [29] was used to calculate group contributions to the molecular orbitals (HOMO and LUMO) and prepare the density of the state (DOS) as shown in figure 3. The positive and negative phases are red and green, respectively. It can be seen from the plots that HOMO levels are spread over the entire molecule in the ground state and all positive and negative phases are distributed to the present material. The LUMO of the first excited state is almost uniformly distributed over the molecule without Sn material. The energy gap of HOMO–LUMO explains the eventual

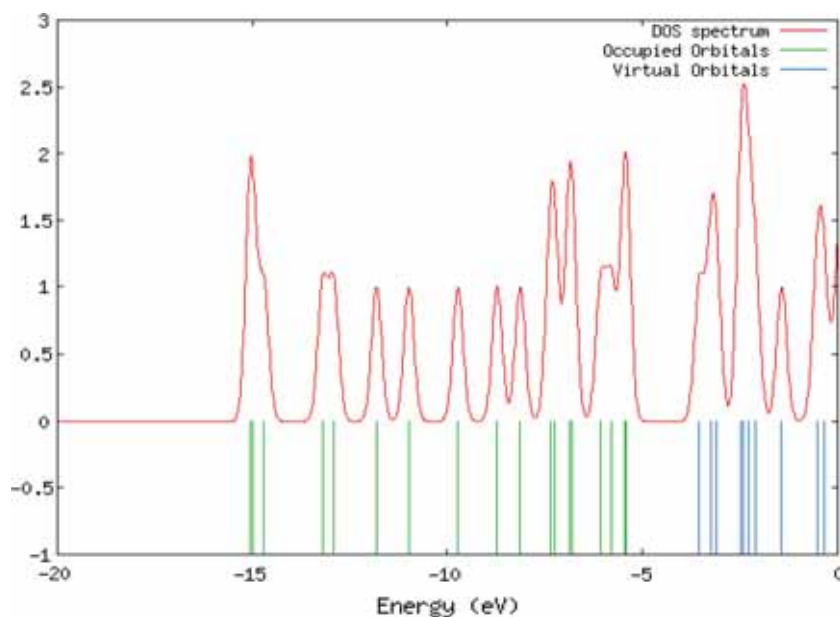
charge transfer interaction within the molecule. The frontier orbital energy gap in Cr₂O₃/SnO₂ is found to be 1.88158 eV. The decrease in energy gap between HOMO and LUMO explains the good NLO properties of the title molecule.

4.4 MEP analysis

The molecular electrostatic potential (MEP) is related to the electronic density and is very useful to understand the sites for electrophilic attack and nucleophilic reactions as well as hydrogen-bonding interactions [30–32]. The MEP was calculated using the DFT/B3LYP/LANL2DZ method and is shown in figure 4. Generally, electrophilic reactivity shown by red colour indicates the negative regions of the molecule and the nucleophilic reactivity shown by blue colour indicates the positive regions of the molecule. In this study, the MEP surfaces are fully surrounded by green colour due to the zero potential order. In addition, the ESP, total density and alpha density surface of the molecule is shown in figure 4.

4.5 Mulliken charge analysis

The total atomic charges of Cr₂O₃/SnO₂ are obtained by Mulliken [33] using DFT/B3LYP/LANL2DZ method and the charges are listed in table 4. The corresponding Mulliken's plot is shown in figure 5 and it gives us information about the charge shifts relative to the title molecule. In this case, the positive charge was found at Sn (Sn6: 1.057562 a.u.) and Cr (Cr1: 0.64124 a.u.

**Figure 3.** DOS spectrum of Cr₂O₃/SnO₂.

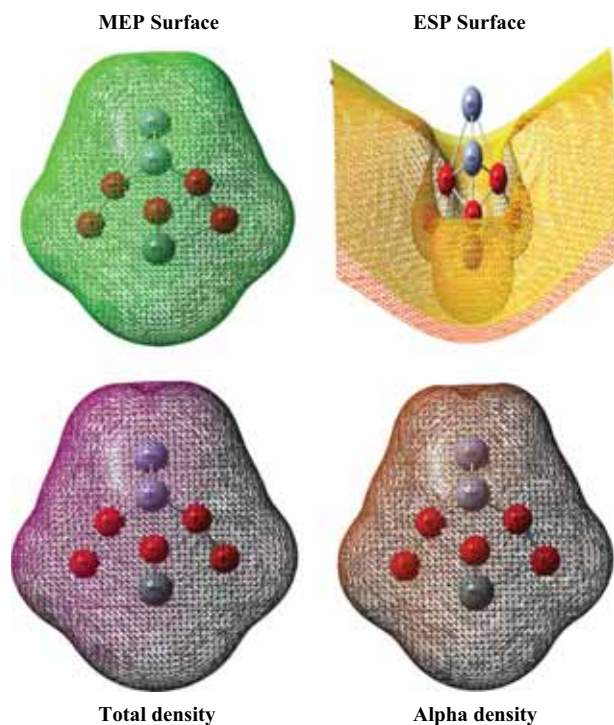


Figure 4. MEP, ESP, alpha density and total density surfaces of $\text{Cr}_2\text{O}_3/\text{SnO}_2$.

Table 4. The Mulliken atomic charges of $\text{Cr}_2\text{O}_3/\text{SnO}_2$.

Atoms	Charges
1Cr	0.641124
2Cr	0.558465
3O	-0.432991
4O	-0.715168
5O	-0.443296
6Sn	1.057262
7O	-0.331563
8O	-0.333833

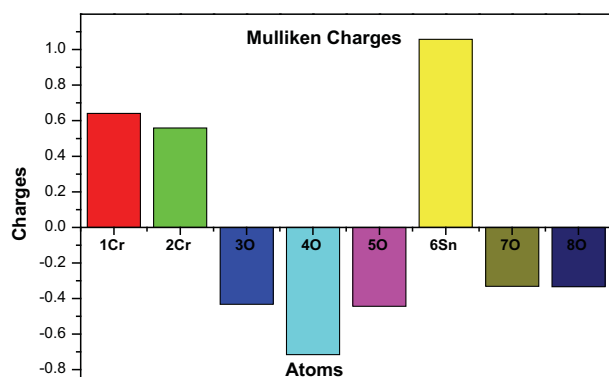


Figure 5. Mulliken atomic charge plot of $\text{Cr}_2\text{O}_3/\text{SnO}_2$.

and Cr2: 0.558465 a.u.). The high positive charge at Sn6/1.057262 a.u. is due to the effect of rare earth materials compared to Cr metal. All the oxygen atoms (O3, O4, O5, O7 and O8) have negative charges, because oxygen is electronegative.

5. Conclusion

The quantum chemical calculations were used for the first time to calculate the theoretical parameters of $\text{Cr}_2\text{O}_3/\text{SnO}_2$ material. The optimised geometrical parameters were calculated using DFT method. The bond distance of metal–oxygen is positively (0.5 \AA) deviated to oxygen–oxygen bonds. As a consequence, the metal–oxygen bond has large ionic character compared to oxygen–oxygen bond. The β_0 value shows the good NLO activity of the title molecule. The energy gap of HOMO–LUMO is only 1.88157 eV, which explains the eventual charge transfer occurring within the molecule and why and it has more optical property. MEP gives the visual representation of the chemically active sites of atoms due to the zero potential of the present system. The Mulliken atomic charges of $\text{Cr}_2\text{O}_3/\text{SnO}_2$ has also been calculated and plotted.

References

- [1] S O Kucheyev, T F Baumann, P A Sterne, Y M Wang, T van Buuren and A V Hamza, *Phys. Rev. B* **72**, 035404 (2005)
- [2] H Song, K H Lee, H Jeong and S H Um, *Nanoscale* **5**, 1188 (2013)
- [3] R Yang, Y G Gu, Y Q Li, J Zheng and X G Li, *Acta Mater. J.* **58**, 866 (2010)
- [4] J Zhang, S R Wang, Y Wang, M J Xu, H J Xia, S M Zhang, W P Huang, X Z Guo and S H Wu, *Sens. Actuators B* **139**, 369 (2009)
- [5] H L Zhang and C G Hu, *Catal. Commun.* **14**, 32 (2011)
- [6] R Hao, J Yuan and Q Peng, *Chem. Lett.* **35**, 1248 (2006)
- [7] T V M Rao, Y Yang and A Sayari, *J. Mol. Catal. A: Chem.* **301**, 152 (2009)
- [8] T V M Rao, E Zahidi and A Sayari, *J. Mol. Catal. A: Chem.* **301**, 159 (2009)
- [9] G Wang, L Zhang, J Deng, H Dai, H He and C Tong, *Appl. Catal. A* **355**, 192 (2009)
- [10] X Pang, K Gao, F Luo, Y Emirov, A A Levin and A A Volinsky, *Thin Solid Films* **517**, 1922 (2009)
- [11] X Hou and K L Choy, *Thin Solid Films* **516**, 8620 (2008)
- [12] D W Kim, S I Shin, J D Lee and S G Oh, *Mater. Lett.* **58**, 1894 (2004)
- [13] P Li, H B Xu, Y Zhang, Z H Li, S L Zheng and Y L Bai, *Dyes and Pigments* **80**, 287 (2009)

- [14] V Teixeira, E Sousa, M F Costa, C Nunes, L Rosa, M J Carvalho, M Collares-Pereira, E Roman and J Gago, *Thin Solid Films* **392**, 320 (2001)
- [15] S Singh and M N Tripathi, *Pramana – J. Phys.* **89**, 5 (2017)
- [16] A Stashans, P Puchaicela and R Rivera, *J. Mater. Sci.* **49**, 2904 (2014)
- [17] Gaussian 03, Revision B 04, M J Frisch, G W Trucks, H B Schlegel, G E Scuseria, M A Robb, J R Cheeseman, J A Montgomery Jr, T Vreven, K N Kudin, J C Burant, J M Millam, S S Iyengar, J Tomasi, V Barone, B Men- nucci, M Cossi, G Scalmani, N Rega, G A Petersson, H Nakatsuji, M Hada, M Ehara, K Toyota, R Fukuda, J Hasegawa, M Ishida, T Nakajima, Y Honda, O Kitao, H Nakai, M Klene, X Li, J E Knox, H P Hratchian, J B Cross, C Adamo, J Jaramillo, R Gomperts, R E Stratmann, O Yazyev, A J Austin, R Cammi, C Pomelli, J W Ochterski, P Y Ayala, K Morokuma, G A Voth, P Salvador, J J Dannenberg, V G Zakrzewski, S Dapprich, A D Daniels, M C Strain, O Farkas, D K Malick, A D Rabuck, K Raghavachari, J B Foresman, J V Ortiz, Q Cui, A G Baboul, S Clifford, J Cioslowski, B B Ste- fanov, G Liu, A Liashenko, P Piskorz, I Komaromi, R L Martin, D J Fox, T Keith, Al-M A Laham, C Y Peng, A Nanayakkara, M Challacombe, P M W Gill, B John- son, W Chen, M W Wong, C Gonzalez and J A Pople, Gaussian, Inc, Pittsburgh PA (2003)
- [18] A D J Becke, *Chem. Phys.* **98**, 5648 (1993)
- [19] C Lee, W Yang and R G Parr, *Phys. Rev. B* **37**, 785 (1988)
- [20] P J Stephens, F J Devlin, C F Chabalowski and M J Frisch, *Phys. Chem.* **98**, 11623 (1994)
- [21] C Andraud, T Brotin, C Garcia, F Pelle, P Goldner, B Bigot and A Collet, *J. Am. Chem. Soc.* **116**, 2094 (1994)
- [22] M Nakano, H Fujita, M Takahata and K Yamaguchi, *J. Am. Chem. Soc.* **124**, 9648 (2002)
- [23] V M Geskin, C Lambert and J L Bredas, *J. Am. Chem. Soc.* **125**, 15651 (2003)
- [24] N B Colthup, L H Daly and S E Wiberly, *Introduction to infrared and Raman spectroscopy* (Academic Press, New York, 1990)
- [25] I Fleming, *Frontier orbitals and organic chem- ical reactions* (John Wiley & Sons, New York, 1976)
- [26] L Li, Z Zhou, X Wang, W Huang, Y Hec and M Yang, *Phys. Chem. Chem. Phys.* **10**, 6829 (2008)
- [27] A Datta and S K Pati, *J. Phys. Chem. A* **108**, 9527 (2004)
- [28] S M Pratik, A Nijamudheen and A Datta, *Chem. Phys. Chem.* **17**, 2373 (2016)
- [29] N M O'Boyle, A L Tenderholt and K M Langer, *J. Com- put. Chem.* **29**, 839 (2008)
- [30] E Scrocco and J Tomasi, *Adv. Quantum Chem.* **11**, 115 (1979)
- [31] F J Luque, J M Lopez and M Orozco, *Theor. Chem. Acc.* **103**, 343 (2000)
- [32] N Okulik and A H Jubert, *Int. Electron. J. Mol. Des.* **4**, 17 (2005)
- [33] R S Mulliken, *J. Chem. Phys.* **23**, 1833 (1955)