A systematic investigation of acetylene hydrohalogenation catalyzed by gold cluster via density functional theory

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The mechanisms for the addition of HX (X = F, Cl, Br and I) on acetylene catalyzed by neutral acetylene Au_3 cluster has been investigated within the formalism of density functional theory (DFT). The gold cluster is shown to play role as the bridge for the transfer of electron from highest occupied molecular orbital (HOMO) of Au_3-C_2H_2 complex to the lowest unoccupied molecular orbital (LUMO) of hydrogen halide (HX). The reaction mechanism of the addition of HX on acetylene consists of two transition states, one intermediate, one de-adsorption product that leads to the final product. The addition of HF proceeds through barrier less transition state, while barrier for the first transition state enroute addition of HBr, HCl and HI 0.44, 5.64 and 6.27 kcal/mol respectively. The activation energy for hydrochlorination obtained in the current work is less than the ones reported in literature, the study reinforces the suitability of small sized gold cluster as an efficient catalyst for acetylene activation and subsequent hydrohalogenetion.

Keywords: DFT, acetylene, hydrohalogenation, Au_3 cluster, activation energy, catalyzed.

1. Introduction

Gold clusters (Au_n) have attracted substantial interest owing to their excellent catalytic properties in contrast to its bulk form. There has been a continuous increase in the number of experimental and theoretical studies on the structure and catalytic properties of Au_n clusters after the first successful study on their catalytic activity performed by Haruta et al.[1]. Role of Au_n clusters with appropriate size has been studied in numerous organic reactions such as rupture of S-H bond in mercaptan and thiophenol[2,3], hydrogen peroxide synthesis[4], oxidation of carbon monoxide[5–8], acetylene hydrogenation[9], selective oxidation of alcohol and olefin[10,11], water gas shift[12,13] and acetylene hydrochlorination[14–21].

For the hydrochlorination of acetylene, supported Au_n clusters act as "green material" substitute for mercuric chloride. Literature reports suggest that Au(3+) is the most effective species for the hydrochlorination of acetylene in comparison to Au(0) and Au(1+)[14] and confirmed that $AuCl_3$ could be a more environmentally friendly catalyst in acetylene hydrochlorination[22,23]. Kang et al.[24] established this conclu-

sion theoretically by studying the reaction mechanism of C_2H_3Cl over a MCl_x (M = Hg, Au, Ru; x = 2, 3) catalyst. However, $AuCl_3$ catalyst deactivation was found to be unstable and deactivation mechanism over $AuCl_3$ dimer model catalyst have been studied via Zhang et al.[25] using density functional theory (DFT). Corma et al.[26] have suggested improvement in catalyst preparation by preparing isolate gold atoms supported on functionalized carbon nanotubes and concluded that single Au atom does not show catalytic activity while their aggregation into Au_n clusters under reaction conditions shows considerable catalytic activity. Though, Au_n clusters do not show catalytic activity when they grow into larger nanoparticles. Using Au_{3-10} clusters, Wang et al.[27] have illustrated the mechanism for the hydrochlorintion of acetylene and reinforced that smaller Au_n clusters exhibits better catalytic activity in comparison to larger Au_n clusters.

Hydrochlorination of acetylene acquires significant consideration due to its extensive range of industrial and economics benefits[27]. Like acetylene hydrochlorination, its fluorination results in the formation of vinyl monofluoride, mono-

mer unit of the polymer polyvinyl fluoride (PVF) that is used for the flammability-lowering coatings of photovoltaic module backsheets and of airplane interiors. Likewise, vinyl monobromide used to manufacture polymer polyvinyl bromide while vinyl monoiodide act as valuable substrates for the transition metal cross-coupling reaction and can be converted to suitable Grignard reagents[28].

While catalytic activity of Au_n clusters for the hydrochlorination of acetylene has been widely studied addition of other hydrogen halides H-X (X = F, Br and I) to acetylene has not been explored yet. Present paper employs density functional calculations to addition of H-X (X = F, Cl, Br and I) to acetylene with the aid of Au_n cluster. The study deciphers the role of cluster as catalyst in the addition reaction by tracing the reaction route. Effect of size and electronegativity of X atom toward the addition of H-X to acetylene has also been illustrated through rigorous computations.

2. Computational details

All geometry optimizations have been performed using spin polarized generalized gradient approximation (GGA)[29] using Perdew-Wang (PW91) functional[30,31] within density functional theory (DFT) formalism using the Gaussian-09 software package[32]. For small gold clusters, the GGA-PW91 exchange-correlation functional is reported to be reliable[33]. The Stuttgart/Dresden effective core potential basis set (SDD) has been adopted for the description of $5s^2 5p^6 5d^{10} 6s^1$ outermost valence electrons of the Au atom in conjunction with 6-311++G(d,p) basis set for carbon, hydrogen and X i.e. flourine, chlorine and bromine while SDD basis set was used for iodine. All the optimized geometries were subjected to frequency check at the same level of theory that also provided the zero point correction energy. The connectivity of transition state (TS) with congruous reactant and product was established by performing intrinsic reaction coordinate (IRC) calculations.

As the calculation of weak intermolecular interactions is reported to suffer from overestimation due to incomplete basis[34,35], basis set superposition error (BSSE) was corrected by re-optimizing all the geometries along the reaction pathways using counterpoise correction.

Adsorption energy (E_{ads}) is calculated according to below equation:

$$E_{ads} = E_{ads\ state} - (E_{C_2H_2} + E_{HX} + E_{Au_3}) \qquad (1)$$

where $E_{ads\ state}$ is the total energy of the system in which both reactants are coadsorbed onto the catalyst while $E_{C_2H_2}$, E_{HX} and E_{Au_3} represents the energies of isolated acetylene, HX and Au_3 cluster, respectively.

3. Results and discussion

It has been demonstrated by Wang et al.[27] in their study on Au_n cluster catalyzed hydrochlorination of acetylene that for n = 3-10, all Au_n clusters follow the same catalytic cycle, the present study employs Au_3 cluster as the model of cluster catalyst to facilitate the addition of HX to acetylene owing to computational simplicity. The value of binding energy (E_b = E (Au_n) – nE(Au)) for Au_3 cluster at the employed level of theory is –2.80 eV, it is in good agreement with the literature values (–2.87 eV[36]).

The complete cycle for the addition of H-X on activated acetylene is shown in Scheme 1. It has been reported that Au_n cluster catalyses the hydrochorination reaction by facilitating the electron transfer from the highest occupied molecular orbital (HOMO) of Au_n-C_2H_2 complex to the lowest unoccupied molecular orbital (LUMO) of HCl when C_2H_2 and HCl are co-adsorbed on the Au_n cluster[27,37,38]. In order to understand the electron flow between Au_n-C_2H_2 complex and H-X (X = F, Cl, Br and I), we calculated the energy gap between the frontier orbitals of reacting species (see Table 1). The values indicate that it is easier to transfer electron from
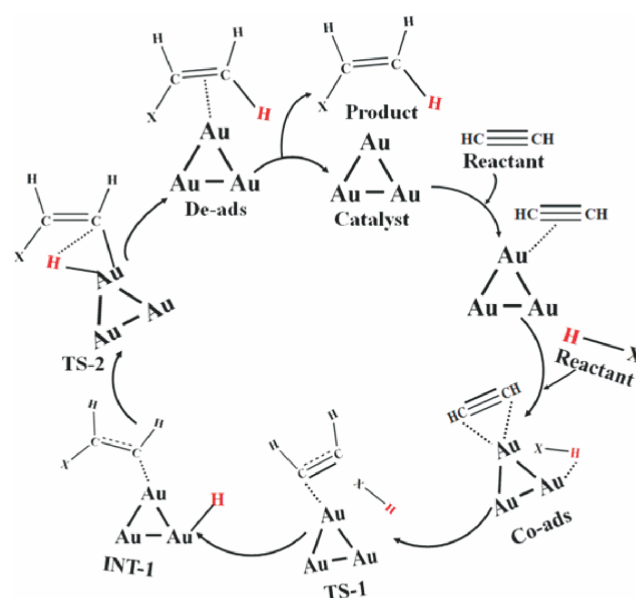
Scheme 1. Catalytic cycle for selective addition of H-X on acetylene catalyzed via using Au_3 cluster, where X = F, Cl, Br and I.

Table 1. The orbital energies on LUMO and HOMO of H-X (X = F, Cl, Br and I) and Au_3-C_2H_2 and their different energy gaps between HX and Au_3-C_2H_2 (energies values are in eV)

	LUMO	HOMO	HOMO-LUMO H-X→Au_3-C_2H_2	HOMO-LUMO Au_3-C_2H_2→H-X
Au_3-C_2H_2	−0.10	−0.17	–	–
HF	−0.04	−0.35	0.24	0.13
HCl	−0.04	−0.29	0.18	0.12
HBr	−0.05	−0.27	0.16	0.11
HI	−0.08	−0.38	0.28	0.09

HOMO of Au_n-C_2H_2 complex to LUMO of H-X (X = F, Cl, Br and I).

First step in the addition of H-X (X = F, Cl, Br and I) to acetylene is the formation of stable co-adsorption structure (Co-ads) formed via the co-adsorption of acetylene and HX on Au_3 cluster. As shown in Scheme 1, formation of product comprise of two TS i.e. TS-1 and TS-2. In the first step, X atom moves to one carbon of acetylene while hydrogen atom moves to Au atom of Au_3 cluster leads to formation of intermediate (INT-1) via TS-1 and this step is the rate determine step. The INT-1 undergoes transfer of hydrogen atom from Au atom to halogen atom attached with acetylene leads to the formation of desorption (De-ads) product via TS-2. De-ads product leads to the formation of final product (P). Elongation of C-C triple bond (1.21 Å in acetylene, 1.32 Å invinyl monohalide) confirms the conversion of triple bond of acetylene to double bond.

The reaction profiles along with the optimized geometries of all the reacting species for the addition of H-X on acetylene catalyzed via Au_3 are shown in Figs. 1, 2, 3 and 4 for X being F, Cl, Br and I respectively. The co-adsorbed complex of C_2H_2 and HX has been taken as the starting point for all the reaction profile, the energy of the Co-ads structure has been taken as zero and energies of all the species in the reaction profile have been scaled with respect to that of Co-ads structure. All the halides follow the same mechanistic route for their addition to acetylene. The addition of HF involves barrier less TS (TS-1 in Fig. 1) while activation energy (E_{act}) for the addition of HCl, HBr and HI are 5.64 kcal/mol, 0.44 kcal/mol and 6.27 kcal/mol as shown in Figs. 2, 3 and 4, respectively.

It is important to note here that the activation barrier obtained in the current work with BSSE correction are consid-
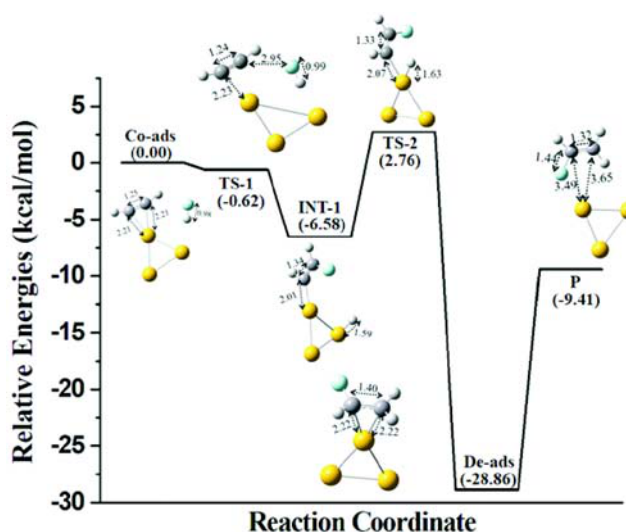
Fig. 1. Energy diagrams of the most favorable pathways of acetylene hydrofluorination on Au_3 cluster: Co-adsorbed (Co-ads), transition states (TSs), intermediate (INT), desorption products (De-ads) and products (P) with the optimized geometries of all stationary points (distance in Å).
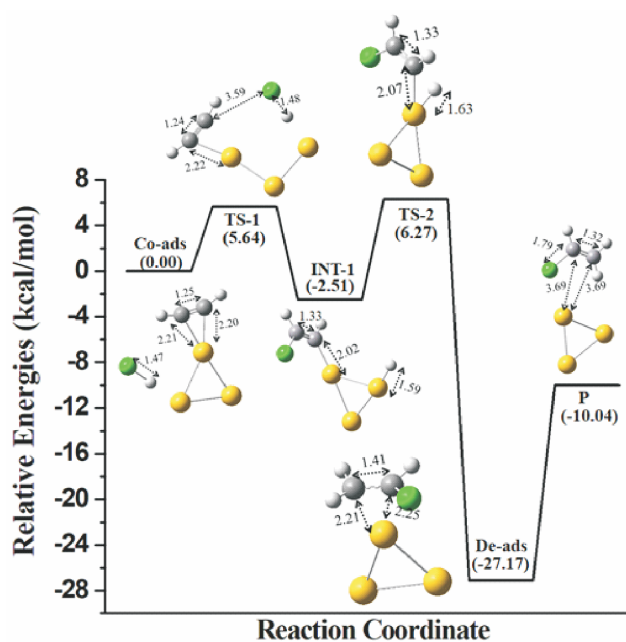
Fig. 2. Energy diagrams of the most favorable pathways of acetylene hydrochlorination on Au_3 cluster: Co-ads, TS, INT, De-ads product and products (P) with the optimized geometries of all stationary points (distance in Å).

erably lower than the ones reported in literature that have been obtained without counterpoise correction. For instance,
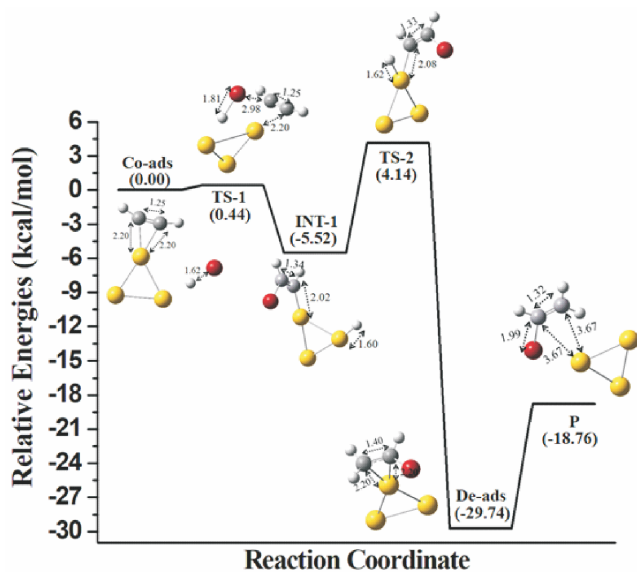
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Fig. 3. Energy diagrams of the most favorable pathways of acetylene hydrobromination on Au_3 cluster: Co-ads reactant, TS, INT, De-ads product and products (P) with the optimized geometries of all stationary points (distance in Å).

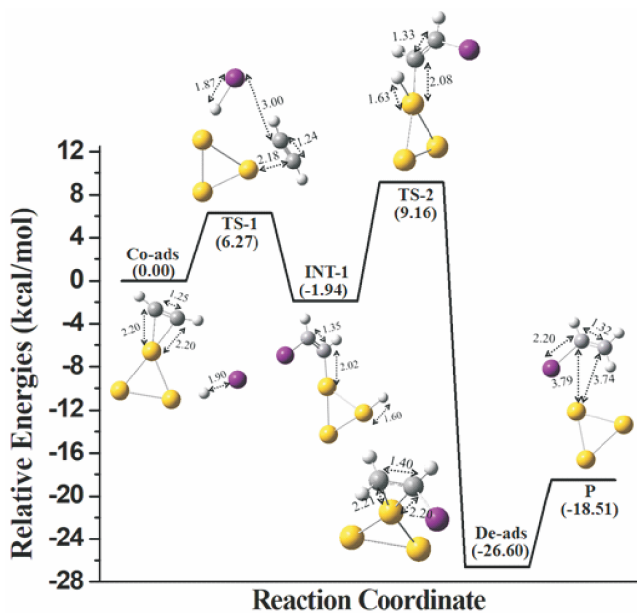**Fig. 4.** Energy diagrams of the most favorable pathways of acetylene hydroiodination on Au_3 cluster: Co-ads, TS, INT, De-ads product and products (P) with the optimized geometries of all stationary points (distance in Å).

Wang et al.[27] reported the formation of vinyl monofluoride through the E_{act} value of 22.2 kcal/mol catalyzed via Au_3

cluster while Zhao et al.[37] reported the mechanisms for the acetylene hydrochlorination reaction on pristine Au_7 and Au_8 clusters and on the Si-doped Au clusters through the values of E_{act},18.23, 19.22, 21.83 and 16.69 kcal, respectively.

4. Conclusion

The current work demonstrates the systematic adsorption and activation of C_2H_2 molecules on the Au_3 cluster and the subsequent addition of HX (X = F, Cl, Br and I) on activated C_2H_2. The whole process involves two transition states (TS), one intermediate, desorption adduct leading to the product. First TS (TS-1) denotes the dissociation of HX, the second TS (TS-2) comprises of hydrogen transfer from Au_3 cluster to haloethenyl. The small sized Au_3 cluster shows excellent catalytic performance, the addition of HF proceeds through barrier less TS, addition of HBr, HCl and HI are offered a low lying barrier of 0.44 kcal/mol, 5.64 kcal/mol, and 6.27 kcal/mol to TS-1 respectively. The barrier less addition of HF to acetylene is attributed to high electronegativity of F atom (3.98). It has been established that Au_3 cluster forms a Co-ads complex with acetylene and HX that facilitates the electron transfer from HOMO of Au_3-C_2H_2 to the LUMO of HX. It is pertinent to mention here that the activation barriers obtained in the current work are significantly lower than the barrier reported for hydrochlorination of acetylene reported in literature. This is owing to the counterpoise correction employed in the current work, the study reinforces the necessity of BSSE correction while investigating reaction mechanisms in density functional formalism.

References

1. M. Haruta, T. Kobayashi, H. Sano and N. Yamada, *Chem. Lett.,* 1987, **16**, 405.

2. A. P. Woodham, G. Meijer and A. Fielicke, *J. Am. Chem. Soc.,* 2013, **135**, 1727.

3. A. Corma, P. Concepcion, M. Boronat, M. J. Sabater, J. Navas, M. J. Yacaman, E. Larios, A. Posadsas, M. A. Lopez-Quintela, D. Buceta, E. Mendoza, G. Guilera and A. Mayoral, *Nat. Chem.,* 2013, **5**, 775.

4. M. D. Hughes, Y. Xu, P. Jenkins, P. McMorn, P. Landon, D. I. Enache, A. F. Carley, G. A. Attard, G. J. Hutchings, F. King, E.

H. Stitt, P. Johnston, K. Griffin and C. J. Kiely, *Nature*, 2005, **437**, 1132.

5. M. Haruta, N. Yamada, T. Kobayashi and S. Iijima, *J. Catal.*, 1989, **115**, 301.

6. H. Y. Kim, H. M. Lee and G. Henkelman, *J. Am. Chem. Soc.*, 2012, **134**, 1560.

7. J. Lu, C. Aydin, N. D. Browning and B. C. Gates, *Angew. Chem.*, 2012, **124**, 5944.

8. C. Liu, Y. Tan, S. Lin, H. Li, X. Wu, L. Li, Y. Pei and X. Zeng, *J. Am. Chem. Soc.*, 2013, **135**, 2583.

9. B. Yang, R. Burch, C. Hardacre, G. Headdock and P. Hu, *ACS Catal.*, 2012, **2**, 1027.

10. J. E. Bailie and G. J. Hutchings, *Chem. Commun.*, 1999, 2151.

11. P. Landon, P. J. Collier, A. J. Papworth, C. J. Kiely and G. J. Hutchings, *Chem. Commun.*, 2002, 2058.

12. Q. Fu, H. Saltsburg and M. Flytzani-Stephanopoulos, *Science*, 2003, **301**, 935.

13. F. Shi, X. Li, Y. Xia, L. Zhang and Z. Yu, *J. Am. Chem. Soc.*, 2007, **129**, 15503.

14. G. J. Hutchings, *J. Catal.*, 1985, **96**, 292.

15. G. J. Hutchings, *Gold Bull.*, 1996, **29**, 123.

16. M. Conte, A. F. Carley, C. Heirene, D. J. Willock, P. Johnston, A. A. Herzing, C. J. Kiely and G. J. Hutchings, *J. Catal.*, 2007, **250**, 231.

17. C. Huang, M. Zhu, L. Kang and B. Dai, *Catal. Commun.*, 2014, **54**, 61.

18. C. Huang, M. Zhu, L. Kang, X. Li and B. Dai, *Chem. Eng. J.*, 2014, **242**, 69.

19. X. Li, M. Zhu and B. Dai, *Appl. Catal. B*, 2013, **142**, 234.

20. X. Li, Y. Wang, L. Kang, M. Zhu and B. Dai, *J. Catal.*, 2014, **311**, 288.

21. X. Li, X. Pan, L. Yu, P. Ren, X. Wu, L. Sun, F. Jiao and X. Bao, *Nat. Commun.*, 2014, **5**, 3688.

22. B. Nkosi, N. J. Coville and G. J. Hutchings, *J. Chem. Soc., Chem. Commun.*,1988, 71.

23. M. Conte, A. F. Carley, C. Heirene, D. J. Willock, P. Johnston, A. A. Herzing, C. J. Kiely and G. J. Hutchings, *J. Catal.*, 2007, **250**, 231.

24. M. Zhu, L. Kang, Y. Su, S. Zhang and B. Dai, *Can. J. Chem.*, 2013, **91**, 120.

25. J. Zhang, Z. He, W. Li and Y. Han, *RSC Adv.*, 2012, **2**,

4814.

26. A. Corma, P. Concepcion, M. Boronat, M. J. Sabater, J. Navas, M. J. Yacaman, E. Larios, A. Posadsas, M. A. Lopez-Quintela, D. Buceta, E. Mendoza, G. Guilera and A. Mayoral, *Nat. Chem.*, 2013, **5**, 775.

27. Y. Wang, M. Zhu, L. Kang and B. Dai, *RSC Adv.*, 2014, **4**, 38466.

28. M. Xie, J. wang, W. Zhang and S. Wang, *J. Organomet. Chem.*, 2009, **694**, 2258.

29. J. P. Perdew, in: 'Electronic Structure of Solids' 91, eds. P. Ziesche and H. Eschrig, Akademie Verlag, Berlin, 1991.

30. J. P. Perdew and Y. Wang, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1992, **45**, 13244.

31. B. Delley, *J. Chem. Phys.*, 1990, **92**, 508; B. Delley, *Int. J. Quantum Chem.*, 1998, **69**, 423; B. Delley, *J. Chem. Phys.*, 2000, **113**, 7756.

32. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery (Jr.), J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Farkas Ö, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, Gaussian 09, Revision E.01, Gaussian Inc, Wallingford CT, 2009.

33. A. V. Walker, *J. Chem. Phys.*, 2005, **122**, 094310.

34. C. J. Cramer, "Essentials of Computational Chemistry: Theories and Models", 2nd ed., John Wiley & Sons Inc, New York, 2004.

35. S. F. Boys and F. Bernardi, *Mol. Phys.*, 1970, **19**, 553.

36. N. Jabr and A. Kodlaa, *CMR*, 2017, **9**, 17.

37. S. Gautam and A. D. Sarkar, *Phys. Chem. Chem. Phys.*, 2016, **18**, 13830.

38. Y. Zhao, F. Zhao and Lihua Kang, *J. Mol. Model.*, 2018, **61**, 1.