Density functional investigation of the adsorption of nitric oxide on palladium clusters (PDN n=1-6)

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Abstract
The adsorption of nitric oxide molecule on small palladium clusters (Pd$_n$;n=1–6) has been investigated by the density functional theory. The orientations of nitric oxide to get a nitrosyl (-NO) and Isonitrosyl (-ON) ligands were implemented. The most stable palladium clusters have been used as adsorbate. The resulting nitrosyl and Isonitrosyl palladium complexes always chemisorbs in a bent geometry. The nitrosyl complexes showed higher binding energy, charge donation, HOMO-LUMO gap and υ(NO) than their isonitrosy counterparts. Looking to the thermodynamic and kinetic stability of the cluster and their interaction with nitric oxide.

1. Introduction
The need to eliminate air pollutants prompted a series of theoretical and experimental studies to identify potential decontamination mechanisms, especially for Nitric oxide uptake and reduction and the removal of nitric oxide and carbon monoxide from exhaust gases is an important scientific challenge [1]. Nano clusters such as clusters of transition metals of group 10 (Ni, Pd, Pt), offer unique physical and chemical behavior, with the possibility of fine-tuning size and structures; palladium has a greater control over chemical properties and better ionization energy, has magnetic properties, facilitates the study of spectral properties and has better binding energies than the other metals in its group (Ni, Pt, Pd), and the stability of palladium structures is high at different temperatures [2-3]. Palladium in particular, is a promising material as catalyst in various applications [2-6]. Previous studies have indicated to the importance of palladium clusters during the adsorption of nitric oxide, which transforms triple bonds to double bonds [4, 6]. The nitric oxide adsorption on small palladium clusters in the framework of the density functional theory (DFT) has been considered [4]. This method is based on the determination of the electronic density and is able to predict numerous properties related with the reactivity of such systems. Early theoretical works dealing with NO adsorption on palladium were reviewed by Whitten and Yang [5]. The magnetic and the symmetries of the clusters varies with the direction of the magnetization, even for a 3d metal such as Ni, the change in the magnetic symmetry leads to small geometric distortions of the cluster structure, which are even more pronounced for the 4d palladium metal; the experimental detection of the exact geometric structure of clusters is still a hard task, structures and cohesive energies of clusters cannot be obtained directly from gas phase or molecular beam experiments [7-10]. Theoretically, the adsorption of NO (-NO, -O and -N), as well as the possible spontaneous dissociation of NO on the small cluster of Pd4 has been considered [6, 9]. Although Pd is less reactive in NO reduction, it could be a good alternative to Rh due to low cost compared to Rh, making Pd (especially the ones supported on oxide surface) a most industrially preferable catalyst [9]. It has been documented that theoretical investigations play an important role in cluster studies; it is possible to make effective theoretical predictions using density functional theory (DFT), the investigation showed that the most stable geometry of Pd4 is a regular tetrahedron with Td symmetry [9,10]. Nitric oxide (NO) is a hetero-nuclear diatomic molecule. The NO molecule has a singly occupied π* molecular orbital, therefore, it is more reactive and the chemical properties of adsorbed NO are quite different from other diatomic molecules [9-13]. The σ-donor and π-acceptor interaction between nitric oxide and metal are well recognized [14-16]. The aim of this work is to investigate the isonitrosyl (-ON) adsorption on small palladium clusters and compare it with previously reported nitrosyl ligand [6, 9]. We are going to prove the results of the previous experimental and theoretical studies to justify our methodology. The adsorption energy and charge transfer, charge donation and back-donation when nitric oxide interacts with palladium clusters are of interest. Finally we are going to look for any correlation between the electronic properties under consideration.

2. The methodology Section
The Gaussian 09 package [17] was used for the calculations. The B3PW91 exchange and correlation functional were used for all the calculations in the current investigation [18]. Copper was described with the [6s5p3d] SDD valence basis set and the quasi-relativistic ECP10MWB effective core potential [19], while Nitrogen and oxygen atoms were described using the 6-311++G (d,p) basis set. Full geometry optimization was carried out in each case and stationary points were confirmed to be genuine minima by harmonic vibrational frequencies analysis. In order to gain a deeper understanding of the chemical bonds evolution, Charge decomposition analysis (CDA) [20] was implemented to estimate the charge donation and back-donation between the copper cluster and nitric oxide fragments in complexes. The Multi wfn

software [21] was used, along with the optimized geometry generated in the quantum-mechanical calculations.

3. Results and Discussion
3.1 Geometries and energetics
To study the adsorption of nitric oxide on neutral palladium clusters (n=1–6), we first optimized the geometries of all neutral clusters to get the lowest energy structure. Excluding palladium monomer the triplet state are the most stable state for Pd_2 to Pd_5. The singlet state is lower in energy than the triplet state for palladium monomer. The Structures of the nitrosyl and isonitrosyl palladium complexes are given in Figure 1.
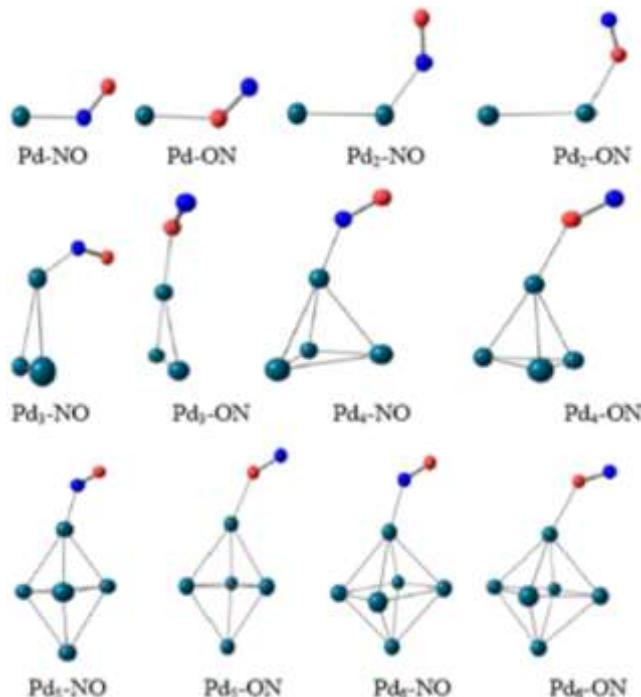

Fig 1: Structures of the nitrosyl and isonitrosyl palladium complexes.

The adsorption of nitric oxide molecule can take place via nitrogen end atom or oxygen end atom. These two different orientations of nitric oxide are showed a significant change in some properties, for instance, the NO stretching frequencies in nitrosyl complexes are showed higher values than their corresponding isonitrosyl complexes Table 1.

Table 1: The selected bond length (Å) and stretching frequencies (cm^{-1}) of the complexes.

sys	N-O	Pd-(NO)	υ NO	υ Pd-(NO)
Pd_1-NO	1.16368	1.89176	1815	503
Pd_2-NO	1.15344	1.81096	1861	599
Pd_3-NO	1.15222	1.81265	1855	611
Pd_4-NO	1.15486	1.80195	1856	575
Pd_5-NO	1.15351	1.79437	1871	537
Pd_6-NO	1.15660	1.80036	1840	599
Pd_1-ON	1.16282	2.11481	1794	278
Pd_2-ON	1.15935	2.05781	1775	320
Pd_3-ON	1.15900	2.08922	1773	290
Pd_4-ON	1.16681	2.06539	1648	310
Pd_5-ON	1.15192	1.94044	1826	439
Pd_6-ON	1.16980	2.09652	1650	268

Furthermore the binding energies of O-end atom complexes are smaller than their N-end atom counterparts Table 2. The effect of the NO orientation on the palladium clusters structures once more noted for example, the Pd_6 structure is compared using Root-Mean-Square-Distances (RMSDs), the difference of the Pd_6 structures in the Pd_6-NO and Pd_6-ON is 0.086, which is corresponding to the highest RMSD among the clusters of the complexes Table 3. Moreover, the structure of the Pd_6 bare cluster is the most affected after the interaction with nitrosyl and isonitrosyl since the RMSD is noted as 0.089 and 0.082 respectively in comparison with Pd_6 bare cluster Table 3. As expected the smallest bare cluster Pd_2 is almost unaffected by the interaction since the RMSD is 0.018 and 0.047 attributed to Pd_2-NO and Pd_2-ON respectively.

The computed bond length of NO is 1.159Å at 6-311++G (d, p) level of theory which is in agreement with the experimental value of 1.153Å [22].

Table 2: Electronic ground state electron donation (D) and back-donation (BD binding energy (BE eV), charge transfer (CT) and HOMO-LUMO gap (H-Lg eV))

Sys	state	D	BD	BE	CT	HL g
Pd_1-NO	Cs-2A'	0.077	0.127	1.38	0.150	2.31
Pd_2-NO	Cs-2A'	0.147	0.123	2.04	0.027	2.08
Pd_3-NO	C1-2A	0.119	0.097	1.99	-0.013	1.84
Pd_4-NO	C1-2A	0.132	0.114	2.61	0.009	2.29
Pd_5-NO	C1-2A	0.131	0.118	2.37	0.006	1.73
Pd_6-NO	C1-2A	0.147	0.101	1.92	0.004	1.64
Pd_1-ON	Cs-2A'	0.012	0.128	0.32	0.135	2.08
Pd_2-ON	C1-2A	0.053	0.095	0.58	0.076	1.87
Pd_3-ON	C1-2A	0.020	0.108	0.56	0.037	1.93
Pd_4-ON	C1-2A	0.030	0.113	1.22	0.098	1.64
Pd_5-ON	C1-2A	0.054	0.103	0.62	0.016	1.37
Pd_6-ON	C1-2A	0.052	0.101	0.67	0.122	1.61

Table 3: The RMSDs between nitrosyl and isonitrosyl complexes.

sys	Rmsd between complexes	Rmsd Between Bare And No	Rmsd between bare and on	Rmsd between complexes
Pd1-NO	0.734	-	-	
Pd2-NO	0.124	0.018	0.047	0.029
Pd3-NO	0.724	0.084	0.077	0.020
Pd4-NO	0.391	0.081	0.077	0.031
Pd5-NO	0.168	0.100	0.100	0.061
Pd6-NO	0.148	0.089	0.082	0.086

The ground state valence electronic configuration of NO is $(1\sigma)^2(2\sigma^*)^2(1\pi)^4(3\sigma)^2(2\pi^*)^1$. Obviously the HOMO $((2\pi^*)^1)$ has one electron with no bonding character, this means that the NO molecule can be consider a potential Lewis base. Recently the molecular orbital and spin density distribution of nitric oxide have been investigated [23], the study showed the spin density of 0.719 and 0.281 au for the nitrogen and oxygen atom respectively. This result is identical with the current values of Table 4. The both orientation of NO molecule always chemisorbs in a bent geometry (Figure 1), this bent structure is related to the symmetry and the shape of $(2\pi^*)^1$ orbital of NO molecule this phenomena is interpreted previously [24]. In these bent complexes a clear effect has been noted on the structure of Pd_1-Pd_6 clusters. Our calculations show that NO adsorbs on an isolated Pd atom in a bent geometry, with a Pd–N–O angle of 129.5∘.The N–O bond-length is stretched to 1.164Å, and this is reflected in a red-shift of

the harmonic N–O stretching frequency from 2009 cm^{-1} to 1815 cm^{-1} and finally 239 cm-1 and 503 cm-1 attributed to Bending mode of Pd-N-O and Pd-N stretching respectively. These values are in good agreement with the experimental values [25].

The calculations of the binding energy demonstrate that the nitrosyl complexes have higher values than their corresponding isonitrosyl Table 2. The N-O bond length calculations showed that the nitrosyl complexes have lower N-O bond length than their isonitrosyl counterparts which are in the same trend as the binding energies, for example the bond length elongates from 1.145 Å to 1.164 Å and 1.163 Å, upon nitrosyl and isonitrosyl adsorption on palladium monomer (Pd-(NO)) respectively. Similarly, the analysis of (NO) stretching frequencies showed that the nitrosyl complexes exhibit a higher υ(NO) than their corresponding isonitrosyl complexes. This increase in the N-O bonds after adsorption on palladium clusters indicates the catalytic activation properties.

The charge transfer values of the complexes are listed in Table 2, Figures 2, 3. The strong adsorption on the palladium clusters is accompanied by the charge transfer from/to the adsorbate. The additional of the positive or negative charge on the palladium clusters can considerably promote their catalytic activity. The analysis of charge transfer showed that there is a considerable amount of charge transferred from the metal clusters to the nitric oxide ligands furthermore, the nitrosyl complexes exhibited larger charge transfer than their isonitrosyl counterparts. The calculations revealed that the nitrosyl complexes have higher charge donation than the isonitrosyl ones, the back donations are very much similar for the complexes in the both series. Similar trend have been realized for charge transfer subsequently similar charge transfer are noted for nitrosyl complexes and isonitrosyl. For example, the values 0.150e and -0.135e are measured for Pd$_1$-NO and Pd$_1$-ON complexes respectively.

It is well documented that the HOMO-LUMO gap reflects the stability of the molecular structure; a large HOMO-LUMO gap is a mark of the chemical stability. The following values of 2.31, 2.08, 1.84, 2.29, 1.73, 1.64 eV are extracted as the HOMO-LUMO gaps for the nitrosyl complexes from Pd$_1$-NO to Pd$_6$-NO respectively. The corresponding isonitrosyl complexes showed lower HOMO-LUMO gap values than their nitrosyl counterparts. The spin density is distributed evenly for the terminal palladium atoms and decreased upon constraint could be rationalized by John Teller distortion, which can be seen starting from Pd$_3$-NO complex Table 4, Figure 4. The spin density values decreased from 0.526 to 0.046. The spin density for the Pd$_2$-NO distributed equally on the palladium atoms whereas in Pd$_2$-ON structure a different spin distribution has been noted. The spin density of the

binding palladium atoms in the complexes showed lower value in the isonitrosyl complexes than their nitrosyl counterparts excluding Pd$_3$ and Pd$_4$ complexes.
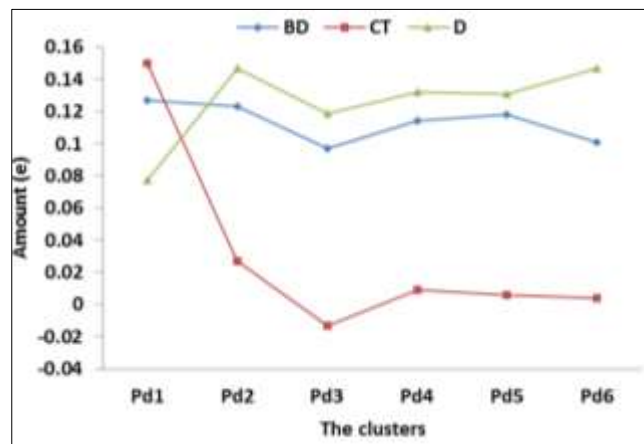
Fig 1: The variation in back-donation (BD), charge transfer (CT) and Donation (D) as a function of nitrosyl complexes.
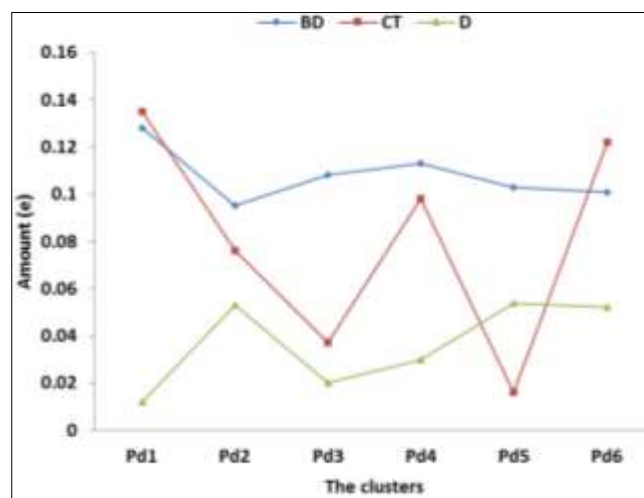

Fig 4: The variation in back-donation (BD), charge transfer (CT) and Donation (D) as a function of isonitrosyl complexes.

The spin density of the free and bonded nitric oxide ligand is examined Table 4 and Figure 5. The spin density values in nitrosyl complexes decrease gradually as the size of the cluster increase while the isonitrosyl complexes showed huge difference in spin density this indicated a limited delocalization of the spin density from the oxygen lone pairs through the O-Pd bond.

Table 4: The spin density distribution on the free NO and the complexes.

sys	O	N	Pd$_1$	Pd$_2$	Pd$_3$	Pd$_4$	Pd$_5$	Pd$_6$
NO	0.281	0.719						
Pd$_1$-NO	0.267	0.428	0.305					
Pd$_2$-NO	0.110	0.165	0.155	0.570				
Pd$_3$-NO	-0.038	-0.059	0.046	0.526	0.526			
Pd$_4$-NO	-0.153	-0.173	0.162	0.399	0.382	0.382		
Pd$_5$-NO	-0.082	-0.084	-0.005	0.325	0.325	0.102	0.419	
Pd$_6$-NO	-0.061	-0.059	0.052	0.046	0.367	0.294	0.318	0.043
Pd$_1$-ON	0.197	0.770	0.033					
Pd$_2$-ON	0.159	0.783	-0.260	0.317				
Pd$_3$-ON	-0.141	-0.814	0.552	0.745	0.658			

Pd$_4$-ON	-0.138	-0.912	0.549	0.492	0.494	0.516		
Pd$_5$-ON	0.004	0.074	-0.067	0.253	0.322	0.012	0.402	
Pd$_6$-ON	0.185	0.904	-0.367	0.339	0.302	0.322	-0.373	-0.312
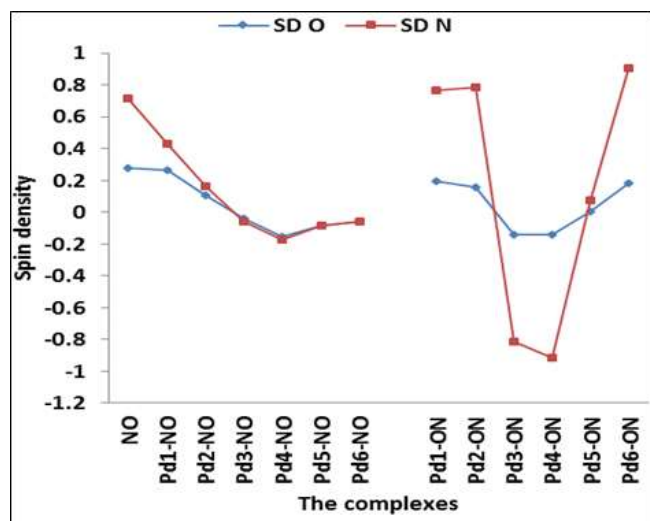
Fig 4: The spin distribution (SD) of nitrogen and oxygen atoms in the nitrosyl (left) and isonitrosyl (right) complexes.

Conclusion

The study revealed that the nitrosyl complexes possessed higher binding energy than their isonitrosyl counterparts. The adsorption leads to significant odd-even (number of Pd atoms) variation of the spin density differences. There is a linear relationship between the spin density differences and the NO stretching frequencies for the complexes. In looking in to the spin distribution of nitrogen and oxygen of the complexes a huge change in nitrogen distribution is noted in comparison between the nitrosyl and isonitrosyl complexes. The NO stretching frequencies in nitrosyl complexes are showed higher values than their corresponding isonitrosyl complexes. The both orientation of NO molecule always chemisorbs in a bent geometry and the harmonic N-O stretching attributed to bending mode of Pd-N-O and Pd-N stretching respectively. The nitrosyl complexes exhibited larger HOMO-LUMO gap, charge transfer and charge donation than their isonitrosyl counterparts, the back donations are very much similar for the complexes in the both series. The spin density values in nitrosyl complexes decrease gradually as the size of the cluster increase.

References

1. Venezia AM, Liotta LF, Deganello G, Terreros P, Pen MA, JL G Fierro, et al. Langmuir. 1999; 15:1176-1181.
2. Kalita B, Deka Rh. Catal J. Soc. India. 2006; 5:110-120.
3. Singh N. B. and Sarkar U., Molecular Simulation, 2014, 1255-1264:861903.
4. Lacaze-Dufaure C, Roques J, Mijoule C, Sicilia E, Russo N, Alexiev V, Mineva T, et al. J. Molecular Catalysis. 2011; 341:28-34.
5. Whitten JL, Yang H. Surface Science Reports. 1996; 24(55-57):59-124.
6. Bertin V, del Angel G, Mora MA, Poulain E, Olvera O, López-Rendón R. J. Mex. Chem. Soc. 2008; 52(1):93-98.
7. Błonski P, Hafner J, J. Phys. Condens. Matter. 2011; 23:136001.
8. Böyükataa M, Belchior JC, CCACAA. 2008; 2:289-297.
9. Begum P, Pakiza B, International Journal of Quantum Chemistry. 2015, 837-845.
10. Manuel J, Pérez K. Somasundram V, Termath NC Handy. Surface science. 1997; 380(1):83-90.
11. Grybosa R, Benco L, Bučko T, Hafnerb J, J. chem. Phys. 2009; 130:104503.
12. Srivastava RK, Hall RE, Lani BW, Journal of the Air & Waste Management Association. 2005; 55:1367-1388.
13. Myers AL, Belfort G. Elsevier sciences, 1993, 206-433.
14. Loffreda D, Delbecq F, Simon D, Sautet P, J. Chem. Phys. 2001; 115:8101.
15. Wörz AS, Judai K, Abbet S, Heiz U. J. Am. Chem. Soc. 2003; 125(26):7964-7970.
16. Johnston RL. "Atomic and Molecular Clusters", Taylor and Francis, London, ISBN 9781420055771, 2002.
17. Frisch MJ. Gaussian 09, Revision D.01.Gaussian, Inc., Wallingford CT, 2013.
18. Perdew JP, Chevary JA, Vosko SH, Jackson KA, Pederson MR, Singh DJ, et al. Phys. Rev. B. 1992; 46:6671-6687.
19. Dolg M, Wedig U, Stoll H, Preuss H. J. Chem. Phys. 1987; 86:866-872.
20. Dapprich S, Frenking G. J Phys. Chem. 1995; 99: 9352-9362.
21. Lu T, Chen F. Comput J. Chem. 2012; 33:580-592.
22. Huber KP, Herzberg G. Van Nostrand New York, (1979). (Experimental bond length of NO), 1979.
23. Orenha RP, Galembeck SE. J. Chem. Educ. 2014; 91:1064-1069.
24. Michael D, Mingos P. Struct. Bond. 2014; 113:103-170.
25. Michael D, Mingos P. "Nitrosyl Complexes in Inorganic Chemistry, Biochemistry and Medicine II", Springer ISBN 978-3-642-41159-5, 2014.