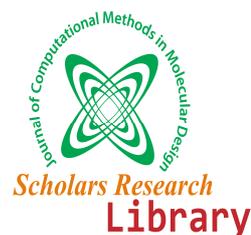




Scholars Research Library
(<http://scholarsresearchlibrary.com/archive.html>)



ISSN : 2231- 3176
CODEN (USA): JCMMDA

Ab initio study of Transition metal nitride clusters -(ZnN)_n n=1-4

Neeraj Misra^{1*}, Apoorva Dwivedi¹

¹Department of Physics, Lucknow University, Lucknow, 226007, India.

ABSTRACT

Structural, vibrational and electronic properties of the Transition metal Nitride clusters (ZnN)_n where n=1-4 are calculated to investigate the changes in, when an electron is either added or removed from the corresponding neutral clusters by Density functional theory with the B3LYP exchange-correlation functional using DGDZVP as the basis set. As the first step of calculation, geometrical optimizations of the nanoclusters have been done. In the next step, these optimized geometries are used to calculate the binding energy and HOMO–LUMO gap (band gap) of the clusters. The calculated results tell that the addition of an electron to the neutral clusters induces significant structural changes relative to the case when an electron is removed. The changes in vibrational properties can be explained in terms of the variation of the interatomic distances upon removing or adding the electron.

Keywords: Zinc nitride, Structure, Stability, DFT

INTRODUCTION

The extensive research in the area of transition metal chemistry has invited a lot of speculation over the last twenty five years and it continues to be a rapidly expanding area of chemical investigation. Historically, transition metal nitrides are fundamentally and technologically important because of their strength and durability, and are useful for their optical, electronic and magnetic properties. Transition metal nitrides already have practical uses. For example, titanium aluminum nitride has become ubiquitous in wear-, corrosion-, and diffusion- resistant coatings for products such as cutting tools. The new alloys have enabled the use of copper interconnects in integrated circuits through the creation of improved diffusion barrier thus paving the way for a new generation of faster computer chips [1]. Transition metal nitrides are fundamentally and technologically important because of their strength, durability and their optical, electronic, and magnetic properties [2–4].

The 3d transition-metal nitrides have deserved more experimental and theoretical attention than the 4d transition-metal nitrides. The ScN, TiN, VN, and CrN compounds have been synthesized in the fcc (NaCl-type) structure. ScN was identified as a semiconductor [5], TiN and VN as superconductors [6]. FeN films synthesized by sputtering appear, depending on the experimental conditions, either in the NaCl structure or in the ZnS (zinc-blende) structure [7]. CoN films, in the zinc-blende phase have also been synthesized [8]. On the theoretical side, *ab initio* calculations show that the 3d transition-metal nitrides usually exhibit a NaCl structure with lower energy than the zinc-blende structure. Though transition metal nitrides are important and have practical uses, to the best of our knowledge no thorough study of Zinc nitride clusters have been done in any of the states.

MATERIAL AND METHODS

The electronic structure calculations were performed on several structural isomers of $(\text{ZnN})_n$ ($n=1-4$) clusters using the GAUSSIAN 09 program [9]. All calculations were carried out by solving the Kohn–Sham equations in the framework of the Density Functional Theory (DFT) [10]. The gradient corrected Density Functional Theory (DFT) with the three-parameter hybrid functional (B3) [11] for the exchange part and the Lee–Yang–Parr (LYP) correlation function [12] has been employed. The double zeta valence plus polarization (DGDZVP) basis sets optimized for the Density Functional Theory orbital were used for these atoms [13]. For the lowest energy isomer, the vibrational frequencies under harmonic approximation were also computed.

RESULTS AND DISCUSSION

Structural analysis (Clusters like ZnN , Zn_2N_2 , Zn_3N_3 and Zn_4N_4)

The calculated spectroscopic constants, i.e., bond length (R_e), vibrational frequency (ω), and binding energy (De), dipole moment and band gap of the Zinc nitride monomers are collected in Table 1. The calculated spectroscopic constants, i.e., bond length (R_e), and binding energy (De), and band gap of the Zinc nitride clusters like Zn_2N_2 , Zn_3N_3 and Zn_4N_4 are collected in Table 2. For Zn_2N_2 , the initial rhombic structure (2) in Fig 1 with the C_1 symmetry is found to be the most stable in neutral state but distorted linear (2c) in Fig-1 with the C_1 symmetry is found to be the most stable in cationic and anionic states, respectively.

For Zn_3N_3 , the initial distorted rectangular (3) structure in Fig 1 with the C_1 symmetry is found to be the most stable in neutral and cationic states but benzene ring type structure (3b) in Fig 1 with the C_1 symmetry is found to be the most stable in anionic state. For Zn_4N_4 , the initial square type shaped structure (4) in Fig 1 with the C_1 symmetry is found to be the most stable in neutral and anionic states but distorted pyramidal type structure (4c) in Fig 1 with the C_1 symmetry is found to be the most stable in cationic state.

Neutral state

The calculated bond length (R_e) for neutral ZnN is 1.84 \AA , whereas the corresponding vibrational frequency (ω) is 560 cm^{-1} , respectively. The calculated bond lengths (R_e) for neutral Zn_2N_2 are 1.91 \AA for Zn–N and 2.51 \AA for Zn–Zn, respectively. The calculated bond length (R_e) for neutral Zn_3N_3 varies from $1.86-2.11 \text{ \AA}$, respectively. For Zn_4N_4 , The value of the Zn–N bond length is 1.82 \AA . These calculated values can prove to be very helpful while carrying out experimental studies on such type of clusters.

Cationic state

For the cationic case (the ionized electron comes out from a bonding orbital), the calculated bond length (R_e) for ZnN is 1.91 \AA , respectively, whereas the corresponding vibrational frequency (ω) is 536 cm^{-1} , respectively. Zn is 3d element with all filled electrons in outer surface as we remove an electron from it; it shows an increase in bond length (1.91 \AA) and decrease of the frequency value (536 cm^{-1}) indicating that the bond in cationic state is weaker than the corresponding one in the neutral monomer. For the cationic case, the calculated bond length (R_e) for Zn_2N_2 varies from $1.89-1.93 \text{ \AA}$. The calculated bond length (R_e) for Zn_3N_3 varies from $1.86-1.96 \text{ \AA}$, respectively. For Zn_4N_4 , The values of the Zn–Zn, Zn–N and N–N bond lengths are 2.51 , 1.97 and 1.31 \AA respectively.

Anionic state

The calculated bond length (R_e) for ZnN is 1.78 \AA , whereas the corresponding vibrational frequency (ω) is 608 cm^{-1} . Decrease in bond length and increase of the frequency value indicates that the bond in anionic state is stronger than the corresponding one in the neutral monomer. The calculated bond length (R_e) for Zn_2N_2 varies from $1.80-1.92 \text{ \AA}$. The calculated bond length (R_e) for all Zn_3N_3 varies from $1.85-1.96 \text{ \AA}$. For Pd_4O_4 , The value of the Zn–N bond length varies from $1.84-1.91 \text{ \AA}$.

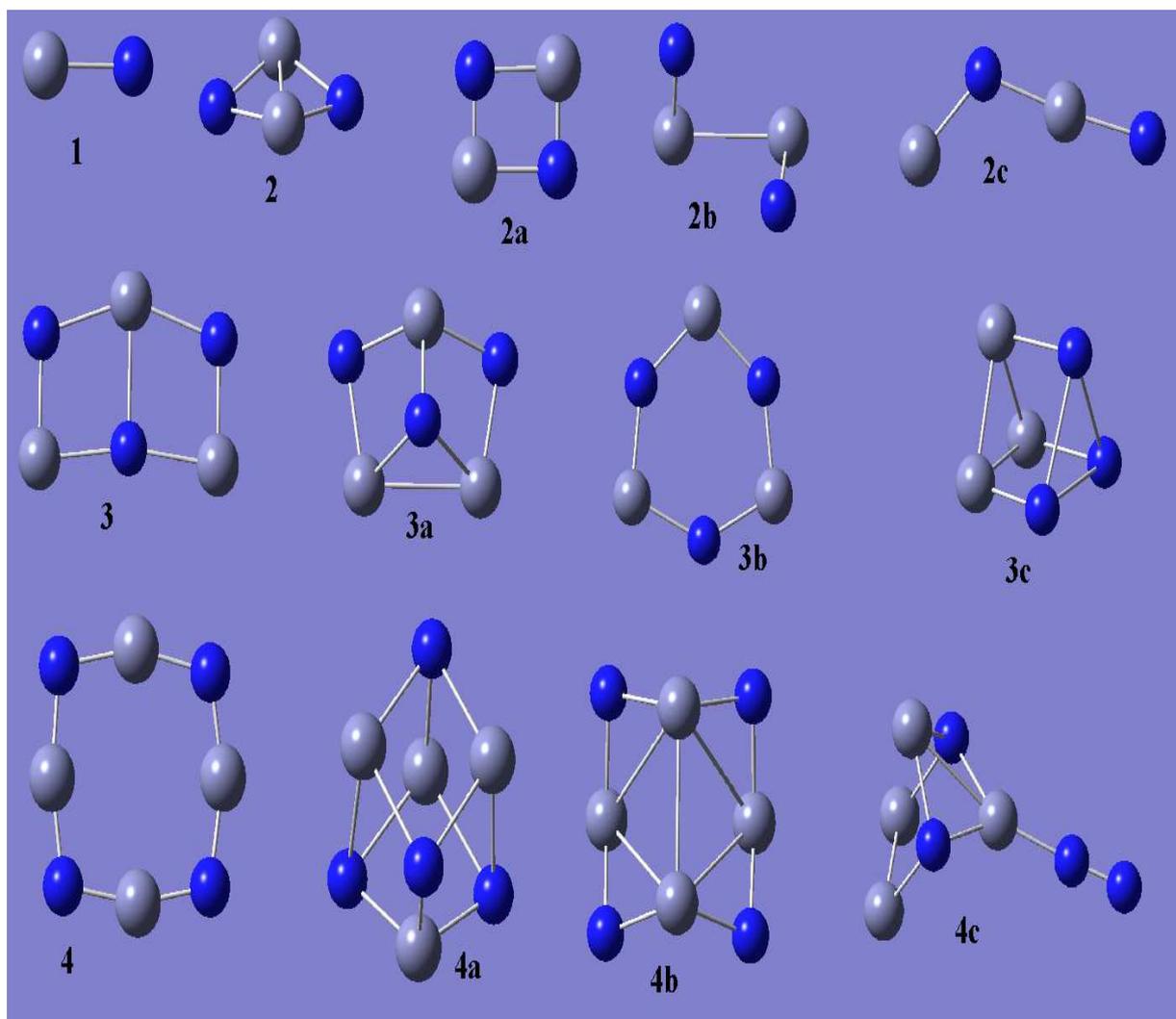


Fig-1 Different Structures of $(\text{ZnN})_n$ Molecules

Table 1 Symmetry, Bond Lengths (\AA), Vibrational frequencies (cm^{-1}) and some other parameters of monomer ZnN

Parameters	Symmetry	Bond Length (\AA)	Vibrational frequency (cm^{-1})	Binding energy	Dipole moment	Band gap
ZnN	C_{infv}	1.84	560	1.06	4.25	$\alpha=3.25$ $\beta=2.71$
ZnN^+	C_{infv}	1.91	536	0.84	2.98	1.78
ZnN^-	C_{infv}	1.78	608	1.12	5.29	2.28

Table 2 Symmetry, Bond Lengths (\AA), binding energy and band gap for Zn_2N_2 , Zn_3N_3 and Zn_4N_4 like clusters

Parameters (Symmetry)	R (Zn-Zn) (\AA)	R (Zn-N) (\AA)	R (N-N) (\AA)	B.E. (ev)	BandGap (ev)
Zn_2N_2 (C_1)	2.51	1.91	-	1.75	1.15
Zn_2N_2^+ (C_1)	-	1.89-1.93	-	4.88	$\alpha=3.07$ $\beta=2.64$
Zn_2N_2^- (C_1)	-	1.80-1.92	-	2.47	$\alpha=3.14$ $\beta=2.23$
Zn_3N_3 (C_1)	-	1.86-2.11	-	2.15	$\alpha=1.72$ $\beta=1.59$
Zn_3N_3^+ (C_1)	-	1.86-1.96	-	5.56	1.45
Zn_3N_3^- (C_1)	-	1.85-1.96	-	2.50	1.21
Zn_4N_4 (C_1)	-	1.82	-	2.44	1.27
Zn_4N_4^+ (C_1)	2.51-2.58	1.97	1.31	7.19	$\alpha=1.58$ $\beta=1.31$
Zn_4N_4^- (C_1)	-	1.84-1.91	-	2.95	$\alpha=1.61$ $\beta=2.18$

Binding energy (E_b) and HOMO–LUMO gap (E_g)-

Binding energy per atom of the $(ZnN)_n$ clusters is defined as follows-

$$\text{For neutral clusters } E_{BE} = (n \cdot E [Zn] + n \cdot E [N] - E [(ZnN)_n]) / (2n)$$

$$\text{For cationic clusters } E_{BE} = (n \cdot E [Zn^+] + n \cdot E [N] - E [(ZnN)_n^+]) / (2n)$$

$$\text{For anionic clusters } E_{BE} = (n \cdot E [Zn] + n \cdot E [N^-] - E [(ZnN)_n^-]) / (2n)$$

The values of binding energy per atom and forbidden band gap (HOMO-LUMO gap) of all clusters (ZnN , Zn_2N_2 , Zn_3N_3 and Zn_4N_4) are given in Tables 1 & 2 respectively. The variation of binding energy per atom of all clusters shows same trend for neutral and ionic states given in figure 2. For ZnN like clusters, HOMO-LUMO gap of cationic ZnN cluster is lowest them all ie. 1.78 eV. For Zn_2N_2 like clusters, HOMO-LUMO gap of neutral cluster is lowest them all ie. 1.15 eV. For Zn_3N_3 like clusters, HOMO-LUMO gap of anionic cluster is 1.21 eV. For Zn_4N_4 like clusters, HOMO-LUMO gap of neutral cluster is 1.27 eV. So neutral Zn_2N_2 cluster is most reactive among them all having lowest band gap. The variation of Band gap of all clusters is given in Figure 3.

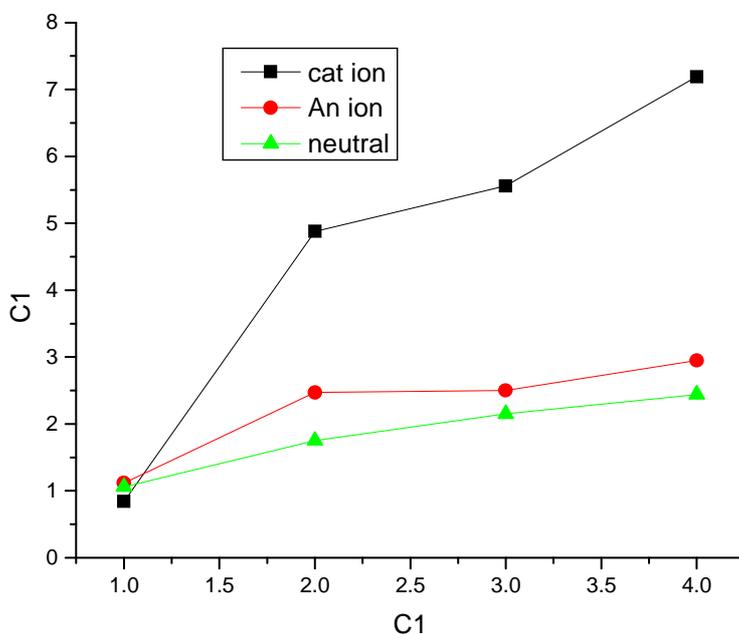


Fig-2 Variation of binding energy per atom for neutral, cationic and anionic clusters

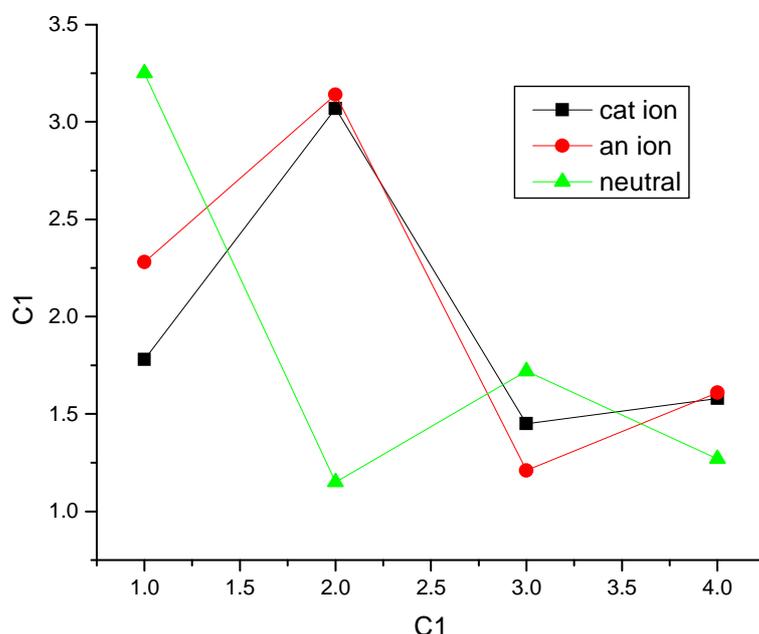


Fig-3 Variation of HOMO-LUMO gap with different combinations for neutral, cationic and anionic clusters

Electron Affinity, Ionization potential, chemical potential and chemical hardness for Monomers, Dimers, Trimers and Tetramers

The calculated electron affinity, the ionization potential, chemical potential and chemical hardness for the monomers, dimer, trimers and tetramers are listed in Table 3. We define the electron affinity to be $EA = E(\text{neutral}) - E(\text{anion})$ and the ionization potential to be $IP = E(\text{cation}) - E(\text{neutral})$. We define the chemical potential to be $\mu = -(IP+EA)/2$ and chemical hardness to be $\eta = (IP-EA)/2$.

Table 3 Electron Affinity and Ionization potential, chemical potential and chemical hardness for Monomers, Dimers, trimers and tetramers of ZnN

Structures	Electron Affinity (ev)	Ionization potential (ev)	Chemical potential (ev)	Chemical Hardness (ev)
ZnN	0.28	9.97	5.13	4.84
Zn ₂ N ₂	3.23	6.53	4.88	1.65
Zn ₃ N ₃	2.60	8.54	5.57	2.97
Zn ₄ N ₄	4.72	0.15	2.44	2.28

Vibrational analysis of Different (ZnN)_n

Analysis of the normal vibrational modes of monomers, dimer, trimers and tetramers is carried out in this subsection. The study of the normal modes was used to judge the stability of the lowest lying isomers for the Zinc Nitride clusters. We have considered four different structures (Rhombus, square, bend, and distorted linear) for Zn₂N₂ configuration, four different structures (distorted rectangular, distorted triangular, benzene ring type and triangular) for Zn₃N₃ configuration and four different structures (square, cubic, squarer bend and distorted pyramidal) for Zn₄N₄ configuration here for calculations. In Table 1 the vibrational frequencies and their dipole moments of the monomers are collected. For Dimer, trimer and tetramers, the frequencies with their modes and their dipole moments values for the most stable structure are given in Table-4.

Table 4 Vibrational frequencies and Dipole moment of Different (ZnN)_n most stable structures [cm⁻¹]

Structures	Frequency Values (Mode) [cm ⁻¹]	Dipole moment (Debye)
Zn ₂ N ₂	147, 220, 433, 447, 540, 576	1.83
Zn ₂ N ₂ ⁺	69, 110, 128, 366, 529, 630	6.38
Zn ₂ N ₂ ⁻	80, 148, 150, 442, 501, 708	1.65
Zn ₃ N ₃	59, 103, 165, 196, 213, 232, 309, 408, 431, 495, 560, 1521	2.78
Zn ₃ N ₃ ⁺	31, 63, 85, 124, 140, 155, 396, 507, 513, 540, 603, 643	5.69
Zn ₃ N ₃ ⁻	65, 145, 161, 169, 171, 237, 430, 458, 504, 559, 610, 620	0.56
Zn ₄ N ₄	71, 77, 108, 111, 119, 126, 153, 191, 201, 233, 441, 501, 519, 601, 654, 723, 743, 779	0.00
Zn ₄ N ₄ ⁺	34, 39, 101, 103, 106, 137, 166, 179, 188, 202, 241, 389, 411, 438, 464, 473, 591, 2440	1.43
Zn ₄ N ₄ ⁻	45, 84, 88, 96, 136, 143, 148, 169, 184, 186, 349, 488, 494, 525, 562, 606, 668, 671	3.04

CONCLUSION

The geometrical structures, stability and the electronic properties etc of the (ZnN)_n clusters have been studied by Density functional theory with the B3LYP exchange-correlation functional using DGDZVP as the basis set. The descriptors like chemical potential, chemical hardness and binding energy of the clusters provide additional information for the experimentalists to build new materials of industrial importance.

Acknowledgements

The authors are grateful to the University Grants Commission, New Delhi, for providing the financial assistance.

REFERENCES

- [1] J. S.Chun, I. Petrov, J.E.Green, *J Appl Phys* 86 (1999)3633
- [2] W.R.L Lambrecht, M.S Miao, P. Lukashev, *J Appl Phys* 97(2005) 10D306
- [3] Young, Sanloup C, Gregoryanz E, Scandolo S, Hemley RJ, Ho-kwang Mao (2006) *Phys Rev Lett* 96:155501. doi:10.1103/PhysRevLett.96.155501
- [4] M.S Miao, P. Lukashev, A.Herwadkar, W.R.L Lambrecht, *Phys Stat Sol (c)* 27 : (2005)2516
- [5] P. J. Dismukes, M. W. Yim, and S. V. Ban, *J. Cryst. Growth* 13-14 (1972)365
- [6] H. F. George and H. K. John, *Phys. Rev.* 93 (1954)1004
- [7] H. Nakagawa, S. Nasu, H. Fujii, M. Takahashi, and F. Kanamaru, *Hyperfine Interact.* 69 (1991)455
- [8] K. Suzuki, T. Kaneko, H. Yoshida, H. Morita, and H. Fujimori, *J. Alloys Compd.* 224 (1995)232
- [9] Frisch, M. J. et al Gaussian 09; *Gaussian, Inc.*, Pittsburgh, PA, (2009)
- [10] P. Hohenberg, W. Kohn, *Phys. Rev.* 136 (1964)13864
- [11] A.D. Becke, *J. Chem. Phys* 98 (1993)5648
- [12] C. Lee, W. Yang, R.G. Parr, *Phys. Rev. B* 37 (1988)785
- [13] Extensible computational chemistry environment basis set database, version 1.0. Molecular Science Computing Facility, E. Laboratory, M. S. Pacific Northwest Laboratory, Richland, WA, (1999)