



DFT Calculations of Vibrational Frequencies of Aluminum and Phosphorous Doped-Carbon Clusters

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We have designed numerous models of aluminum (C_nAl_m) and phosphorus (C_nP_m) doped carbon clusters ($n = 3$ and $m = 4$). The geometry optimization, bond length and calculation of vibrational frequency were carried out in each case by DFT in local density approximation. We also try other widely used functionals but local density approximation functional works well in our study. Numerous cluster structures of aluminum and phosphorus were prepared because of their different bonding preference. In addition, the total energies of the C_nAl_m and C_nP_m clusters were also discussed.

Key Words: DFT, Binary clusters, Vibrational frequencies, Energies.

INTRODUCTION

Atomic clusters have become the field of interest from last few years due to their significant role as bridge between microscopic atoms and macroscopic condensed matter. Doping with molecular species adds further multidimensionality to the cluster structure and property variations, which can be useful for practical applications such as catalysis, new (nanostructured) materials, or molecular devices¹. The electronic structure calculation, based on density functional theory (DFT) and the local density approximation (LDA) are the reliable and computationally tractable tool in materials science²⁻⁵. A deep investigation of the properties of the doped carbon clusters is desirable, because the hetero-atoms are expected to play special role in their physical and chemical properties.

Zhan and Iwata⁶ optimized the geometric structures of C_nP^* ($n = 1-7$) using *ab initio* calculations. Pascoli and Lavendy proposed structures of carbon and phosphorus clusters (C_nP , C_nP^* , C_nP^+ ($n = 1-7$) and $C_nP^+_p$ ($n + p = 3-6$)) based on data collected in DFT calculations⁷⁻⁹. Liu and his coworkers carried out calculations on linear C_nP^* ($n = 1-11$) by using the HF method^{10,11}. Fisher *et al.*¹² conducted density functional calculations on structures of some carbon phosphide anions. C_nP_2 ($n = 3-9$) clusters have been analyzed theoretically by DFT calculations¹³, whereas various geometries of C_3P and C_3PC have been investigated by other *ab initio* approaches¹⁴. Various studies have been reported on aluminum clusters like C_2Al and C_2Al_2 in order to relate the geometry with stability^{15,16}.

Recently, Naumkin¹ studied the stable geometries, which correspond to the flat-structural motives of CAI_3 units. His content of "stability" refers to the energies among a predetermined set of clusters. The resemblances of C_2Al_3 with C_2Al_2 have been reported but many apparent questions regarding the geometries of C_nAl_m remain unanswered¹⁷. To the best of our knowledge no work on the theoretical study of phosphorous and aluminum-doped carbon clusters ($n = 3$ and $m = 4$) has been reported. Since the physical and chemical properties of a small metal cluster rely on its atomic structure, determining the lowest-energy structures of clusters is a fundamental step in understanding and utilizing their properties. In view of these facts, the present study has been undertaken to have a better understanding of the physical and chemical properties in phosphorous and aluminum-doped carbon clusters.

COMPUTATIONAL METHOD

DFT is a commonly used, reliable and accurate approach in searching for the lowest-energy structures of C_nAl_m and C_nP_m doped carbon clusters. When the cluster becomes larger, *i.e.*, n increases, the number of energy minima for a given cluster size increases rapidly. For this reason, an impartial search for the lowest-energy structure is extremely vital. DFT is used to obtain the solution of the Schrödinger equation within the local-density approximation (LDA). The Amsterdam density-functional theory (ADF) package using the double zeta wave functions was utilized in this study. The theory on determining the vibrational frequencies has been well described earlier¹⁸.

All possible clusters were made starting from the simplest one with only two atoms. For this cluster, the electronic energy is calculated as a function of distance between atoms and hence the lowest energy distances can be determined. The lowest-energy configuration is considered to be the stable one and the others with maximum energy are considered to be unstable and discarded. In a second step, the vibrational frequencies were calculated for the stable structures. In short, the optimization of the electronic energy determines the structure and the vibrational frequencies were always obtained for the optimized structure. We build all of the possible clusters and retain only the stable ones. All structures of clusters were fully optimized freely and only those structures that had a symmetry property were retained in this study. The reason is that we propose the larger structures may be built up from these elementary units which possess some symmetrical property.

RESULTS AND DISCUSSION

The present work deals with the theoretical study of aluminum and phosphorous-doped carbon clusters. We present the vibrational frequencies, zero point energies and total energies of the various aluminum and phosphorous-doped carbon clusters. These clusters are very interesting from the theoretical point of view because of the geometry difference between two different pairs (C_nAl_m and C_nP_m) of heterodoped carbon clusters. Both aluminum (group III) and phosphorus (group V) are adjacent to carbon (group IV) in periodic table and relative to carbon, aluminum can be considered to be electron poor and phosphorus electron rich. Hence, it is interesting to make comparisons between the two types because of their different group properties. Ball and stick models are used to represent clusters of C_nAl_m and C_nP_m (Figs. 1 and 2). Bigger balls represent the aluminum and phosphorus atoms and smaller ones denote carbon atoms. The geometries of most of the clusters depicted here has never been reported before.

Geometries of C_nAl_m and C_nP_m systems

CAI_n clusters (CAI , CAI_2 , CAI_3 and CAI_4): We made the diatomic molecule CAI [Fig. 1(i)] and optimized the structure for the minimum energy. Adding a single Al atom to C can produce a linear isomer, which could formally be associated with the C-Al bond length of 1.964 Å and the appreciable lowest vibrational frequency of 750.5 cm^{-1} . In the linear model CAI_2 linear [Fig. 1(ii)], the carbon atom is kept in the center and two aluminum atoms are located on each side of C so that the Al-C-Al atoms are aligned in a straight line. The bond length of C-Al is found to be 1.818 Å. The results of the vibrational frequencies of significant intensity allow us to consider the following isomers. The CAI_3 (triangular) model [Fig. 1(iii)] is formed by three atoms of Al which sit on three corners of a triangle and C sits in the center of the triangle. The CAI bond length is found to be 1.917 Å and in square model CAI_4 [Fig. 1(iv)] in which the four Al atoms sit on the corners of a square and one C is located in the center of the square. The CAI bond length is 2.471 Å. All the vibrational frequencies are given in Table-1.

C_nAl clusters (C_2Al , C_3Al): Adding a single Al atom to C_2 molecule can produce a linear isomer C_2Al [Fig. 1(v)] with one Al in the center and two C on two corners. The C-Al bond length is found to be 2.200 Å and in the triangular model C_2Al [Fig. 1(vi)] the CAI distance is found to be 2.045 Å and C-C distance is 1.271 Å. In the C_3Al pyramidal model, [Fig. 1(vii)] the three carbon atoms form a triangle and the Al atom sits at the top position. The C-Al bond distance is 1.975 Å and the C-C bond length is 1.499 Å and in the C_3Al triangular model [Fig. 1(viii)] the three C atoms form a triangle and one Al atom sits at the center. In this case the C-Al bond length is 1.953 Å. All the calculated vibrational frequencies are represented in Table-1.

C_nAl_m clusters (C_2Al_2 , C_2Al_3 , C_3Al_2 and C_3Al_3): Figs. 1(ix) to 1(xiv) list, respectively, the different geometries of the cluster systems. Optimized bond lengths of C_nAl_m clusters

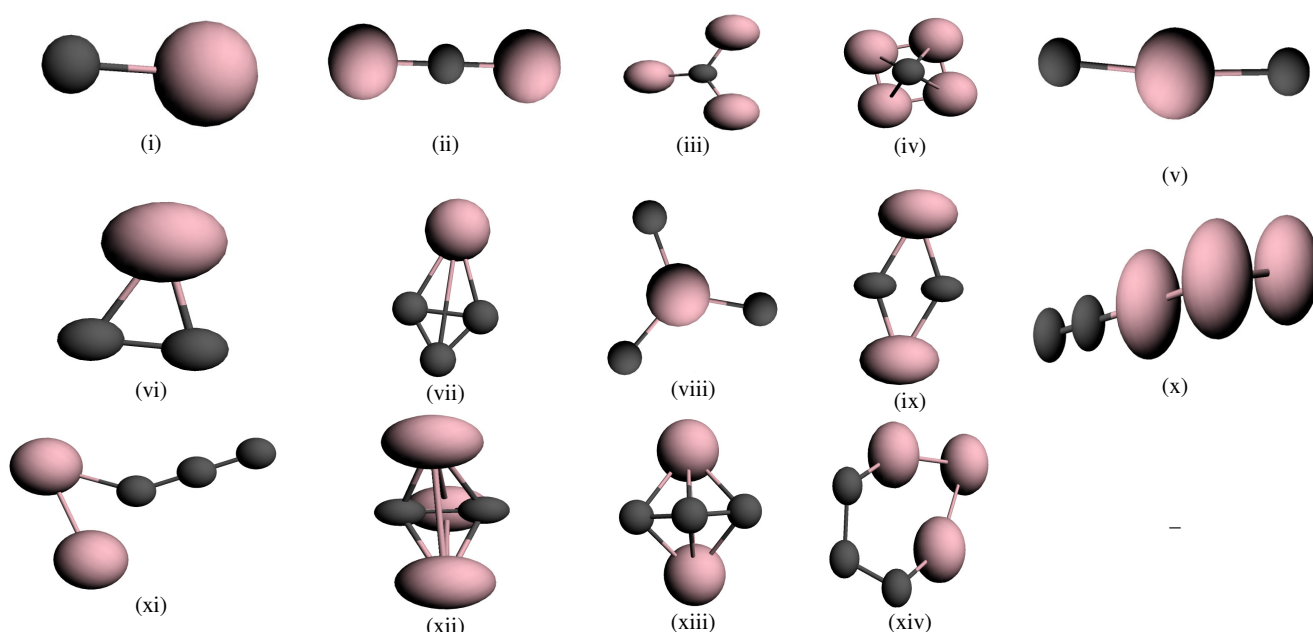


Fig. 1. Qualitative geometry of C_nAl_m clusters (i) to (xiv) shown by ball and stick models without electronic density contours

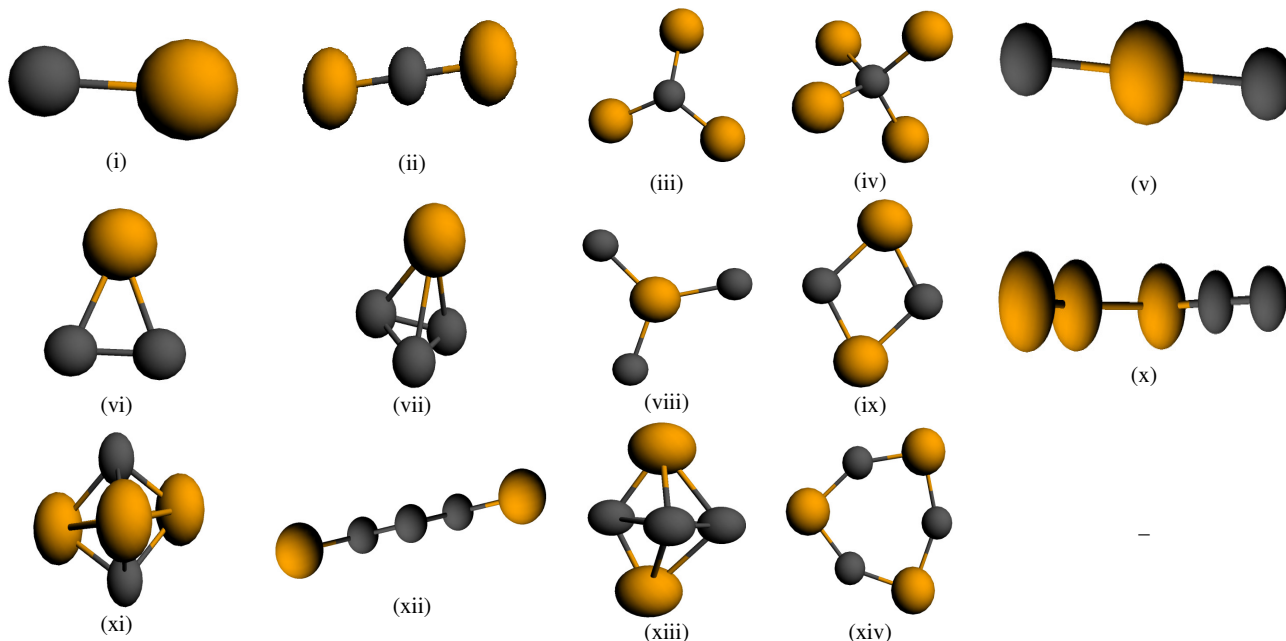


Fig. 2. Qualitative geometry of clusters (i) to (xiv) shown by stick-ball models without electronic structure

TABLE-1 VIBRATIONAL FREQUENCIES OF VARIOUS CLUSTERS CALCULATED FROM THE FIRST ORDER PRINCIPLES				
S. No.	Cluster	Frequency (cm ⁻¹)	Intensity (km/mol)	Degeneracy
CAI _n clusters				
1	CAI ₂ (linear)	82.8	97.9	1
2	CAI ₂ (linear)	454.9	0.01	1
3	CAI ₂ (linear)	1043.9	36.5	1
4	CAI ₃ (triangular)	449.3	2.05	2
5	CAI ₃ (triangular)	210.3	15.21	1
6	CAI ₃ (triangular)	395.5	0.01	1
7	CAI ₃ (triangular)	820.3	361.9	2
8	CAI ₄ (square)	103.2	0.01	2
9	CAI ₄ (square)	184.1	8.7	3
10	CAI ₄ (square)	330.2	0.01	1
11	CAI ₄ (square)	586.7	250.0	3
C _n Al clusters				
1	C ₂ Al (linear)	192.0	30.5	1
2	C ₂ Al (linear)	325.3	0.1	1
3	C ₂ Al (linear)	474.5	44.5	1
4	C ₂ Al (triangular)	149.3	8.1	1
5	C ₂ Al (triangular)	579.1	174.8	1
6	C ₂ Al (triangular)	1785.1	15.4	1
7	C ₃ Al (pyramidal)	261.7	0.01	1
8	C ₃ Al (pyramidal)	266.4	25.6	1
9	C ₃ Al (pyramidal)	433.8	137.9	1
10	C ₃ Al (pyramidal)	790.1	25.1	1
11	C ₃ Al (pyramidal)	1256.9	0.33	1
12	C ₃ Al (pyramidal)	1462.2	27.0	1
13	C ₃ Al (triangular)	422.6	22.2	1
14	C ₃ Al (triangular)	526.6	0.01	1
15	C ₃ Al (triangular)	723.7	15.5	2
C _n Al _m clusters				
1	C ₂ Al ₂ (rectangular)	280.2	0.01	1
2	C ₂ Al ₂ (rectangular)	430.8	805.4	1
3	C ₂ Al ₂ (rectangular)	1784.6	0.01	1
4	C ₂ Al ₃ (linear)	88.7	11.8	1
5	C ₂ Al ₃ (linear)	196.7	4.7	1
6	C ₂ Al ₃ (linear)	317.0	18.6	1

7	C ₂ Al ₃ (linear)	347.7	32.1	1
8	C ₂ Al ₃ (linear)	467.7	0.17	1
9	C ₂ Al ₃ (linear)	656.6	6.8	1
10	C ₂ Al ₃ (linear)	1899.6	536.4	1
11	C ₂ Al ₃ (bipyramidal)	249.1	2.4	2
12	C ₂ Al ₃ (bipyramidal)	380.2	0.01	1
13	C ₂ Al ₃ (bipyramidal)	396.1	0.01	2
14	C ₂ Al ₃ (bipyramidal)	487.2	62.0	1
15	C ₂ Al ₃ (bipyramidal)	570.8	83.4	2
16	C ₂ Al ₃ (bipyramidal)	678.5	0.01	1
17	C ₃ Al ₂ (linear)	101.2	2.5	1
18	C ₃ Al ₂ (linear)	169.2	0.7	1
19	C ₃ Al ₂ (linear)	172.0	8.1	1
20	C ₃ Al ₂ (linear)	290.4	8.0	1
21	C ₃ Al ₂ (linear)	434.6	5.2	1
22	C ₃ Al ₂ (linear)	439.4	41.4	1
23	C ₃ Al ₂ (linear)	620.5	219.7	1
24	C ₃ Al ₂ (linear)	1186.8	0.04	1
25	C ₃ Al ₂ (linear)	1878.3	657.5	1
26	C ₃ Al ₂ (bipyramidal)	280.0	53.3	1
27	C ₃ Al ₂ (bipyramidal)	409.2	8.5	1
28	C ₃ Al ₂ (bipyramidal)	417.1	9.9	1
29	C ₃ Al ₂ (bipyramidal)	541.5	37.8	1
30	C ₃ Al ₂ (bipyramidal)	546.4	97.1	1
31	C ₃ Al ₂ (bipyramidal)	725.7	1.5	1
32	C ₃ Al ₂ (bipyramidal)	989.4	37.4	1
33	C ₃ Al ₃ (ring)	82.0	33.5	1
34	C ₃ Al ₃ (ring)	126.1	0.05	1
35	C ₃ Al ₃ (ring)	161.4	64.9	1
36	C ₃ Al ₃ (ring)	169.1	1.4	1
37	C ₃ Al ₃ (ring)	217.2	11.3	1
38	C ₃ Al ₃ (ring)	298.4	1.2	1
39	C ₃ Al ₃ (ring)	346.7	3.0	1
40	C ₃ Al ₃ (ring)	428.1	0.2	1
41	C ₃ Al ₃ (ring)	445.6	14.2	1
42	C ₃ Al ₃ (ring)	493.3	143.7	1
43	C ₃ Al ₃ (ring)	571.6	26.5	1

and the C_n and Al_m alternation effect are also exhibited for the various clusters. In the C₂Al₂ rectangular model [Fig. 1(ix)]

the atoms are alternately arranged with the bond length 2.308 Å. The C₂Al₃ linear model [Fig. 1(x)] is obtained with two Al atoms and one C atom which lies in the center and one C and Al at the ends. The Al-Al bond length is 2.586 Å and C-C distance observed is 1.268 Å. The C₃Al₂ [Fig. 1(xi)] linear model is represented by two C and Al atoms which lie at the center and C and Al at the ends. The Al-Al distance is 2.6192 Å and C-C distance is 1.2952 Å at the ends. On optimization of the linear isomer, the bent geometry is displayed with no linearity in structure. The bipyramidal model [Fig. 1(xii)] C₂Al₃ is formed by three aluminum atoms, which form a triangle and one C atom sits on the top position and another in the bottom position. The CAI distance is found to be 2.364 Å and the Al-Al distance 3.934 Å. Similarly, in the C₃Al₂ bipyramidal structure [Fig. 1(xiii)] the three carbon atoms form a triangle and one Al atom is at the top position and another at the bottom position. The CAI distance is 2.295 Å and Al-Al distance is 3.196 Å. The C₃Al₃ [Fig. 1(xiv)] model is a hexagonal ring with three sites occupied by C on one side of the ring and three Al atoms on the other side. All the vibrational frequencies calculated from the first principles⁹ are given in Table-1.

CP_n clusters (CP, CP₂, CP₃ and CP₄): We now consider CP_n clusters and the corresponding geometries are displayed in Fig. 2. In each case, the geometry is optimized starting from several initial configurations obtained by adding the various atoms. Using the same principles as previously described we make the diatomic molecule CP [Fig. 2(i)] and optimized the structure for minimum energy. This calculation gives the CP bond length of 1.613 Å with vibrational frequency calculated as 1165.8 cm⁻¹. Another CP₂ linear [Fig. 2(ii)] model is obtained by adding two phosphorus atoms on each side of C, which is kept at the center so that P-C-P atoms are aligned in a straight line. The bond length of C-P is found to be 1.664 Å. Addition of three atoms of P to C which occupies the center and P which sit on three corners of a triangle results in a triangular CP₃ [Fig. 2(iii)] model. The CP bond length is found to be 1.773 Å. Another model of CP₄ [Fig. 2(iv)] is a square in which the four P atoms are on the corners of a square and one C located in the center of the square. The CP bond length is 1.818 Å. All the vibrational frequencies are given in Table-2.

TABLE-2
VIBRATIONAL FREQUENCIES OF VARIOUS CLUSTERS
CALCULATED FROM THE FIRST ORDER PRINCIPLES

S. No.	Cluster	Frequency (cm ⁻¹)	Intensity (km/mol)	Degeneracy
CP _n clusters				
1	CP ₂ (linear)	475.3	41.3	2
2	CP ₂ (linear)	545.1	0.5	1
3	CP ₂ (linear)	1401.3	198.7	1
4	CP ₃ (triangular)	222.8	7.17	2
5	CP ₃ (triangular)	441.8	0.3	1
6	CP ₃ (triangular)	659.8	27.7	1
7	CP ₃ (triangular)	972.4	1.1	2
8	CP ₄ (square)	103.4	0.01	1
9	CP ₄ (square)	211.8	0.8	2
10	CP ₄ (square)	272.6	0.02	1
11	CP ₄ (square)	428.3	6.5	2
12	CP ₄ (square)	432.4	1.1	1
13	CP ₄ (square)	466.6	0.01	1
14	CP ₄ (square)	568.9	6.2	1

C _n P clusters				
1	C ₂ P (linear)	200.0	4.8	1
2	C ₂ P (linear)	542.4	0.01	1
3	C ₂ P (linear)	563.9	80.1	1
4	C ₂ P (triangular)	649.0	5.0	1
5	C ₂ P (triangular)	672.6	2.0	1
6	C ₂ P (triangular)	1422.0	17.0	1
7	C ₃ P (pyramidal)	421.5	39.8	1
8	C ₃ P (pyramidal)	479.3	3.5	1
9	C ₃ P (pyramidal)	661.1	46.7	1
10	C ₃ P (pyramidal)	995.9	31.2	1
11	C ₃ P (pyramidal)	1381.6	17.5	1
12	C ₃ P (triangular)	189.1	3.0	2
13	C ₃ P (triangular)	349.0	21.6	1
14	C ₃ P (triangular)	603.9	0.01	1
15	C ₃ P (triangular)	668.2	22.2	2
C _n P _m clusters				
1	C ₂ P ₂ (rectangular)	297.6	53.3	1
2	C ₂ P ₂ (rectangular)	468.9	0.01	1
3	C ₂ P ₂ (rectangular)	742.7	0.01	1
4	C ₂ P ₂ (rectangular)	792.7	148.0	1
5	C ₂ P ₂ (rectangular)	962.7	0.02	1
6	C ₂ P ₃ (linear)	44.2	3.7	1
7	C ₂ P ₃ (linear)	111.0	4.3	1
8	C ₂ P ₃ (linear)	148.2	6.3	1
9	C ₂ P ₃ (linear)	223.4	0.8	1
10	C ₂ P ₃ (linear)	338.9	14.8	1
11	C ₂ P ₃ (linear)	381.1	9.4	1
12	C ₂ P ₃ (linear)	647.3	11.9	1
13	C ₂ P ₃ (linear)	718.0	27.8	1
	C ₂ P ₃ (linear)	1787.3	311.3	1
14	C ₂ P ₃ (bipyramidal)	200.5	16.7	2
15	C ₂ P ₃ (bipyramidal)	330.1	26.5	1
16	C ₂ P ₃ (bipyramidal)	446.6	0.01	1
17	C ₂ P ₃ (bipyramidal)	644.3	0.5	2
18	C ₂ P ₃ (bipyramidal)	690.8	0.01	1
19	C ₂ P ₃ (bipyramidal)	771.5	16.2	2
20	C ₃ P ₂ (bipyramidal)	128.8	30.1	1
21	C ₃ P ₂ (bipyramidal)	272.7	3.1	1
22	C ₃ P ₂ (bipyramidal)	307.5	11.5	1
23	C ₃ P ₂ (bipyramidal)	349.5	9.5	1
24	C ₃ P ₂ (bipyramidal)	461.0	2.0	1
25	C ₃ P ₂ (bipyramidal)	628.1	9.4	1
26	C ₃ P ₂ (bipyramidal)	679.9	4.4	1
27	C ₃ P ₂ (bipyramidal)	976.5	25.1	1
28	C ₃ P ₂ (bipyramidal)	978.4	0.4	1
29	C ₃ P ₃ (ring)	281.0	0.01	2
30	C ₃ P ₃ (ring)	385.4	51.4	1
31	C ₃ P ₃ (ring)	386.7	72.3	2
32	C ₃ P ₃ (ring)	485.1	9.8	2
33	C ₃ P ₃ (ring)	490.7	0.01	1
34	C ₃ P ₃ (ring)	788.3	0.02	1
35	C ₃ P ₃ (ring)	861.6	0.01	1
36	C ₃ P ₃ (ring)	1126.5	76.4	2
37	C ₃ P ₂ (linear)	218.9	18.1	1
38	C ₃ P ₂ (linear)	247.7	0.2	1
39	C ₃ P ₂ (linear)	299.0	0.01	1
40	C ₃ P ₂ (linear)	339.8	0.03	1
41	C ₃ P ₂ (linear)	353.1	1.2	1
42	C ₃ P ₂ (linear)	503.8	4.9	1
44	C ₃ P ₂ (linear)	709.2	1.4	1
45	C ₃ P ₂ (linear)	710.1	172.8	1
46	C ₃ P ₂ (bipyramidal)	324.9	0.9	1
47	C ₃ P ₂ (bipyramidal)	524.5	12.3	1
48	C ₃ P ₂ (bipyramidal)	529.5	0.2	1
49	C ₃ P ₂ (bipyramidal)	624.9	0.09	1
50	C ₃ P ₂ (bipyramidal)	724.1	8.2	1

51	C ₃ P ₂ (bipyramidal)	775.5	45.7	1
52	C ₃ P ₂ (bipyramidal)	947.6	220.2	1
53	C ₃ P ₂ (bipyramidal)	1130.7	2.1	1

C_nP clusters (C₂P, C₃P): Formally adding a single P to the C₂ molecule can produce a linear model of C₂P [Fig. 2(v)] similar to that of C₂Al in which Al sits at the center and two C at the two sides. The CP bond length is found to be 1.870 Å. In the triangular model C₂P [Fig. 2(vi)] the CP distance is 186.2 Å and C-C distance 1.342 Å. The pyramidal model C₃P [Fig. 2(vii)] is obtained by three carbon atoms which form a triangle and one P atom which sits at the top position. The C-P bond distance is 1.925 Å and the C-C bond length is 1.462 Å. While in C₃P [Fig. 2(viii)] which is triangular, the three carbon atoms form a triangle and one phosphorus atom sits in the center. In this case the C-P bond length is 1.828 Å. The calculated vibrational frequencies are given in Table-2.

C_nP_m clusters (C₂P₂, C₂P₃, C₃P₂ and C₃P₃): In C₂P₂ which is rectangular [Fig. 2(ix)] all the atoms are alternatively arranged with bond length 1.870 Å and in the linear C₂P₃ [Fig. 2(x)] P and C are located at the ends and two P and C lies in the center of the cluster. Interestingly the structure showed no linearity under optimization. The CP bond length is 1.6982 Å and C-C bond length is 1.2900 Å. Another C₂P₃ [Fig. 2(xi)] bipyramidal structure was obtained where the three phosphorus atoms form a triangle and one C atom sits on top position and another at the bottom position. The CP distance is found to be 1.913 Å and the P-P distance 2.901 Å. In C₃P₂ [Fig. 2(xii)] which is linear, three C atoms lie at the center and two P atoms at the ends. The CP distance at the ends is 1.870 Å. The bipyramidal C₃P₂ cluster [Fig. 2(xiii)] is obtained by three carbon atoms which form a triangle and a P atom which is at the top position and another in the bottom position. The CP distance is 2.295 Å and the P-P distance is 3.196 Å. Another C₃P₃ structure [Fig. 2(xiv)] forms a hexagonal ring with alternate sites occupied by C and P atoms. All the vibrational frequencies are given in Table-2.

Energies of various clusters: A perusal of Table-3 presents the zero point energies and total energies of the C_nAl_m and C_nP_m clusters. These values are graphically represented in Fig. 3, which show that the total energies increase with increase in the number of cluster atoms. The sequence of the total energies of the cluster model C_nAl_m is as follows: CAI (L), C₂Al (L) C₂Al₂ (L), C₂Al (T), C₃Al (T) < C₂Al₂ (R), C₃Al₂ (L), C₃Al₂ (BP) C₂Al₃ (L) < C₂Al₃ (BP), C₃Al₃ (R), CAI₄ (S). A comparison with the neighboring heteroatom-containing species that is C_nP_m clusters have also been predicted. For each set {----} where each member of form C_nP_m is an increasing sequence in the total energy, we can further distinguish the groups of sets energetically as follows: {CP (L), C₂P (L), C₂P (T), C₃P (T), C₃P (P), C₂P (L)} < {C₂P₂ (RA), C₃P₂ (L), C₃P₂ (BP)} < {CP₃ (T), C₂P₃ (L), C₂P₃ (BP), C₃P₃ (R), CP₄ (S)}. This grouping suggests that in general (there are exceptions) linear and triangular isomers seems to have less energies than isomers of other symmetries. However, the comparison between the two C_nAl_m and C_nP_m in Fig. 3 suggest that C_nAl_m isomers are usually less in energy than the C_nP_m type. According to the results of our calculations, the less energy structures of the cluster models of C_nAl_m and C_nP_m can be regarded as the corresponding outcomes

TABLE-3
ZERO POINT VIBRATIONAL ENERGIES (ZPE) AND
TOTAL ENERGIES (TE) OF VARIOUS CLUSTERS

S. No.	Cluster	Zero point vibrational energies (eV)	Total energies (eV)
C _n Al _m cluster			
1	CAI (linear)	0.0465	-278.8127
2	CAI ₂ (linear)	0.0980	-520.3326
3	CAI ₃ (triangular)	0.1577	-716.7942
4	CAI ₄ (square)	0.1766	-1003.2028
5	C ₂ Al (linear)	0.0614	-316.3943
6	C ₂ Al (triangular)	0.1558	-316.6618
7	C ₂ Al ₂ (rectangular)	0.1559	-558.0945
8	C ₂ Al ₃ (linear)	0.2463	-799.4108
9	C ₂ Al ₃ (bipyramidal)	0.2466	-799.3859
10	C ₃ Al (pyramidal)	0.2771	-354.3275
11	C ₃ Al (triangular)	0.1485	-353.9456
12	C ₃ Al ₂ (linear)	0.3281	-595.7709
13	C ₃ Al ₂ (bipyramidal)	0.2641	-595.7200
14	C ₃ Al ₃ (ring)	0.2068	-837.0267
C _n P _m cluster			
1	CP (linear)	0.0722	-377.6220
2	CP ₂ (linear)	0.1796	-717.7843
3	CP ₃ (triangular)	0.2164	-1057.8079
4	CP ₄ (square)	0.2542	-1397.8502
5	C ₂ P (linear)	0.0809	-415.1766
6	C ₂ P (triangular)	0.1700	-415.2982
7	C ₂ P ₂ (rectangular)	0.2023	-755.3707
8	C ₂ P ₃ (linear)	0.2727	-1095.4947
9	C ₂ P ₃ (bipyramidal)	0.2913	-1095.4931
10	C ₃ P (pyramidal)	0.2442	-452.8670
11	C ₃ P (triangular)	0.1653	-452.6463
12	C ₃ P ₂ (linear)	0.2096	-793.0214
13	C ₃ P ₂ (bipyramidal)	0.3464	-792.9778
14	C ₃ P ₃ (ring)	0.4392	-1133.1905

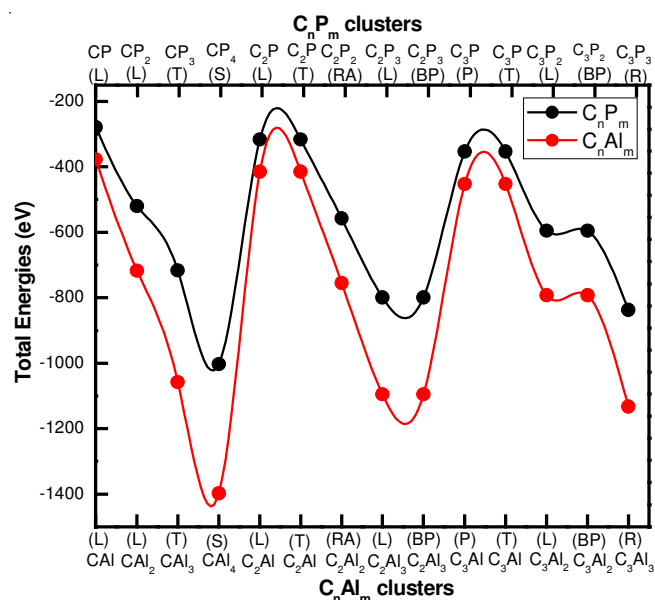


Fig. 3. Curves of total energies of the C_nAl_m and C_nP_m clusters versus number of cluster atoms of different geometries L (linear), T (triangular), S (square), RA (rectangular), P (pyramidal), BP (bipyramidal) and R (ring)

of lengthening the carbon chain or the aluminum component atoms in the cluster models. As expected, the results obtained in our study for the two different types of cluster systems show that

the values of the total energies varies and increases as the number of atoms in the isomers increases from CAI to C_nAl_m and from CP to C_nP_m .

Conclusion

Density functional computations have been carried out on aluminum and phosphorous doped carbon clusters. Interesting results have been obtained, for example, comparison of frequencies of CAI₃ (triangular) with C₃Al (triangular) shows that CAI₃ has a vibrational frequency 210.3 cm⁻¹ whereas C₃Al has a vibrational frequency 422.6 cm⁻¹. Comparing C₃P (triangular) with CP₃ (triangular) we observe that shows that CP₃ has vibrational frequency 222.8 cm⁻¹ whereas C₃P has vibrational frequency 189.1 cm⁻¹ as the lowest frequency. It is observed that the effect of force constant is much stronger than the effect of the mass and our calculations are clear about the bond distance, which depends on the structures of various clusters. The sequences of the total energies of various isomers were obtained. Considerable effect due to the number of hetero atoms linked to carbon has been observed. We hope that the present work will serve to stimulate experimental studies of binary aluminum and phosphorus doped carbon clusters.

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