Electronic Supplementary Information (ESI).

Onset of carbon-carbon bonding in the Nb_5C_y (y = 0-6) clusters: a threshold photo-ionisation and density functional theory study.

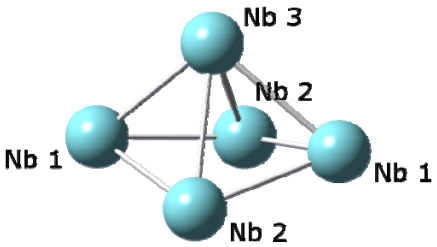
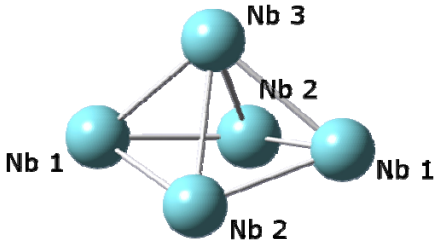
Dryza *et al*, *PCCP*, 2008.

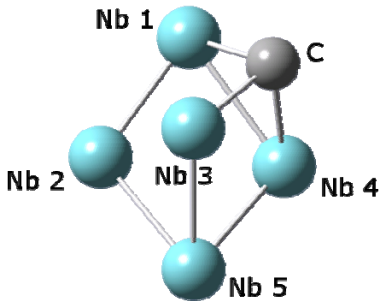
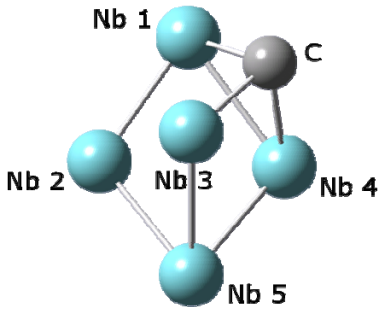
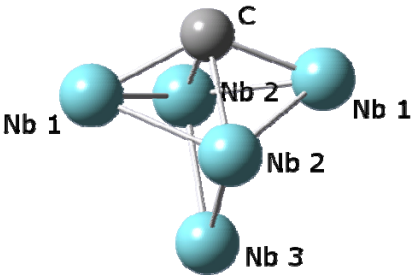
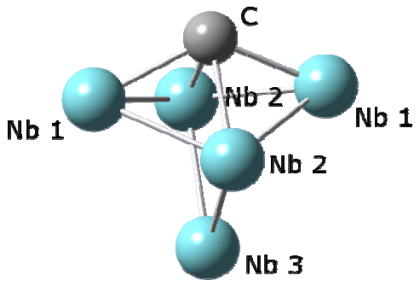
Tables displaying the electronic state, structural symmetry, absolute energies (B3P86/Nb SDD, C aug-cc-pVTZ) and relative energies for the neutral and cationic niobium-carbide cluster isomers.

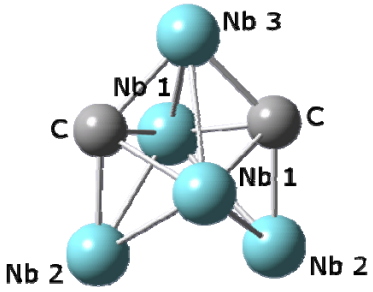
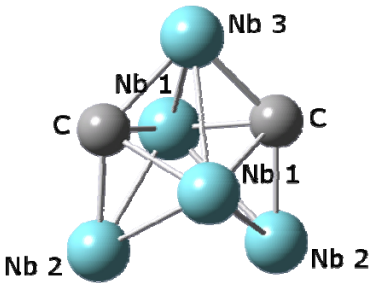
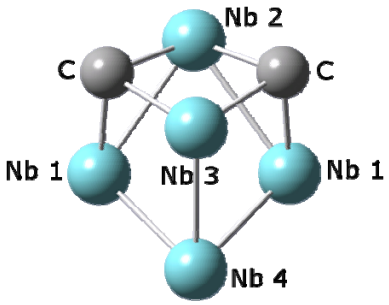
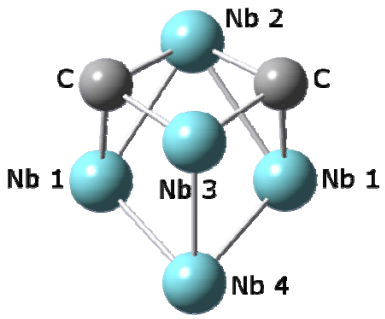
Cluster	Electronic State	Symmetry	Absolute Energy (a.u)	Relative Energy (eV)
Nb_5				
I A	$^2B_1$	C_{2v}	-286.19471	0.000
	$^4A'$	C_s	-286.18519	0.259
Nb_5C				
II A	^2A	C_1	-324.45092	0.000
	^4A	C_1	-324.44134	0.261
II B	$^2A_1$	C_{2v}	-324.44827	0.072
	$^4A_2$	C_{2v}	-324.43165	0.525
Nb_5C_2				
III A	$^2B_1$	C_{2v}	-362.72514	0.000
	$^4A'$	C_s	-362.68986	0.960
III B	$^2A'$	C_s	-362.72081	0.118
	$^4A'$	C_s	-362.68881	0.989
Nb_5C_3				
IV A	$^2A_1$	C_{3v}	-400.99418	0.000
	^4A	C_1	-400.95252	1.133
Nb_5C_4				
V A	$^2A'$	C_s	-439.18649	0.000
	$^4A'$	C_s	-439.16810	0.500
V B	$^2A''$	C_s	-439.18164	0.132
	$^4A''$	C_s	-439.17039	0.438
V C	$^2A_1$	C_{2v}	-439.16836	0.493
	$^4B_2$	C_{2v}	-439.16499	0.585
V D	^2A	C_2	-439.16261	0.650
	^4B	C_2	-439.14220	1.205
Nb_5C_5				
VI A	$^2A'$	C_s	-477.42246	0.000
	$^4A''$	C_s	-477.41498	0.204
VI B	$^2A'$	C_s	-477.41022	0.333
	$^4A''$	C_s	-477.38019	1.150
VI C	^2A	C_1	-477.40806	0.392
	^4A	C_1	-477.38997	0.884
VI D	^2A	C_1	-477.40043	0.599

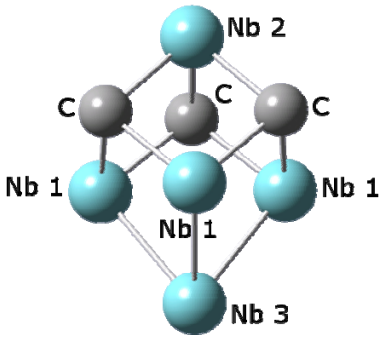
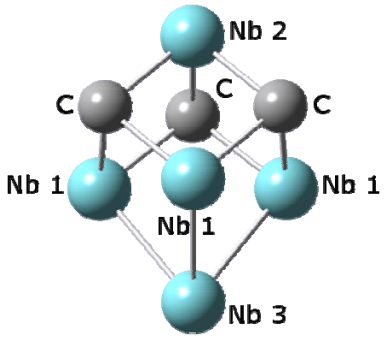
	^4A	C_1	-477.38799	0.938
Nb_5C_6				
VII A	$^2A_1$	C_{2v}	-515.68800	0.000
	$^4A_2$	C_{2v}	-515.66640	0.588
VII B	$^2B_1$	C_{2v}	-515.64714	1.112
	$^4B_1$	C_{2v}	-515.63360	1.480
Nb_5^+				
I A^+	$^1A_1$	C_{2v}	-285.97582	0.243
	$^3A_1$	C_{2v}	-285.98476	0.000
Nb_5C^+				
II A^+	^1A	C_1	-324.23732	0.016
	^3A	C_1	-324.23354	0.118
II B^+	$^1A'$	C_s	-324.23115	0.184
	$^3B_2$	C_{2v}	-324.23790	0.000
$Nb_5C_2^+$				
III A^+	$^1A_1$	C_{2v}	-362.54234	0.000
	$^3B_1$	C_{2v}	-362.50838	0.924
III B^+	$^1A'$	C_s	-362.50144	1.113
	$^3A''$	C_s	-362.50676	0.968
$Nb_5C_3^+$				
IV A^+	$^1A_1$	C_{3v}	-400.80894	0.000
	^3A	C_1	-400.75789	1.389
$Nb_5C_4^+$				
V A^+	$^1A'$	C_s	-438.96981	0.295
	$^3A'$	C_s	-438.97561	0.138
V B^+	$^1A'$	C_s	-438.97730	0.091
	$^3A''$	C_s	-438.97740	0.089
V C^+	$^1A_1$	C_{2v}	-438.98066	0.000
	$^3A_1$	C_{2v}	-438.96724	0.365
V D^+	^1A	C_2	-438.96437	0.443
	^3A	C_1	-438.94266	1.034
$Nb_5C_5^+$				
VI A^+	$^1A'$	C_s	-477.22490	0.000
	^3A	C_1	-477.21208	0.349
VI B^+	$^1A'$	C_s	-477.21260	0.335
	$^3A'$	C_s	-477.17682	1.308
VI C^+	^1A	C_1	-477.19408	0.839
	^3A	C_1	-477.19117	0.918
VI D^+	^1A	C_1	-477.19589	0.790
	^3A	C_1	-477.18627	1.051
$Nb_5C_6^+$				
VII A^+	$^1A_1$	C_{2v}	-515.48703	0.000
	$^3A_1$	C_{2v}	-515.46049	0.722
VII B^+	$^1A_1$	C_{2v}	-515.43207	1.495
	$^3B_1$	C_{2v}	-515.41564	1.943

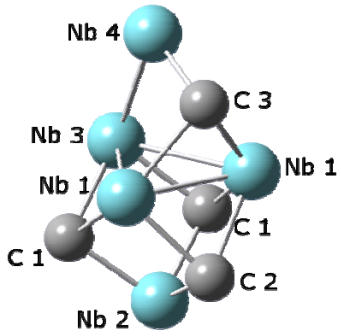
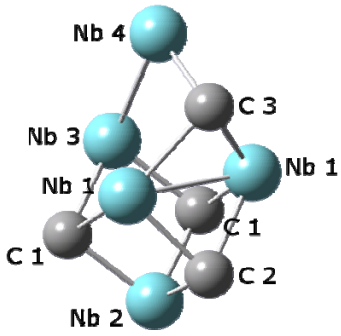
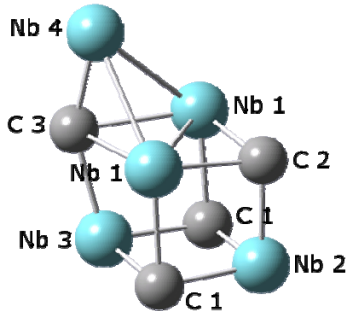
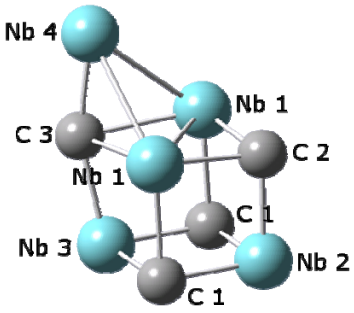
Tables displaying the geometrical parameters and atomic charges for the neutral and cationic niobium-carbide cluster isomers (B3P86/Nb SDD, C aug-cc-pVTZ).

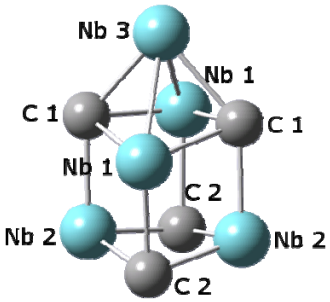
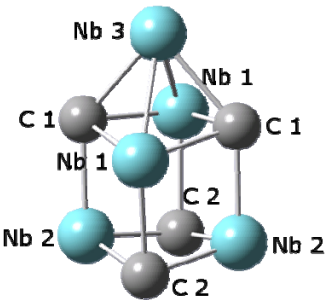
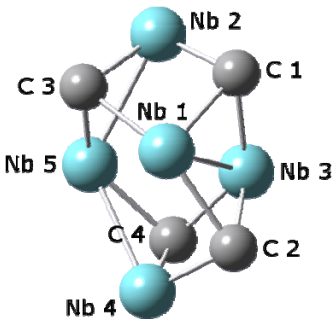
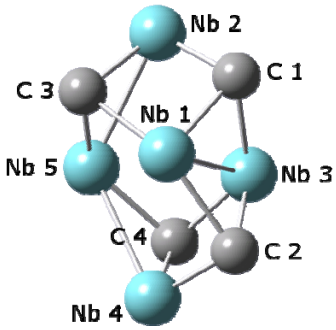
Cluster	Geom. Parameters	Charges
Nb_5 I A $^2B_1$ C_{2v} 	**Nb1-Nb1 = 3.950 Å** **Nb1-Nb2 = 2.491 Å** **Nb1-Nb3 = 2.614 Å** **Nb2-Nb2 = 2.874 Å** **Nb2-Nb3 = 2.632 Å**	**Nb1 = –0.20** **Nb2 = +0.15** **Nb3 = +0.10**
Nb_5^+ I A$^+$ $^3A_1$ C_{2v} 	**Nb1-Nb1 = 3.961 Å** **Nb1-Nb2 = 2.502 Å** **Nb1-Nb3 = 2.624 Å** **Nb2-Nb2 = 2.914 Å** **Nb2-Nb3 = 2.627 Å**	**Nb1 = +0.25** **Nb2 = +0.18** **Nb3 = +0.15**

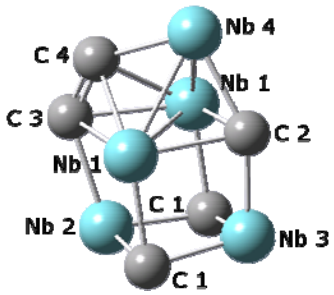
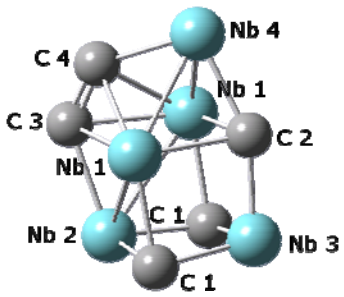
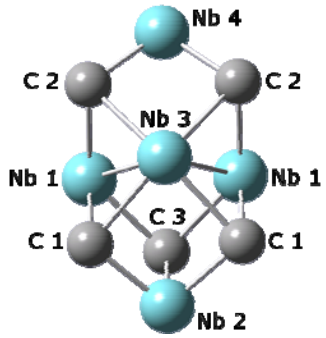
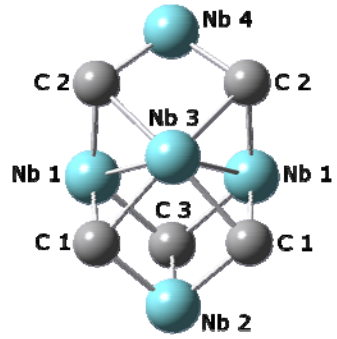
Cluster	Geom. Parameters	Charges
Nb_5C II A ^2A C_1 	Nb1-Nb2 = 2.343 Å Nb1-Nb3 = 2.994 Å Nb1-Nb4 = 2.519 Å Nb2-Nb3 = 2.776 Å Nb2-Nb4 = 2.877 Å Nb2-Nb5 = 2.557 Å Nb3-Nb4 = 2.809 Å Nb3-Nb5 = 2.492 Å Nb4-Nb5 = 2.449 Å Nb1-C = 2.089 Å Nb3-C = 1.924 Å Nb4-C = 2.068 Å	Nb1 = +0.28 Nb2 = –0.13 Nb3 = +0.49 Nb4 = +0.39 Nb5 = –0.15 C = –0.88
Nb_5C^+ II A^+ ^1A C_1 	Nb1-Nb2 = 2.367 Å Nb1-Nb3 = 2.958 Å Nb1-Nb4 = 2.500 Å Nb2-Nb3 = 2.764 Å Nb2-Nb4 = 2.860 Å Nb2-Nb5 = 2.487 Å Nb3-Nb4 = 2.849 Å Nb3-Nb5 = 2.553 Å Nb4-Nb5 = 2.474 Å Nb1-C = 2.032 Å Nb3-C = 1.919 Å Nb4-C = 2.118 Å	Nb1 = +0.59 Nb2 = +0.04 Nb3 = +0.61 Nb4 = +0.41 Nb5 = +0.16 C = –0.81
Nb_5C II B $^2A_1$ C_{2v} 	Nb1-Nb2 = 2.499 Å Nb1-Nb3 = 3.149 Å Nb2-Nb2 = 3.108 Å Nb2-Nb3 = 2.469 Å Nb1-C = 2.043 Å Nb2-C = 2.149 Å	Nb1 = +0.14 Nb2 = +0.30 Nb3 = +0.02 C = –0.89
Nb_5C^+ II B^+ $^3B_2$ C_{2v} 	Nb1-Nb2 = 2.497 Å Nb1-Nb3 = 3.131 Å Nb2-Nb2 = 3.123 Å Nb2-Nb3 = 2.479 Å Nb1-C = 2.056 Å Nb2-C = 2.156 Å	Nb1 = +0.54 Nb2 = +0.31 Nb3 = +0.19 C = –0.88

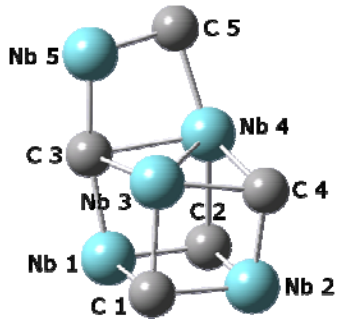
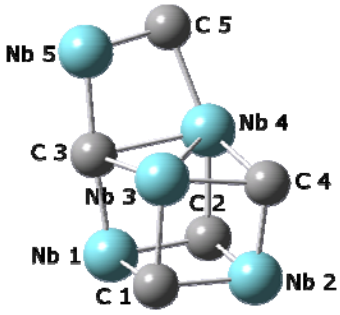
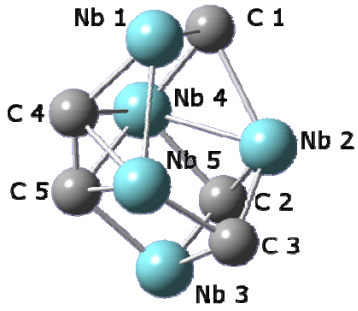
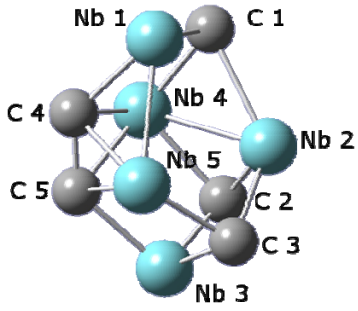
Cluster	Geom. Parameters	Charges
Nb_5C_2 III A $^2B_1$ C_{2v} 	Nb1-Nb1 = 3.101 Å Nb1-Nb2 = 2.529 Å Nb1-Nb3 = 2.600 Å Nb2-Nb2 = 2.809 Å Nb1-C = 2.164 Å Nb2-C = 2.030 Å Nb3-C = 2.024 Å	Nb1 = +0.39 Nb2 = +0.25 Nb3 = +0.41 C = –0.84
$Nb_5C_2^+$ III A$^+$ $^1A_1$ C_{2v} 	Nb1-Nb1 = 3.087 Å Nb1-Nb2 = 2.541 Å Nb1-Nb3 = 2.581 Å Nb2-Nb2 = 2.852 Å Nb1-C = 2.156 Å Nb2-C = 2.021 Å Nb3-C = 2.024 Å	Nb1 = +0.64 Nb2 = +0.35 Nb3 = +0.61 C = –0.80
Nb_5C_2 III B $^2A'$ C_s 	Nb1-Nb1 = 3.012 Å Nb1-Nb2 = 2.598 Å Nb1-Nb3 = 2.863 Å Nb1-Nb4 = 2.462 Å Nb2-Nb3 = 2.898 Å Nb3-Nb4 = 2.493 Å Nb1-C = 1.990 Å Nb2-C = 2.039 Å Nb3-C = 2.002 Å	Nb1 = +0.30 Nb2 = +0.63 Nb3 = +0.63 Nb4 = –0.24 C = –0.82
$Nb_5C_2^+$ III B$^+$ $^3A''$ C_s 	Nb1-Nb1 = 2.901 Å Nb1-Nb2 = 2.625 Å Nb1-Nb3 = 2.909 Å Nb1-Nb4 = 2.507 Å Nb2-Nb3 = 2.877 Å Nb3-Nb4 = 2.520 Å Nb1-C = 2.015 Å Nb2-C = 1.997 Å Nb3-C = 1.995 Å	Nb1 = +0.46 Nb2 = +0.80 Nb3 = +0.72 Nb4 = +0.07 C = –0.76

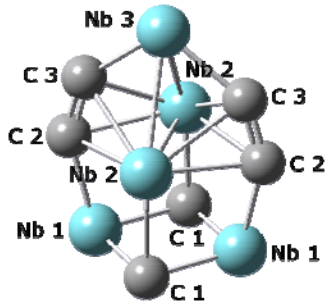
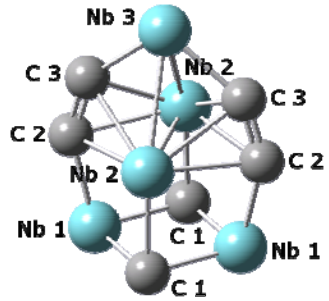
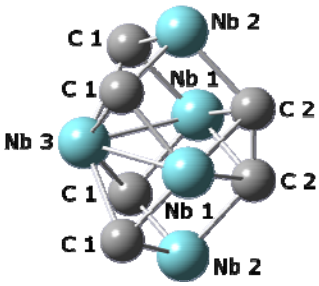
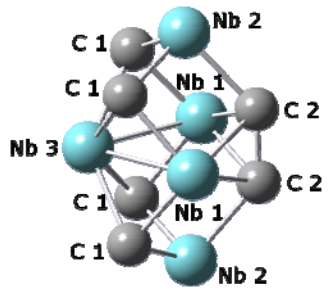
Cluster	Geom. Parameters	Charges
Nb_5C_3 IV A $^2A_1$ C_{3v} 	**Nb1-Nb1 = 2.901 Å** **Nb1-Nb2 = 2.914 Å** **Nb1-Nb3 = 2.470 Å** **Nb1-C = 2.016 Å** **Nb2-C = 1.997 Å**	**Nb1 = +0.62** **Nb2 = +0.79** **Nb3 = –0.26** **C = –0.80**
$Nb_5C_3^+$ IV A^+ $^1A_1$ C_{3v} 	**Nb1-Nb1 = 2.920 Å** **Nb1-Nb2 = 2.876 Å** **Nb1-Nb3 = 2.483 Å** **Nb1-C = 2.021 Å** **Nb2-C = 1.959 Å**	**Nb1 = +0.71** **Nb2 = +1.07** **Nb3 = –0.01** **C = –0.73**

Cluster	Geom. Parameters	Charges
Nb_5C_4 V A $^2A'$ C_s 	Nb1-Nb1 = 2.516 Å Nb1-Nb2 = 2.913 Å Nb1-Nb3 = 2.739 Å Nb1-Nb4 = 2.955 Å Nb2-Nb3 = 2.875 Å Nb3-Nb4 = 2.656 Å Nb1-C1 = 2.108 Å Nb1-C2 = 2.070 Å Nb1-C3 = 2.132 Å Nb2-C1 = 1.967 Å Nb2-C2 = 1.936 Å Nb3-C1 = 2.029 Å Nb4-C3 = 1.882 Å	Nb1 = +0.78 Nb2 = +0.89 Nb3 = +0.53 Nb4 = +0.33 C1 = –0.83 C2 = –0.77 C3 = –0.87
$Nb_5C_4^+$ V A$^+$ $^3A'$ C_s 	Nb1-Nb1 = 2.589 Å Nb1-Nb2 = 2.919 Å Nb1-Nb3 = 2.766 Å Nb1-Nb4 = 2.959 Å Nb2-Nb3 = 2.881 Å Nb3-Nb4 = 2.703 Å Nb1-C1 = 2.094 Å Nb1-C2 = 2.050 Å Nb1-C3 = 2.108 Å Nb2-C1 = 1.964 Å Nb2-C2 = 1.934 Å Nb3-C1 = 2.003 Å Nb4-C3 = 1.857 Å	Nb1 = +0.86 Nb2 = +1.00 Nb3 = +0.62 Nb4 = +0.65 C1 = –0.75 C2 = –0.69 C3 = –0.80
Nb_5C_4 V B $^2A''$ C_s 	Nb1-Nb1 = 2.618 Å Nb1-Nb2 = 2.942 Å Nb1-Nb3 = 2.757 Å Nb1-Nb4 = 2.676 Å Nb2-Nb3 = 2.848 Å Nb1-C1 = 2.157 Å Nb1-C2 = 2.044 Å Nb1-C3 = 2.273 Å Nb2-C1 = 1.960 Å Nb2-C2 = 1.972 Å Nb3-C1 = 1.996 Å Nb3-C3 = 2.057 Å Nb4-C3 = 1.901 Å	Nb1 = +0.71 Nb2 = +0.87 Nb3 = +0.85 Nb4 = +0.11 C1 = –0.80 C2 = –0.80 C3 = –0.85
$Nb_5C_4^+$ V B$^+$ $^3A''$ C_s 	Nb1-Nb1 = 2.680 Å Nb1-Nb2 = 2.928 Å Nb1-Nb3 = 2.846 Å Nb1-Nb4 = 2.700 Å Nb2-Nb3 = 2.849 Å Nb1-C1 = 2.127 Å Nb1-C2 = 2.025 Å Nb1-C3 = 2.241 Å Nb2-C1 = 1.962 Å Nb2-C2 = 1.971 Å Nb3-C1 = 1.983 Å Nb3-C3 = 2.006 Å Nb4-C3 = 1.911 Å	Nb1 = +0.77 Nb2 = +1.00 Nb3 = +0.96 Nb4 = +0.51 C1 = –0.74 C2 = –0.73 C3 = –0.80

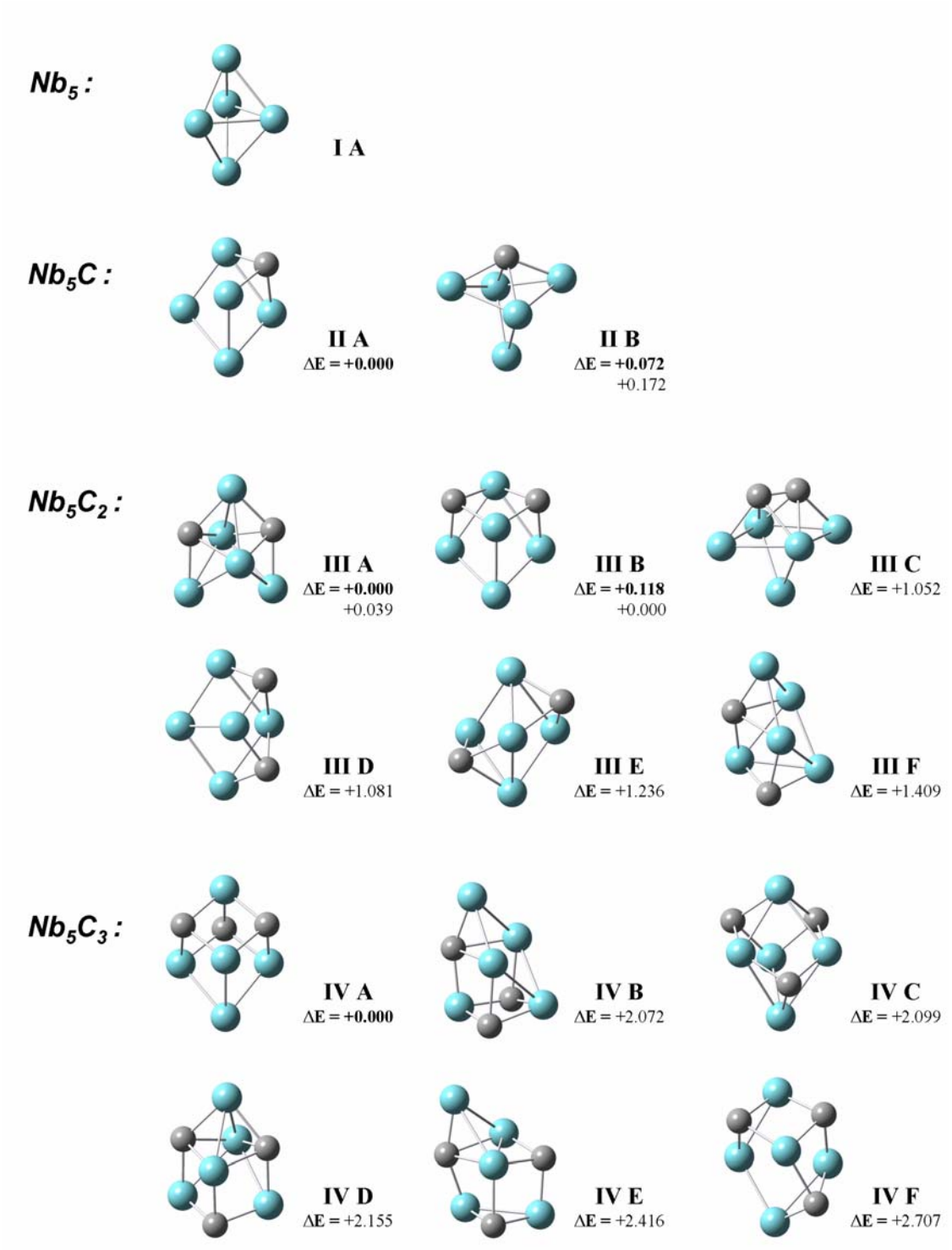
Cluster	Geom. Parameters	Charges
Nb_5C_4 V C $^2A_1$ C_{2v} 	Nb1-Nb1 = 3.180 Å Nb1-Nb2 = 2.794 Å Nb1-Nb3 = 2.464 Å Nb2-Nb2 = 2.783 Å Nb1-C1 = 2.129 Å Nb1-C2 = 2.135 Å Nb2-C1 = 2.123 Å Nb2-C2 = 1.974 Å Nb3-C1 = 2.107 Å	Nb1 = +0.71 Nb2 = +0.87 Nb3 = +0.21 C1 = –0.86 C2 = –0.83
$Nb_5C_4^+$ V C^+ $^1A_1$ C_{2v} 	Nb1-Nb1 = 3.108 Å Nb1-Nb2 = 2.809 Å Nb1-Nb3 = 2.435 Å Nb2-Nb2 = 2.771 Å Nb1-C1 = 2.101 Å Nb1-C2 = 2.168 Å Nb2-C1 = 2.125 Å Nb2-C2 = 1.958 Å Nb3-C1 = 2.148 Å	Nb1 = +0.86 Nb2 = +1.02 Nb3 = +0.45 C1 = –0.84 C2 = –0.77
Nb_5C_4 V D ^2A C_2 	Nb1-Nb2 = Nb3-Nb4 = 2.841 Å Nb1-Nb3 = 2.584 Å Nb1-Nb4 = Nb2-Nb3 = 2.910 Å Nb1-Nb5 = Nb3-Nb5 = 2.803 Å Nb2-Nb5 = Nb4-Nb5 = 2.663 Å Nb1-C1 = Nb3-C2 = 2.040 Å Nb1-C2 = Nb3-C1 = 2.188 Å Nb1-C3 = Nb3-C4 = 2.049 Å Nb2-C1 = Nb4-C2 = 1.911 Å Nb2-C3 = Nb4-C4 = 1.963 Å Nb5-C3 = Nb5-C4 = 2.116 Å	Nb1 = +0.76 Nb2 = +0.72 Nb3 = Nb1 Nb4 = Nb2 Nb5 = +0.34 C1 = –0.80 C2 = C1 C3 = –0.84 C4 = C3
$Nb_5C_4^+$ V D^+ ^1A C_2 	Nb1-Nb2 = Nb3-Nb4 = 2.827 Å Nb1-Nb3 = 2.607 Å Nb1-Nb4 = Nb2-Nb3 = 2.987 Å Nb1-Nb5 = Nb3-Nb5 = 2.800 Å Nb2-Nb5 = Nb4-Nb5 = 2.707 Å Nb1-C1 = Nb3-C2 = 2.019 Å Nb1-C2 = Nb3-C1 = 2.195 Å Nb1-C3 = Nb3-C4 = 2.035 Å Nb2-C1 = Nb4-C2 = 1.896 Å Nb2-C3 = Nb4-C4 = 1.948 Å Nb5-C3 = Nb5-C4 = 2.096 Å	Nb1 = +0.86 Nb2 = +0.88 Nb3 = Nb1 Nb4 = Nb2 Nb5 = +0.57 C1 = –0.73 C2 = C1 C3 = –0.78 C4 = C3

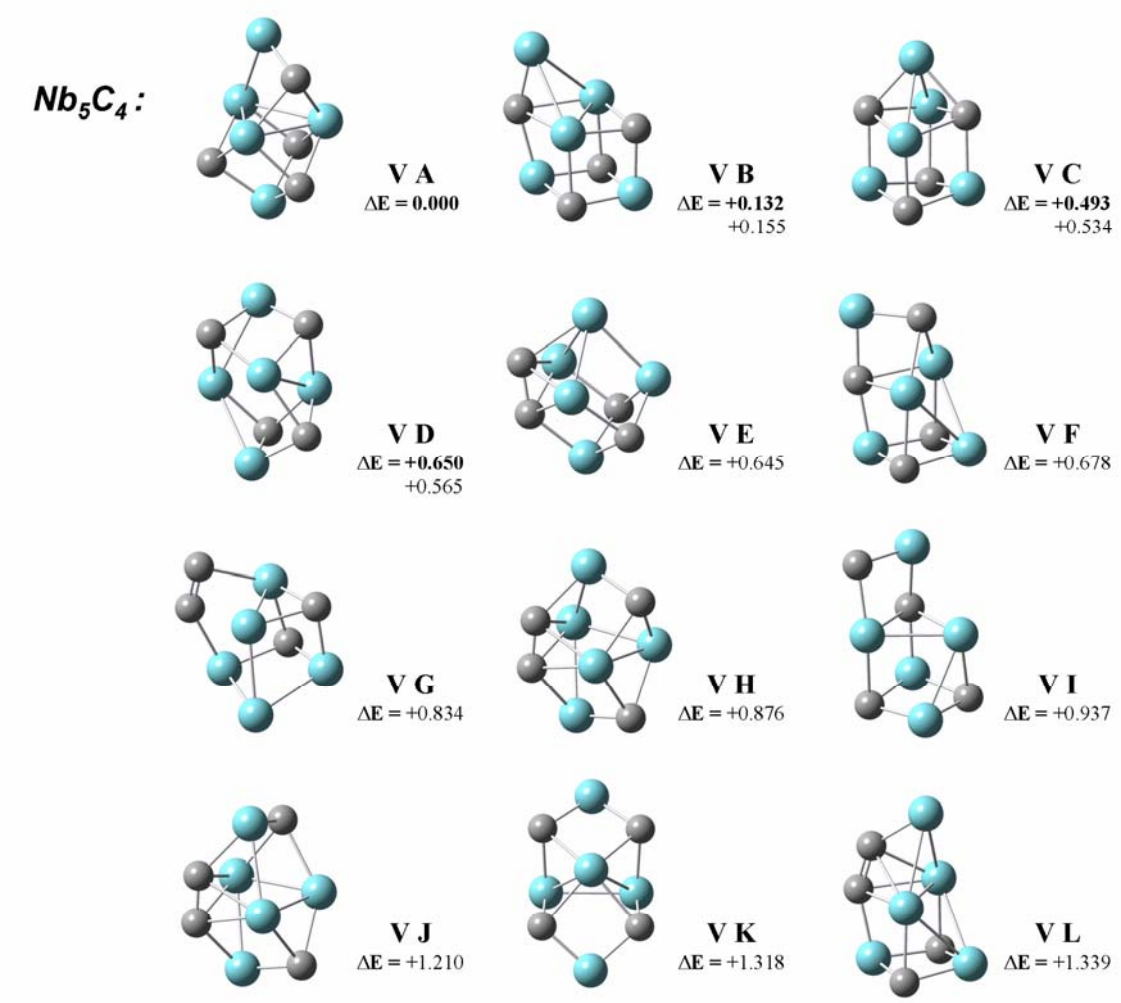
Cluster	Geom. Parameters	Charges
Nb_5C_5 VI A $^2A'\ C_s$ 	Nb1-Nb1 = 2.689 Å Nb1-Nb2 = 2.754 Å Nb1-Nb3 = 2.842 Å Nb1-Nb4 = 2.529 Å Nb2-Nb3 = 2.872 Å Nb1-C1 = 2.151 Å Nb1-C2 = 2.199 Å Nb1-C3 = 2.280 Å Nb1-C4 = 2.218 Å Nb2-C1 = 1.989 Å Nb2-C3 = 2.188 Å Nb3-C1 = 1.976 Å Nb3-C2 = 2.036 Å Nb4-C2 = 2.087 Å Nb4-C4 = 2.164 Å C3-C4 = 1.346 Å	Nb1 = +0.80 Nb2 = +0.77 Nb3 = +0.89 Nb4 = +0.39 C1 = –0.83 C2 = –0.86 C3 = –0.58 C4 = –0.55
Nb_5C_5 VI A^+ $^1A'\ C_s$ 	Nb1-Nb1 = 2.799 Å Nb1-Nb2 = 2.703 Å Nb1-Nb3 = 2.903 Å Nb1-Nb4 = 2.533 Å Nb2-Nb3 = 2.844 Å Nb1-C1 = 2.140 Å Nb1-C2 = 2.194 Å Nb1-C3 = 2.299 Å Nb1-C4 = 2.245 Å Nb2-C1 = 1.974 Å Nb2-C3 = 2.181 Å Nb3-C1 = 1.974 Å Nb3-C2 = 1.998 Å Nb4-C2 = 2.079 Å Nb4-C4 = 2.116 Å C3-C4 = 1.332 Å	Nb1 = +0.89 Nb2 = +0.96 Nb3 = +1.02 Nb4 = +0.65 C1 = –0.77 C2 = –0.81 C3 = –0.53 C4 = –0.52
Nb_5C_5 VI B $^2A'\ C_s$ 	Nb1-Nb1 = 2.767 Å Nb1-Nb2 = 2.880 Å Nb1-Nb3 = 2.634 Å Nb1-Nb4 = 3.004 Å Nb2-Nb3 = 2.994 Å Nb3-Nb4 = 2.965 Å Nb1-C1 = 2.010 Å Nb1-C2 = 2.101 Å Nb1-C3 = 2.083 Å Nb2-C1 = 1.934 Å Nb2-C3 = 1.975 Å Nb3-C1 = 2.171 Å Nb3-C2 = 2.175 Å Nb4-C2 = 1.879 Å	Nb1 = +0.77 Nb2 = +0.87 Nb3 = +0.85 Nb4 = +0.59 C1 = –0.72 C2 = –0.79 C3 = –0.84
Nb_5C_5 VI B^+ $^1A'\ C_s$ 	Nb1-Nb1 = 2.885 Å Nb1-Nb2 = 2.881 Å Nb1-Nb3 = 2.650 Å Nb1-Nb4 = 3.038 Å Nb2-Nb3 = 3.018 Å Nb3-Nb4 = 2.922 Å Nb1-C1 = 1.977 Å Nb1-C2 = 2.097 Å Nb1-C3 = 2.060 Å Nb2-C1 = 1.932 Å Nb2-C3 = 1.981 Å Nb3-C1 = 2.178 Å Nb3-C2 = 2.152 Å Nb4-C2 = 1.861 Å	Nb1 = +0.87 Nb2 = +1.00 Nb3 = +0.93 Nb4 = +0.89 C1 = –0.66 C2 = –0.73 C3 = –0.78

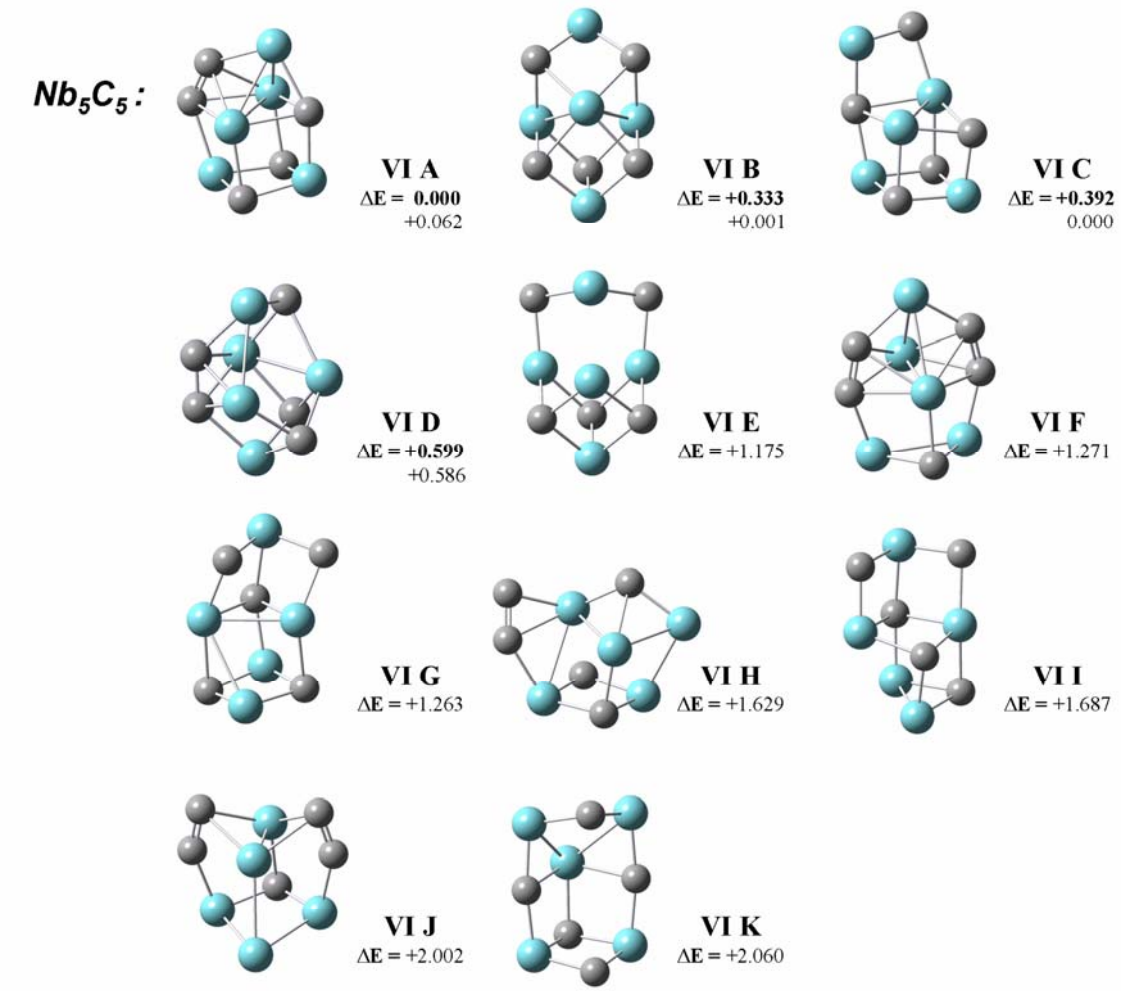
Cluster	Geom. Parameters	Charges
Nb_5C_5 VI C ^2A C_1 	Nb1-Nb2 = 2.834 Å Nb1-Nb3 = 2.859 Å Nb1-Nb4 = 2.886 Å Nb2-Nb3 = 2.909 Å Nb2-Nb4 = 2.979 Å Nb3-Nb4 = 2.538 Å Nb3-Nb5 = 2.800 Å Nb4-Nb5 = 2.858 Å Nb1-C1 = 1.999 Å Nb1-C2 = 1.961 Å Nb1-C3 = 1.978 Å Nb2-C1 = 1.980 Å Nb2-C2 = 2.001 Å Nb2-C4 = 1.910 Å Nb3-C1 = 2.115 Å Nb3-C3 = 2.277 Å Nb3-C4 = 2.072 Å Nb4-C2 = 2.210 Å Nb4-C3 = 2.222 Å Nb4-C4 = 2.153 Å Nb4-C5 = 2.036 Å Nb5-C3 = 2.001 Å Nb5-C5 = 1.840 Å	Nb1 = +0.91 Nb2 = +0.91 Nb3 = +0.70 Nb4 = +0.77 Nb5 = +0.56 C1 = –0.82 C2 = –0.81 C3 = –0.86 C4 = –0.76 C5 = –0.61
$Nb_5C_5^+$ VI C$^+$ ^1A C_1 	Nb1-Nb2 = 2.832 Å Nb1-Nb3 = 2.915 Å Nb1-Nb4 = 2.909 Å Nb2-Nb3 = 2.895 Å Nb2-Nb4 = 2.954 Å Nb3-Nb4 = 2.583 Å Nb3-Nb5 = 2.978 Å Nb4-Nb5 = 2.894 Å Nb1-C1 = 1.984 Å Nb1-C2 = 1.966 Å Nb1-C3 = 1.965 Å Nb2-C1 = 2.000 Å Nb2-C2 = 2.000 Å Nb2-C4 = 1.906 Å Nb3-C1 = 2.072 Å Nb3-C3 = 2.217 Å Nb3-C4 = 2.061 Å Nb4-C2 = 2.154 Å Nb4-C3 = 2.204 Å Nb4-C4 = 2.124 Å Nb4-C5 = 2.051 Å Nb5-C3 = 1.999 Å Nb5-C5 = 1.810 Å	Nb1 = +1.02 Nb2 = +1.04 Nb3 = +0.87 Nb4 = +0.84 Nb5 = +0.84 C1 = –0.76 C2 = –0.75 C3 = –0.86 C4 = –0.70 C5 = –0.54
Nb_5C_5 VI D ^2A C_1 	Nb1-Nb2 = 2.963 Å Nb1-Nb4 = 2.840 Å Nb1-Nb5 = 2.545 Å Nb2-Nb3 = 2.821 Å Nb2-Nb4 = 2.686 Å Nb2-Nb5 = 2.836 Å Nb3-Nb4 = 2.873 Å Nb3-Nb5 = 2.777 Å Nb4-Nb5 = 3.345 Å Nb1-C1 = 1.932 Å Nb1-C4 = 2.070 Å Nb2-C1 = 2.241 Å Nb2-C2 = 2.053 Å Nb2-C3 = 2.019 Å Nb3-C2 = 1.935 Å Nb3-C3 = 1.935 Å Nb3-C5 = 2.084 Å Nb4-C1 = 2.027 Å Nb4-C2 = 2.088 Å Nb4-C4 = 2.156 Å Nb4-C5 = 2.220 Å Nb5-C3 = 2.100 Å Nb5-C4 = 2.158 Å Nb5-C5 = 2.122 Å C4-C5 = 1.427 Å	Nb1 = +0.62 Nb2 = +0.81 Nb3 = +0.92 Nb4 = +0.86 Nb4 = +0.65 C1 = –0.85 C2 = –0.81 C3 = –0.88 C4 = –0.65 C5 = –0.64
Nb_5C_5 VI D$^+$ ^1A C_1 	Nb1-Nb2 = 2.991 Å Nb1-Nb4 = 2.787 Å Nb1-Nb5 = 2.604 Å Nb2-Nb3 = 2.838 Å Nb2-Nb4 = 2.585 Å Nb2-Nb5 = 2.905 Å Nb3-Nb4 = 2.855 Å Nb3-Nb5 = 2.784 Å Nb4-Nb5 = 3.283 Å Nb1-C1 = 1.915 Å Nb1-C4 = 2.050 Å Nb2-C1 = 2.306 Å Nb2-C2 = 2.043 Å Nb2-C3 = 2.003 Å Nb3-C2 = 1.912 Å Nb3-C3 = 1.996 Å Nb3-C5 = 2.116 Å Nb4-C1 = 2.014 Å Nb4-C2 = 2.133 Å Nb4-C4 = 2.111 Å Nb4-C5 = 2.209 Å Nb5-C3 = 2.040 Å Nb5-C4 = 2.139 Å Nb5-C5 = 2.085 Å C4-C5 = 1.436 Å	Nb1 = +0.84 Nb2 = +0.92 Nb3 = +1.03 Nb4 = +0.97 Nb4 = +0.78 C1 = –0.80 C2 = –0.78 C3 = –0.80 C4 = –0.61 C5 = –0.59

Cluster	Geom. Parameters	Charges
Nb_5C_6 VII A $^2A_1$ C_{2v} 	Nb1-Nb1 = 2.843 Å Nb1-Nb2 = 2.876 Å Nb2-Nb2 = 2.487 Å Nb2-Nb3 = 2.689 Å Nb1-C1 = 1.969 Å Nb1-C2 = 2.040 Å Nb2-C1 = 2.199 Å Nb2-C2 = 2.278 Å Nb2-C3 = 2.302 Å Nb3-C3 = 2.015 Å C2-C3 = 1.353 Å	Nb1 = +0.84 Nb2 = +0.84 Nb3 = +0.51 C1 = –0.83 C2 = –0.54 C3 = –0.57
$Nb_5C_6^+$ VII A$^+$ $^1A_1$ C_{2v} 	Nb1-Nb1 = 2.877 Å Nb1-Nb2 = 2.882 Å Nb2-Nb2 = 2.514 Å Nb2-Nb3 = 2.702 Å Nb1-C1 = 1.972 Å Nb1-C2 = 2.009 Å Nb2-C1 = 2.165 Å Nb2-C2 = 2.273 Å Nb2-C3 = 2.278 Å Nb3-C3 = 2.004 Å C2-C3 = 1.354 Å	Nb1 = +1.00 Nb2 = +0.92 Nb3 = +0.76 C1 = –0.75 C2 = –0.50 C3 = –0.54
$Nb_5C_6^+$ VII B$^+$ $^2B_1$ C_{2v} 	Nb1-Nb1 = 3.455 Å Nb1-Nb2 = 2.865 Å Nb1-Nb3 = 2.708 Å Nb2-Nb3 = 2.954 Å Nb1-C1 = 2.007 Å Nb1-C2 = 2.199 Å Nb2-C1 = 1.933 Å Nb2-C2 = 2.059 Å Nb3-C1 = 2.204 Å C2-C2 = 1.449 Å	Nb1 = +0.87 Nb2 = +0.93 Nb3 = +0.90 C1 = –0.79 C2 = –0.67
$Nb_5C_6^+$ VII B$^+$ $^1A_1$ C_{2v} 	Nb1-Nb1 = 3.352 Å Nb1-Nb2 = 2.855 Å Nb1-Nb3 = 2.681 Å Nb2-Nb3 = 2.993 Å Nb1-C1 = 1.994 Å Nb1-C2 = 2.169 Å Nb2-C1 = 1.930 Å Nb2-C2 = 2.068 Å Nb3-C1 = 2.196 Å C2-C2 = 1.469 Å	Nb1 = +1.04 Nb2 = +1.03 Nb3 = +0.97 C1 = –0.71 C2 = –0.64

All isomers considered for the Nb_5Cy clusters. The relative energies are given for the SDD basis set (normal) and extended basis set (bold).

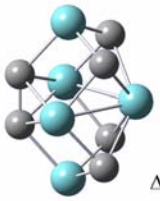




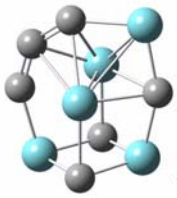


Nb_5C_6 :

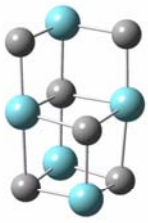
XIX A
ΔE = 0.000



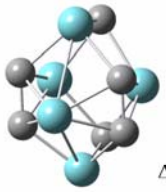
XIX B
ΔE = +1.112
+0.719



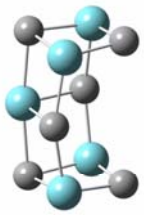
XIX C
ΔE = +1.028



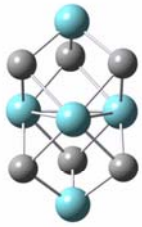
XIX D
ΔE = +1.420



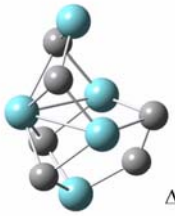
XIX E
ΔE = +1.434



XIX F
ΔE = +1.462



XIX G
ΔE = +1.690



XIX H
ΔE = +1.869