

## Supporting Information

### Theoretical Insights into the CO Dimerization and Trimerization on Pt Nanocluster

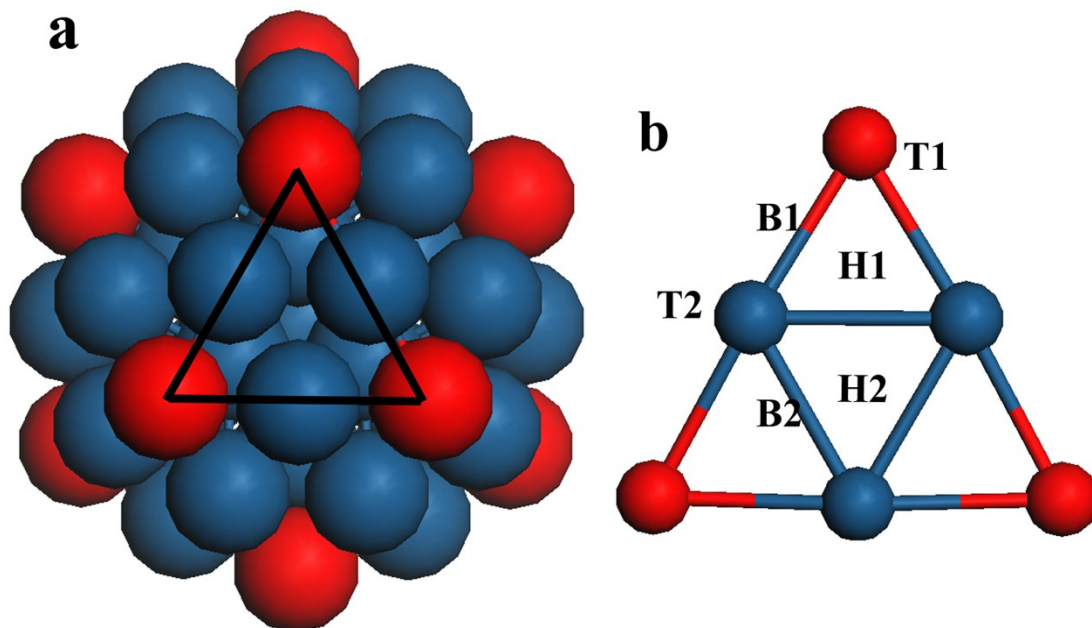
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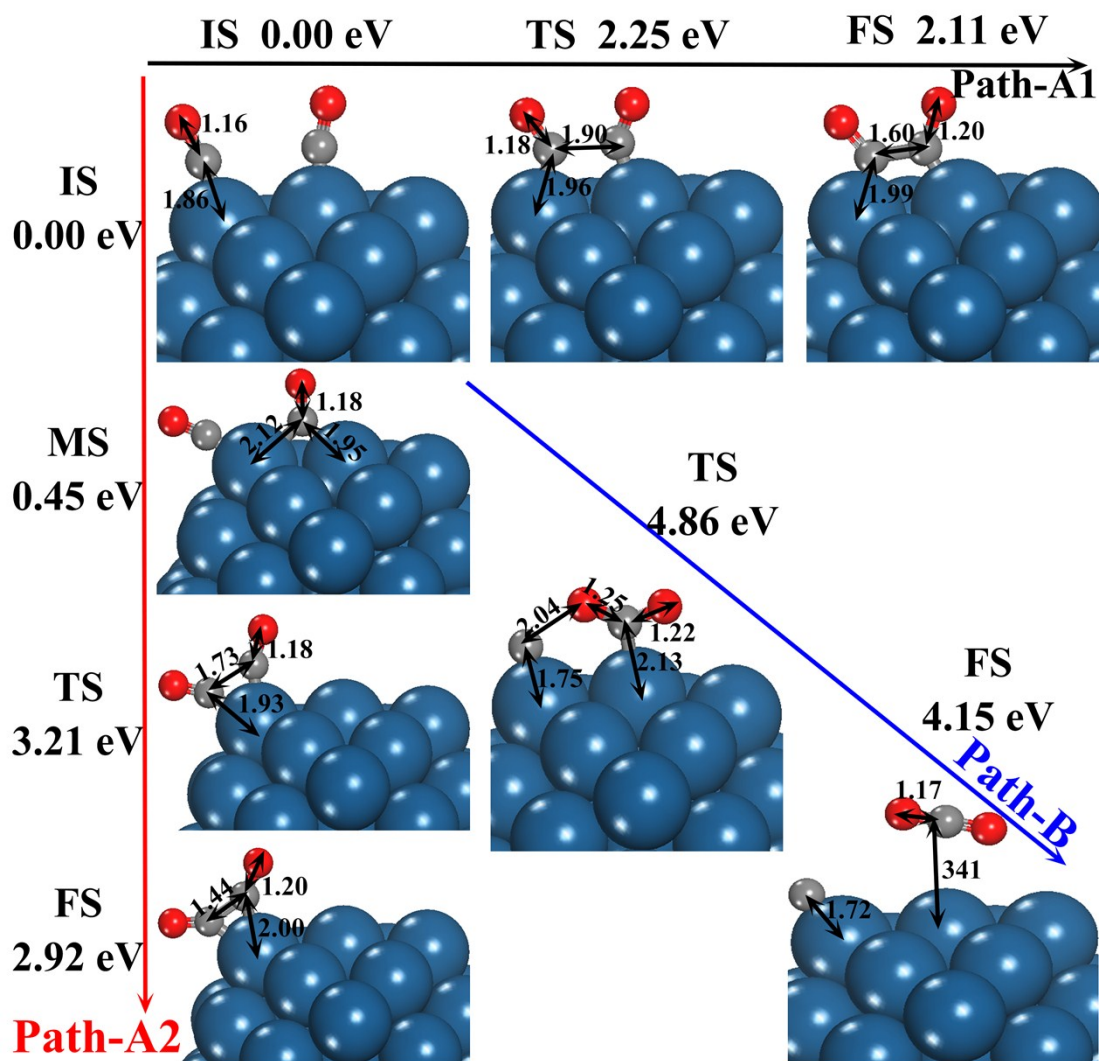
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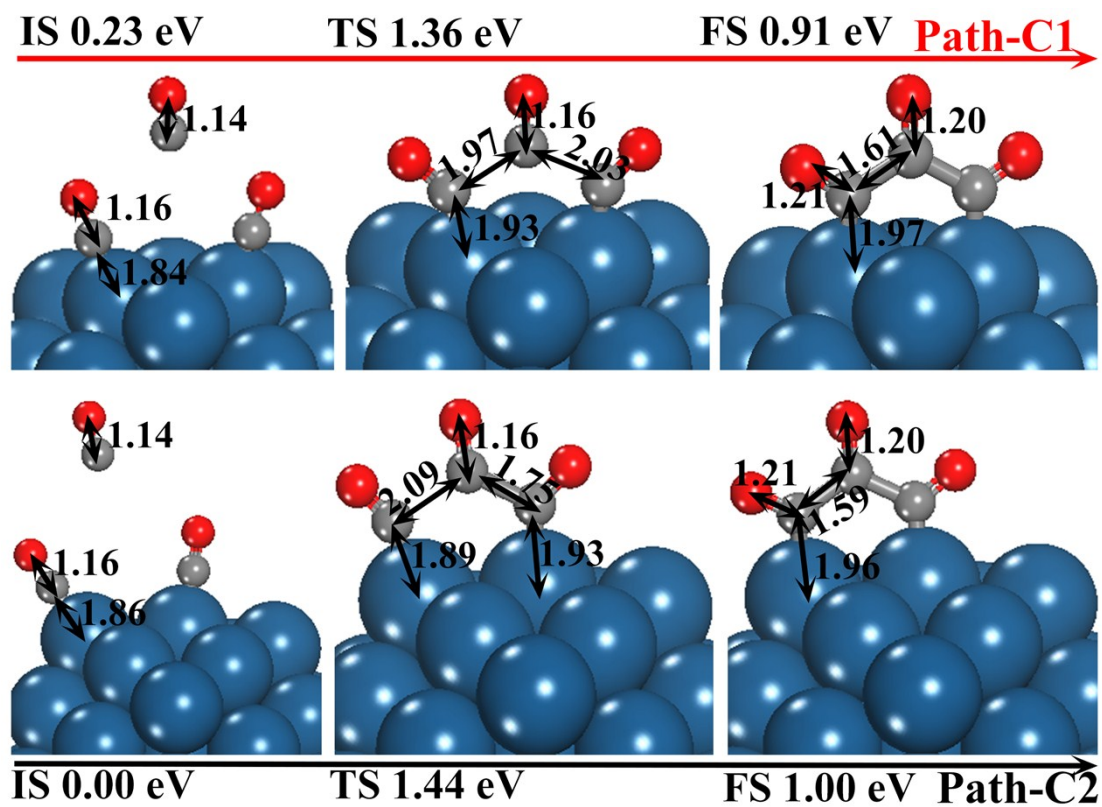
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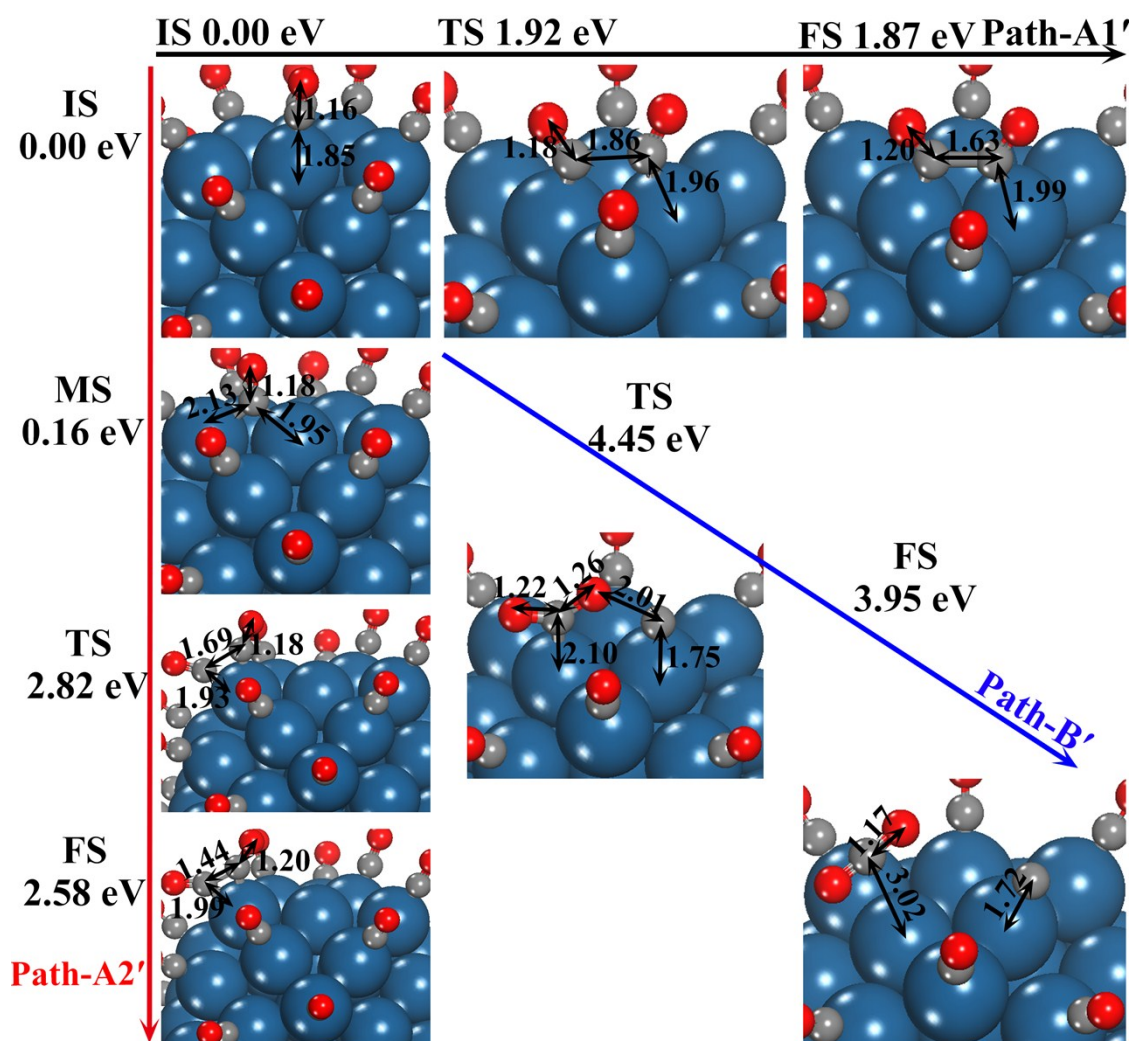
**Fig. S1.** Geometrical structures of icosahedral Pt<sub>55</sub> cluster (a) and one of the (1 1 1) facets (b). Red atoms are the corner Pt, and blue atoms are edge Pt at the surface.



**Fig. S2.** Relative energies and geometrical parameters of all the minima and transition states involved in the reactions of CO dimerization on two neighboring corner and edge Pt atoms (Path-A1), CO dimerization on one corner Pt atom (Path-A2), and CO disproportionation on two neighboring corner and edge Pt atoms (Path-B).

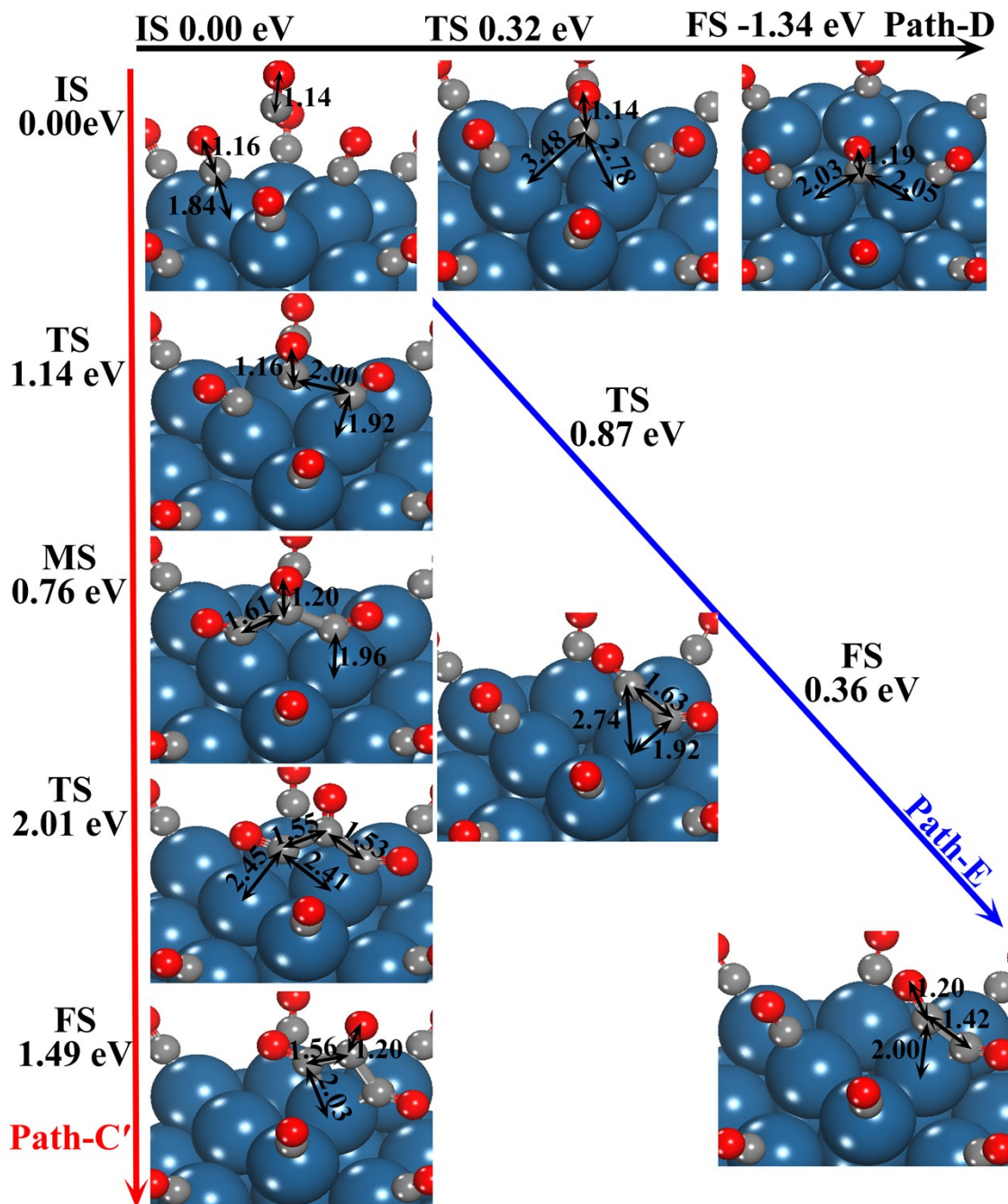


**Fig. S3.** Relative energies and geometrical parameters of all the minima and transition states involved in the reactions of CO trimerization on two edge Pt atoms (Path-C1) and CO trimerization on two neighboring corner and edge Pt atoms (Path-C2).

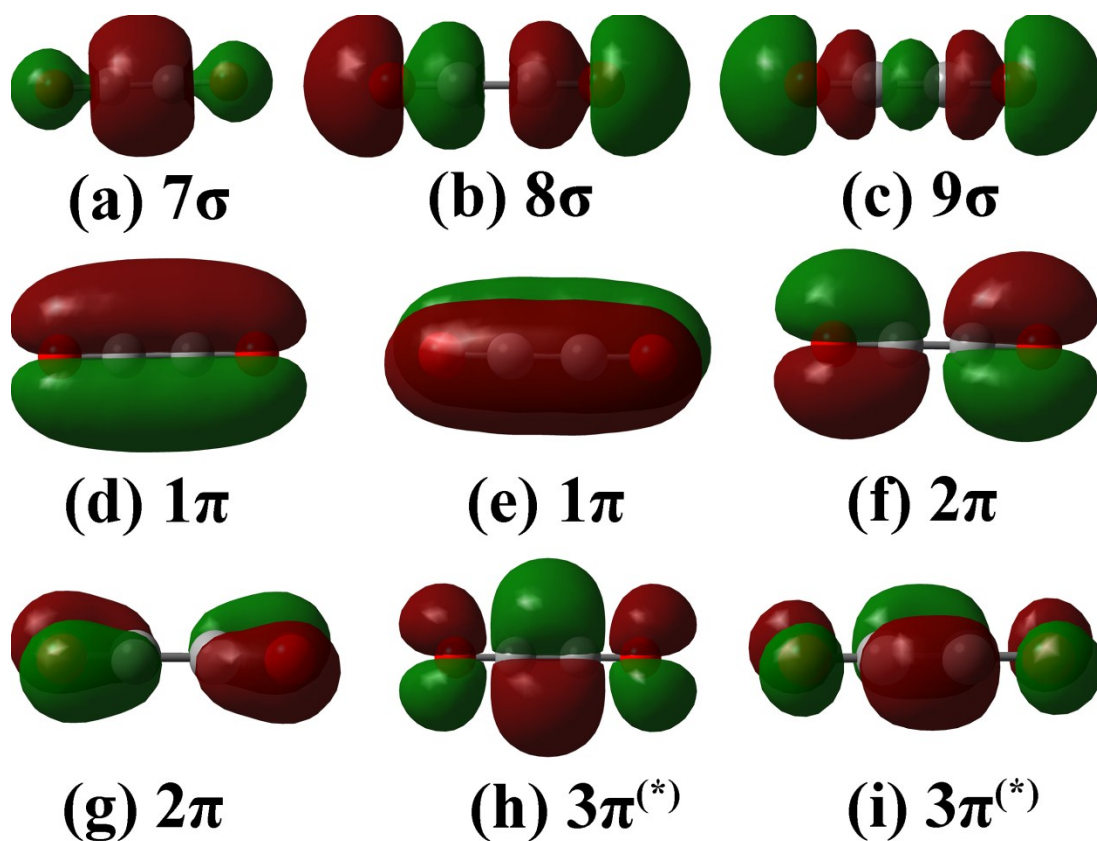


**Fig. S4.** Relative energies and geometrical parameters of all the minima and transition states involved in the reactions of CO dimerization on two neighboring corner and edge Pt atoms (Path-A1'), CO dimerization on one corner Pt atom (Path-A2'), and CO disproportionation on two neighboring corner and edge Pt atoms (Path-B') with high CO coverage effect.

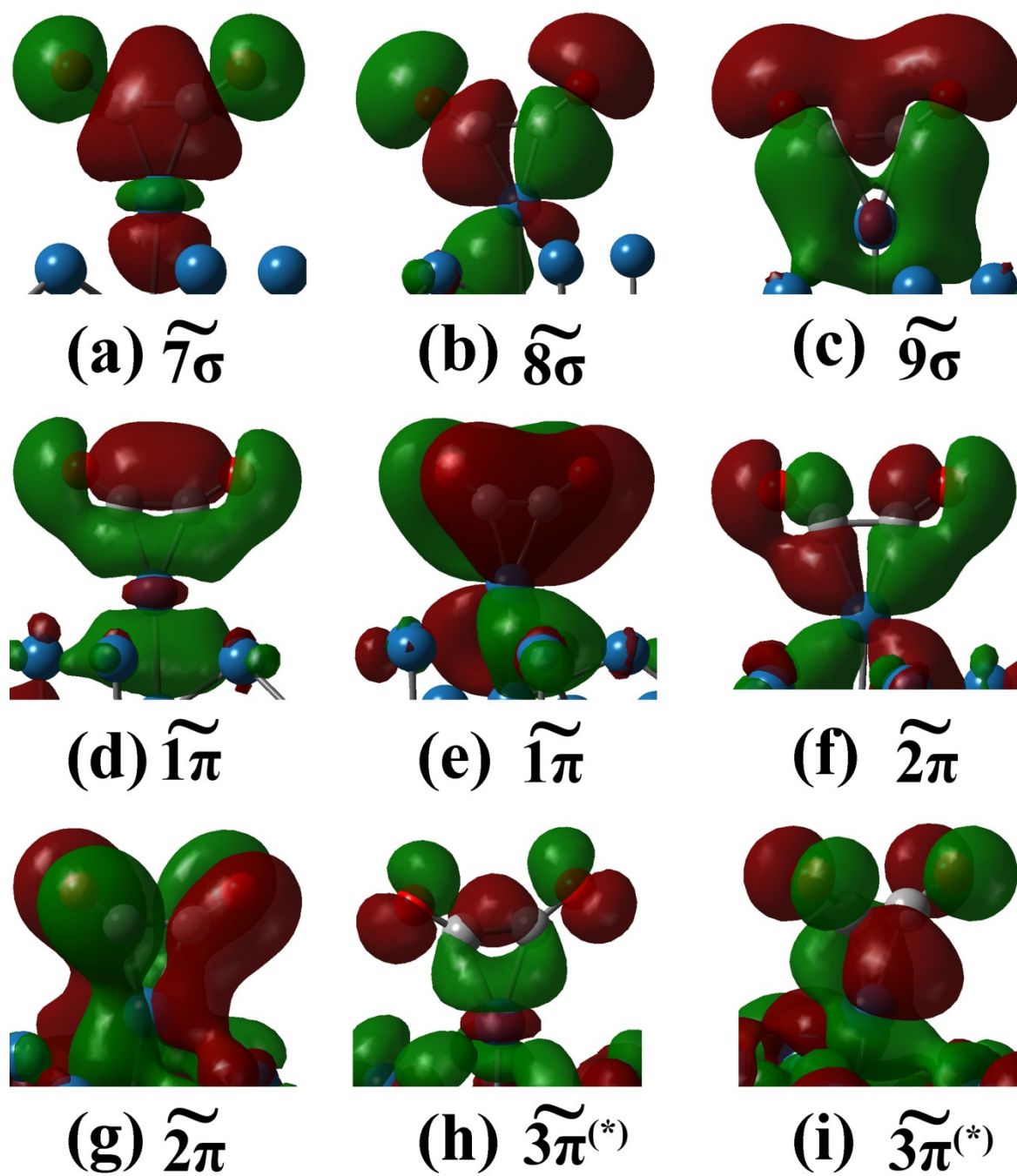




**Fig. S5.** Relative energies and geometrical parameters of all the minima and transition states involved in the reactions of an additional free CO adsorbed at B1 site (Path-D), CO dimerization between an free CO molecule and corner CO\* on one corner Pt atom (Path-E), and CO trimerization on two edge Pt atoms (Path-C1') with high CO coverage effect.



**Fig. S6.**  $7\sigma$  (a),  $8\sigma$  (b),  $9\sigma$  (c),  $1\pi$  (d) and (e),  $2\pi$  (f) and (g), and  $3\pi^{(*)}$  (h) and (i) orbitals of  $C_2O_2$  before adsorption. The symbol (\*) in  $3\pi^{(*)}$  indicates this orbital contains one electron.



**Fig. S7**  $7\sigma$  (a),  $8\sigma$  (b),  $9\sigma$  (c),  $1\pi$  (d,e),  $2\pi$  (f,g) and  $3\pi^{(*)}$  (h,i) orbitals of  $C_2O_2$  when  $C_2O_2$  is adsorbed on one Pt atom.