Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary Information

Bulk Carbide Fractional Coordinates

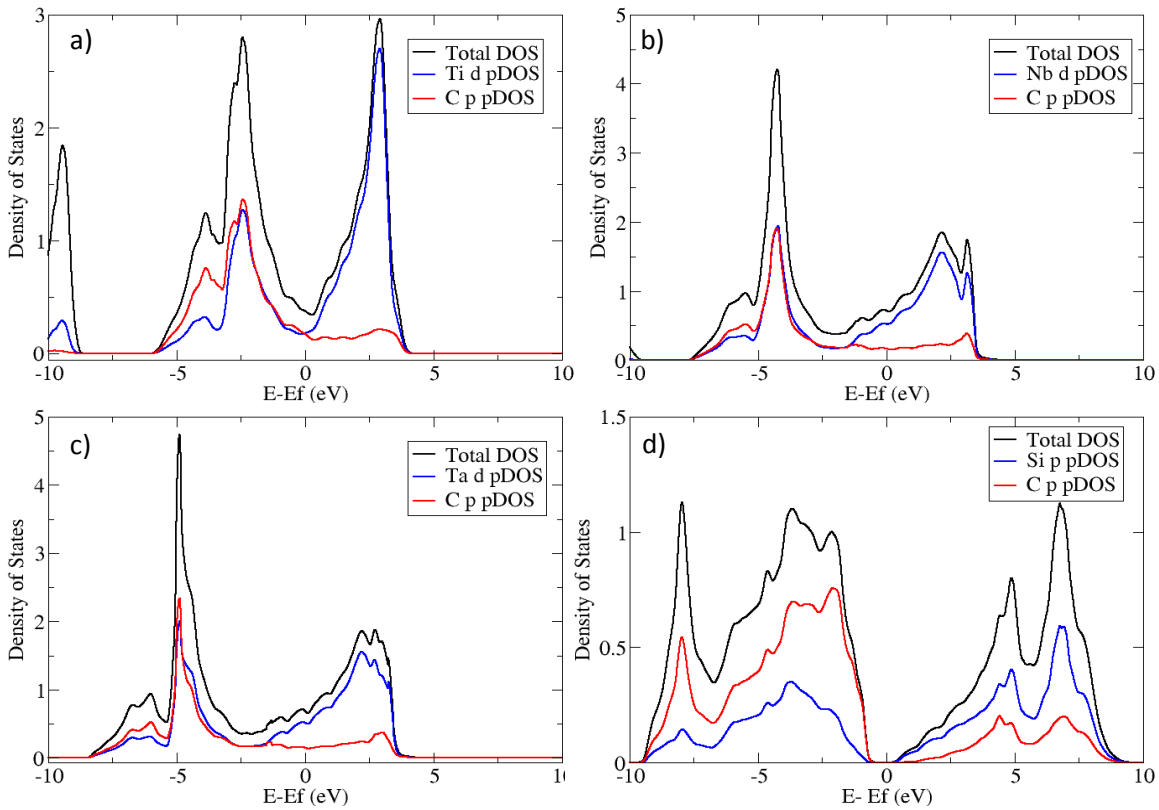
TiC/NbC/TaC/fccWC	hcp WC	SiC β
Space Group 225	Space Group 187	Space Group 216
TM: 0.0, 0.0, 0.0	W: 0.0, 0.0, 0.0	Si: 0.25, 0.25, 0.25
C: 0.5, 0.5, 0.5	C: ⅔, ⅓, 0.5	C: 0.0, 0.0, 0.0

Bulk Carbide DOS Plots and Analysis

The fcc carbides exhibit valence bands with a large degree of TM d- and carbon p-overlap below E_f, while the unfilled conduction bands above E_f are dominated by the TM d-states. As the d-band is filled moving across the period, both the conduction and valence bands are shifted negatively in energy resulting in an increased number of states at E_f, and improved conductivity. The gap between the valence and conduction band centres (Δ) increases going down the series from TiC to Nb to Ta signifying a widening in the bonding anti-bonding splitting which is indicative of the compounds' stability.[1]

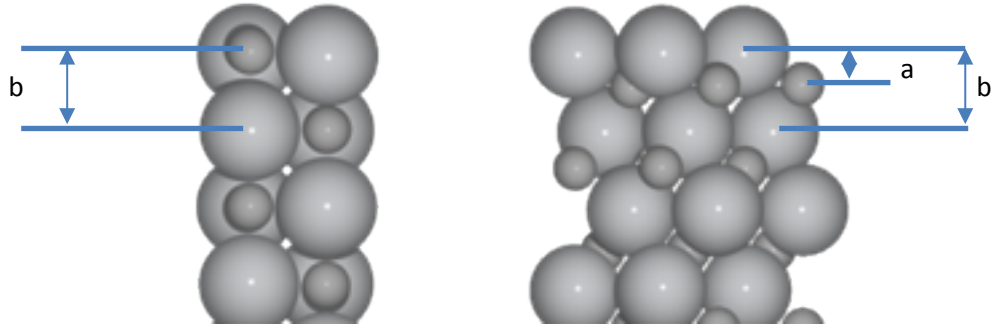
The hcp WC DOS also exhibits valence and conduction bands connected by a pseudogap at E_f. It is similar to TiC in terms of the positioning of the bands with regards to E_f although with a much larger Δ value. The proximity of the hcp WC conduction band to E_f results in a positive E_d which is also more reminiscent of TiC than of fcc WC (see article Table 1). SiC differs from the TM carbides as it is a semiconductor. Excellent overlap in noted between the C and Si p-bands as expected for a covalent compound with C contributions dominating the valence band and unfilled Si p-states the conduction band. Δ is once again very large as the conduction band is well separated from E_f.

Figure1. Total and projected Density of States (DOS) around the Fermi level (E_f) a) TiC, b) NbC, c)TaC and d) SiC



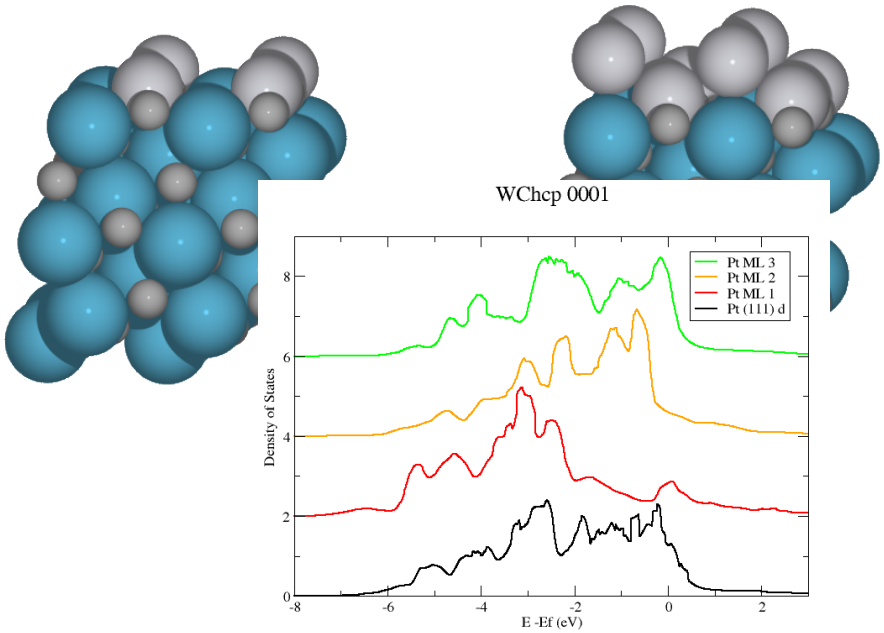
Surface Relaxations

Figure 2. Schematic showing a) intralayer and b) interlayer distances in (100) and (111) surfaces.



Hcp WC(11-20) Overlayer Formation

Figure 3. Surface structure of hcp WC(11-20) illustrating partial coverage of the carbide upon filling of the preferred surface sites.

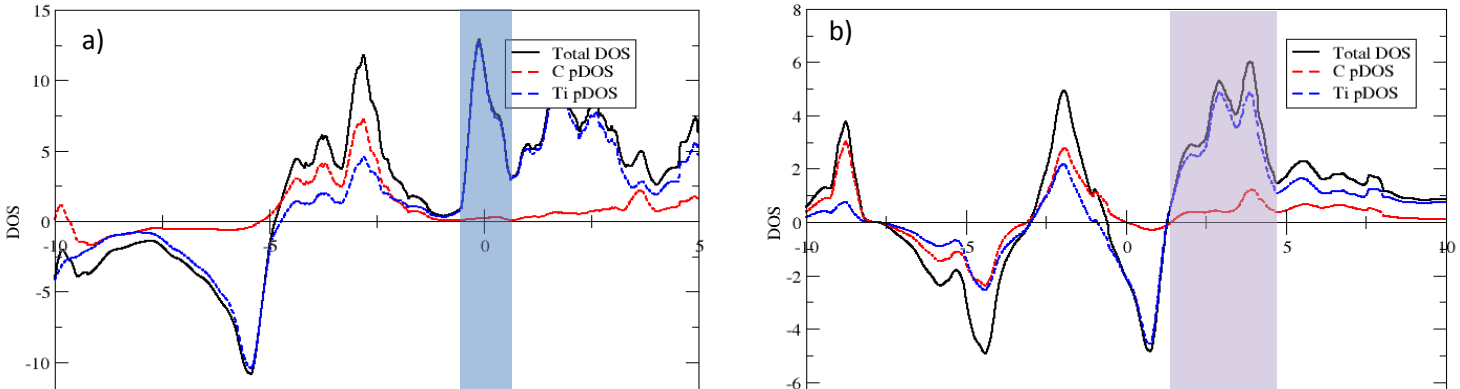


Overlayer Electronic structure for hcp WC(0001)

Figure 4. Projected Density of States diagram for the d-band of Pt ML on hcp WC(0001), each ML d-band is offset for clarity

Surface Specific Electronic Structure

Figure 5. Difference Density of States plots (surface-bulk) for fcc carbide surfaces a) TiC(111), b) TiC(100), c) NbC(111), d) NbC(100), e) TaC(111) ,f)TaC(100) g) fcc WC(111) and h) fcc WC (100) TMSRs are highlighted in blue and other regions of interest in purple



c)

d)

e)

f)

g)

h)

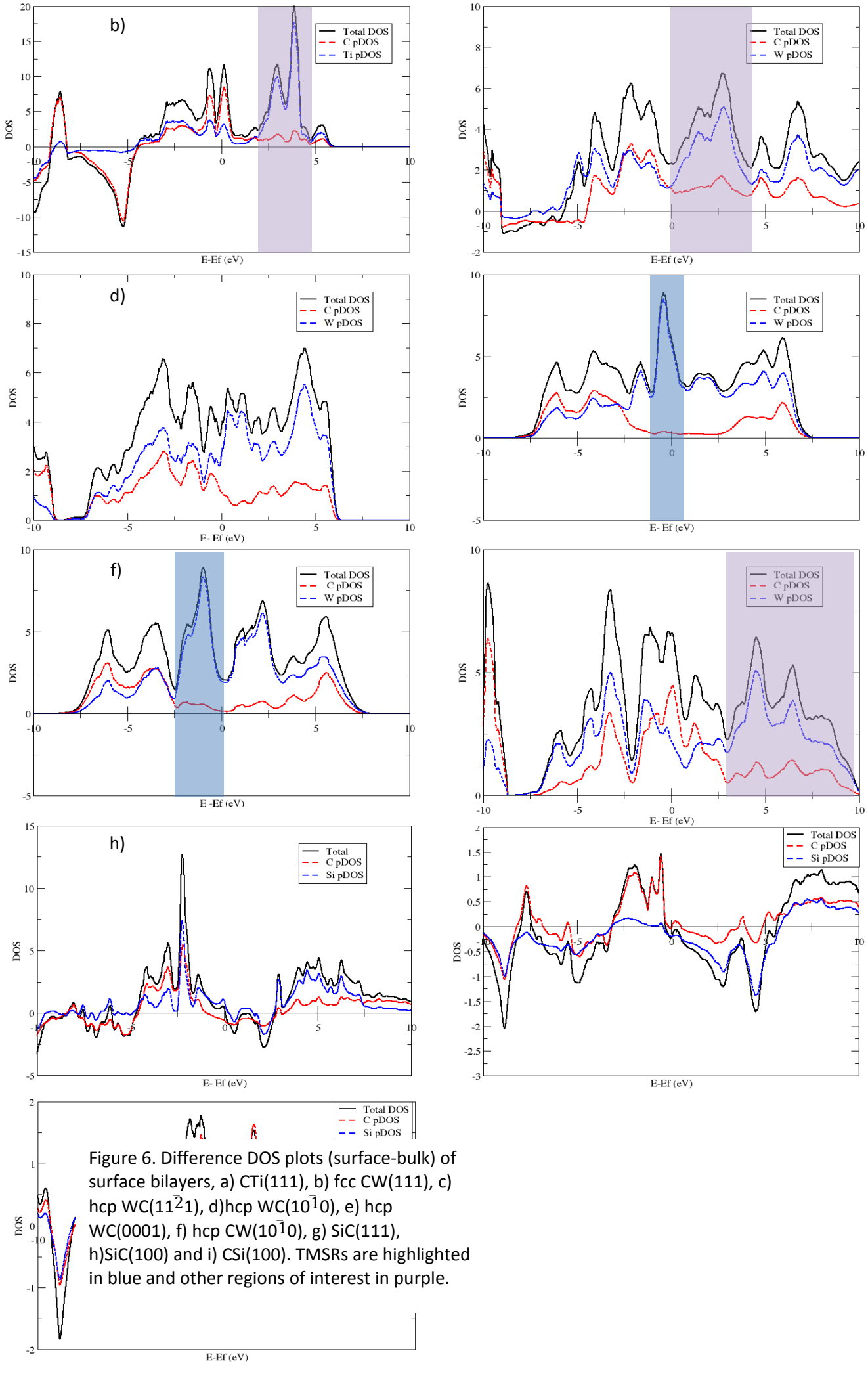
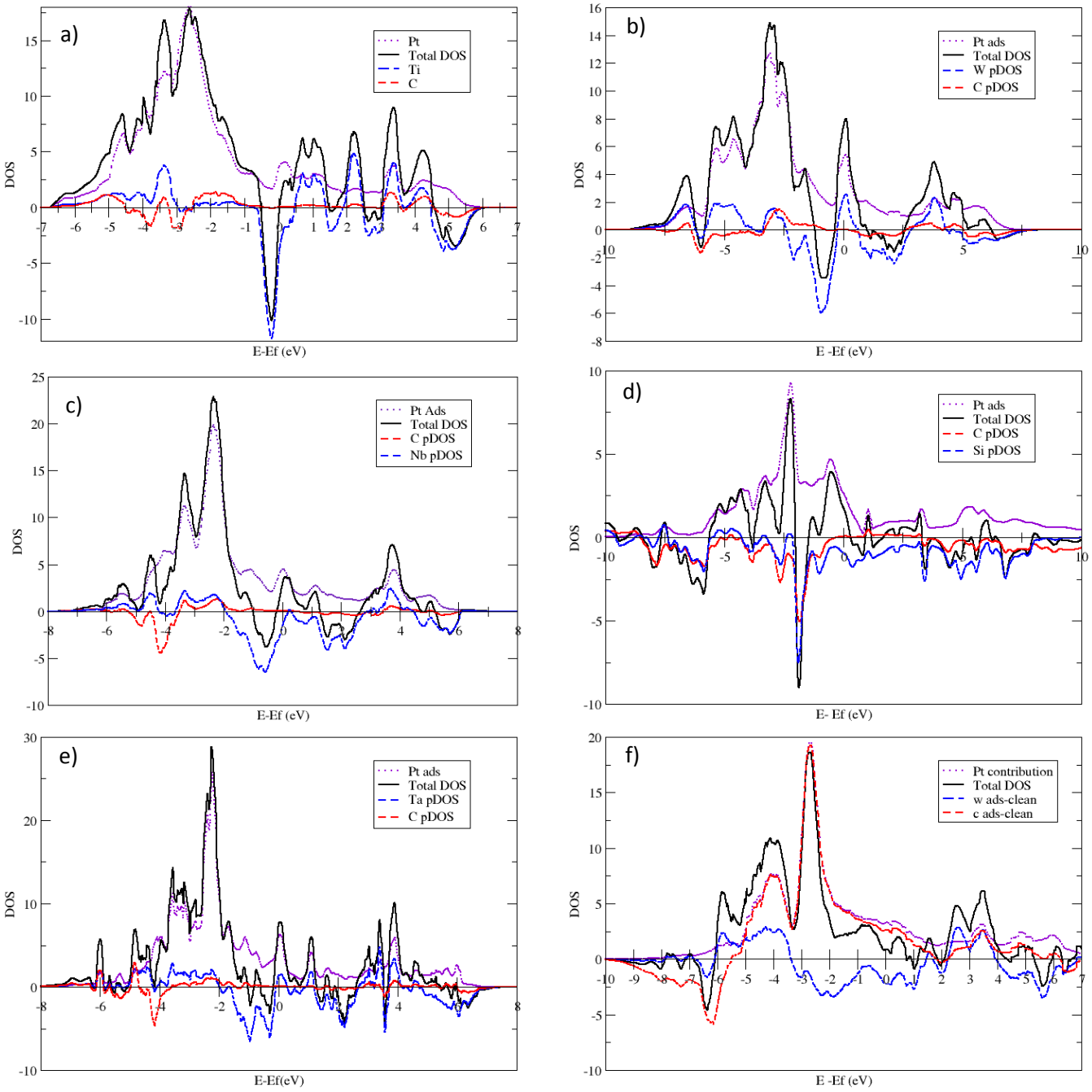


Figure 6. Difference DOS plots (surface-bulk) of surface bilayers, a) CTi(111), b) fcc CW(111), c) hcp WC(11$\bar{2}$1), d)hcp WC(10$\bar{1}$0), e) hcp WC(0001), f) hcp CW(10$\bar{1}$0), g) SiC(111), h)SiC(100) and i) CSi(100). TMSRs are highlighted in blue and other regions of interest in purple.

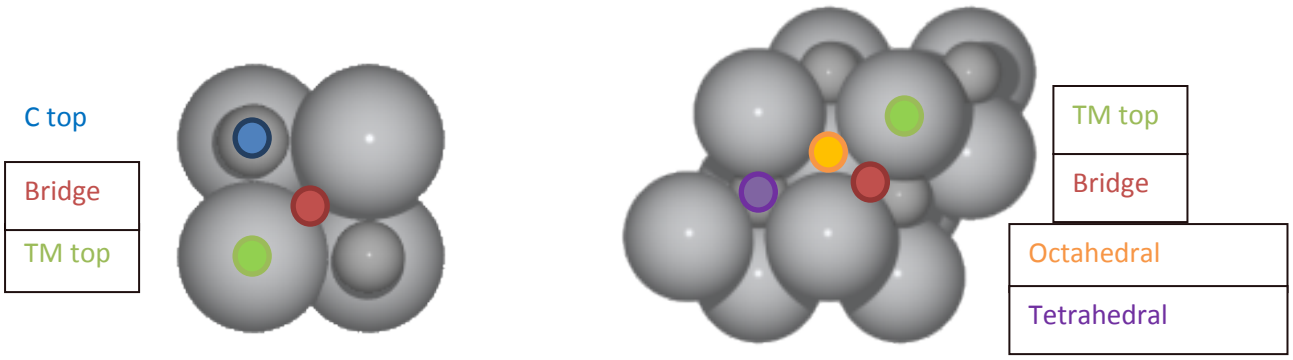
TMSR Depletion Upon Pt Adsorption

Figure 7. Difference DOS plots of surface bilayers upon Pt overlayer adsorption. a) TiC(111) b) hcp WC(0001), c) NbC(111) d) SiC(111), e) TaC(111) and f) fcc WC(111)



Adsorption Sites

Figure 8. Schematic for different adsorption sites on fcc(100) and (111) surfaces.



References

1. F. Viñes, C. Sousa, P. Liu, J. A. Rodriguez, and F. Illas, *J. Chem. Phys.*, 2005, **122**, 174709.