Adsorption of Phenol on Zinc (10-10), (0001)

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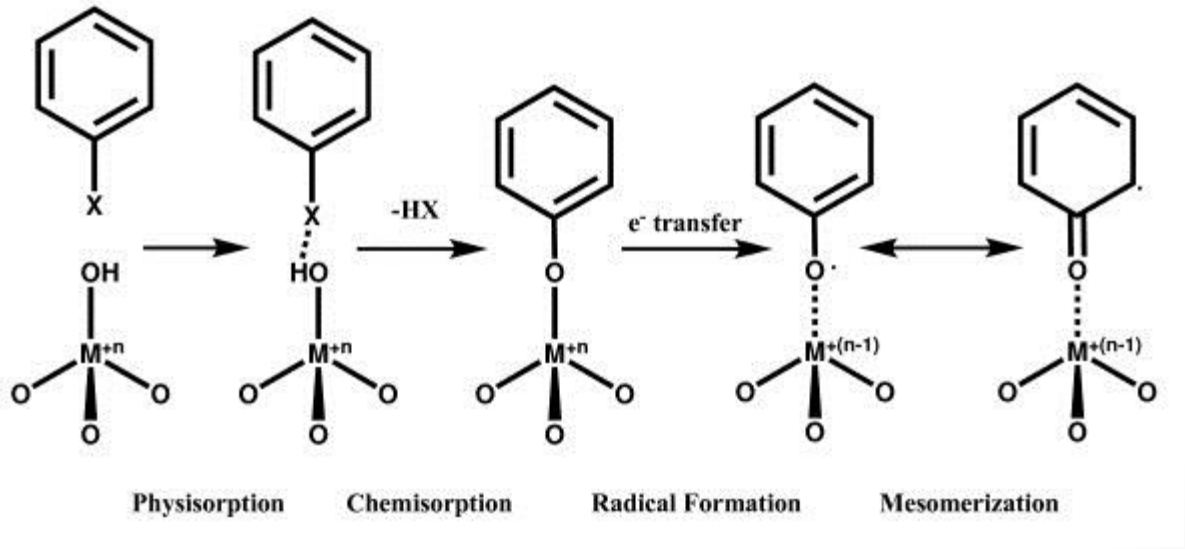
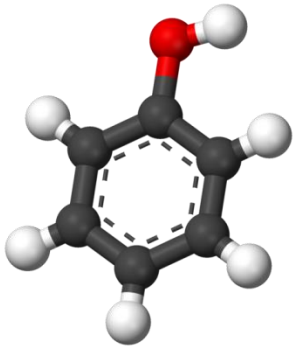
Environmentally Persistent Free Radicals

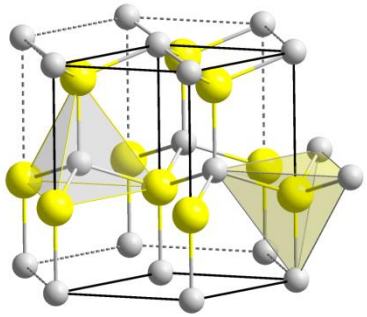
- Environmentally persistent free radicals (EPFRs) have been known to cause cancer within biological organisms
- EPFRs have been shown to be present in many disease causing materials such as particulate matter in the air as well as within the tar balls that appeared after the Deep Water Horizon oil spill



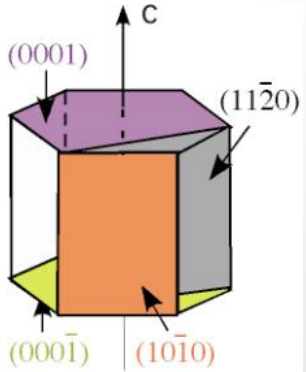
Zinc Oxide (10-10), (0001)

- It has been observed that Phenol attaches itself to Zinc Oxide, propagating a free radical.



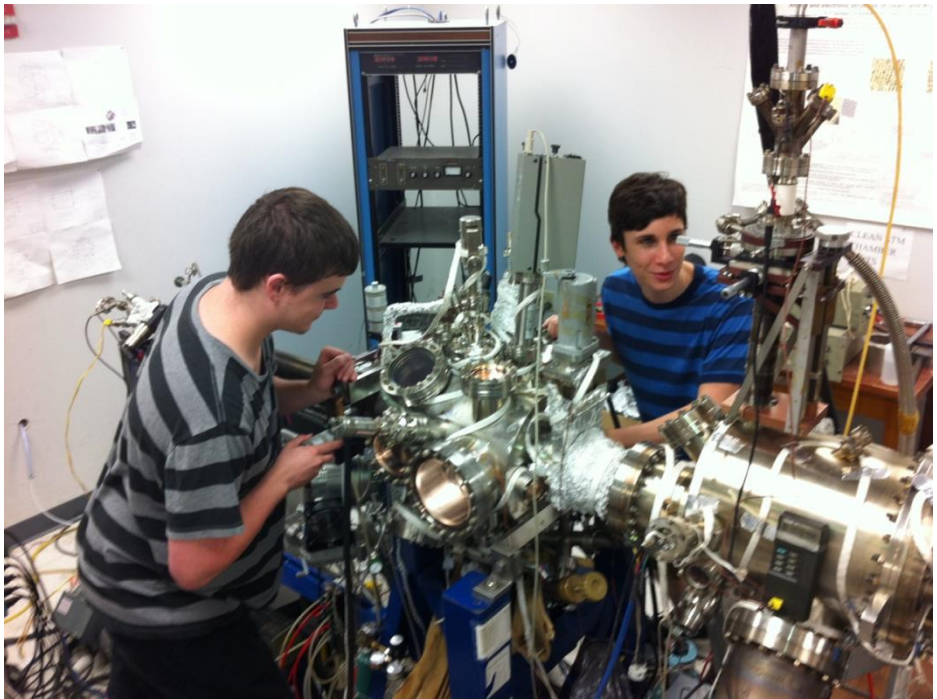


- (10-10) refers to a ZnO surface that alternates zinc and oxygen atoms, (0001) refers to one that has only zinc atoms.

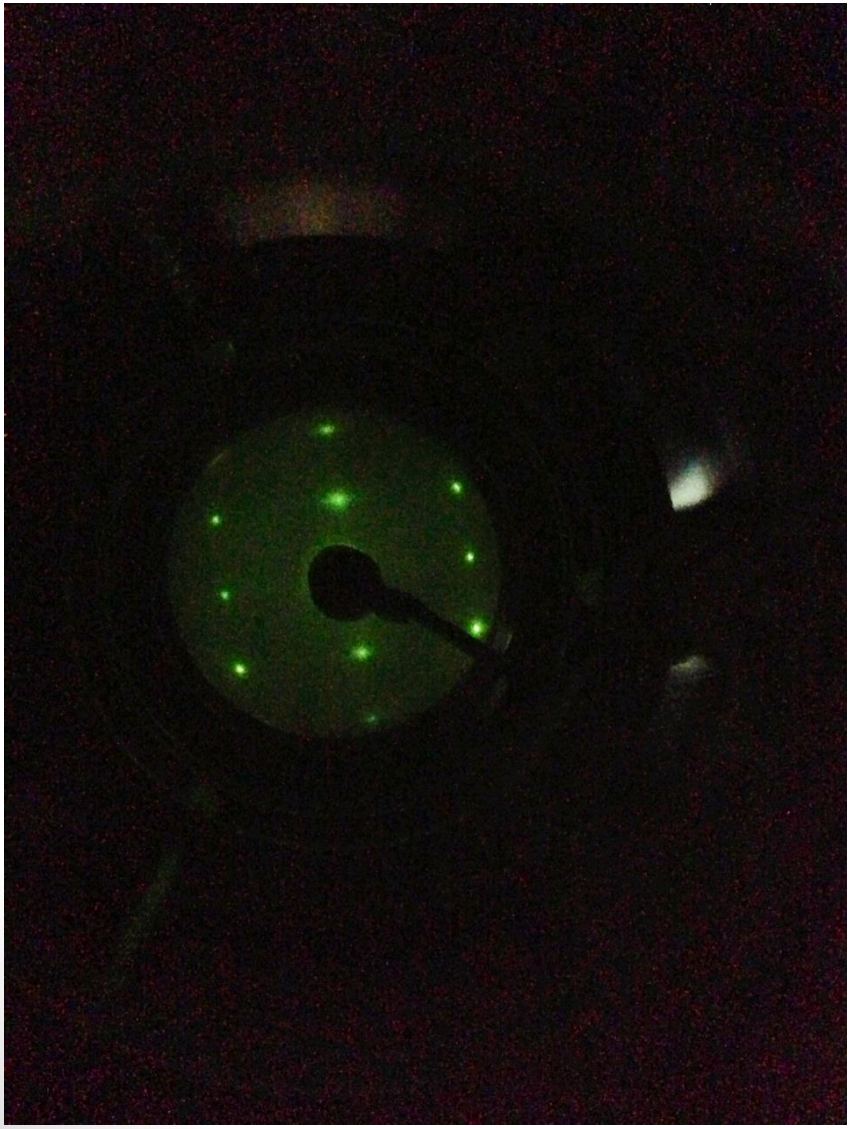


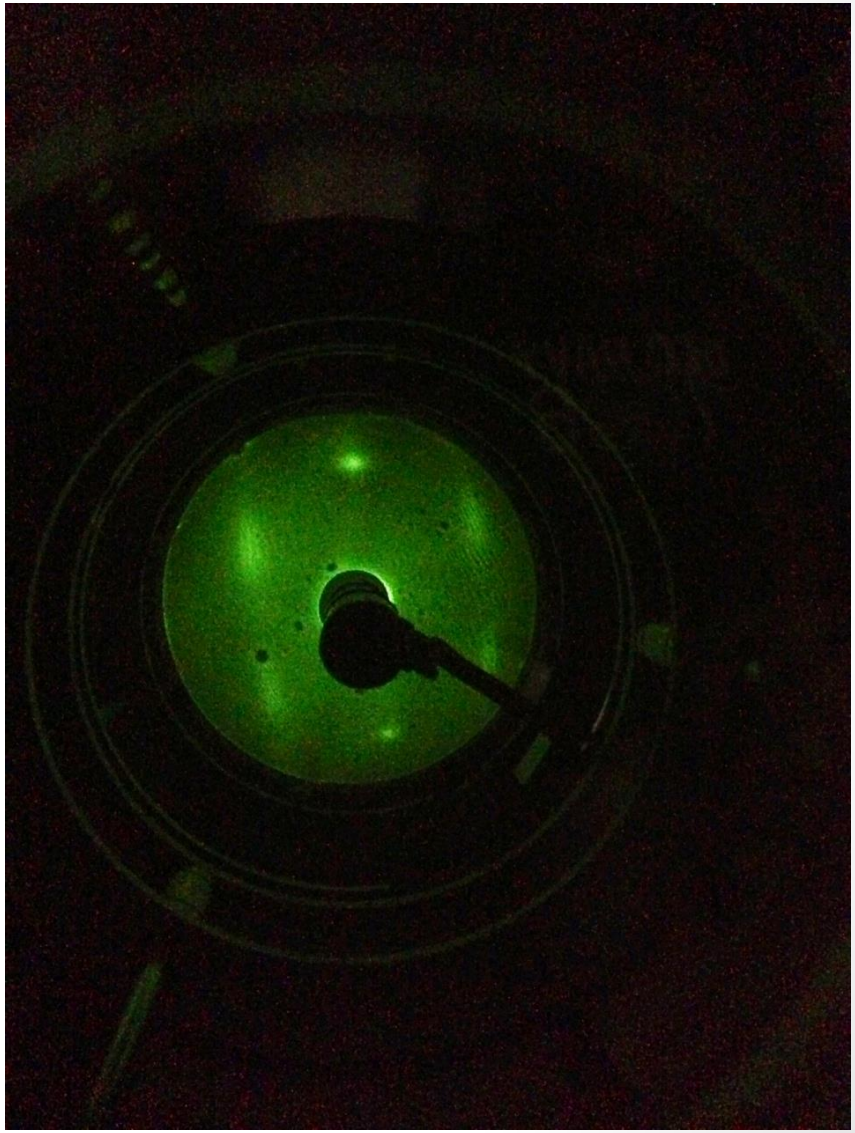
Method

- All tests are done under Ultra High Vacuum
- This is due to needing a vacuum for sample quality as well as for experimental methods (i.e. air molecules being in the way of a laser).
- These tests only depend on the surface, not the bulk properties.

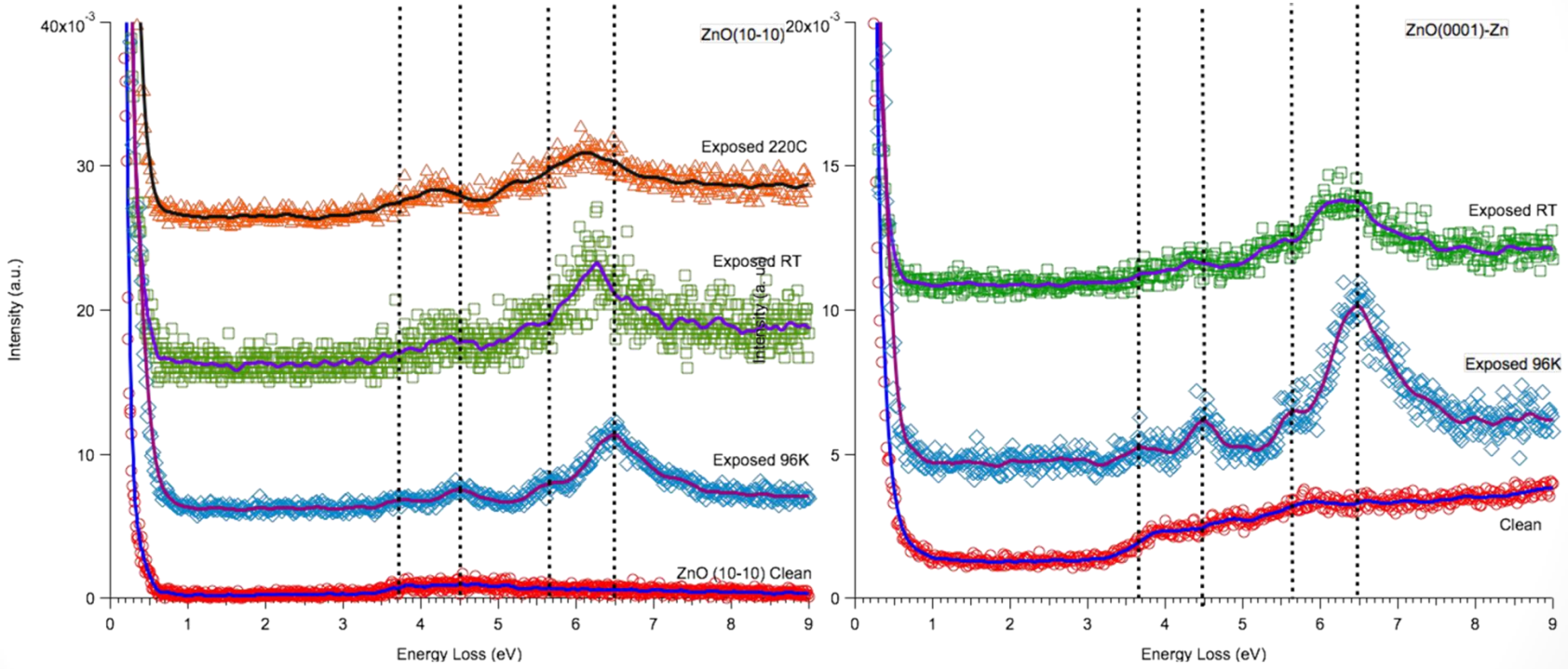


Low Energy Electron Diffraction

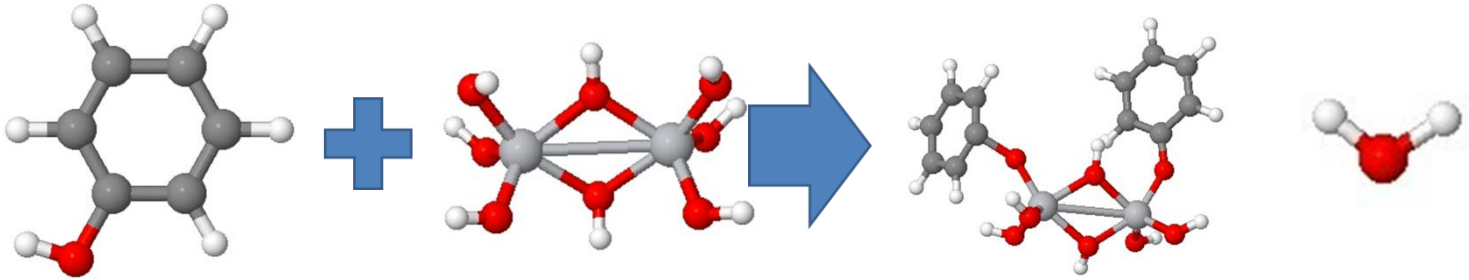




Electron Energy Loss Spectroscopy



Surface Structure Optimization



Phenol TiO_2 Cluster TiO_2 Cluster dosed with phenol Water

	Delta E (hartrees)	HOMO LUMO (eV)
InverseDiTiNatural.out	-2305.925152	6.124584356
Phenol.out	-307.478467	5.982000288
Water.out	-76.41973662	9.72238311
DiTiPhenol.out	-2536.989303	4.416024503
Delta E (hartrees)	-0.005421304	
Delta E (eV	-3.40191995	

	Delta E (hartrees)	HOMO LUMO (eV)
InverseDiTiNatural.out	-2305.925152	6.124584356
2*Phenol.out	-614.956934	5.982000288
2*Water.out	-152.8394732	9.72238311
DiTiDiPhenol.out	-2768.063136	4.271263579
Delta E (hartrees)	-0.020523419	
Delta E (eV)	-12.87864014	

The calculations of ΔE and HOMO-LUMO for the adding of one phenol and two phenol to ZnO surface. The structures and energies were calculated using b3lyp/631g**.

Conclusions

- The phenol is ordered upon the surface of ZnO in one direction (the lack of streaking horizontally of the LEED) and a little spread out in the other (the vertical streaking).
- The 6.5 eV peak on the EELS is caused by the π to π* transition of the same energy within phenol. The lesser peaks are also π to π* transitions, but are forbidden.
- The slight shift of the peak to lower energies at higher and higher temperatures indicates that the π to π* transition shrinks slightly at higher temperatures. This could potentially indicate that the ZnO-phenol bond could be getting more stable.
- The intensity of the peak at -177 ℃ indicates that the phenol is only physisorbed at -177 ℃ and is chemisorbed at room temperature and 220 ℃.
- Due to the similarity between the (10-10) and (0001) EELS, we can conclude the site of bonding between ZnO and phenol is the zinc.

Questions?