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

Informing Air-Carbon Ablation Modeling with Theoretical Calculations of Atomic Oxygen and Nitrogen Interacting with Carbon Surfaces

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Supporting Materials

S-I. Test of functionals in characterizing the interlayer distance in graphite.

We tested the performance of different functionals in characterizing the interlayer distance of a graphite surface. Due to the fact that van der Waals forces play an important role in holding the graphite layers together, functionals that include the van der Waals interaction, such as vdW-DF,[1] optPBE-vdW,[2] and DFT-D3 methods,[3] perform much better than the standard GGA PBE functional,[4] as shown in Table S1 where the optimized interlayer distance is compared with experiment. We chose the optPBE-vdW functional based on its good performance in reproducing the interlayer distance of graphite surface.

1. M. Dion, H. Rydberg, E. Schröder, D. C. Langreth and B. I. Lundqvist, *Physical review letters*, 2004, **92**, 246401.
2. J. Klimeš, D. R. Bowler and A. Michaelides, *Journal of Physics: Condensed Matter*, 2009, **22**, 022201.
3. S. Grimme, J. Antony, S. Ehrlich and H. Krieg, *The Journal of chemical physics*, 2010, **132**, 154104.
4. J. P. Perdew, K. Burke and M. Ernzerhof, *Physical review letters*, 1996, **77**, 3865.

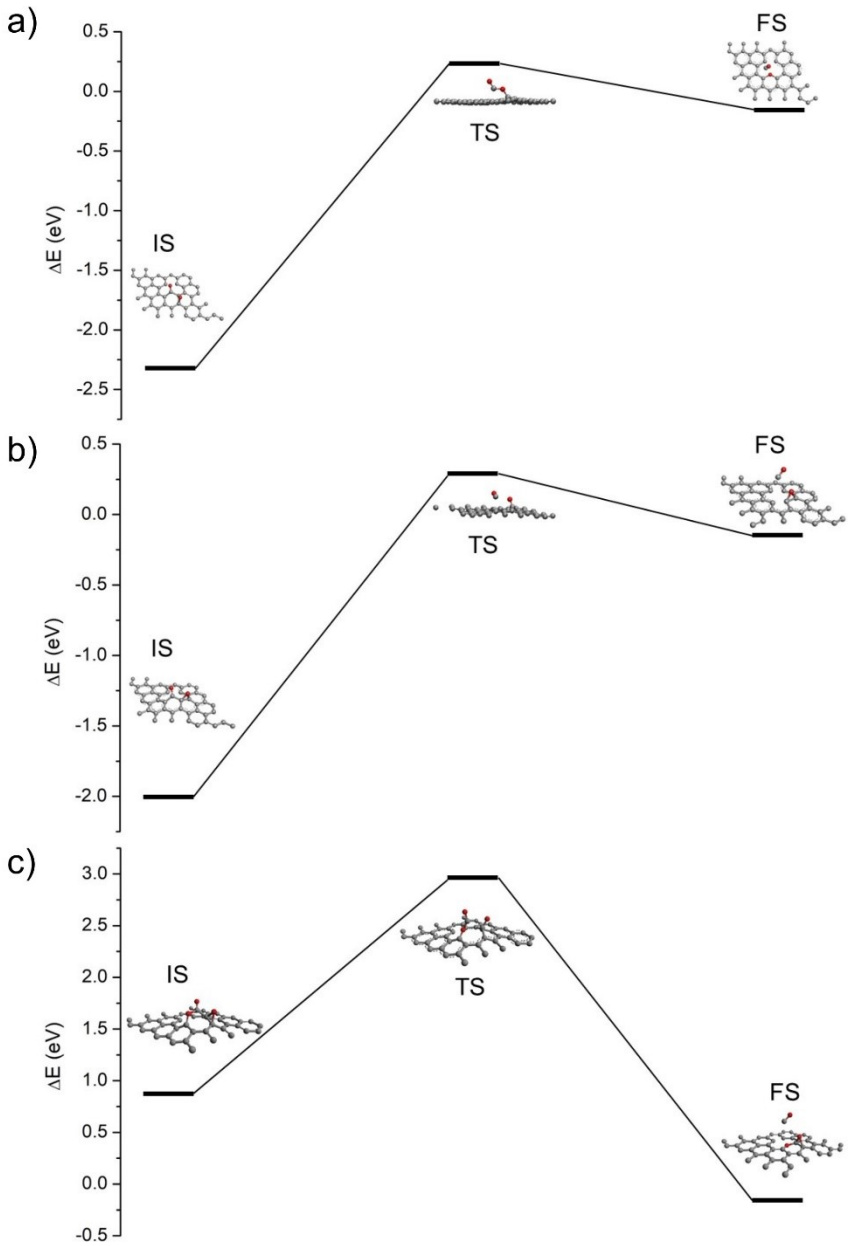

Figure S1: Energy profile for CO desorption from the SV defect with a) a neighboring epoxide group away the SV defect, b) a neighboring epoxide group at the SV defect, and c) a lactone group at the leaving CO and a neighboring epoxide group away from the SV defect. Associated geometry configurations are provided for the IS, TS, and FS.

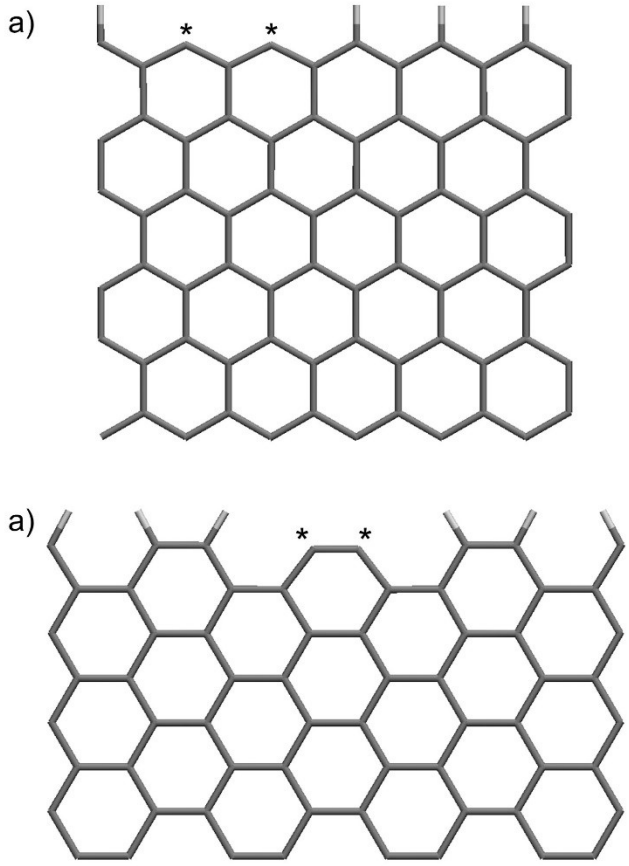

Figure S2: Geometric configurations of the a) ZZ and b) AC edge sites with two unsaturated sites left by the recombinative desorption of O_2. The radical sites have been marked with asterisks (*).