Nature of the Hydrogen Binding in Metal Organic Frameworks with Exposed Transition Metal Sites

WEI ZHOU, NIST and UMD, TANER YILDIRIM, NIST and UPENN — MOFs with exposed transition metal (TM) sites were recently found to exhibit significantly larger experimental heat of H₂ adsorption than classical MOFs, thus attracted great attention. [1, 2] Understanding the nature of the H₂ interaction with the exposed metal sites is of critical importance for the further development of these materials. Using Mn₄Cl-MOF as an example, here we show that the H₂ binding with the exposed TM site is not of the expected Kubas type, in strong contrast to “similar” systems investigated previously (e.g., ref. [3] and [4]). In Mn₄Cl-MOF, there are a) no charge transfer from TM to H₂, b) no significant H-H bond elongation, and c) no evidence of any H₂-σ* Mn-d orbital hybridization. We also study the H₂ binding as a function of Mn₄-magnetic spin configurations, and find no significant effect of the magnetic state on the binding energy. We further reveal that the major contribution to the overall binding is classical Coulomb interaction arising from the small charge overlap of H₂-σ and Mn-d orbitals. This coulomb interaction is very anisotropic, and when the quantum nature of H₂-orientation is taken into account, the actual binding energy is significantly reduced from the calculated classical binding energy. [1] J. Am. Chem. Soc. 128, 16876 (2006). [2] Angew. Chem. Int. Ed. 46, 1419 (2007). [3] Phys. Rev. Lett. 94, 087205 (2005). [4] Phys. Rev. B 76, 085434 (2007).