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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 H_2 adsorption than classical MOFs, thus attracted great attention. [1, 2] Understanding the nature of the H_2 interaction with the exposed metal sites is of critical importance for the further development of these materials. Using Mn_4Cl-MOF as an example, here we show that the H_2 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 Mn_4Cl-MOF, there are a) no charge transfer from TM to H_2, b) no significant H-H bond elongation, and c) no evidence of any H_2-σ^* Mn-d orbital hybridization. We also study the H_2 binding as a function of Mn_4-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 H_2-σ and Mn-d orbitals. This coulomb interaction is very anisotropic, and when the quantum nature of H_2-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).

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