Experimental and theoretical study on hydrogen interaction with unsaturated Metal Organic Frameworks

NOUR NIJEM, JEAN FRANÇOIS VEYAN, University of Texas at Dallas, YONGGANG ZHAO, LINGZHU KONG, JING LI, DAVID C. LANGRETH, Rutgers University, YVES J. CHABAL, University of Texas at Dallas — Infrared absorption spectroscopy (IRAS) is useful to study the interaction of H\textsubscript{2} molecules inside various materials, since the frequency of its internal stretch mode depends on the adsorption site. Unsaturated Metal Organic Frameworks (MOFs) are particularly interesting due to their high H\textsubscript{2} uptakes with relatively large isosteric heats of adsorption (Q\textsubscript{st} > 8 kJ/mol). Our study focuses on H\textsubscript{2} in M\textsubscript{2}(dhtp), dhtp=2,5-dihydroxyterephthalate (M= Zn, Ni, Co, Mg) and combines temperature-dependent IRAS measurements and vdW-DF calculations. Results show that the H\textsubscript{2} stretch frequencies are very sensitive to the chemical environment, with no correlation between binding energies and frequency shifts, as previously observed for saturated MOFs. Moreover, the H\textsubscript{2} stretch vibration closest to the metal site exhibits a strong shift from -30 cm\textsuperscript{-1} to -68 cm\textsuperscript{-1} upon population of neighboring sites (e.g. “oxygen” site).

\textsuperscript{1}This work is supported fully by DOE Grant No. DE-FG02-08ER46491.
\textsuperscript{2}N. Nijem et al. submitted to J.A.C.S 2009