MOLECULAR HYDROGEN INTERACTIONS WITHIN METAL-ORGANIC FRAMEWORKS

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There is much interest in understanding the details of molecular hydrogen physisorption within highly porous materials that could be used for hydrogen storage applications. Unfortunately, the structures of the most promising materials are too complex for ab inito calculations and DFT models are notoriously unreliable for weak interactions. A new approach based on so-called van der Waals DFT has been proposed for explaining the behavior of molecular hydrogen within metal-organic frameworks.[1] In this talk we will present IR spectra of adsorbed hydrogen within a series of isostructural MOFs containing Mg^{2+} and various first-row transition metal cations. The data clearly show that H_2 binds first at an open metal site, with a large vibrational redshift that correlates with the magnitude of the site binding energy. These spectra show minimal effects due to $H_2 \cdots H_2$ interactions and are significantly different from the recent findings of the Chabal group.[1] After collecting spectra over a wide range of temperature and H_2 pressure, we could only reproduce their experimental observations by exposing samples to moist air, which is well-known to cause occupation of the open metal sites by water. This calls into question the appropriateness of the van der Waals DFT models that were used to support their interpretations.[1] We are hopeful that the spectra we present will inspire improved parametrization of such advanced computational models, or prompt the development of superior ones.

1. Nijjem *et al.*, J. Am. Chem. Soc. **132**, 14834 (2010).