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Spectroscopic Evidence for the Influence of the Benzene Sites on Tightly Bound H_2 in Metal−Organic Frameworks with Unsaturated Metal Centers: MOF-74-Cobalt

Nour Nijem,[†] Lingzhu Kong,[‡] Yonggang Zhao,[§] Haohan Wu,[§] Jing Li,[§] David C. Langreth,[‡] and Yves J. Chabal[*,†]

[†]Department of Materials Science and Engineering, University of Texas at Dallas, Richardson, Texas 75080, United States

[‡]Department of Physics and Astronomy and [§]Department of Chemistry and Chemical Biology, Rutgers University, Piscataway, New Jersey 08854, United States

Supporting Information

ABSTRACT: The role of low binding energy sites on the adsorption of H_2 in metal−organic frameworks (MOFs) with unsaturated metal centers has not been identified. For instance, the importance of the benzene sites on H_2 adsorption at the metal site in MOF-74 has not been established. We report here experimental evidence that unambiguously shows that the internal mode of H_2 adsorbed at the metal site undergoes both a frequency shift and a marked change in its *dynamic dipole moment* when H_2 is adsorbed at the **next** nearest neighbor "benzene" site in MOF-74-Co. The effect of loading (i.e., occupation of all benzene sites) also induces spectroscopic shifts in H_2 at the metal site. These interactions highlight the role of lower binding energy sites in H_2 adsorption.

The weak H_2 binding energy (BE ~4 kJ/mol) of H_2 in Metal−Organic Frameworks (MOFs) is a major drawback in their use for onboard H_2 storage, requiring a BE of ~20−25 kJ/mol.[1] Strategies targeting the increase of H_2 BE in these systems include postsynthetic modification,[2−4] incorporation of reactive metal centers,[5] and exploration of spillover mechanisms.[6] One of the routes to increasing the binding energy is the incorporation of unsaturated metal centers in their structure.[7−13] For instance, MOF-74 (M_2(dhtp)), dhtp = 2,5-dihydroxyterephthalate) characterized by a 1-D pore structure of ~12 Å in diameter with unsaturated metal centers connecting the benzenedicarboxylate ligands has shown an enhanced adsorption of H_2 at 77 K.[7,10,11] The adsorption sites of H_2, determined by neutron scattering,[7] are from highest to lowest binding energy: metal, oxygen, benzene, and pore-center sites. Enhanced adsorption at 77 K is possible because of the proximity of H_2 in neighboring sites (e.g., metal and oxygen) (~2.9 Å for D_2−D_2 at 4 K).[7] This results in noticeable H_2−H_2 interactions as evidenced by large variations of H−H stretch frequencies and dynamic dipole moments in MOF-74-Zn (or Mg).[14] Results associated with such ***pairing*** interactions between neighboring H_2 molecules are summarized in Figure S1, along with an illustration of the four adsorption sites.

Theoretical calculations have predicted signatures of next nearest H_2 neighbor interactions, such as variations of both H−H stretch frequencies and dynamic dipole moments of H_2 adsorbed at the metal site when the benzene sites are occupied in MOF-74-(Zn,Mg).[14] There has however been no experimental evidence of such long-range interactions. Yet MOF-74 with Co and Ni differ from MOF-74 with Zn and Mg in that the binding energy of H_2 at the metal site is stronger and the H_2−metal distance is shorter.[15] Focusing on the H_2 molecule adsorbed on the metal site in MOF-74-Co, we show spectroscopic evidence for next-nearest neighbor interactions.

The spectral location of the H−H stretch mode for an isolated H_2 molecule at the highest binding site is best obtained from IR absorption measurements at room temperature and moderate H_2 pressures (24−55 bar). Under these conditions, the total loading does not exceed ~1 wt % (see Figure S2), ensuring that H_2 is mostly located at the metal site. Figure 1 (bottom) shows that the H_2 internal vibration occurs at 4125 cm^{-1}, i.e. is shifted by ~ −30 cm^{-1} from the unperturbed ortho-H_2 band at 4155 cm^{-1}.[16] This shift is similar to what was observed for MOF-74-M (M = Zn, Mg, and Ni).[14] The sidebands at 4060 and 4223 cm^{-1}, not observed in MOF-74 (Zn, Mg), may be associated with rotational and frustrated translational modes (possibly due to the H_2−Co distance ~2.13 Å)[15] and are not the focus of the present work.

A dramatic shift occurs in the H_2 internal mode at higher H_2 loading, achieved at 77 K as shown in Figure 2. The strongest mode is now located at 4041 cm^{-1} at low pressures, i.e. ~ −121 cm^{-1} away from the unperturbed para-H_2 at 4161 cm^{-1} (at 77 K, most H_2 undergoes an ortho to para transition). Similar large shifts have been observed for MOF-74-Ni[17] and weaker shifts (~ −70 cm^{-1}) for MOF-74 (Mg, Zn).[14] The shifts have been shown to arise from H_2−H_2 interactions for the Mg and Zn systems using vdW-DFT calculations[14] but could not be calculated for Co or Ni because of the magnetic nature of these metals. For H_2 in a paired configuration, the mode of H_2 at the oxygen site (expected at ~4120 cm^{-1})[14] is weak as shown in Figure 2 and discussed in the Supporting Information (Figure S3). While the frequency of isolated H_2 is very similar in many systems with both saturated and unsaturated metal centers[14] with no correlation between H_2 frequency shifts and binding

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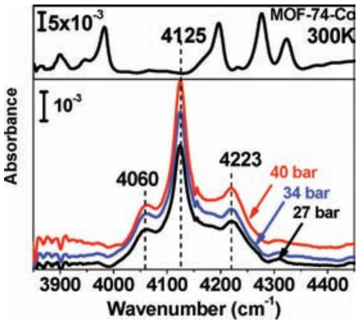

Figure 1. IR absorbance spectra at 300 K of (top) activated MOF-74-Co pressed on a KBr pellet referenced to KBr in vacuum, and (bottom) difference spectra of hydrogen referenced to deuterium (subtraction is necessary to minimize variations in the MOF infrared absorption when guest molecules are introduced).

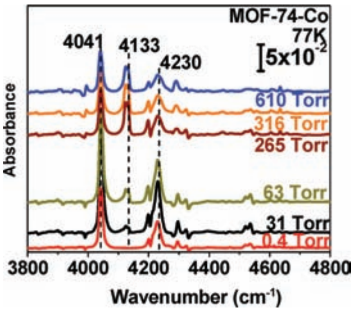

Figure 2. IR absorbance spectra of H_2 adsorbed into MOF-74-Co at 77 K as a function of pressure (0.4−610 Torr). The spectra are references to the MOF sample in vacuum.

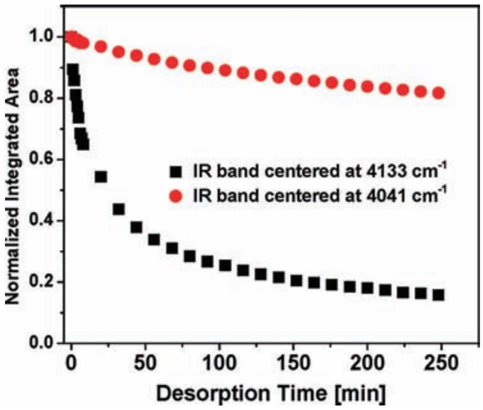

Figure 3. Integrated areas of 4133 and 4041 cm^{-1} bands normalized to their maximum obtained value at t = 0 min at 77 K (integrated in the range 4086−4155 cm^{-1}) as a function of time in the desorption process. A faster decrease of the bands centered at 4133 cm^{-1} is observed.

energies,[16] the frequency of paired H_2 in MOF-74 is affected by the H_2−metal distance.

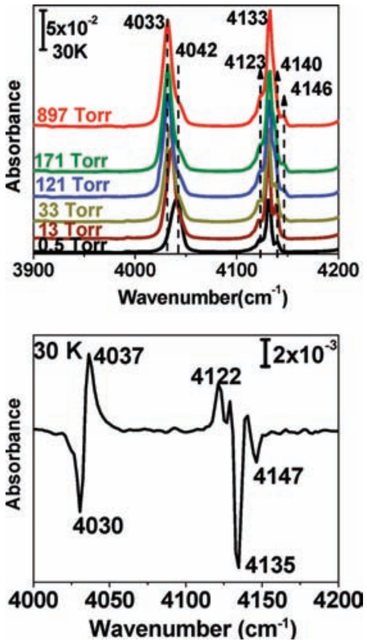

Figure 4. (Top) IR absorbance spectra of H_2 adsorbed at 30 K as a function of pressure (0.5−897 Torr) and (bottom) differential absorbance measured at t = 120 min after lowering the pressure to 0.04 Torr, referenced to the initial absorbance at t = 0 min, highlighting changes occurring over time.

As more H_2 is loaded into the MOF, the intensity of the 4041 cm^{-1} band decreases markedly as that of the 4133 cm^{-1} band increases, as shown Figure 2, and was confirmed by time-dependent measurements at constant pressure (Figure S4). The dependence of the integrated areas on pressure is summarized in Figure S5 showing that the population of the site giving rise to the 4133 cm^{-1} band leads to a decrease of the dynamic dipole moment of H_2 at the metal site. The assignment of the band centered at 4133 cm^{-1} is established by evacuating MOF-74-Co after loading at 900 Torr at 77 K and measuring the time dependence of the IR absorption (Figure 3). The fast decrease of this band intensity indicates that ∼90% of the band is related to H_2 at the low binding-energy benzene site. The remaining 10% is most likely associated with H_2 adsorbed at the oxygen site. In contrast, the band at 4041 cm^{-1} decreases very slowly as H_2 is removed from the oxygen site, i.e. as H_2 pairs are broken. These findings are consistent with theoretical predictions for MOF-74 (Mg, Zn) and from previous observations that H_2−H_2 pairing effectively stabilizes H_2 at the oxygen site.[14]

Although kinetic limitations restrict H_2 penetration into the MOF at low temperatures (T < 50 K) even after 2 h (Figure S6), large loadings can be achieved in the periphery of the crystallites, as shown in Figure 4 at 30 K as a function of pressure. Indeed, the appearance and growth of IR bands in the 4125−4133 cm^{-1} range can be associated with H_2 adsorbed at the lower binding energy sites (i.e., benzene or center sites), consistent with a larger local loading at 30 K than what can be achieved at 77 K. Even though the local loading in the periphery is higher than that at 77 K, the total integrated area of all the H_2 absorption bands is less than that at 77 K, precisely because the regions deep inside the crystallites are not accessible at 30 K.

Figure 4 (top) shows that the 4041 cm^{-1} band shifts by an additional −9 cm^{-1} and saturates upon further loading (P > 10 Torr). This observation indicates that this additional shift is associated with the complete occupation of all benzene sites within the pore (i.e., all metal and oxygen sites are occupied as well). That is, the frequency of H_2 at metal sites is affected by the **cooperative** effect of H_2 at benzene sites. To test the dependence of this change on loading, IR spectra were taken as a function of time (over a 2 h period) at 30 K after evacuation (0.04 Torr). The overall change is summarized in the bottom part of Figure 4. The decrease in intensity of the band at 4133 cm^{-1} is attributed to the removal of H_2 adsorbed at the benzene site. The IR band at 4030 cm^{-1} blue shifts back $\sim+8$ cm^{-1} with the partial removal of H_2 at the benzene site. A small increase in absorption at 4122 cm^{-1} is attributed to variations (increase) of the dipole moment of H_2 at the oxygen site.

This same -9 cm^{-1} shift is observed at the largest pressure (900 Torr) as a function of time (for a 2 h period) for samples at 77 K (Figure S7). A red shift is observed in the IR band corresponding to H_2 adsorbed at the metal site (4041 cm^{-1}) as the benzene site is occupied (increase in the band at 4133 cm^{-1}). This observation indicates that this shift can only occur when **all** of the benzene sites are occupied in the unit cell. However, the magnitude of this effect is small, indicating that only a very small fraction of the unit cells have full benzene site occupation under these conditions.

In summary, by focusing on the H_2 internal mode frequency of H_2 located at the metal site in MOF-74-Co, we have shown that next-nearest neighbor interactions with H_2 at lower binding energy sites are important. Specifically, the occupation of the benzene site affects H_2 at the metal site, and the full occupation of all benzene sites further modifies the frequency of H_2 at the metal site. It is possible that the long-range H_2-H_2 interactions observed in MOF-74-Co are mediated by the open d-shell nature of the cobalt metal center. This could occur if the second H_2 adsorption would change the crystal field and thus the d-orbital splitting sufficiently to affect the partial hybridization between the Co and the adsorbed H_2 (see Supporting Information section 8). These results show that, even though the binding energy of H_2 adsorbed at the benzene sites is small, there are interactions that affect hydrogen adsorbed at the higher binding energy sites that need to be taken into consideration when a material is considered for hydrogen storage and gas separation.

ASSOCIATED CONTENT

Supporting Information. Schematic of hydrogen adsorption sites in MOF-74, isotherms of H_2 adsorption at 300 K as a function of loading, verification of the weak intensity of H_2 adsorbed at the oxygen site, dependence of the dynamic dipole moment of H_2 loading as a function of time, kinetic limitation for adsorption at low temperatures, IR shifts of H_2 adsorbed at the metal site when the benzene site is occupied, materials synthesis, X-ray diffraction and TGA, and suggested mechanisim for the effect of the Co metal center on long-range H_2-H_2 interactions. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author
Chabal@utdallas.edu

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