Infrared Spectroscopy of H₂ in MOFs

1) More than just a characterization technique
2) Experimental probe of H₂⋯MOF interactions
3) Requires some specialized equipment
4) Storage, quantum sieving, catalysis
5) CO₂, CH₄, N₂, other gases
Infrared Spectroscopy! Are you crazy?
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The atoms are neutral
No Dipole moment
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Interactions with MOF can polarize $\text{H}_2$
Infrared Spectroscopy! Are you crazy?

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Interactions with MOF can polarize H₂
Infrared Spectroscopy! Are you crazy?

The atoms are neutral
No Dipole moment

Interactions with MOF can polarize $\text{H}_2$

$\text{H}_2$ polarizability is almost isotropic
Mostly activates pure vibrational transitions
H₂ Quadrupole Mechanism

H₂ quadrupole moment can polarize MOF atoms

Quadrupole moment highly anisotropic
Vibrations and Ro-vibrations are activated

Hydrogen polarizes MOF atoms
Diffuse Reflectance Infrared Spectroscopy

1) Long effective optical path length
2) Powder sample require no processing
3) Typically use 10 mg of powder
4) Sample chamber can be quite small
Diffuse Reflectance Spectroscopy: Cryostat Assembly

Samples are mounted in a glove-box
Quantum Dynamics of Adsorbed $\text{H}_2$

- **Vibration**
  
  $E_v = (\nu + 1/2) \nu_0$
  
  $\nu_0 = 4161 \text{ cm}^{-1}$ for free $\text{H}_2$

- **Rotation**

  $E_J = J(J+1)B_0$

  $B_0 = 59 \text{ cm}^{-1}$ for free $\text{H}_2$

- **Translation**

  Center-of-mass

  On the order of $100 \text{ cm}^{-1}$
Spectroscopic notation of possible transitions

- Pure Vibrational modes called Q transitions $\Delta J = 0$
  - Q(0) and Q(1) are very close in energy $\sim 6$ cm$^{-1}$ apart
- Rotational Sidebands called S Transitions $\Delta J = 2$

- Para $H_2$
  - $\nu = 0, J = 0$
  - $\nu = 1, J = 0$

- Ortho $H_2$
  - $\nu = 0, J = 0$
  - $\nu = 1, J = 1$

$\nu = 0$ transition energies:
- Para $H_2$: $Q(0) = 4161$ cm$^{-1}$, $S(0) = 4498$ cm$^{-1}$
- Ortho $H_2$: $Q(1) = 4155$ cm$^{-1}$, $S(1) = 4713$ cm$^{-1}$
Typical Spectra for $\text{H}_2$ in MOFs at 30 K

- MOF-5
- MOF-74
- HKUST-1
- ZIF-8
Vibrational Redshift as a Function of Binding Energy

![Graph showing the relationship between isosteric heat (kJ/mol) and redshift (cm⁻¹) for various MOF materials.](image-url)
Temperature Dependent Spectra Co-MOF-74
Spectra as a function of concentration (Mg-MOF-74 at 35 K)

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Quantum Dynamics of Adsorbed $\text{H}_2$

- **Vibration**
  \[ E_v = (\nu + 1/2) \nu_0 \]
  \[ \nu_0 = 4161 \text{ cm}^{-1} \text{ for free } \text{H}_2 \]

- **Rotation**
  \[ E_J = J(J+1)B_0 \]
  \[ B_0 = 59 \text{ cm}^{-1} \text{ for free } \text{H}_2 \]

- **Translation**
  Center-of-mass
  On the order of $150 \text{ cm}^{-1}$
Translational mode energy (quantum sieving?)
Back of the Envelope Calculation

\[
ZPE = \frac{3}{2} h \omega
\]

\[
\omega \approx 200 \text{ cm}^{-1}
\]

\[
\Rightarrow ZPE = 300 \text{ cm}^{-1} = 420 \text{ K}
\]

\[
\omega_D = \frac{1}{2} \omega_{H_2}
\]

\[
\Rightarrow ZPE_{D_2} \approx 300 \text{ K}
\]

\[
\Delta ZPE = 120 \text{ K}
\]

\[
e^{\frac{\Delta E}{kT}} \text{ at } 77 \text{ K}
\]

\[
e^{\frac{120}{77}} = 4.75
\]

\[E = 0\]
Selectivity vs Translational Frequency


Dashed line shows simple back of the envelope
Solid line shows full (harmonic) thermodynamic calculation
H₂ and D₂ Mixtures in Mg-MOF-74
H₂ and D₂ Mixtures (After sitting at room temperature)
Mass Spectroscopy HD formation at room temperature
Mass Spectroscopy HD formation at room temperature

Graph showing the HD/(H₂+HD+D₂) ratio over time for two conditions: Pristine and Air-Exposed.
Mass Spectroscopy HD formation at room temperature

- Pristine
- Air-Exposed
- Reactivated 180 °C
H$_2$ and D$_2$ Mixtures (After sitting at room temperature)
Deuterium in MOF-5

Pure MOF-5

MOF-5 with D₂

Fundamental

Overtone
Frequency Shift Fundamental versus Overtone


![Graph showing absorbance vs. frequency shift for different isotopes: D$_2$, HD, H$_2$, Q(1), Q(0)]

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Supporting Information

ABSTRACT: In order for hydrogen gas to be used as a fuel, it must be stored in sufficient quantity on board the vehicle. Efforts are being made to increase the hydrogen storage capabilities of metal–organic frameworks (MOFs) by introducing unsaturated metal sites into their linking element(s), as hydrogen adsorption centers. In order to devise successful hydrogen storage strategies there is a need for a fundamental understanding of the weak and elusive hydrogen physisorption interaction. Here we report our findings from the investigation of the weak intermolecular interactions of adsorbed hydrogen molecules on MOF-linkers by using cluster models. Since physical interactions such as dispersion and polarization have a major contribution to attraction energy, our approach is to analyze the adsorption interaction using energy decomposition analysis (EDA) that distinguishes the contribution of the physical interactions from the charge-transfer (CT) “chemical” interaction. Surprisingly, it is found that CT from the adsorbent to the $\sigma^*(H_2)$ orbital is present in all studied complexes and can contribute up to approximately $-2$ kJ/mol to the interaction. When metal ions are present, donation from the $\sigma^*(H_2)$ to metal Rydberg-like orbital, along with the adsorbent $\sigma^*(H_2)$ contribution, can contribute from $-2$ to $-10$ kJ/mol, depending on the coordination mode. To reach a sufficient adsorption enthalpy for practical usage, the hydrogen molecule must be substantially polarized. Ultimately, the ability of the metalated linker to polarize the hydrogen molecule is highly dependent on the geometry of the metal ion coordination site where a strong electrostatic dipole or quadrupole moment is required.

INTRODUCTION

Hydrogen ($H_2$) gas is a promising candidate for future use as an energy carrier for mobile applications such as vehicles and aircrafts. Hydrogen has almost three times higher gravimetric energy content than gasoline, and its combustion or utilization in a fuel cell is a “zero emission” process that results in the formation of water without emitting any compounds that pollute the environment or disrupt the climate. Since $H_2$ is an extremely volatile gas under standard conditions, the energy available per unit volume (volumetric energy density) is too low for practical application, requiring its storage at high pressures or as a liquid at cryogenic temperatures on board a vehicle. An efficient method for the storage of $H_2$ is therefore a necessary technology for its effective use as a fuel. The 2017 DoD target values for an onboard hydrogen storage system for light-duty fuel cell vehicles are a gravimetric capacity of 5.5 wt % ($kg_{H_2}/kg$) and a volumetric capacity of 4.0 vol % ($kg_{H_2}/L$) at an operating temperature of $-40$ to $-100^\circ$C. To the best of our knowledge, these targets have yet to be met by any known material upon incorporation into a storage system.

Metal–organic frameworks (MOFs) are a family of compounds consisting of metal ions or clusters coordinated to organic ligands (linkers), which form extended network structures. These materials have attracted attention for their potential use as gas-storage media.1 MOF structures often have sizable pores that can be filled with guest molecules, many of which are adsorbed to the internal surfaces. Moreover, the MOF composition and structure can be modified and tuned for many purposes, such as catalysis1 and chemical separations.1,4

A reversible mechanism for adsorption and release of $H_2$ from its storage material is needed for any practical storage application. In this respect, the weak physisorption of $H_2$ in MOFs is advantageous, since $H_2$ can reversibly adsorb to pores surfaces within the MOF and be easily released when needed. However, the weak adsorption enthalpy ($H_{ads}$) of $H_2$ to most known MOFs poses a challenge. At ambient temperatures, an adsorption enthalpy of $\sim-15$ to $\sim-30$ kJ mol$^{-1}$ is needed for optimum hydrogen storage–delivery cycles depending upon

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Direct Experimental Evidence of Binding Mechanism?

How could we most directly determine the relative contribution of these three mechanisms?

“More direct” implies less need for theoretical modelling.

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Typical Spectra for H$_2$ in MOFs at 30 K

Absorbance

Frequency (cm$^{-1}$)

Q(0) and Q(1)

S(0)

S(1)

MOF-74

HKUST-1

ZIF-8

MOF-5
Binding Sites in MOF-5


MOF-5 Temperature Dependence

![Graph showing the temperature dependence of MOF-5 with absorbance on the y-axis and frequency (cm⁻¹) on the x-axis, with peaks labeled Q(0) and Q(1) at different temperatures (15K, 20K, 25K).]
Concentration Dependence

![Graph showing the concentration dependence of absorbance across different frequencies. The x-axis represents frequency in cm\(^{-1}\), and the y-axis represents absorbance. Lines of different colors represent various concentrations of \(H_2\) per cluster, with 0.7, 1.3, 2.0, 2.7, and 4.0 \(H_2\) per cluster distinguished by line color.](image-url)
MOF-5 with H$_2$ Molecules at Primary Site
Stick Spectrum for Interacting ortho-H₂ Pairs
Ortho to Para Conversion with Time

![Graph showing absorbance vs frequency over time](image.png)
H₂ and D₂ Mixture

Absorbance

Frequency (cm⁻¹)

- 0.7 H₂ per Cluster
- 0.7 H₂ and 2.7 D₂
CO$_2$ in Different Metal MOF-74

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