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# Supporting Information

## Hydrogen adsorption in metal-organic framework MIL-101(Cr) – Adsorbate densities and enthalpies from sorption, neutron scattering, *in-situ* X-ray diffraction, calorimetry, and molecular simulations

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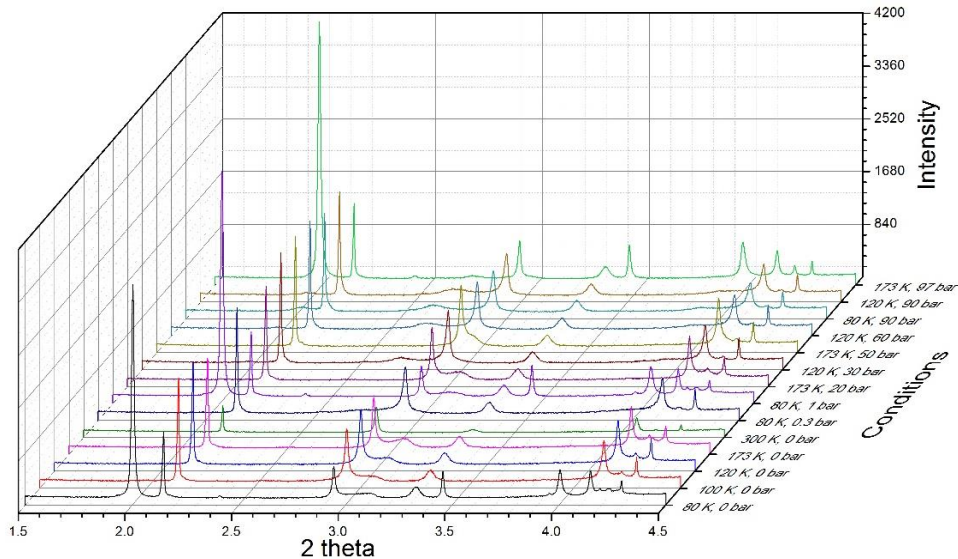
### Samples

The MIL-101(Cr) and MIL-53(Al) samples were synthesised and activated as reported previously in Sharpe et al [1].

### *In-situ* synchrotron X-ray diffraction

The experiments were performed at instrument ID31 at the European Synchrotron Radiation Facility (ESRF) in Grenoble. The MIL-101(Cr) and MIL-53(Al) samples were loaded into a high-pressure quartz capillary using a glovebox. The capillary is then glued using an epoxy to a brass holder, Swagelok fittings and ferrules and mounted on a goniometer, which is then aligned in the beam. In addition to vacuum measurements, the setting allows gas dosing and measurements using high-purity hydrogen at 10 MPa. The system is also equipped with a cryostream system

that allows measurements between 80 and 500 K, with a ramp rate of 360 K/hr. The X-ray diffractograms were collected using synchrotron radiation for both materials at 0 and 10 MPa and at temperatures 100 and 300 K for the MIL-101(Cr), and at temperatures 80 to 173 K for the MIL-53(Al).



**Figure S1** – Low-angle in-situ synchrotron X-ray diffraction pattern for the MIL-53(Al) from 0 – 9.7 MPa and from 80 to 173 K

### Molecular simulations

The atomic structure of MIL-101(Cr) was constructed in a three-step process based on experimental crystallographic data and computational methods, as reported previously by Chen et al [2]. The unit cell was energetically minimized using Materials Studio, in which the framework atoms were represented by the universal force field (UFF) [3]. The atomic charges of MIL-101(Cr) was estimated by density functional theory (DFT). The DFT calculation was conducted in Materials Studio using the Becke exchange plus Lee-Yang-Parr correlation functional, along with the double- $\xi$  numerical polarization (DNP) basis set. From the calculated electrostatic potentials, the atomic charges were fitted using the Merz-Kollman (MK) scheme [4].

The interactions between MIL-101(Cr) framework atoms and hydrogen molecules were represented by additive pair-wise Lennard-Jones (LJ) and Coulombic potentials

$$u_{ij}(r) = \sum_{\substack{\alpha \in i \\ \beta \in j}} \left\{ 4\epsilon_{\alpha\beta} \left[ \left( \frac{\sigma_{\alpha\beta}}{r_{\alpha\beta}} \right)^{12} - \left( \frac{\sigma_{\alpha\beta}}{r_{\alpha\beta}} \right)^6 \right] + \frac{q_{\alpha}q_{\beta}}{4\pi\epsilon_0 r_{\alpha\beta}} \right\}$$

where  $\sigma_{\alpha\beta}$  and  $\epsilon_{\alpha\beta}$  are the collision diameter and well depth, respectively; the cross LJ interaction parameters were calculated by the Lorentz-Berthelot combining rules;  $\epsilon_0 = 8.8542 \times 10^{-12} \text{ C}^2 \text{ N}^{-1} \text{ m}^{-2}$  is the permittivity of the vacuum and  $q_\alpha$  is the charge on atom  $\alpha$ . The LJ parameters of the framework atoms were adopted from the UFF. The MIL-101(Cr) structure was assumed to be rigid and perfect without defect.  $\text{H}_2$  was represented as a single-site Buch model [5] with  $\sigma = 2.96 \text{ \AA}$  and  $\epsilon/k_B = 34.2$ . It is known that quantum dispersion effects play a substantially important role in determining the properties of  $\text{H}_2$  at cryogenic temperatures [6-7]. To estimate these effects, we calculated the *de Broglie* wavelength:

$$\Lambda = h / \sqrt{2\pi m_{\text{H}_2} k_B T}$$

where  $h$  is the Planck constant ( $6.62608 \times 10^{-34} \text{ J s}$ ),  $m_{\text{H}_2}$  is the mass of  $\text{H}_2$  molecule ( $3.34524 \times 10^{-27} \text{ kg}$ ),  $k_B$  is the Boltzmann constant ( $1.38066 \times 10^{-23} \text{ J K}^{-1}$ ), and  $T$  is temperature. At 77 K,  $\Lambda$  is approximately 1.402  $\text{\AA}$  for  $\text{H}_2$ , in the same magnitude as the range of intermolecular distance. Consequently, the quantum dispersion effects cannot be neglected at 77 K, especially at high pressures. Two methods are commonly used to take into account the quantum dispersion effects, namely, path integral (PI) formalism and Feynman-Hibbs (FH) variational approach. The PI formalism is theoretically exact but computationally more expensive. In this study, the quantum dispersion effects for  $\text{H}_2$  were incorporated by the FH effective potential [8]:

$$u_{\text{FH}}(r) = u_{\text{LJ}}(r) + \frac{\beta \hbar^2}{24\mu} \left[ u_{\text{LJ}}''(r) + \frac{2u_{\text{LJ}}'(r)}{r} \right] \\ + \frac{\beta^2 \hbar^4}{1152\mu^2} \left[ u_{\text{LJ}}''''(r) + \frac{4u_{\text{LJ}}'''(r)}{r} + \frac{15u_{\text{LJ}}'(r)}{r^3} \right]$$

where  $\beta = 1/k_B T$ ,  $\hbar$  is the reduced Planck constant ( $= h/2\pi$ ), and  $\mu$  is the reduced mass. This gives the quartic approximation of the FH effective potential and is superior to the quadratic approximation in a confined system [6].

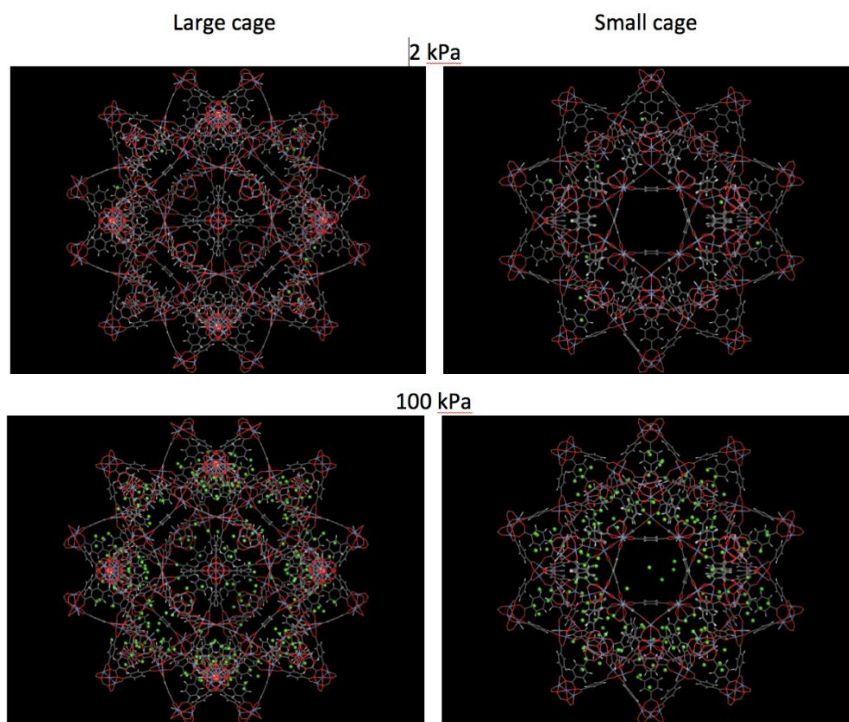
$\text{H}_2$  adsorption in MIL-101(Cr) was simulated by Gibbs ensemble Monte Carlo (GEMC) method. This approach precludes the need to use an empirical equation of state to convert chemical potential to pressure (which is the case by grand canonical Monte Carlo method at a fixed chemical potential  $\mu$ , volume and temperature). In the GEMC simulation, two simulation boxes are used (one for the adsorbent and the other for the bulk adsorbate), the total number of adsorbate molecules is fixed, but allowing molecules to swap between the two boxes. Thus, the adsorption at a given pressure is directly simulated, along with the direct determination of bulk density and enthalpy, which allows the calculation of excess adsorption data. In our GEMC

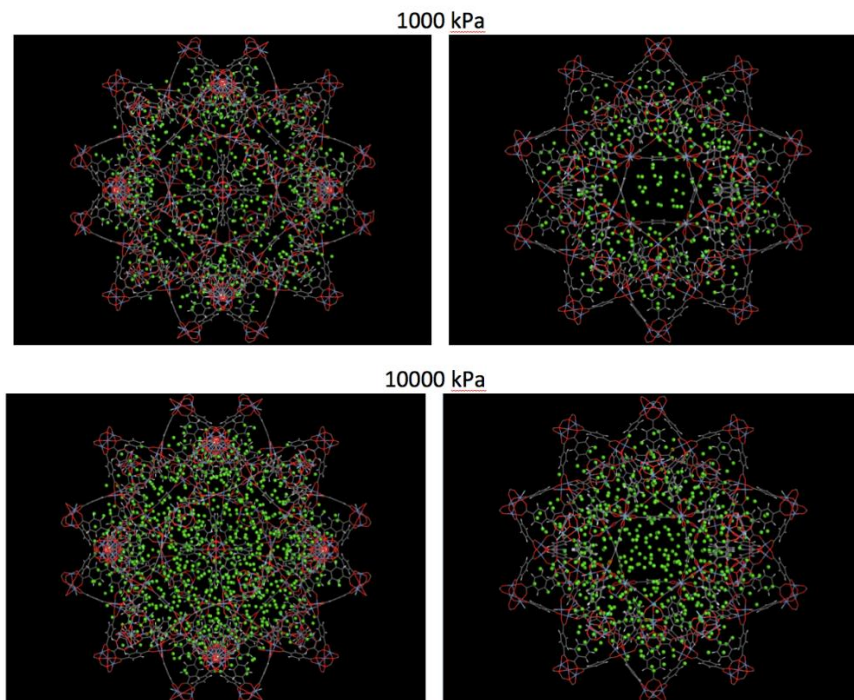
simulations, MIL-101(Cr) was assumed to be rigid and the framework atoms were fixed. The LJ interactions were evaluated using a spherical cutoff of 15 Å with long-range corrections added, while the Coulombic interactions were calculated using the Ewald sum method. The number of trial moves in a typical GEMC simulation was  $2 \times 10^7$ , with the first  $10^7$  moves for equilibration and the subsequent  $10^7$  moves for ensemble averages. Three types of trial moves were randomly attempted: displacement and regrowth in each box, and swap between two boxes.

To evaluate the interaction strength between adsorbate and adsorbent, the heat of adsorption  $Q_{st}$  was calculated by

$$Q_{st} = RT - \left( \frac{\partial U_{adsp}}{\partial N} \right)_{T,V}$$

where  $R$  is the gas constant,  $U_{adsp}$  is the adsorption energy, and  $N$  is the number of adsorbate molecules.





**Figure S2** – Simulation snapshots of hydrogen adsorption (green balls) in MIL-101(Cr) in both small and large cages from 0.002 to 10 MPa at 77 K.

### Inelastic neutron scattering experiments

Inelastic neutron scattering experiments were performed on the TOSCA instrument at the ISIS facility at the Science and Technology Facilities Council's (STFC's) Rutherford Appleton Laboratories in the UK, which currently allows measurement at high resolution ( $\Delta E / E < 1.25\%$ , where  $E$  is the energy lost by the incoming neutron) over the widest range of energy transfer of any INS instrument in the world. The measurement of the elastic line (where little or no energy is transferred between the incident neutron and the target  $H_2$  molecule,  $\sim 0$  meV in INS energy loss spectra) was made possible by recent modifications, which gave improved high resolution at low energies allowing quantitative analysis of the elastic region of a scattering spectrum as a function of gas pressure, with simultaneous monitoring of the recoil features in the inelastic region. Both elastic and inelastic regions contain information on the state (gaseous, liquid or solid) of the  $H_2$  in the pores.

INS spectra were collected on  $H_2$  dosed onto a  $\sim 7$  cm<sup>3</sup> sample of MIL-101(Cr) at 77 K, at eight gas pressures in the range 0.016-3.5 MPa, with  $\sim 12$  h data collection periods.

## Differential Scanning Calorimetry

High-pressure Differential Scanning Calorimetry (DSC) was done on a Setaram  $\mu$ DSC7 Evo module equipped with high-pressure sample holder. Stepwise pressure measurements were performed with the DSC connected to a Setaram Hy-Energy PCTPro-2000 to supply the required pressure doses. Air Products high purity hydrogen gas was dosed at  $\sim 1$  MPa pressure intervals up to a max pressure of 11 MPa and allowed to equilibrate for  $\sim 20$  mins between each dose. The pressure was measured once the sample equilibrated. Data was collected and analysed using Calisto software from Setaram and Origin 2018b software (OriginLab Corporation, Northampton, MA, USA). The data was acquired at room temperature to reduce uncertainties associated with temperature control at cryogenic temperatures.

To calculate the enthalpies from the DSC, the first peak was integrated and divided by the mass of the sample (54.04 mg of MIL-101(Cr)). The integrated peak is equal to 2.83 J per gram of MIL-101(Cr). The equilibrium pressure that corresponded to the exothermic peak was 1.344 MPa and this pressure had to be correlated with uptake, to calculate heat per mol of hydrogen. Using the experimental data at 292 K (experimental data is more accurate than using modelling, and close to room temperature there will not be much difference at low pressures between absolute and excess uptakes), we interpolate the data at 1.344 MPa and the corresponding uptake is 0.118 wt%. After converting to moles, the integrated peak value ( $2.83 \text{ J g}^{-1}$ ) was divided by the uptake in mol  $\text{H}_2$  per g of adsorbent to yield J per mol of  $\text{H}_2$  ( $4.84 \text{ kJ mol}^{-1}$ ).

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