Supporting Information

The Temperature Dependence of the Langmuir Adsorption Model for a Single-Site Metal-Organic Framework

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Absolute Adsorption Approximation

The maximum correction term in Equation 3 in the main text ($\rho_g V_a$) was determined by assuming that the maximum adsorbed phase volume is equal to the total pore volume of the adsorbent.

For the MOF used in this study, $Ni_3(pzdc)_2(ade)_2(H_2O)_4$, the total pore volume accessible to H_2 was calculated using a standard software package (Zeo++) using the experimentally determined crystal structure (measured by K. C. Stylianou et al.[S1]) and a probe radius of 1.2 Å (corresponding to H_2); it was found to be 0.119 mL g^{-1}. Furthermore, the densest gas phase of hydrogen encountered under the experimental conditions explored in this work (calculated using NIST Refprop) was 0.139 mmol mL^{-1} at 70 K and 810 mbar.

By combining these two quantities, the maximum possible correction term is 0.0166 mmol g^{-1} which is ~0.7% of the measured (excess) uptake quantity at 70 K and 810 mbar. This is below the standard error associated with the measurement and is hence negligible.

Clausius-Clapeyron Approximation

In general, adsorption equilibria obey the Clapeyron equation which is a general relation for any two phases in thermal and mechanical equilibrium:

$$\Delta_{ads}H[T,P] = T\,\Delta_{ads}S = T\left(\frac{\partial P}{\partial T}\right)_\theta \Delta_{ads}v = T\left(\frac{\partial P}{\partial T}\right)_\theta \left(v_a - v_g\right)$$

When one of the two phases in equilibrium is an ideal gas and the other is a condensed phase (e.g., an adsorbed phase), it is common to employ an approximation that the condensed phase molar volume is negligible compared to the gas and thus derive the Clausius-Clapeyron subvariant:

$$q_{st}[T,P] = -\Delta_{ads}H[T,P] = \frac{RT^2}{P}\left(\frac{\partial P}{\partial T}\right)_\theta$$

The above equations can be explicitly solved for all of the models explored in this work, each giving rise to a specific form of the partial derivative and therefore a specific relationship between the fitting parameters and the isosteric enthalpy of adsorption. These relationships are summarized in Equation 12 in the main text.

Powder X-Ray Diffraction Analysis

The phase purity of $Ni_3(pzdc)_2(ade)_2(H_2O)_4$ was assessed by powder X-ray diffraction (XRD) methods, as shown in **Figure S1**.

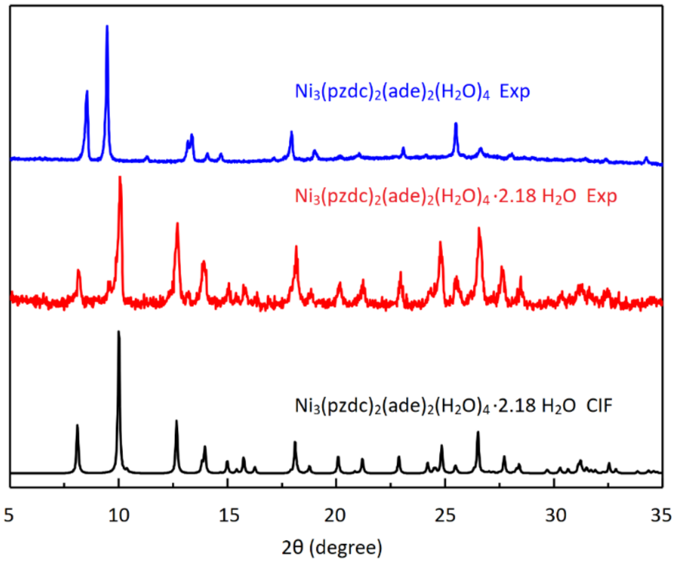

Figure S1. XRD pattern of $Ni_3(pzdc)_2(ade)_2(H_2O)_4$ and $Ni_3(pzdc)_2(ade)_2(H_2O)_4 \cdot 2.18H_2O$ compared to a simulated pattern (based on the single-crystal XRD structure of $Ni_3(pzdc)_2(ade)_2(H_2O)_4 \cdot 2.18H_2O$[S1]).

Cryostat Temperature Calibration

The cryostat temperature was calibrated by comparison to boiling nitrogen, as shown in **Figure S2**.

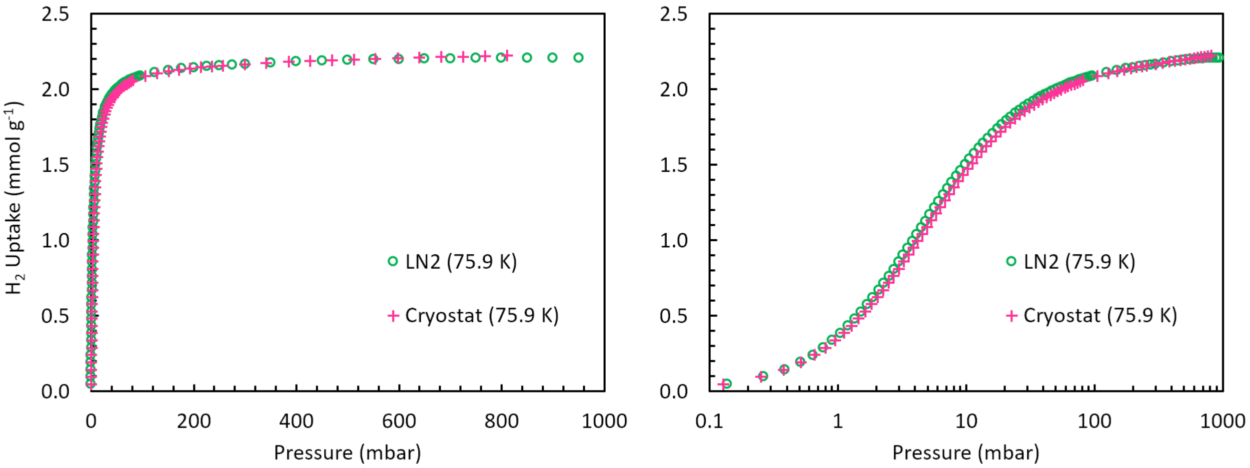

Figure S2. Equilibrium excess adsorption uptake of H_2 on $Ni_3(pzdc)_2(ade)_2(H_2O)_4$ in a liquid nitrogen bath (N_2 boils at 75.9 K in Bozeman, Montana) and at the same set-point using a cryostat (75.9 K).

Langmuir Adsorption Theory

In the "classic" (also known as the single-site monolayer) Langmuir model, there are three simple assumptions used to define the adsorption system:

1. Every adsorption site is identical, independent, and distinguishable (hence "single-site")
2. Each adsorption site can accommodate up to 1 adsorbate molecule (hence "monolayer")
3. The chemical reservoir is an ideal gas

The third assumption is necessary to obtain the classic Langmuir equation from first principles, but is not always strictly ensured by the system of study. In this case, the conditions investigated experimentally meet the criteria to be considering suitably ideal (see Clausius-Clapeyron Approximation above). Therefore, if the adsorbent is crystalline and contains identical sites that can host only a single adsorbate per site, the adsorption isotherm will be described by the Langmuir model.

When held in contact with a thermal reservoir (held at temperature T) and a chemical reservoir (held at chemical potential μ), a single such adsorption site has the following grand canonical partition function (owing to two possible states, empty or singly occupied, according to the first assumption):

$$\xi[\beta, \beta\tilde{\mu}] = \sum_{i\ (states)} q_i e^{-\beta E_i} e^{\beta\tilde{\mu}N_i} = 1 + q[\beta]e^{-\beta\varepsilon}e^{\beta\tilde{\mu}}$$

$$\beta = \frac{1}{k_B T}$$

$$\beta\tilde{\mu} = \frac{\tilde{\mu}}{k_B T} = \frac{1}{k_B T}\left(\frac{\partial G}{\partial N}\right)_{T,P}$$

In the above equations, q is the canonical partition function for the adsorbate when occupying the adsorption site, and ε is the binding energy (difference in energy between the bulk adsorbate and the bound adsorbate).

The total grand canonical partition function for the surface (containing N_s identical, independent, and distinguishable sites, according to the second assumption) is then:

$$\mathcal{Z}[\beta, \beta\tilde{\mu}] = \prod_{j\ (sites)} \xi_j = \xi^{N_s} = \left(1 + q[\beta]e^{-\beta\varepsilon}e^{\beta\tilde{\mu}}\right)^{N_s}$$

Finally, following the usual thermodynamic relations, the expectation value for the number of sites occupied, which is equivalent to the adsorption equation, is:

$$\langle N\rangle[\beta, \beta\tilde{\mu}] = N_s \cdot \frac{q[\beta] \cdot e^{-\beta\varepsilon} \cdot e^{\beta\tilde{\mu}}}{1 + q[\beta] \cdot e^{-\beta\varepsilon} \cdot e^{\beta\tilde{\mu}}}$$

This is much more commonly expressed in terms of the pressure of the chemical reservoir, P^*. To do so requires invoking the third assumption. The chemical potential of an ideal (monatomic) gas is:

$$P^* = \frac{(2\pi\widetilde{m})^{1.5}\,(k_B T)^{2.5}}{h^3} e^{\beta\widetilde{\mu}}$$

Therefore:

$$\langle N\rangle[T, P^*] = N_s \cdot \frac{A[T]\cdot e^{-\frac{\varepsilon}{k_B T}}\cdot P^*}{1 + A[T]\cdot e^{-\frac{\varepsilon}{k_B T}}\cdot P^*}$$

The fractional occupancy is simply:

$$\theta[T, P^*] = \frac{\langle N\rangle}{N_s} = \frac{A[T]\cdot e^{-\frac{\varepsilon}{k_B T}}\cdot P^*}{1 + A[T]\cdot e^{-\frac{\varepsilon}{k_B T}}\cdot P^*}$$

The pre-exponential term, $A[T]$, varies depending on the treatment of the bound molecule on the adsorption site (see **Table S1**). We note that, in general, the form of $A[T]$ is independent of the nature of the ideal gas adsorbate (i.e., monatomic, diatomic, etc.), as long as the same internal degrees of freedom are retained in the adsorbed state as in the gas state.

Adsorption Site Descriptions and A[T]

To derive $A[T]$, an explicit form of $q[\beta]$ (i.e., $q[T]$) is needed. Four representative examples are explored below and a more systematic list is given in **Table S1**.

Fixed (i.e., "model -2.5"):

If the bound molecule has no degrees of freedom (the adsorption site is either "on" or "off", "occupied" or "empty"), then the canonical partition functions of the adsorbed molecule in all three spatial dimensions are simply:

$$q_{DF}[\beta] = 0 + 1 = 1$$

In other words:

$$q_{Fix,x}[\beta] = q_{DF,x}[\beta] = 1$$
$$q_{Fix,y}[\beta] = q_{DF,y}[\beta] = 1$$
$$q_{Fix,z}[\beta] = q_{DF,z}[\beta] = 1$$

Together:

$$q_{Fix}[\beta] = q_{DF,x}[\beta] \times q_{DF,y}[\beta] \times q_{DF,z}[\beta] = 1 \times 1 \times 1 = 1$$

Then, following the statistical mechanics above:

$$\xi_{Fix}[\beta, \beta\tilde{\mu}] = 1 + e^{-\beta\varepsilon} e^{\beta\tilde{\mu}}$$

$$A_{Fix}[T] = \frac{h^3}{(2\pi\tilde{m})^{1.5}\,(k_B T)^{2.5}}$$

This is confirmed by using a more general approach which integrates over the entire potential experienced by the adsorbed molecule. For a perfectly fixed adsorbate, the potential is simply an inverted Dirac delta function (whose value is equal to the energy of adsorption, ε, at the origin and infinity everywhere else), centered at the adsorption site. The explicit details of this integration approach are given elsewhere.[S2]

<u>3D Ideal Gas (i.e., "model -1")</u>:

If the bound molecule is treated as a particle in a box in all three spatial dimensions, then the individual partition functions are simply:

$$q_{SP}[\beta] = L\frac{\sqrt{2\pi\tilde{m}}}{h\sqrt{\beta}} = \frac{L}{\Lambda}$$

where:

$$\Lambda = \frac{h}{\sqrt{2\pi\tilde{m}k_B T}} = \frac{h\sqrt{\beta}}{\sqrt{2\pi\tilde{m}}}$$

In other words:

$$q_{3DI,x}[\beta] = q_{SP,x}[\beta] = \frac{L_x}{\Lambda}$$
$$q_{3DI,y}[\beta] = q_{SP,y}[\beta] = \frac{L_y}{\Lambda}$$
$$q_{3DI,z}[\beta] = q_{SP,z}[\beta] = \frac{L_z}{\Lambda}$$

Together:

$$q_{3DI}[\beta] = q_{SP,x}[\beta] \times q_{SP,y}[\beta] \times q_{SP,z}[\beta] = \frac{L_x}{\Lambda} \times \frac{L_y}{\Lambda} \times \frac{L_z}{\Lambda} = \frac{V_s}{\Lambda^3}$$

Then, following the statistical mechanics above:

$$\xi_{3DI}[\beta, \beta\tilde{\mu}] = 1 + \frac{V_s}{\Lambda^3} e^{-\beta\varepsilon} e^{\beta\tilde{\mu}}$$

$$A_{3DI}[T] = \frac{V_s}{k_B T}$$

This is also confirmed by using a more general approach which integrates over the entire potential experienced by the adsorbed molecule. For an adsorbate in a box, the potential along x is simply a square-well of width L_x (whose value is equal to the energy of adsorption, ε, in the box and infinity everywhere else), centered at the adsorption site. The explicit details of this integration approach are given elsewhere.[S2]

Einstein Adsorbed Phase (i.e., "model +0.5"):

If the bound molecule is treated as a harmonic oscillator in all three spatial dimensions, then the individual partition functions are simply:

$$q_{QP}[\beta] = \frac{2\pi}{h\omega\beta}$$

In other words:

$$q_{Ein,x}[\beta] = q_{QP,x}[\beta] = \frac{2\pi}{h\omega_x\beta}$$
$$q_{Ein,y}[\beta] = q_{QP,y}[\beta] = \frac{2\pi}{h\omega_y\beta}$$
$$q_{Ein,z}[\beta] = q_{QP,z}[\beta] = \frac{2\pi}{h\omega_z\beta}$$

Together:

$$q_{Ein}[\beta] = q_{QP,x}[\beta] \times q_{QP,y}[\beta] \times q_{QP,z}[\beta] = \frac{2\pi}{h\omega_x\beta} \times \frac{2\pi}{h\omega_y\beta} \times \frac{2\pi}{h\omega_z\beta}$$

When all three dimensions are taken to have the same natural frequency of oscillation, ω_s:

$$q_{Ein}[\beta] = \left(\frac{2\pi}{h\omega_s\beta}\right)^3$$

Then, following the statistical mechanics above:

$$\xi_{Ein}[\beta, \beta\tilde{\mu}] = 1 + \left(\frac{2\pi}{h\omega_s\beta}\right)^3 e^{-\beta\varepsilon} e^{\beta\tilde{\mu}}$$

$$A_{Ein}[T] = \frac{(2\pi)^{1.5}\ (k_B T)^{0.5}}{{\omega_s}^3\ (\widetilde{m})^{1.5}}$$

This is confirmed by using a more general approach which integrates over the entire potential experienced by the adsorbed molecule. For a harmonic oscillator, the potential along x is simply a quadratic function with a minimum at ε (whose value is equal to $\varepsilon + ½\widetilde{m}{\omega_x}^2 x^2$), centered at the adsorption site. The explicit details of this integration approach are given elsewhere.[S2]

2D Ideal Gas with z-Oscillation (i.e., “model -0.5”):

Instead of treating all three spatial dimensions as equivalent, other models can be developed that treat each dimension differently. For simplicity, the above three types of potential can be interchanged: inverted delta functions, square wells, or quadratic potentials. For example, if the bound molecule is treated as a particle in a 2D box (accounting for the two spatial dimensions along the surface of the adsorbent as square wells) and a harmonic oscillator in the direction orthogonal to the surface (treated as a quadratic potential, nominally in the z direction), then the individual partition functions are:

$$q_{2DO,x}[\beta] = q_{SP,x}[\beta] = \frac{L_x}{\Lambda}$$

$$q_{2DO,y}[\beta] = q_{SP,y}[\beta] = \frac{L_y}{\Lambda}$$

$$q_{2DO,z}[\beta] = q_{QP,z}[\beta] = \frac{2\pi}{h\omega_z\beta}$$

Together:

$$q_{2DO}[\beta] = q_{SP,x}[\beta] \times q_{SP,y}[\beta] \times q_{QP,z}[\beta] = \frac{L_x}{\Lambda} \times \frac{L_y}{\Lambda} \times \frac{2\pi}{h\omega_z\beta} = \frac{A_s}{\Lambda^2}\left(\frac{2\pi}{h\omega_s\beta}\right)$$

Then, following the statistical mechanics above:

$$\xi_{2DO}[\beta, \beta\tilde{\mu}] = 1 + \frac{A_s}{\Lambda^2}\left(\frac{2\pi}{h\omega_s\beta}\right) e^{-\beta\varepsilon} e^{\beta\tilde{\mu}}$$

$$A_{2DO}[T] = \frac{(2\pi)^{0.5}\, A_s}{\omega_s\, (\tilde{m})^{0.5}\, (k_B T)^{0.5}}$$

Other possibilities for mixed-potential adsorption sites are shown in **Table S1** and indexed according to the type of potential in each of the spatial directions (x, y, and z). Upon derivation of the adsorption model, the form of $A[T]$ is unique to each choice of $q[\beta]$. The high-T heat capacity of the adsorbed phase in each model is equal to the order of T in the expression for $q[\beta]$ (e.g., $q_{2DO}[\beta] \propto \beta^{-2} \propto T^2$ so the heat capacity at high temperature is $2k_B T$).

Nomenclature:

Physical Constant	**Variable**	**Value**	**Units**
Boltzmann	k_B	1.381 x 10^{-23}	J K^{-1}
Planck	h	6.626 x 10^{-34}	J s

Quantity	**Variable**	**Typical Order**	**Units**
Number of Adsorption Sites	N_s	10^{23}	molecules
Binding Energy	ε	10^{1}	kJ mol^{-1}
Adsorbate Mass	$\widetilde{m}$	10^{-27}	kg
Adsorption Site Length	L_s	10^{-1}	nm
Adsorption Site Area	A_s	10^{-2}	nm^2
Adsorption Site Volume	V_s	10^{-3}	nm^3
Natural Frequency	ω_s	10^{13}	s^{-1}

Thermal deBroglie Wavelength:

$$\Lambda = \frac{h}{\sqrt{2\pi\widetilde{m}k_B T}} = \frac{h\sqrt{\beta}}{\sqrt{2\pi\widetilde{m}}}$$

Table S1. Partition functions and T-dependence of the adsorption equation for single-site Langmuir models of ideal gases, depending on the number and potential form of the external degrees of freedom in the adsorbed state.

	Single Adsorption Site			**Total Adsorption System**		
Model Name	**Partition Function (x × y × z)**	**Degrees of Freedom**	**High T Heat Capacity (k_BT)**	**Explicit $A[T]$**	**T Dep of A**	**Δ Heat Capacity (RT)**
Einstein Crystal	QP × QP × QP	3	1 + 1 + 1 = 3	$\frac{(2\pi)^{1.5}\,(k_BT)^{0.5}}{\omega_s{}^3\,(\tilde{m})^{1.5}}$	0.5	+1.5
(no physical picture)	QP × QP × SP	3	1 + 1 + 0.5 = 2.5	$\frac{2\pi\,L_s}{\omega_s{}^2\,(\tilde{m})}$	0	+1
2D Lattice Gas	QP × QP × DF	2	1 + 1 + 0 = 2	$\frac{(2\pi)^{0.5}\,h}{\omega_s{}^2\,(\tilde{m})^{1.5}\,(k_BT)^{0.5}}$	-0.5	+0.5
2D Ideal Gas w z-Oscillation	SP × SP × QP	3	0.5 + 0.5 + 1 = 2	$\frac{(2\pi)^{0.5}\,A_s}{\omega_s\,(\tilde{m})^{0.5}\,(k_BT)^{0.5}}$	-0.5	+0.5
(no physical picture)	QP × SP × DF	2	1 + 0.5 + 0 = 1.5	$\frac{h\,L_s}{\omega_s\,(\tilde{m})\,(k_BT)}$	-1	0
3D Ideal Gas	SP × SP × SP	3	0.5 + 0.5 + 0.5 = 1.5	$\frac{V_s}{k_BT}$	-1	0
z-Oscillators	DF × DF × QP	1	0 + 0 + 1 = 1	$\frac{h^2}{\omega_s\,(2\pi\tilde{m}^3)^{0.5}\,(k_BT)^{1.5}}$	-1.5	-0.5
2D Ideal Gas	SP × SP × DF	2	0.5 + 0.5 + 0 = 1	$\frac{h\,A_s}{(2\pi\tilde{m})^{0.5}\,(k_BT)^{1.5}}$	-1.5	-0.5
1D Ideal Gas	SP × DF × DF	1	0.5 + 0 + 0 = 0.5	$\frac{h^2\,L_s}{(2\pi\tilde{m})\,(k_BT)^2}$	-2	-1
Fixed	DF × DF × DF	0	0 + 0 + 0 = 0	$\frac{h^3}{(2\pi\tilde{m})^{1.5}\,(k_BT)^{2.5}}$	-2.5	-1.5

Abbreviations:
DF = delta function
SP = square potential
QP = quadratic potential

Variables in red are fitting constants of the resulting model.

Supporting References

S1. Stylianou, K. C.; Warren, J. E.; Chong S. Y.; Rabone, J.; Bacsa, J.; Bradshaw, D.; Rosseinsky, M. J. "CO_2 Selectivity of a 1D Microporous Adenine-Based Metal-Organic Framework Synthesized in Water." *Chem. Commun.*, 2011, 47, 3389-3392. https://doi.org/10.1039/c0cc05559j

S2. Wang, Z. "Temperature Dependence of Gas Physisorption Energy: Experimental and Computational Studies of Krypton on Porous Carbon." PhD thesis, California Institute of Technology, 2023. https://thesis.library.caltech.edu/15181/ (see section 2.4, "Surface Dynamics")