Towards Rational Design of Metal-Organic Frameworks for Sensing Applications: Efficient Calculation of Adsorption Characteristics in Zero Loading Regime.

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The Henry's constant of adsorption, differential enthalpy of adsorption, free energy barriers between various compartments of the porous space and selectivity are important characteristics of a porous material. These characteristics are directly related to the performance of the porous material in a sensing application and can be used as preliminary criteria for computational screening of the candidate porous materials. All these properties are linked to each other through well established statistical-mechanical relations. In this article we demonstrate that the finely discretized representation of the simulation cell offers a particularly convenient way to exploit these relations and, for rigid molecules in rigid porous materials, the majority of these characteristics can be calculated from a single simulation run. We apply the methodology to calculate the Henry's constants and other characteristics for several small organic and aromatic molecules in two metal-organic frameworks, IRMOF-1 and MIL-47(V). We further provide predictions for TNT adsorption in these structures and discuss the implications of our findings in the context of sensing applications.

1. Additional derivations, related to eq 11:

$$RT\rho_S K_H = \frac{Z_S(1,T,V_S)}{8\pi^2 V_S} = \frac{\iint e^{-U_S(\theta,r)/kT} d\theta dr}{8\pi^2 V_S} = \frac{8\pi^2 \int \left\langle e^{-U_S(\theta,r)/kT} \right\rangle^\theta dr}{8\pi^2 V_S} \approx$$

$$\approx \frac{\sum_{i=1}^{N_{cubelet}} \left\langle e^{-U_S(\theta,r)/kT} \right\rangle_i^{r_i,\theta} \Delta V_S}{V_S} = \frac{1}{N_{cubelet}} \sum_{i=1}^{N_{cubelet}} \left\langle e^{-U_S(\theta,r)/kT} \right\rangle_i^{r_i,\theta}$$

Further details on the link between K_H and $K_{H,i}$:

$$RT\rho_S K_H = \frac{1}{N_{cubelet}} \sum_{i=1}^{N_{cubelet}} \left\langle e^{-U_S(\theta,r)/kT} \right\rangle_i^{r_i,\theta} = \frac{\sum_{i=1}^{N_{cubelet}} 8\pi^2 \Delta V_S \left\langle e^{-U_S(\theta,r)/kT} \right\rangle_i^{r_i,\theta}}{N_{cubelet} 8\pi^2 \Delta V_S} =$$

$$\frac{1}{N_{cubelet}} \sum_{i=1}^{N_{cubelet}} \frac{Z_{S,i}(1,T,\Delta V_S)}{Z_{IG}(1,T,\Delta V_S)} = \frac{1}{N_{cubelet}} \sum_{i=1}^{N_{cubelet}} RT\rho_S K_{H,i}$$

2. Chemical structures of the investigated adsorbate species. From top down and from left to right, benzene (BEN), toluene (TOL), p-xylene (XYL), 1,2,4-trimethylbenzene (3MB), tetralin (TET), trinitrotoluene (TNT), chloroform (CHL), acetone (ACT), and acetaldehyde (ACH) are shown.
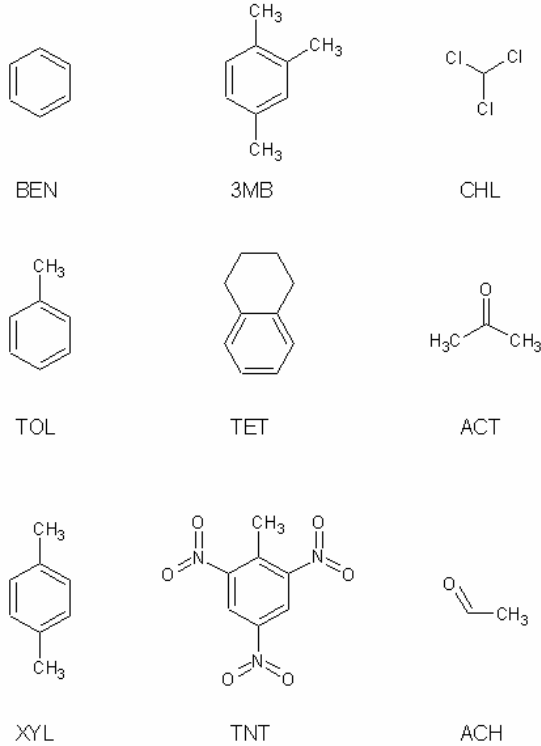
3. UFF interaction parameters[1]:

Atom	σ (Å)	ε (K)
H	2.571	22.14
C	3.431	52.8
O	3.118	30.2
N	3.26	34.7
Cl	3.52	114.1
Zn	2.462	62.38
V	2.801	8.051

4. CO_2 interaction parameters from the TraPPE forcefield[2]:

Atom	σ (Å)	ε (K)	q (e)
C	2.80	27.0	0.70
O	3.05	79.0	-0.35

5. The Henry's constant for CO_2 in IRMOF-1 at 300 K: comparison of the result from this work (with cubelet size d_C=0.5 Å, 50 CO_2 trial orientations, 12.8 Å potential cut-off distance, and electrostatic interactions calculated via the method by Fennell and Gezelter[3]) to the reference results from the standard Widom insertion method with Ewald summations and with the cut-off method by Fennell and Gezelter[3].

Method	K_H [mol/kg/bar]
This work (Lattice/ Fennell-Gezelter[3])	0.890
Widom/Ewald	0.886
Widom/Fennell-Gezelter[3]	0.897

6. Variation of the Henry's constant for CO_2 in IRMOF-1 at 300 K as a function of the cubelet size d_C. Data is for 50 CO_2 orientations in each cubelet and 12.8 Å potential cut-off distance.

d_C, Å	K_H [mol/kg/bar]	CPU time, s
0.2	0.894	15480
0.5	0.890	996
1	0.891	120
2	0.822	13
3	0.759	4

7. Variation of the Henry's constant for CO_2 in IRMOF-1 at 300K as a function of the number of trial orientations R. Data is for d_C=0.5 Å and 12.8 Å potential cut-off distance.

R	K_H [mol/kg/bar]	CPU time, s
1	0.885	39
10	0.896	374
50	0.890	996
500	0.894	25200

Note, that even with a single orientation of the CO_2 molecule probed, a reasonable accuracy of the result is achieved. The explanation is as following. In each cubelet a new orientation of a CO_2 molecule is generated. For a simple small molecule such as CO_2 and crystalline, periodic structure (IRMOF-1), apparently this is sufficient to sample the orientational degrees of freedom. This is not going to be the case for more complex molecules, or for porous structures lacking crystallinity.

8. Red line and right y-axis scale: the difference in the Helmholtz energy for TNT and TOL in IRMOF-1 at 300 K. Black line and left y-axis scale: selectivity for TNT over TOL $S_{TNT-TOL}$ along the reaction coordinate x (Å) in IRMOF-1 at 300 K.
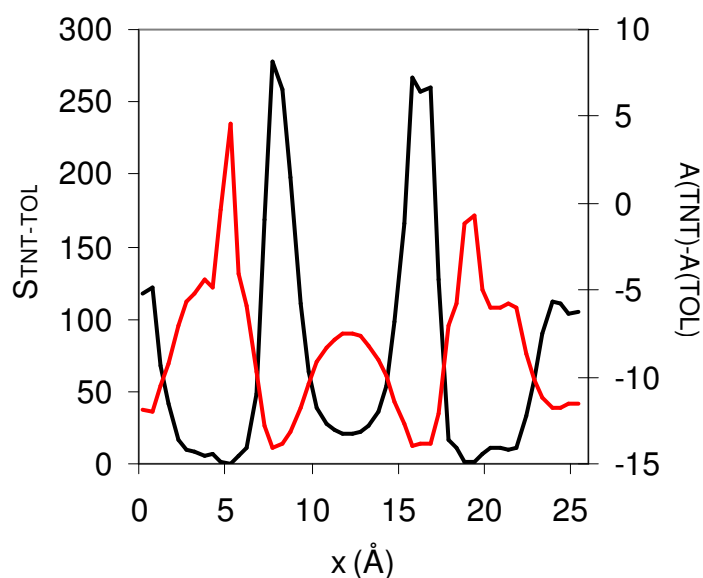
9. Additional visualization of the MIL-47(V) structure. The structure features straight channels, not connected to each other. Each channel is formed by four walls of the benzyl units, connected in the vertices of the channel to the octahedral vanadium complexes.
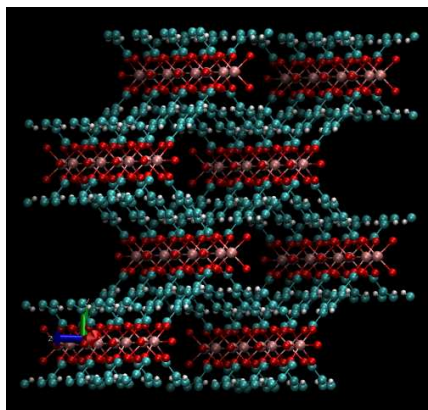
10. The Henry's constant for ACT (acetone) in IRMOF-1 at 473 K: comparison of the result for different charge models:

Method	K_H [mol/kg/bar]
No charge	0. 75070
CHelpG	0.81654
Mullliken	0.82544

(1)   Rappe, A. K.; Casewit, C. J.; Colwell, K. S.; Goddard, W. A.; Skiff, W. M. *Journal of the American Chemical Society* **1992**, *114*, 10024.
(2)   Potoff, J. J.; Siepmann, J. I. *Aiche Journal* **2001**, *47*, 1676.
(3)   Fennell, C. J.; Gezelter, J. D. *Journal of Chemical Physics* **2006**, *124*, 234104.