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SUPPORTING INFORMATION for: First principles Monte Carlo simulations of unary and binary adsorption: CO_2, N_2, and H_2O in Mg-MOF-74

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S1. Simulation details

All simulations are performed using the Monte Carlo (MC) modules[1–4] available in the CP2K software suite.[5] The potential energy of a configuration (defined by the positions of the nuclei) is calculated using Kohn–Sham density functional theory (KS-DFT) with the PBE density functional[6] along with the D3 dispersion correction of Grimme,[7] the double-ζ basis set optimized for molecular systems,[8] the GTH pseudopotentials,[9,10] and a plane wave cutoff of 600 Ry. The sampling of the Brillouin zone is done only at the Γ-point.

The Mg-MOF-74 sorbent is represented by a $1 \times 1 \times 2$ supercell with a total of 324 atoms and with a periodic simulation box with cell parameters of $a = b = 26.136$ Å, $c = 6.942$ Å, $\alpha = \beta = 90°$, and $\gamma = 120°$. Additionally, the system contains 64 sorbate molecules of each type that can distribute between the simulation boxes.

The FPMC simulations are carried out in the NpT-Gibbs ensemble[11] at $T = 313$ K. To reduce the computational cost, the classical partition function of the system is used to describe the system (i.e., nuclear quantum effects are not considered). Several different Monte Carlo moves are employed. In order to efficiently sample concerted motion of the framework and sorbate atoms, a hybrid Monte Carlo (HMC) move is used.[12] During each HMC move, a short microcanonical molecular dynamics (MD) trajectory is launched (20 time steps, each integrating the equation of motion for 0.25 fs), and the MD sequence is accepted using the conventional MC acceptance rule. The overall distribution of MC moves is as follows: 25% of molecule translations, 15% of molecule rotations (both moves only in the sorbent phase), 5% of atom displacements, 30% of HMC moves, and 25% of configurational-bias molecule transfer moves[13,14] with 64 trial insertions per move. Maximum displacements for translational and rotational moves were adjusted to yield 40% acceptance rates.

For each state point, 16 independent simulations are carried out. Each simulation consists of at least 4,000 MC moves for equilibration and at least 6,000 MC moves for production. The standard errors of the mean in the computed loadings are determined from the independent simulations.

IAST data are generated using the pyIAST package.[15]

S2. Numerical data for unary sorption isotherms

Table S1: Calculated loadings in Mg-MOF-74 at different pressures. Uncertainties are provided as the standard error of the mean in.

p_{CO_2} [bar]	Q_{CO_2} [molec/uc]	p_{N_2} [bar]	Q_{N_2} [molec/uc]	p_{H_2O} [mbar]	Q_{H_2O} [molec/uc]
0.01	0.8 ± 0.4	0.01	0.042 ± 0.015	0.1	5.5 ± 1.5
0.1	12.3 ± 0.7	0.1	0.34 ± 0.11	1.0	13 ± 3
0.5	16.7 ± 0.6	0.5	0.96 ± 0.12	10	51 ± 5
1.0	18.4 ± 0.8	1.0	1.71 ± 0.08	20	57 ± 4

S3. Input files for the FPMC simulation in CP2K

All simulations use the same overall energy routine (section &FORCE_EVAL). It should be noted that each atom type in the Mg-MOF-74 (H, C, O, and Mg) is represented as a separate molecule kind in the course of the MC simulations and therefore requires its own topology file and MC parameters, e.g., move probabilities. An example of the &FORCE_EVAL section is given here.

```
  &FORCE_EVAL
METHOD QS
&DFT
 BASIS_SET_FILE_NAME BASIS_MOLOPT
 POTENTIAL_FILE_NAME GTH_POTENTIALS
 &MGRID
   CUTOFF 600
   NGRIDS 5
 &END
 &QS
   EXTRAPOLATION USE_PREV_WF
 &END QS
 &SCF
   EPS_SCF 1.0E-6
   SCF_GUESS RESTART
   MAX_SCF 20
   &OUTER_SCF
     EPS_SCF 1.0E-6
     MAX_SCF 10
   &END OUTER_SCF
   &OT
     MINIMIZER DIIS
     PRECONDITIONER FULL_KINETIC
   &END
 &END
 &XC
   &XC_FUNCTIONAL PBE
   &END
   &VDW_POTENTIAL
     DISPERSION_FUNCTIONAL PAIR_POTENTIAL
     &PAIR_POTENTIAL
        TYPE DFTD3
        REFERENCE_C9_TERM .TRUE.
        LONG_RANGE_CORRECTION .TRUE.
        PARAMETER_FILE_NAME dftd3.DAT
        REFERENCE_FUNCTIONAL PBE
        R_CUTOFF [angstrom] 10.0
        EPS_CN 1.0E-6
     &END PAIR_POTENTIAL
   &END VDW_POTENTIAL
 &END XC
&END

&SUBSYS
```

```
&CELL
  ABC 26.136 26.136 13.884
  ALPHA_BETA_GAMMA 90.0 90.0 120.0
&END CELL
&COORD
  (MOF coordinates are here)
&END COORD
&KIND H
  BASIS_SET DZVP-MOLOPT-SR-GTH
  POTENTIAL GTH-PBE-q1
&END KIND
&KIND O
  BASIS_SET DZVP-MOLOPT-SR-GTH
  POTENTIAL GTH-PBE-q6
&END KIND
&KIND C
  BASIS_SET DZVP-MOLOPT-SR-GTH
  POTENTIAL GTH-PBE-q4
&END KIND
&KIND Mg
  BASIS_SET DZVP-MOLOPT-SR-GTH
  POTENTIAL GTH-PBE-q10
&END KIND
&KIND N
  BASIS_SET DZVP-MOLOPT-SR-GTH
  POTENTIAL GTH-PBE-q5
&END KIND
&KIND CC
  BASIS_SET DZVP-MOLOPT-SR-GTH
  POTENTIAL GTH-PBE-q4
  ELEMENT C
&END KIND
&KIND OO
  BASIS_SET DZVP-MOLOPT-SR-GTH
  POTENTIAL GTH-PBE-q6
  ELEMENT O
&END KIND
&KIND OW
  BASIS_SET DZVP-MOLOPT-SR-GTH
  POTENTIAL GTH-PBE-q6
  ELEMENT O
&END KIND
&KIND HW
  BASIS_SET DZVP-MOLOPT-SR-GTH
```

```
    POTENTIAL GTH-PBE-q1
    ELEMENT H
  &END KIND
  &TOPOLOGY
    CONNECTIVITY MOL_SET
    &MOL_SET
      &MOLECULE
        NMOL 36
        CONN_FILE_NAME topology_fist_Mg.psf
      &END
      &MOLECULE
        NMOL 108
        CONN_FILE_NAME topology_fist_O.psf
      &END
      &MOLECULE
        NMOL 144
        CONN_FILE_NAME topology_fist_C.psf
      &END
      &MOLECULE
        NMOL 36
        CONN_FILE_NAME topology_fist_H.psf
      &END
      &MOLECULE
        NMOL 0
        CONN_FILE_NAME topology_fist_N2.psf
      &END
      &MOLECULE
        NMOL 0
        CONN_FILE_NAME topology_fist_CO2.psf
      &END
      &MOLECULE
        NMOL 0
        CONN_FILE_NAME topology_fist_H2O.psf
      &END
    &END
  &END
 &END SUBSYS
&END FORCE_EVAL
```

The &MOTION section of the input file is similar to other GEMC simulation in CP2K with the addition of two new keywords: LIDEAL and PRESSURE_IG. Logical LIDEAL, if set to **yes** (true), indicates that the second box is treated as ideal with pressures for each molecule type specified by PRESSURE_IG (in bar). An example for a binary CO_2–H_2O mixture is given here.

```
   &MOTION
 MC
  ENSEMBLE GEMC_NVT
  TEMPERATURE 313.0
  IPRINT 1
  LBIAS yes
  LSTOP no
  LIDEAL yes
  PRESSURE_IG 0.0 0.0 0.0 0.0 0.0 0.15 0.001
  NMOVES 8
  NSWAPMOVES 64
  NSTEP 10000
  PRESSURE 1.013
  RESTART yes
  BOX2_FILE_NAME box2.inp
  RESTART_FILE_NAME mc_restart_1
  ETA 0.0 0.0 0.0 0.0 0.0 0.0 0.0
  VIRIAL_TEMPS 300.0
  &MOVE_PROBABILITIES
    PMVOLUME 0.0
    PMSWAP 0.25
    PMHMC 0.55
    PMTRAION 0.11
    PMTRANS 0.67
    PMAVBMC 0.0
    &MOL_PROBABILITIES
      PMAVBMC_MOL 0.0 0.0 0.0 0.0 0.0 0.0 1.0
      PMSWAP_MOL 0.0 0.0 0.0 0.0 0.0 0.5 1.0
      PMTRAION_MOL 0.0 0.0 0.0 0.0 0.0 0.5 1.0
      PMTRANS_MOL 0.0 0.0 0.0 0.0 0.0 0.5 1.0
      PMROT_MOL 0.0 0.0 0.0 0.0 0.0 0.5 1.0
    &END MOL_PROBABILITIES
    &BOX_PROBABILITIES
      PMVOL_BOX 1.0
      PMHMC_BOX 1.0
    &END BOX_PROBABILITIES
  &END MOVE_PROBABILITIES
  &MOVE_UPDATES
```

```
    IUPTRANS 10000
    IUPVOLUME 10000
   &END MOVE_UPDATES
   &MAX_DISPLACEMENTS
    &MOL_DISPLACEMENTS
     RMDIHEDRAL 0.0 0.0 0.0 0.0 0.0 0.0 0.0
     RMANGLE 0.0 0.0 0.0 0.0 0.0 0.15 0.15
     RMBOND 0.0 0.0 0.0 0.0 0.0 0.1 0.1
     RMROT 0.0 0.0 0.0 0.0 0.0 15.0 15.0
     RMTRANS 0.0 0.0 0.0 0.0 0.0 0.3 0.3
    &END MOL_DISPLACEMENTS
    &BOX_DISPLACEMENTS
     RMVOLUME 75.0
    BOX_DISPLACEMENTS
   &END MAX_DISPLACEMENTS
   &AVBMC
    AVBMC_ATOM 1 1 1 1 1 1 1
    AVBMC_RMIN 1.0 1.0 1.0 1.0 1.0 1.0 1.0
    AVBMC_RMAX 5.0 5.0 5.0 5.0 5.0 5.0 5.0
    PBIAS 0.5 0.5 0.5 0.5 0.5 0.5 0.5
   &END AVBMC
  &END MC
  MD
   ENSEMBLE NVE
   STEPS 20
   TIMESTEP 0.25
   TEMPERATURE 313.0
   &PRINT
    &ENERGY
     &EACH
       MD 20
     &END
    &END
   &END PRINT
  &END MD
&END MOTION
```

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