Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information For

Quantum Chemical Modeling of Single and Multiple Hydrogen Binding in Metal-Organic Frameworks: Validation, Insight, Predictions and Challenges.

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Thermochemistry of H_2 binding to MOFs

Thermochemistry computations were performed at B3LYP-D2/def2-SVP level of theory under the standard RRHO approximation with full relaxation of the cluster model on H_2 binding.

MOF-5

Previous research has indicated the H_2 can freely rotate at the binding site to a good approximation. In previous work, free rotation of H2 in the bound configuration was assumed for thermochemistry calculations.[1] Given the more computationally expensive nature of frequency calculations, the formate model for MOF-5 was used for frequency analysis. Figure S1 shows a summary of enthalpy and entropy change as a function of temperature for H_2 binding to the cup MOF-5.

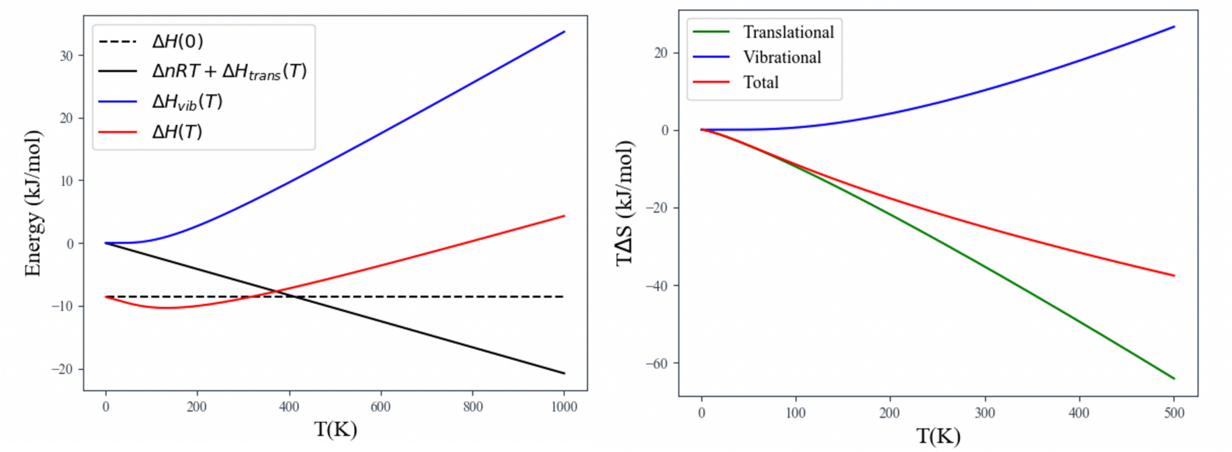

Figure S1: Summary of change in enthalpy and entropy as a function of temperature for H_2 binding at the cup site in MOF-5

Ni_2(m-dobdc)

Relaxing coordinates of the node resulted in artefactual distortion of the overall hexagonal symmetry of the material. Hence the cluster model was optimized with the nuclear coordinates derived from experimental crystal structure of the bare MOF fixed. Fixing part of the cluster for geometry optimizations resulted in difficulty obtaining converged geometries with ωB97M-V, and hence we optimized the geometry at B3LYP-D2/def2-SVP level of theory. The traditional harmonic approximation could not be applied for partially frozen cluster coordinates. Hence we modeled the thermochemistry under a harmonic approximation for frustrated translational and rotational modes for H_2 bound to the Ni(II) site in Ni_2-m-dobdc.

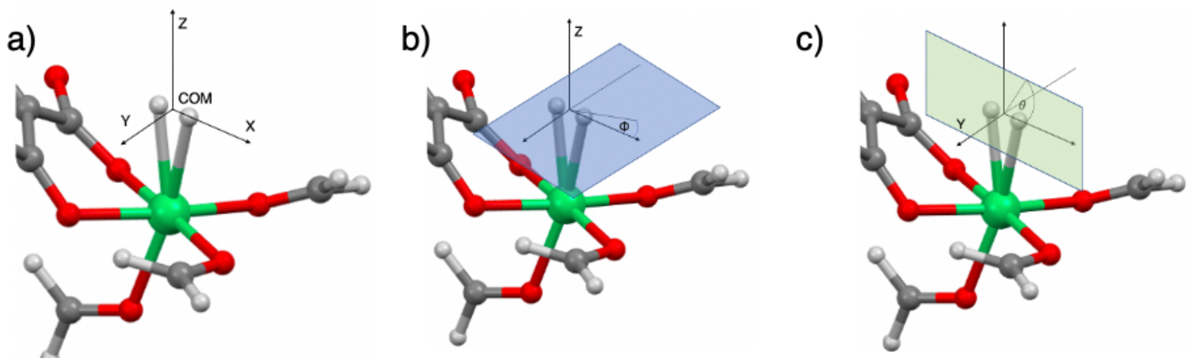

Fig. S1: Frustrated translational and rotational modes of bound H_2 in Ni_2-m-dobdc. X, Y and Z axis for frustrated translations of H2 center of mass (COM) a). Frustrated rotation along the Z axis with rotation angle φ (b), and along the Y axis with rotation angle θ (c).

Frustrated translational and rotational modes of hydrogen in H_2 center of mass (COM) reference frame are shown in Figure 1. Finite difference scans from the equilibrium geometry were performed for the hindered modes of H_2 bound on the MOF OMS. A Fourier Grid Hamiltonian[2] was constructed and solved for each mode to obtain anharmonic vibrational frequencies. The corresponding harmonic ZPVEs were obtained from the curvature of the interpolated potential at equilibrium. 1D anharmonic corrections were applied to zero-point vibrational energies as $\Delta\, 1D^{rigid}_{anharmonic} = \sum \left(\epsilon^{rigid}_{anharmonic} - \epsilon^{rigid}_{harmonic}\right)$. Akin to the case of MOF-5, we assumed free rotation of H_2 in its bound state.

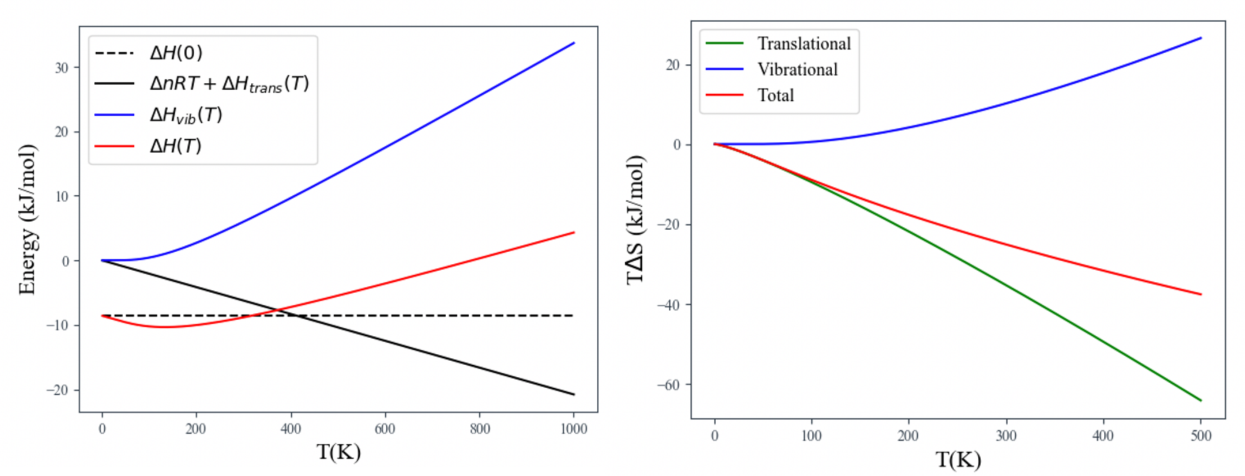

Figure S2: Summary of contributions to enthalpy and entropy changes for H_2 binding to Ni(II) in Ni_2(m-dobdc)

Cu(I)MFU-4*l*

All coordinates of the MOF node were relaxed for frequency calculations. A smaller model of the MOF node truncated at triazolate extremities was utilized for predicting thermochemical observables. The triazolate model for the MOF node has been utilized for frequency calculations for H_2 binding to Cu(I)MFU-4*l* in the past giving decent agreement with experimental values in instances where the optimizated geometries of the loaded node are consistent with experimental observations.[3]

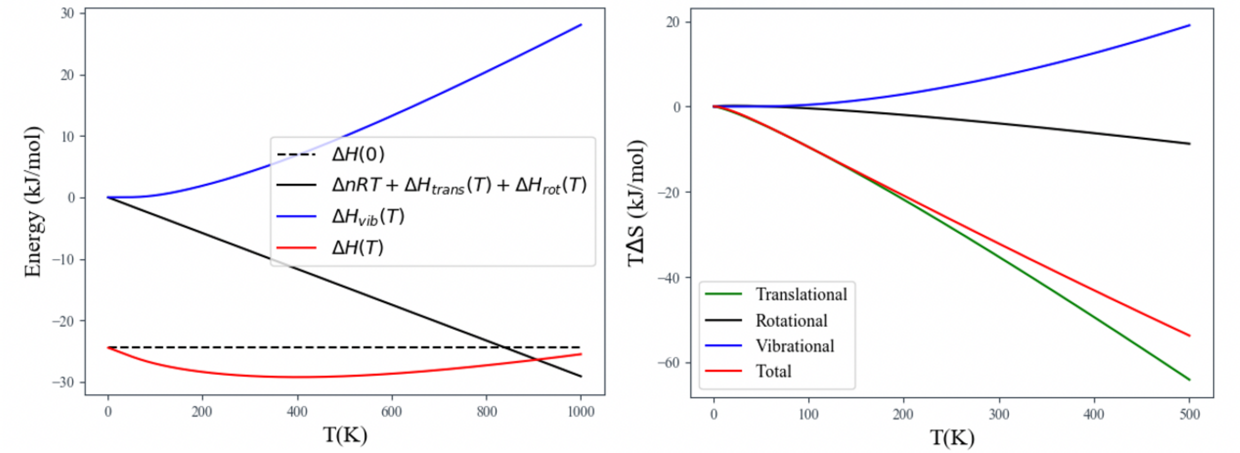

Figure 3: Summary of contributions to enthalpy and entropy changes for H_2 binding to Cu(I) in Cu(I)MFU-4*l*

V$_2$Cl$_x$btdd

All coordinates of the cluster model representing the MOF node were relaxed for thermochemistry calculations. This was done in a similar approach as the one utilized in the original literature.[4]

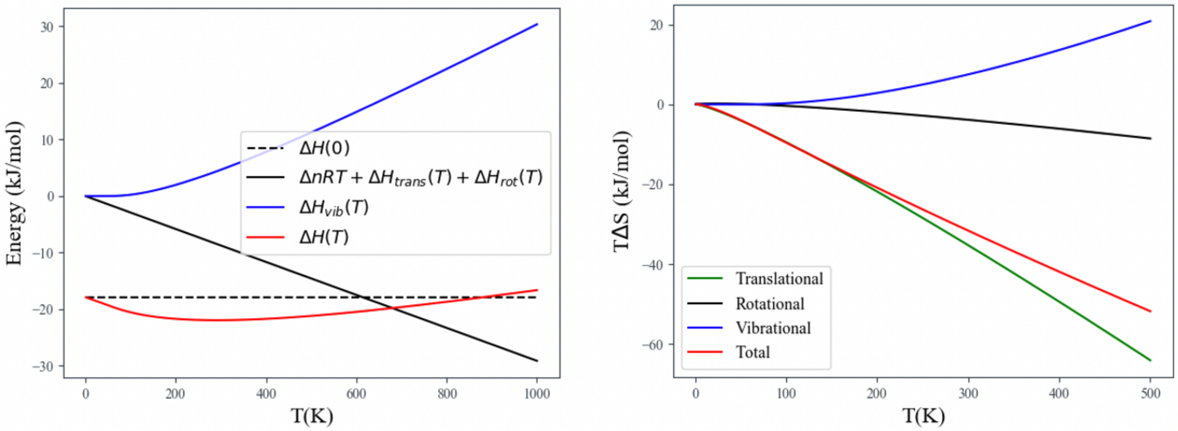

Figure 4: Summary of contributions to enthalpy and entropy change on H_2 binding to V(II) in V_2Cl_xbtdd

Thermochemistry for the ligation of three equivalents of H_2 at Sc(I)- and Ti(I)-MFU-4*l*

Table S2: Thermochemistry of H_2 binding to monovalent metal sites Sc(I) and Ti(I) in MFU-4l at 298 K and 1 atm. Sequential ligation of 1, 2, and 3 equivalents of H_2 at these metal sites occur with similar binding enthalpies of adsorption for three hydrogens.

	Sc(I)			Ti(I)		
Term (kJ/mol)	1	2	3	1	2	3
ΔE	-31.6	-33.1	-34.9	-52.0	-47.6	-42.9
ΔZPVE	11.5	11.2	12.9	12.1	12.4	14.1
ΔH(0)	-20.1	-21.9	-21.9	-39.9	-35.2	-28.9
ΔH(T)	-24.7	-27.9	-26.9	-45.2	-40.2	-34.0
TΔS(T)	-31.4	-35.2	-33.0	-33.5	-32.9	-33.6
ΔG(T)	6.7	7.3	6.1	-11.7	-7.3	-0.5

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