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Diffusion of IPA in UiO-66

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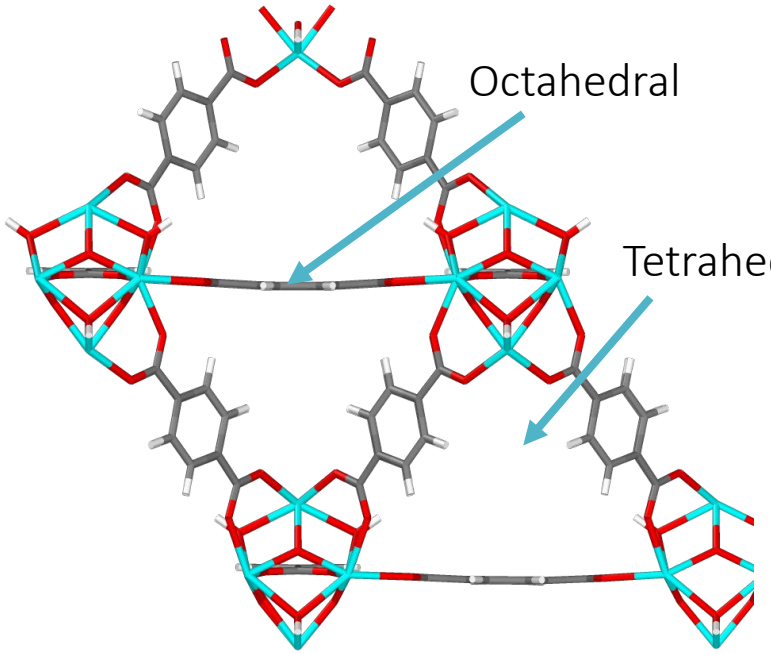
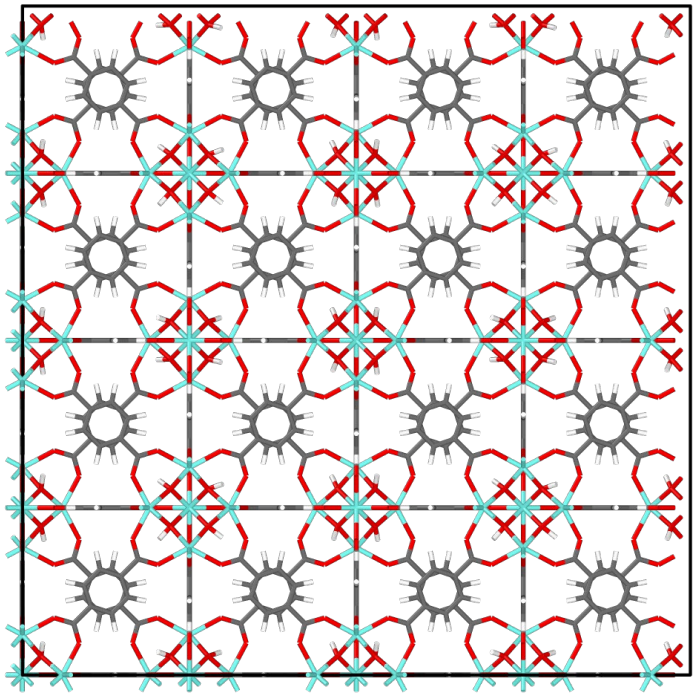
Background and Methods





Molecular Dynamics Outline

1.) Insertion of IPA
2.) 50 ps NVT equilibration
3.) 25 ns NVE production

T = 325K for finite loadings
T = 325K, 350K, 425K for 0 loading

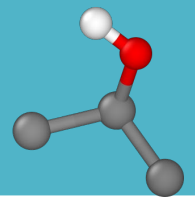
Diffusion Calculations

$$\boldsymbol{D_s} = \lim_{t\to\infty} \frac{1}{2dNt} \left\langle \sum_{i=1}^{N} |r_i(t) - r_i(0)|^2 \right\rangle$$

$$\boldsymbol{D_c} = \lim_{t\to\infty} \frac{1}{2dNt} \left\langle \left| \sum_{i=1}^{N} r_i(t) - r_i(0) \right|^2 \right\rangle$$

MOF Forcefield: Modified Rogge et al.* UiO-66 potential to include hydrogen bonds

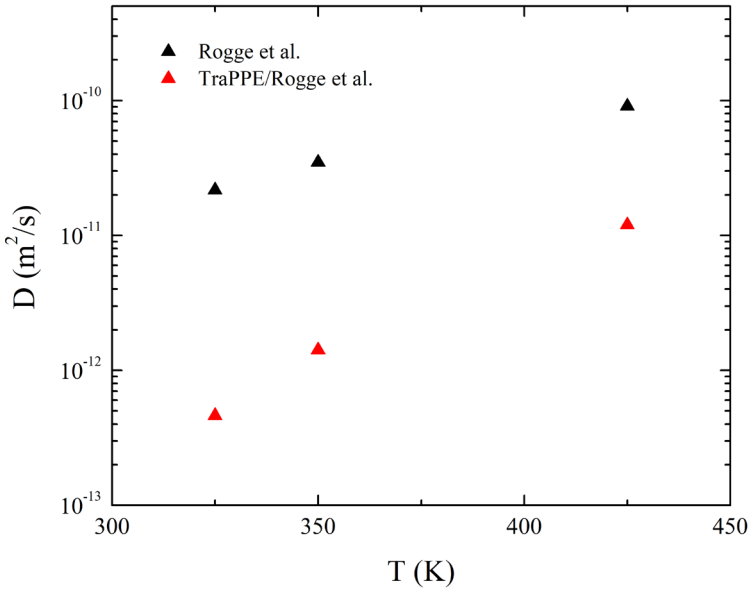
IPA forcefield: TraPPE-United Atom[ŧ]



* Rogge, S. M. J. et al. Thermodynamic Insight in the High-Pressure Behavior of UiO-66: Effect of Linker Defects and Linker Expansion. Chem. Mater.2016,28, 5721−5732.

ŧ B. Chen et al. Monte Carlo calculations for alcohols and their mixtures with alkanes. Transferable potentials for phase equilibria. 5. United-atom description of primary, secondary and tertiary alcohols. J. Phys. Chem. B 105, 3093-3104 (2001).

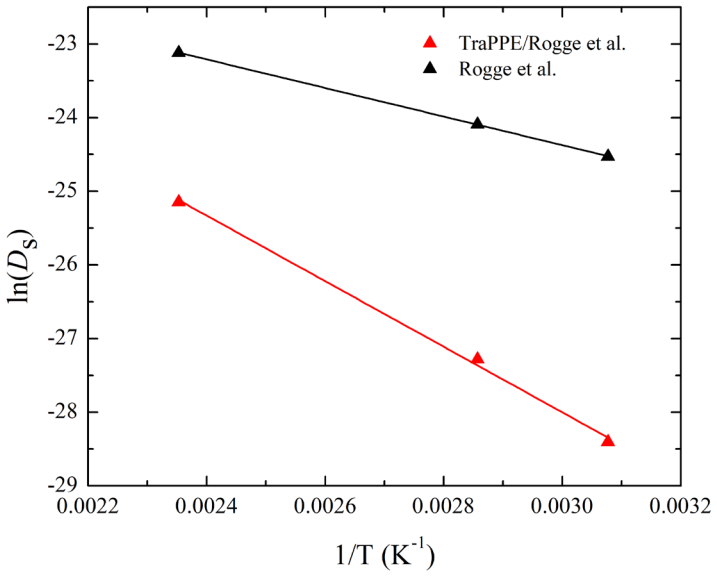
0-Loading



T(K)	a) D_s $[\frac{m^2}{s}]$	b) D_s $[\frac{m^2}{s}]$
325	2.18 x 10^{-11}	4.62 x 10^{-13}
350	3.49 x 10^{-11}	1.42 x 10^{-12}
425	9.11 x 10^{-11}	1.21 x 10^{-11}

Hydrogen bonding has a profound effect on diffusivity

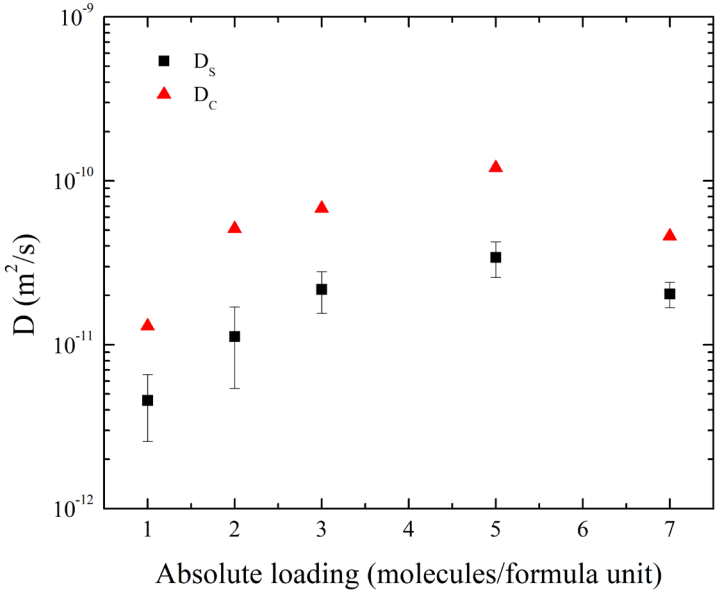
Activation Energy



Model	E_a (kJ/mol)
Rogge et al. (a)	16.14
TraPPE/Rogge (b)	37.02

Hydrogen bonding additionally effects the activation energy to diffusion

Finite Loading

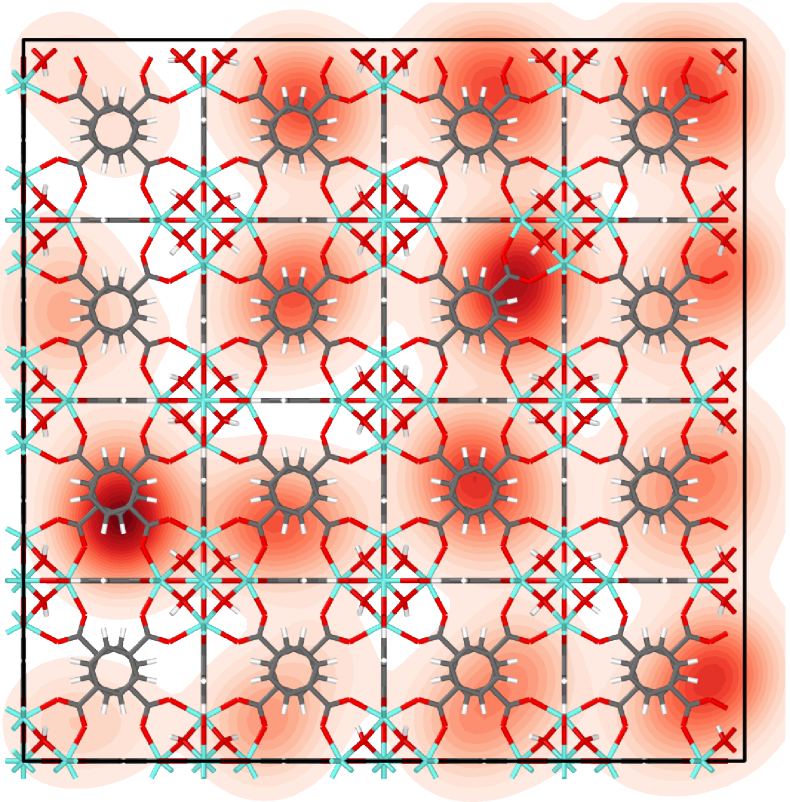


Loading	D_s $[\frac{m^2}{s}]$	D_C $[\frac{m^2}{s}]$
1	4.57 x 10^{-12}	1.3 x 10^{-11}
2	1.12 x 10^{-11}	5.1 x 10^{-11}
3	2.17 x 10^{-11}	6.8 x 10^{-11}
5	3.41 x 10^{-11}	1.2 x 10^{-10}
7	2.04 x 10^{-11}	4.6 x 10^{-11}

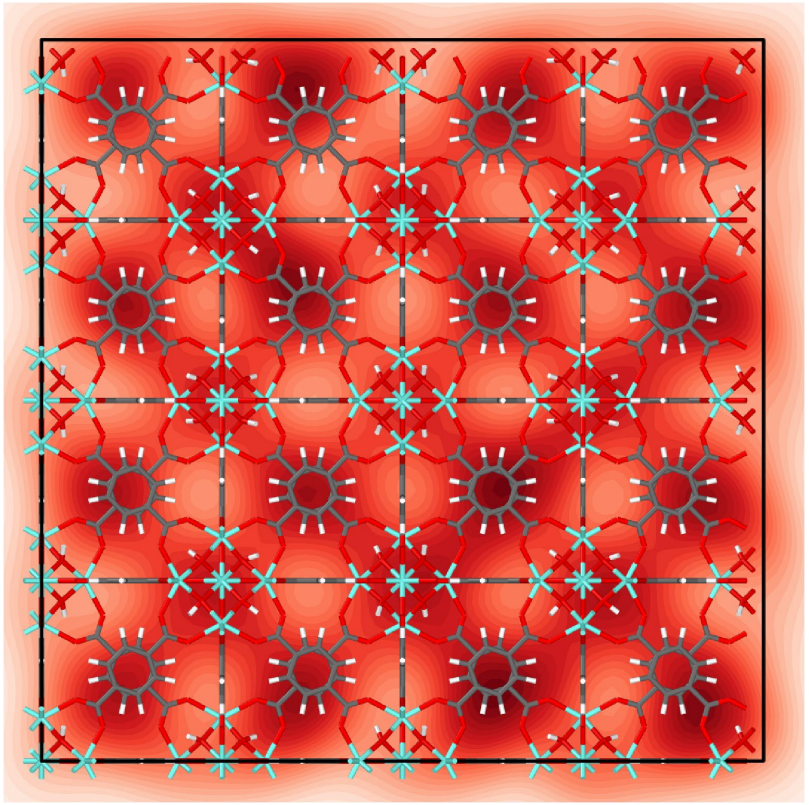
Diffusivity increases until roughly saturation loading, then decreases

Favorable Sites

0 Loading

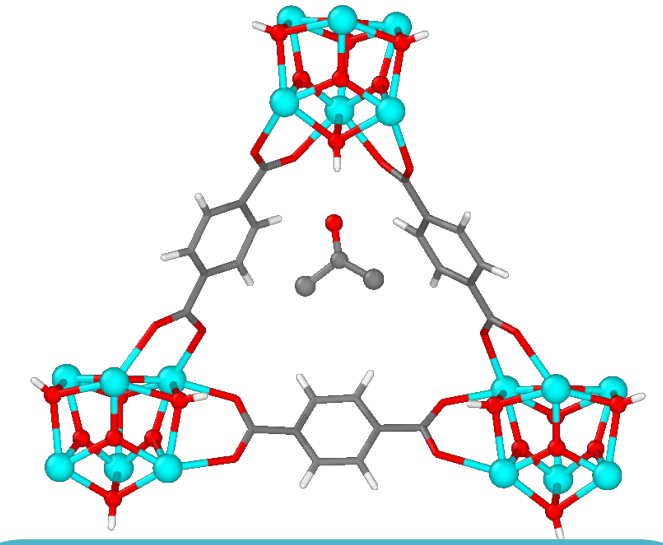


7 Loading



Low loading – hydrogen bonding sites very favorable

High loading – Crowding of hydrogen bonding sites push IPA to less favorable locations



Conclusions

- Hydrogen bonding plays a large role in the diffusion of IPA in UiO-66
- Corrected diffusivities can be used for comparison to experimental transport diffusivity

Future Work

- Collaboration with experimentalists
- Examination of defective UiO-66
- Exploration of free energy curves as guest molecules cage hop

Acknowledgments

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