OAK RIDGE National Laboratory

Theoretical Insight into CO_2 Capture and Conversion

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Oak Ridge National Laboratory

Oak Ridge, Tennessee
May 29, 2024

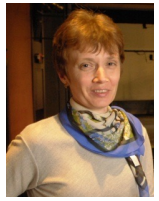
ORNL is managed by UT-Battelle, LLC for the US Department of Energy

U.S. DEPARTMENT OF ENERGY

Acknowledgment

- ORNL
  - **Jingsong Huang**
  - **Syed Islam**
  - **Panchapakesan Ganesh**
  - **David Lingerfelt**
  - **Bobby G. Sumpter**
  - **David S. Sholl**

- University of South Carolina
  - **Sonya Garashchuk**
  - **Vitaly Rassolov**



- North Carolina State University (RMG-DFT)
  - **Jerry Bernholc**
  - **Wenchang Lu**
  - **Emil Briggs**

Spallation Neutron Source (SNS) &
Center for Nanophase Material Science (CNMS)

This work was performed at the Center for Nanophase Materials Sciences, a U.S. Department of Energy Office of Science User Facility.

ACCESS Advancing Innovation | U.S. DEPARTMENT OF ENERGY | Office of Science | OAK RIDGE National Laboratory | CENTER FOR NANOPHASE MATERIALS SCIENCES

Molecular dynamics of nuclei and electrons

Parameterized force fields

Energy and forces on molecules from parameters

Molecules moved: Newton's laws

(MM)

Born-Oppenheimer dynamics

(Time-independent Quantum Mechanics)

Solve electronic Schrödinger Eq. (convergence) at nuclear Configuration

$$\hat{H}\psi(r;t) = E\psi(r;t)$$

Nuclei propagated from gradients (classically)

(BOMD)

Time-dependent Quantum Mechanics (electrons)

Electronic structure:

Quantum dynamics:

$$i\hbar\frac{\partial}{\partial t}\psi(r;t) = \hat{H}\psi(r;t)$$

Nuclei propagated from gradients (classically)

(QD-electrons)

Time-dependent Quantum Mechanics (nuclei)

Electronic structure or force fields

Nuclei propagated quantum dynamically

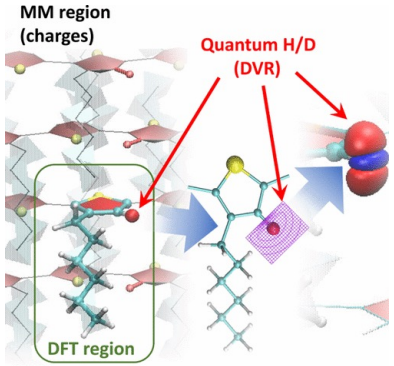
$$i\hbar\frac{\partial}{\partial t}\psi(R;t) = \hat{H}\psi(R;t)$$

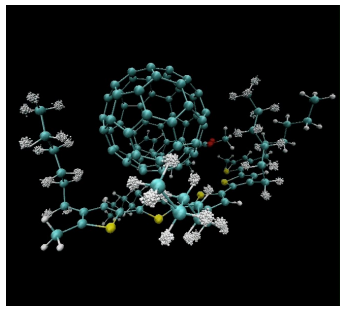
(QD-nuclei)

Jacek Jakowski

Isotopic substitution & quantum nuclear effects

- development of new quantum methods
- deuterations
- electronic structure

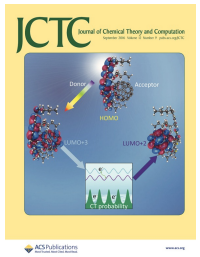




Quantum trajectories

Collaborations:

- Jingsong Huang
- Bobby Sumpter
- Sophya Garashchuk (USC)
- Vitaly Rassolov (USC)



Selected publications:

[1] *J.Chem.Theory Comp* ***12****, 4487-4500. 2016*
[2] *J. Phys. Chem. Lett*, **8**, 4333–4340 (2017)
[3] Macromolecules, (2021), 54, 3555-3584

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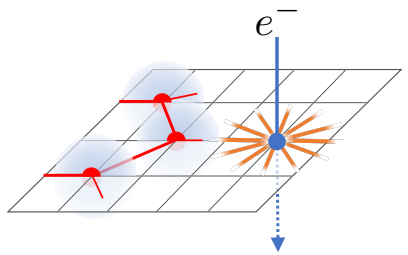
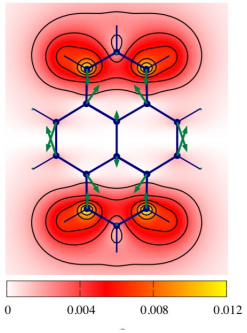
Electron/ion beam interactions with materials

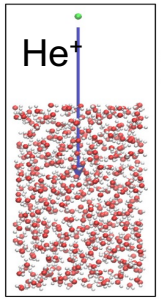
- beam of energetic ions of electrons
- electron dynamics
- excited states





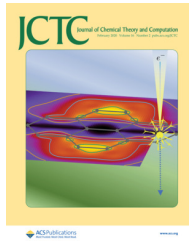
Collaborations:

- David Lingerfelt
- Ganesh Panchakepasan
- Jery Bernholc (NCSU)



Selected publications:

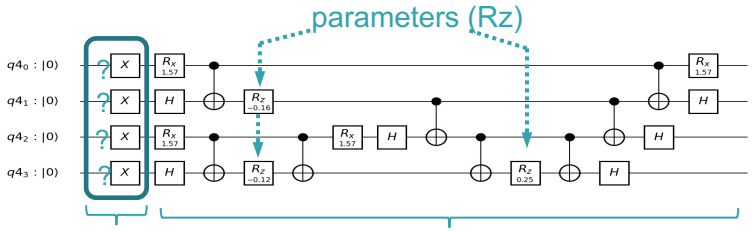
[1] *Nanoscale*, **9**, 12949-12956 (2017)
[2] *Science 363, 525 (2019)*
[3] *J. Chem. Theory Comp (2020)16, 1200*
[4] Theoretical Comp. Chem (2022) 21, 61



Quantum Computing

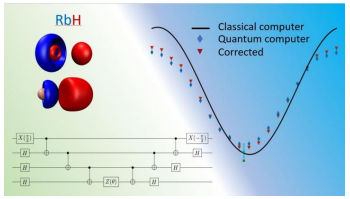
- quantum chemistry benchmarks
- small molecules
- many-body theory $|\psi(\boldsymbol{\theta})\rangle = e^{T-T^\dagger}|\psi_0\rangle$

$$E(\boldsymbol{\theta}) = \langle\psi(\boldsymbol{\theta})|H|\psi(\boldsymbol{\theta})\rangle = \sum_{p,q} h_{pq}\langle\psi(\boldsymbol{\theta})|a_p^\dagger a_q|\psi(\boldsymbol{\theta})\rangle + \frac{1}{2}\sum_{p,q,r,s} h_{pqrs}\langle\psi(\boldsymbol{\theta})|a_p^\dagger a_q^\dagger a_s a_r|\psi(\boldsymbol{\theta})\rangle,$$



Collaborations:

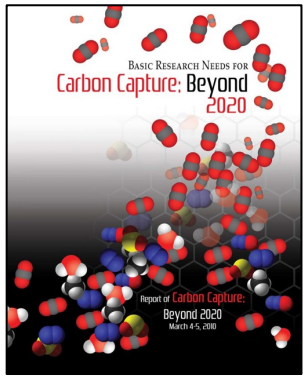
- Titus Morris
- Stephan Irle
- Gonzalo Alvarez
- Ryan Benink



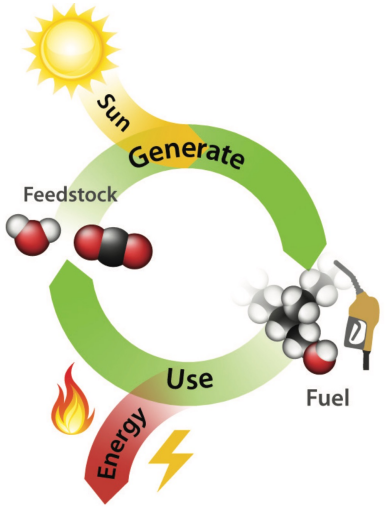
Selected publications:

[1] NPJ-Quantum Inf. (2019) 5:99
[2] Adv. Quantum Techn. (2021) 4, 2100012
[3] ACM Trans. on Quant. Comput. (2023), 4, 27:1-14

Challenge: Closing Carbon Cycle



Solar to Hydrocarbons



Key DOE questions:

How to balance release and capture of CO_2 to mitigate climate change?

- *Reduce emission of CO_2 (solar, wind nuclear energy, efficiency?)*
- *Carbon capture and storage*
- *Conversion of CO_2 to useful chemicals (solar liquid fuels)*

Liquid solar fuels (DOE definition):

- *Energy dense chemicals at (or near) ambient conditions (methanol, hydrocarbons, oxygenated hydrocarbons, and nitrogen-containing compounds)*
- *Catalysis: sequential reduction processes.*

Advances require ***molecular-level understanding*** and control of the microenvironment ***around catalytic sites*** to direct reactions for key bond-making and bond-breaking steps

Overview

- **Part I. Quantum chemistry simulations of CO_2 capture** in reline, a prototypical deep eutectic solvent
  - ab initio dynamics
  - ground state, DFTB

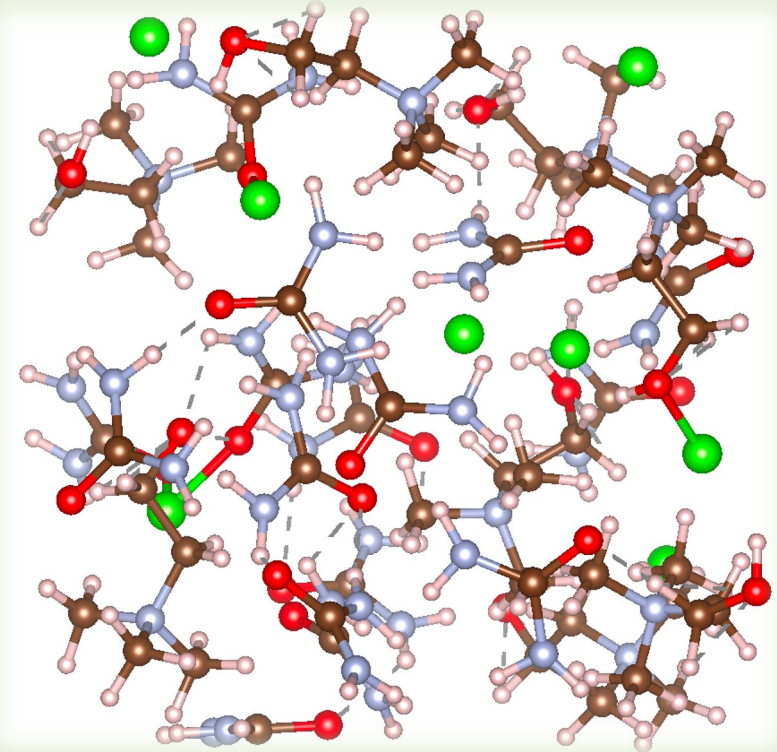
[1] S. Z.Islam, [Ind. & Eng. Chem. Res. (2023) 62, 10,4455
[2] J. Jakowski, et al. J. Phys. Chem. B, (2023), 127, 8888

- **Part II. Towards modeling of CO_2 reduction via real time TDDFT**
  - theory, implementation, benchmarking
  - electronic excitation, non-equilibrium processes

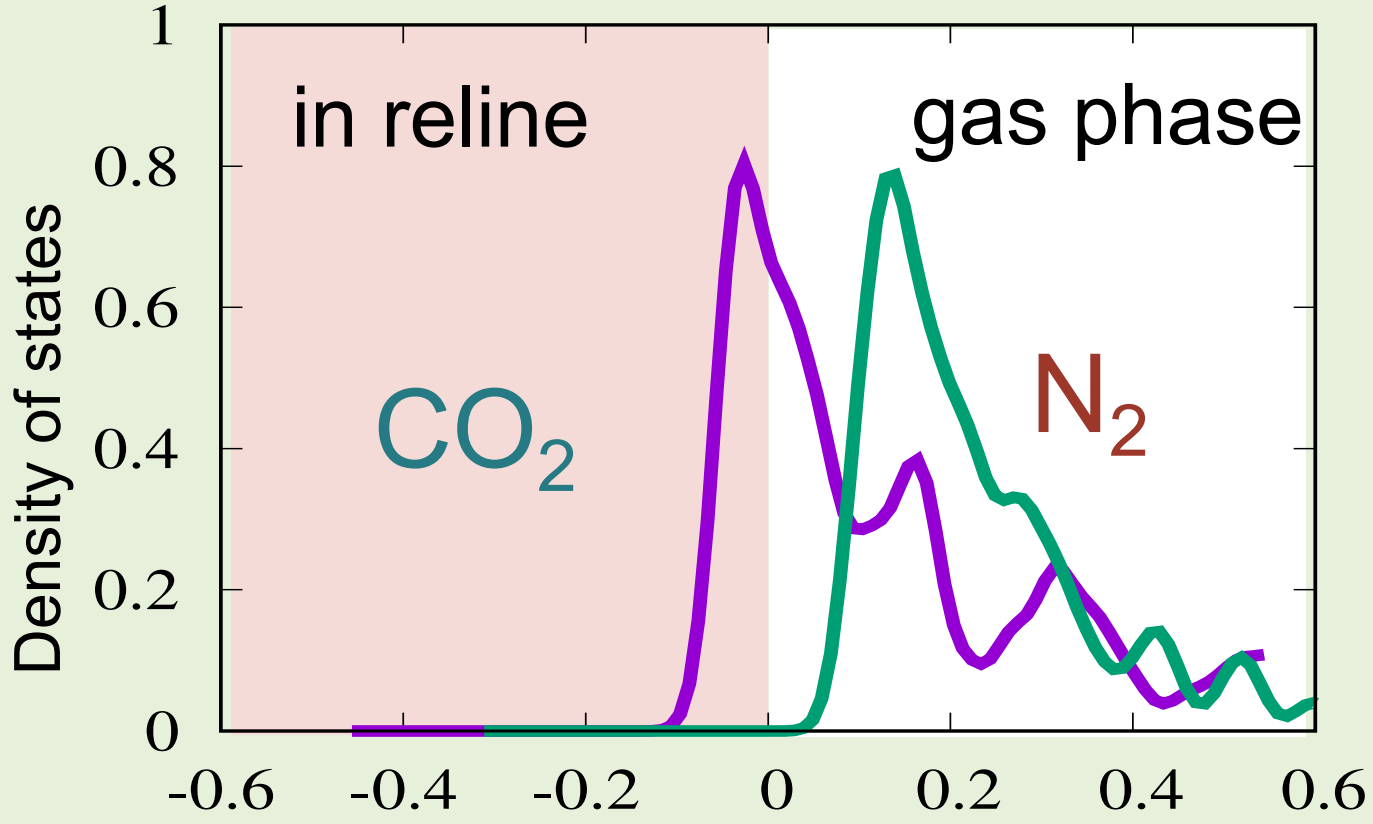
Part I. Quantum chemistry simulations of CO_2 capture in reline, a prototypical deep eutectic solvent

Part I. Summary of Results

Electronic and entropic effects lead to selective capture of CO_2 vs N_2 in reline (DES)



1:2 choline chloride/urea
(Deep Eutectic Solvent)



Quantum Chemical Simulations of CO_2 and N_2 Capture in Reline, a Prototypical Deep Eutectic Solvent

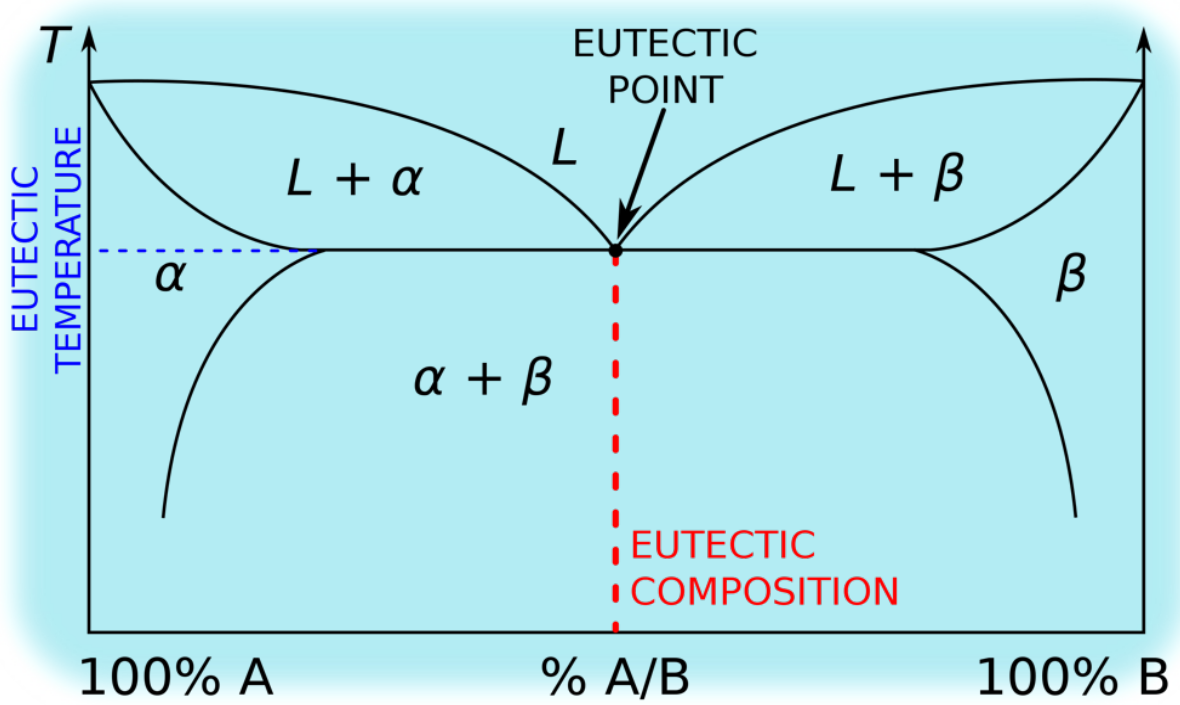
What are Deep Eutectic Solvents?

Eutectic systems

- A binary mixture of A+B (example: metal alloys)
- Eutectic composition (L): homogeneous mixture at eutectic point
- Melting temperature: $T_L < T_A$ and $T_L < T_B$
- Non-eutectic composition:

  -mixture of L (liquid) and solid A or B

A phase diagram of binary mixture of A+B (source: Wikipedia)



α	- solid A
β	- solid B
L+α	- solid A + liquid L
L+β	- solid A + liquid L

Deep Eutectic Solvents (DES)

Properties

- Mixture of hydrogen bond donor (HBD) and acceptor (HBA)
- HBA : salts with cation acting as H-acceptor
- HBD : critical in suppressing melting Temp
- Tunable (modify HBA/ HBD)
- Cheap, biodegradable, low toxicity,
- Low vapor pressure

Example components

- Choline chloride
- Tetraethylammonium bromide
- Urea
- Acetamide
- Glycerol
- Phenol
- Lactose

Applications

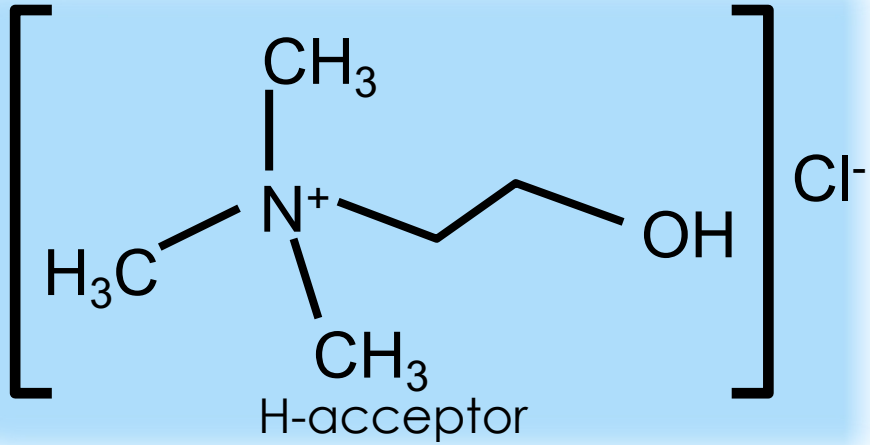
- Pharmaceuticals
- Biocatalysis
- Separation
- Extraction

Reline as a Deep Eutectic Solvent

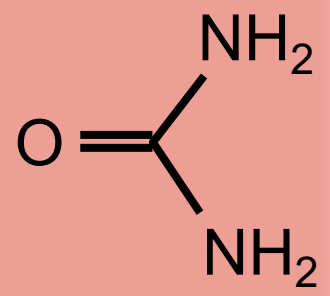
- **Reline:**
  - choline chloride (HBA) + urea (HBD)
  - 1: 2 molar ratio

Melting Temperatures

- Choline chloride: 302 °C
- Urea: 130 °C
- Reline: 12 °C

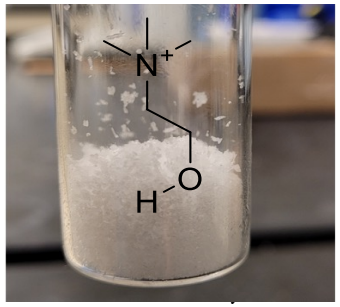


H-acceptor



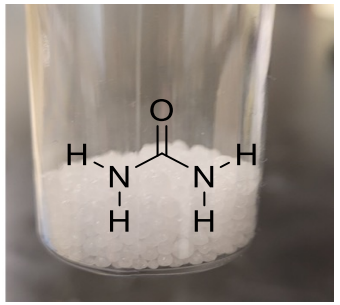
H-donor

Choline chloride

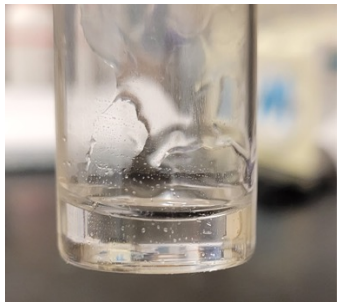


1:2 +

Urea



80°C



Reline

Properties:

- Thermally stable
- Non-toxic
- Biodegradable
- Negligible vapor pressure
- Inexpensive

Experimental work

I&EC research
Industrial & Engineering Chemistry Research
pubs.acs.org/IECR
Article

A Membrane Contactor Enabling Energy-Efficient CO_2 Capture from Point Sources with Deep Eutectic Solvents

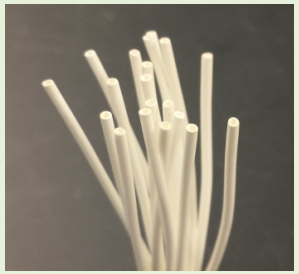
Syed Z. Islam,* Md Arifuzzaman, Gernot Rother, Vera Bocharova, Robert L. Sacci, Jacek Jakowski, Jingsong Huang, Ilia Nicolaevich Ivanov, Ramesh R. Bhave,* Tomonori Saito, and David S. Sholl

Cite This: https://doi.org/10.1021/acs.iecr.3c00080 Read Online

Polymer Hollow Fiber Membrane Contactor

Microporous polymer hollow fiber

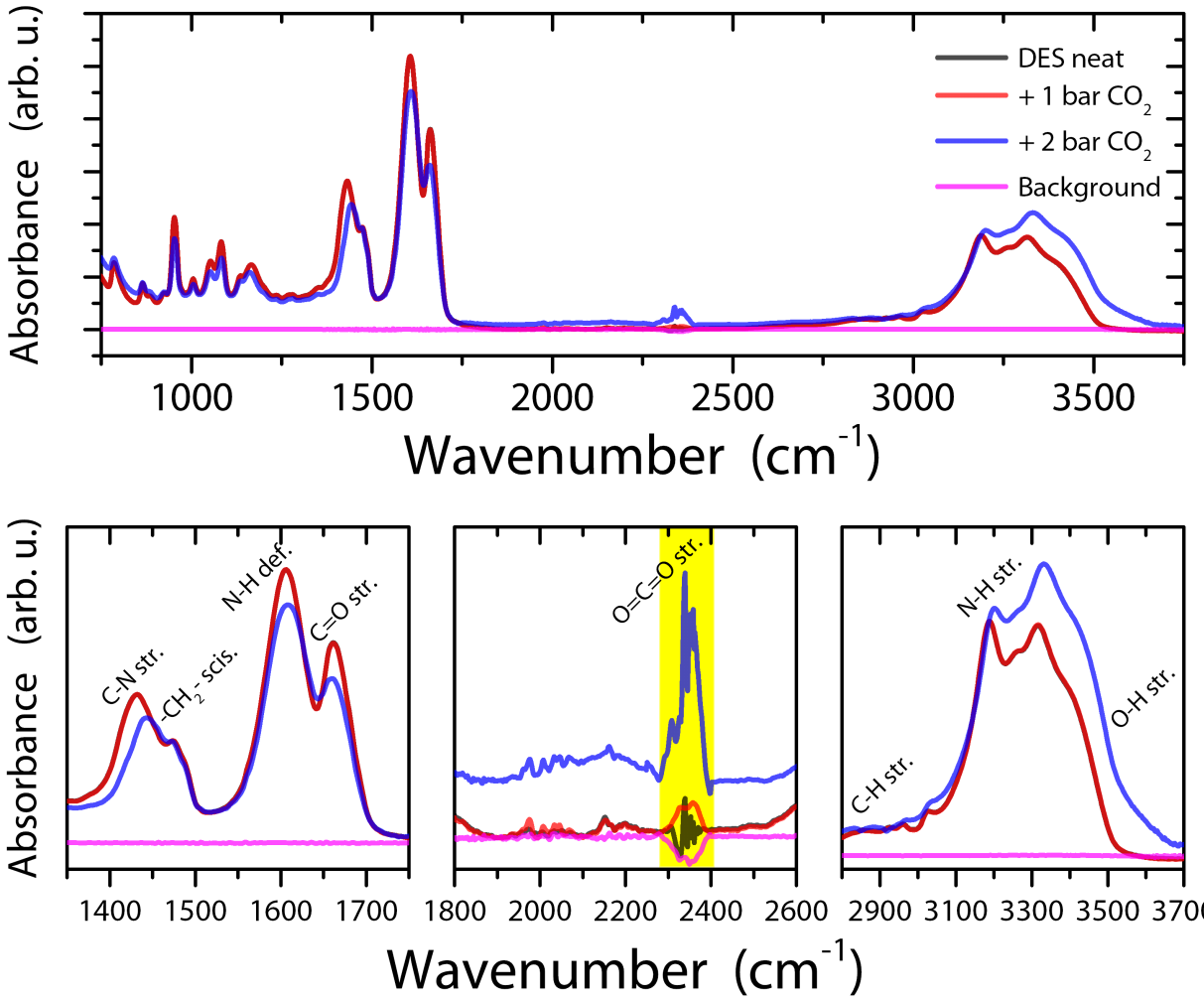
Polypropylene hollow fibers



- **Purity recovered CO_2 of 96.7%**

Experimental results

- Separation of CO_2 with 96.7% purity from 50%/50% mixture of CO_2/N_2
- No N_2 detected
- Input pressure up to 2 bars
- FTIR suggests physisorption
- **Question: what is the mechanism?**



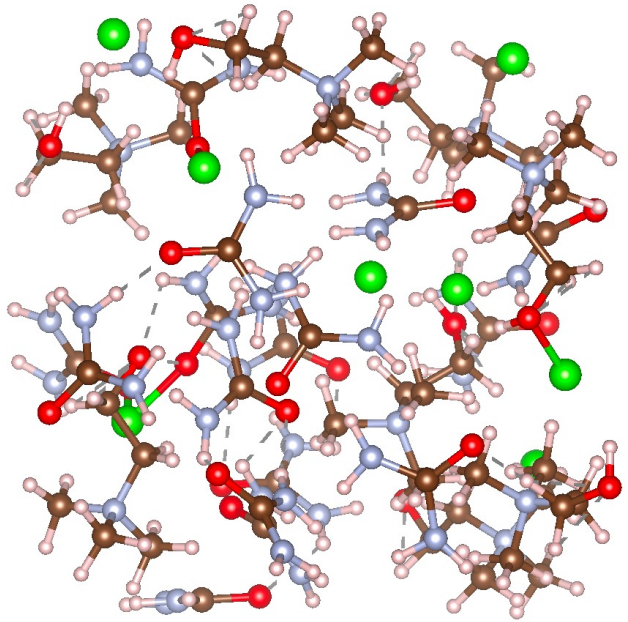
Ind. Eng. Chem. Res. 2023, 62, 10, 4455−4465

Simulations

Computational model:

- urea 8 atoms
- choline 22 atoms
- DES (304 atoms= 8 cholines+16 ureas)
- periodic box: 1.5x1.5x1.5nm

Siepmann, JPCB 2018, 122, 1245



Goal:

- Understand FTIR experimental data
- Explain binding energy and affinity of reline towards CO_2, N_2
- Validate computational model towards search for future DES

Methodology:

- Electronic structure: DFTB(periodic) & DFT
- IR from MD (ACF) vs IR from Hessian
- Binding energy & motifs
- Statistical mechanics
  (ZPE, thermal effects, entropy)
- Temperature: 333.15K

Overview of Density Functional Tight-Binding

Extended Hückel type method using atomic parameters from DFT (PBE, GGA-type), diatomic repulsive potentials from B3LYP

- Seifert, Eschrig (1980-86): STO-LCAO; 2-center approximation
- Porezag *et al.* (1995): efficient parameterization scheme: ***NCC-DFTB***
- Elstner *et al.* (1998): charge self-consistency: ***SCC-DFTB***
- Köhler *et al.* (2001): spin-polarized DFTB: ***SDFTB***
- ***Houraine et al. (2020): DFTB+, a software package***

$$E^{(NCC-)DFTB} = \sum_{i}^{\substack{valence\\orbitals}} n_i \varepsilon_i + \frac{1}{2} \sum_{A \neq B}^{atoms} E_{AB}^{rep}$$

Zeroth-order (TB) Hamiltonian: no e-e interactions

$$E^{(SCC-)DFTB} = E^{(NCC-)DFTB} + \frac{1}{2} \sum_{A \neq B}^{atoms} \gamma_{AB} \Delta q_A \Delta q_B$$

Self-consistent charge-charge interactions

$$E^{S(pin-polarized)DFTB} = E^{(SCC-)DFTB} + \frac{1}{2} \sum_{A}^{atoms} \sum_{l \in A} \sum_{l' \in A} p_{Al} p_{Al'} W_{All'}$$

Self-consistent spin-spin interactions

$$E = Tr[h^{core} + \tfrac{1}{2} G(P)P]$$

$$F = h^{core} + G(P)$$

16

Overview of Density Functional Tight-Binding

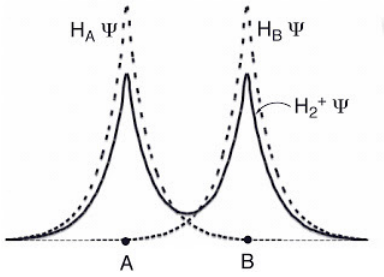
- Only valence electrons considered
  - minimal basis set, 1 to 9 per atom, Slater type orbitals
  - energy obtained by diagonalization of generalized DFTB eigenvalue problem:

$$\mathbf{H}^0\mathbf{C} = \mathbf{SC}\varepsilon \qquad \text{with} \quad S_{\mu\nu} = \langle \chi_\mu | \chi_\nu \rangle$$

$$H^0_{\mu\nu} = \langle \chi_\mu | \hat{H}[\rho_0^M, \rho_0^N] | \chi_\nu \rangle$$

- Coulomb asymptotic for electron-electron term:

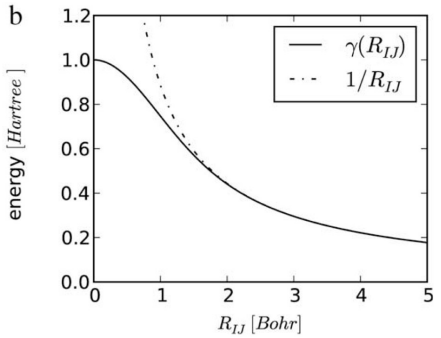
$$E_{el-el} = \frac{1}{2} \sum_{A \neq B}^{atoms} \Delta q_A \cdot \gamma_{AB}(R_{AB}) \cdot \Delta q_B$$



γ_{AB} — distance-dependent charge-charge interaction functional;

$\gamma_{AB} = \gamma_{AB}(U_A, U_B, R_{AB})$ for $R_{AB} \to \infty$: Coulomb potential $1/R_{AB}$

$\gamma_{AA} = \gamma_{AA}(U_A, U_A, R_{AA})$ for $R_{AA} \to 0$: Hubbard $U_A = \frac{1}{2}(IP_A - EA_A)$



- Parameters are publically available and transferable (not all elements are parametrized)

Main repositories (U. of Bremen, Germany)

http://www.dftb-plus.info/

http://www.dftb.org

Overview of Density Functional Tight-Binding

Main Features & Advantages

- Localized A.O. with PBC
- Very fast:
  - routine MD for ~1000 atoms on a desktop
  - 30ps long MD for ~300 atoms within a day timescale
- Accuracy comparable to DFT
- Code is open source
- Many features implemented:
  band structure, transport (NEGF), TDDFT, Grimme dispersion

Weaknesses

- Parameters not comprehensive
- Parameters often deed tweaking & benchmarking before use

Simulations

- Simulations of FTIR: CO_2 in gas phase and liquid reline
- Binding energy: CO_2 vs N_2 in reline
- Thermal, entropy effects
- Binding motifs

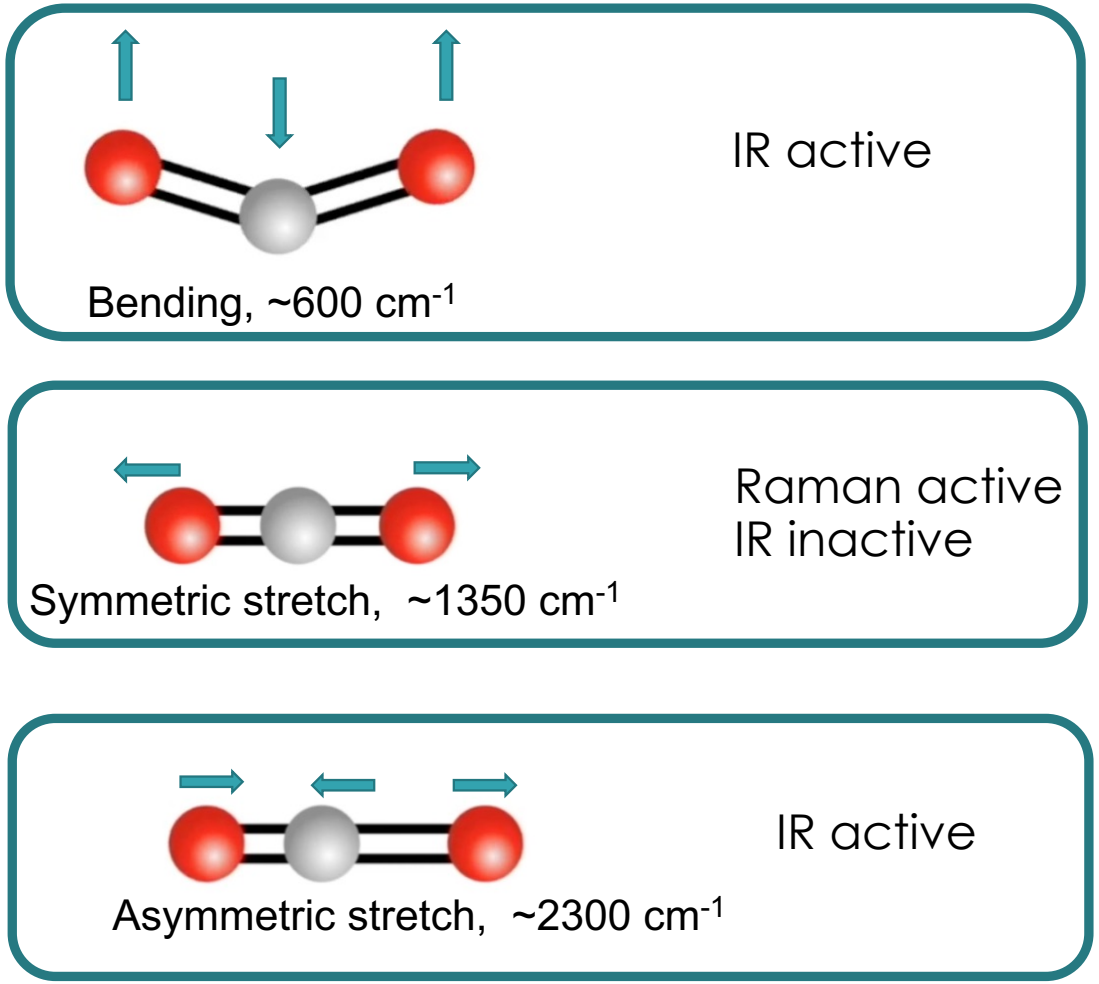
Vibrational spectra of CO_2 in gas phase and in reline

IR of CO_2 molecule (linear)

- 3 atoms ➔ 4 vibrations (=3N-5)

Normal modes analysis

- Bending (double degenerate)
- Symmetric stretching
- Asymmetric stretching



Benchmark: CO_2 molecule gas phase

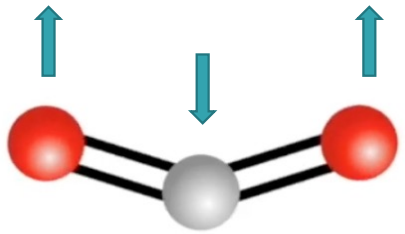
FTIR spectra from MD:

- Save time dependent dipoles
- … or save charges and velocities
- Dipole-dipole autocorrelation function
- Fourier transform it

$$I(\omega)_{cl} = \frac{1}{2\pi\omega^2}\int_{-\infty}^{\infty} dt\, e^{-i\omega t}\left\langle \frac{d\vec{M}(0)}{dt}\cdot\frac{d\vec{M}(t)}{dt}\right\rangle$$

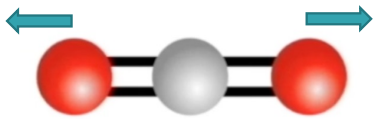
$$= \frac{1}{2\pi\omega^2}\int_{-\infty}^{\infty} dt\, e^{-i\omega t}\left\langle \left(\sum_{i=1}^{n} q_i\vec{v}_i(0)\right)\cdot\left(\sum_{j=1}^{n} q_j\vec{v}_j(t)\right)\right\rangle$$

$$\frac{d\vec{M}}{dt} = \frac{d}{dt}\sum_i q_i(t)\vec{R}_i(t) = \sum_i [\dot{q}(t)R(t) + q(t)\dot{R}(t)]$$



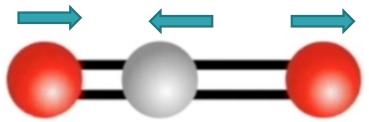
Bending, ~600 cm^{-1}

IR active



Symmetric stretch, ~1350 cm^{-1}

Raman active
IR inactive



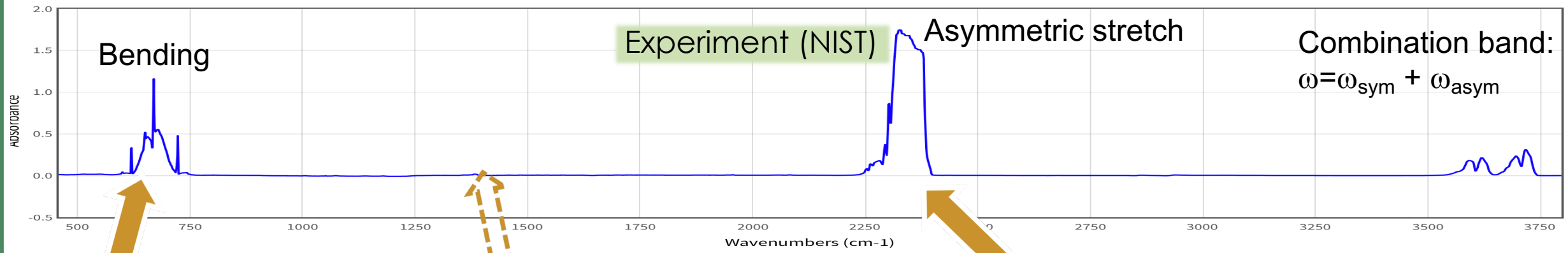
Asymmetric stretch, ~2300 cm^{-1}

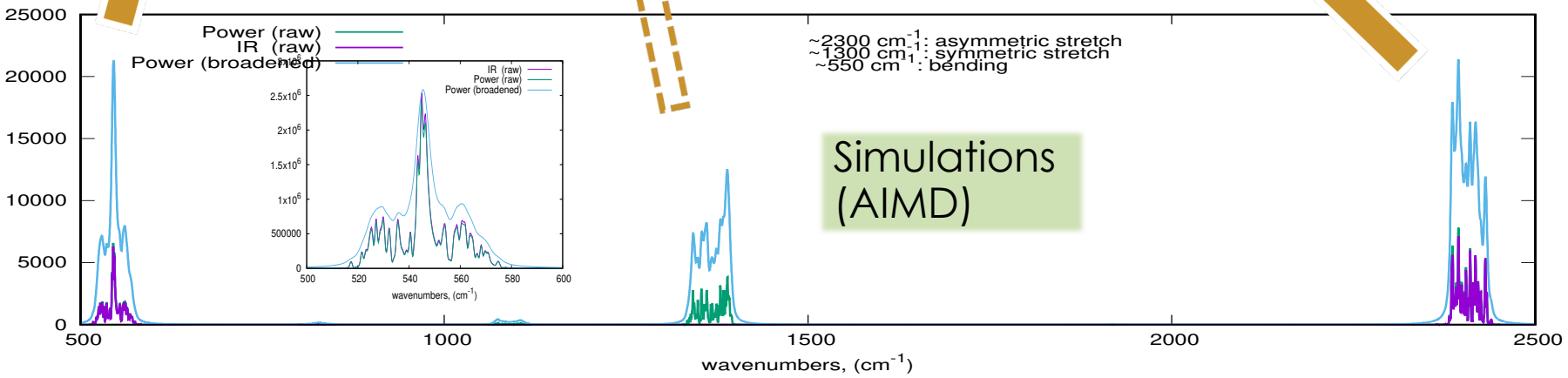
IR active

Benchmark: CO_2 molecule gas phase

- **FTIR from Experiment** (data from NIST): https://webbook.nist.gov/cgi/cbook.cgi?ID=C124389&Type=IR-SPEC&Index=1#IR-SPEC

- **FTIR from Simulations:**
  - calculated as average over **100 MD simulations**
  - NVE with initial random velocities corresponding to T=300K

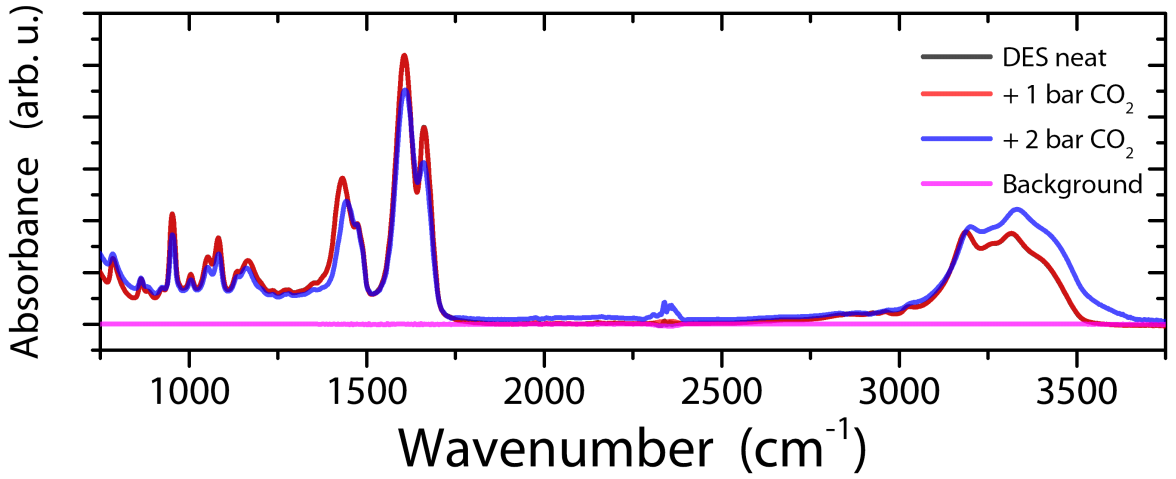




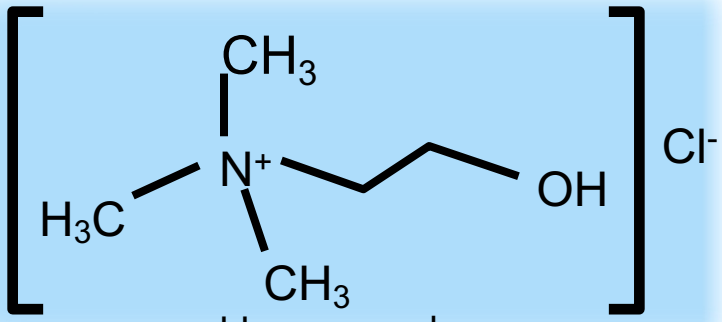
Vibrational spectra of CO_2 in gas phase and in reline

- Experiment:
  no chemistry, physisorption
- What is the effect of reline on CO_2 spectra?
- How does CO_2 binds o reline?

Ind. Eng. Chem. Res. 2023, 62, 10, 4455−4465

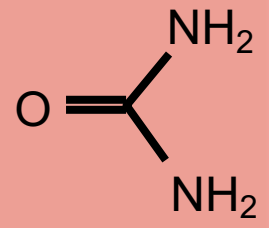


Choline chloride

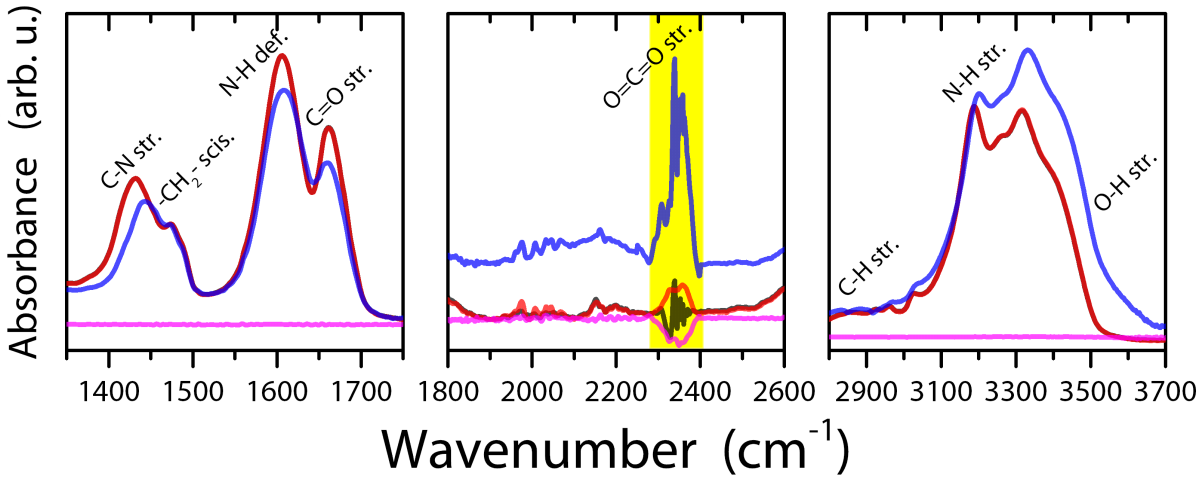


H-acceptor

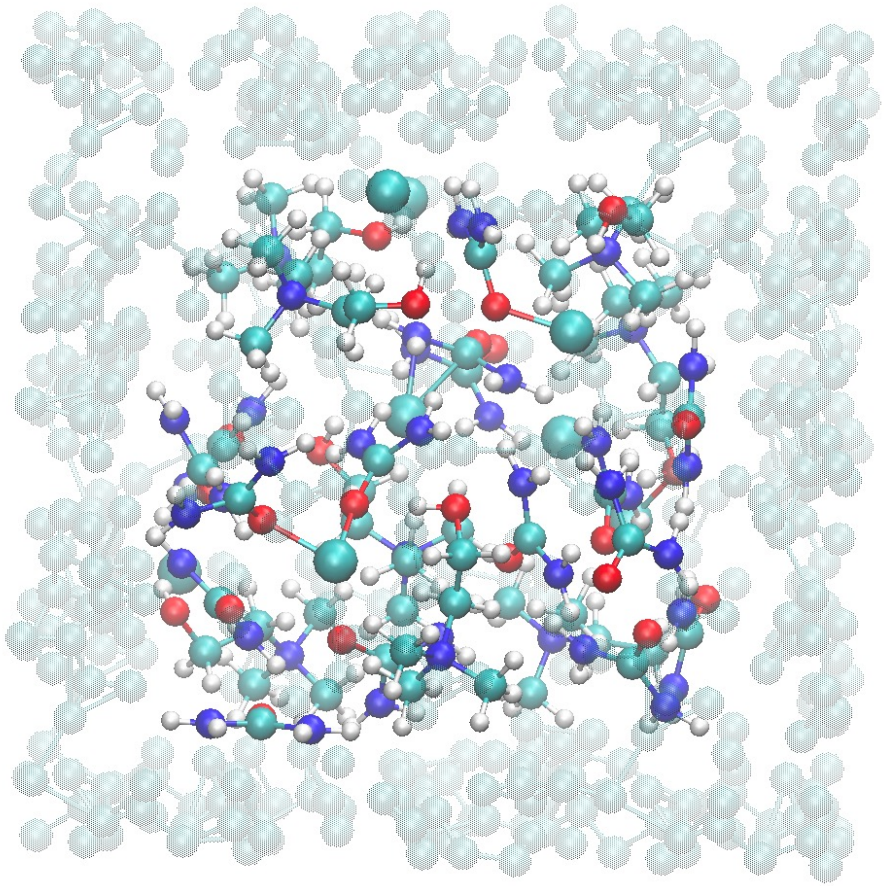
Urea



H-donor



Vibrational spectra of CO_2 in reline

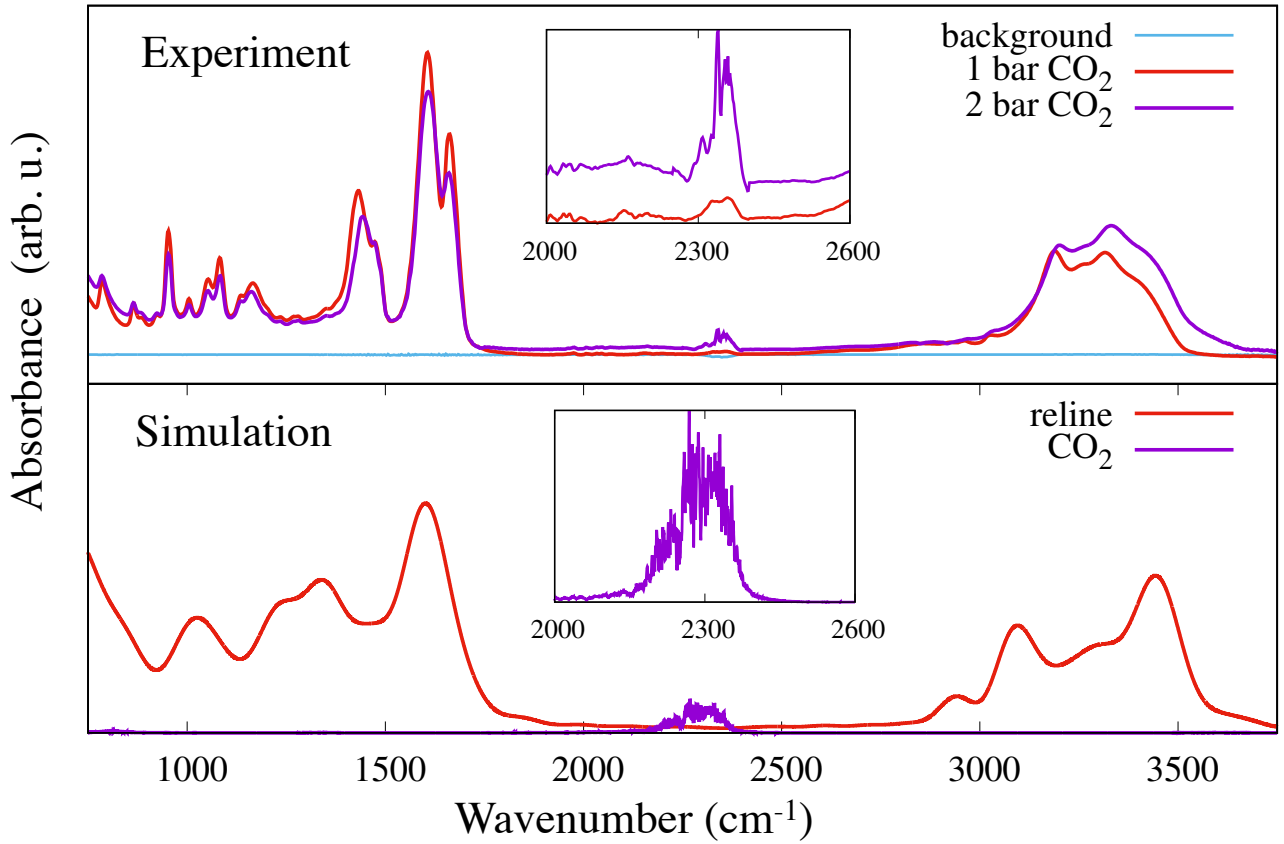


- Molecular dynamics simulations
- Periodic simulation box cube (1.43 nm)
- 10 randomized structures of reline + CO_2:
  8 cholines +16 ureas +1 CO_2 (total 307 atoms)
- Monte Carlo based insertion of of gas
- Electronic structure from DFTB3 +dispersion
- 3ob parametrization
- Periodic boundary condition with Gamma point sampling
- Constant energy microcanonical ensemble
- Initial kinetic energy corresponding to 300 K
- Total time =30ps, time step dt=1ps
- IR /power spectra as average over all simulations
- IR spectra from dipole-dipole autocorrelation function
- All modes (IR+Raman) from velocity-velocity autocorrelation function

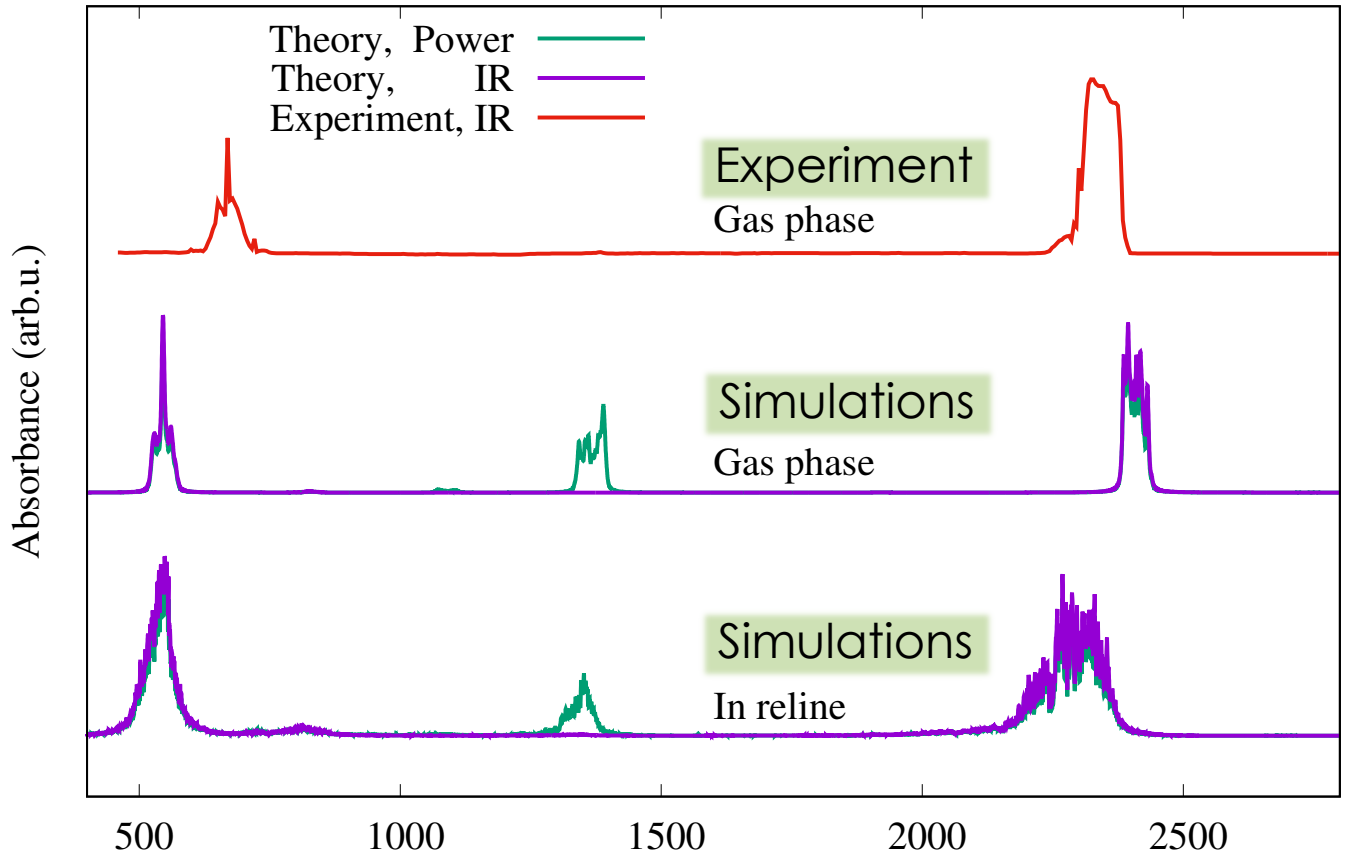
Vibrational spectra of CO_2 in reline

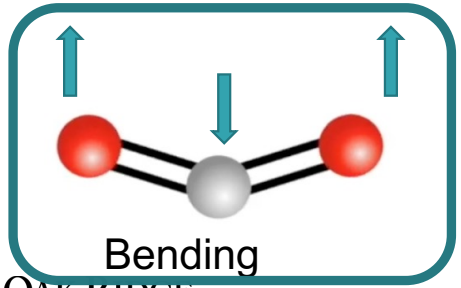
Simulations details

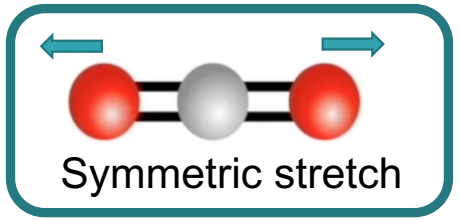
- 3rd order DFTB+dispersion
- Periodic boundary condition
- no chemistry, physisorption
- What is the effect of reline on CO_2 spectra?
- How does CO_2 binds o reline?

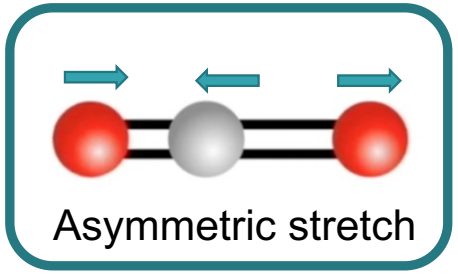


Vibrational spectra of CO_2 in gas phase and in reline









Simulations results

- Power spectrum:
  - velocity autocorrelation
- IR spectrum:
  - dipole autocorrelation
- Bending and symmetric stretch insensitive to reline (broadening)
- Asymmetric stretch redshifted

Correlation of vibrational modes, binding energy and structure descriptors

- Binding of CO_2 vs N_2 in reline
- 10 randomly packed structures of reline (thermalized, NVT)
- Monte Carlo based search for voids
- Optimization: 3rd order DFTB + dispersion, 3ob parameters
- Normal modes analysis (mass weighted Hessian)
- Analysis: binding energy, separation (gas vs. reline), O-C-O angle, IR shift
- ZPE energy, entropy & thermochemistry corrections

Correlation of vibrational modes, binding energy and structure descriptors

- Binding energy (electronic)

$$E^0_{BE} = E(G..S) - E(G) - E(S)$$

- Corrections (ZPE, thermochemistry)

$$\Delta E^X_{BE} = E^X(G_{solvent}) - E^X(G_{gas})$$

$$E^X_{BE} = E^0_{BE} + \Delta E^X_{BE}$$

Thermochemistry (standard, harmonic approximation)

Internal energy (U)

$$U = RT^2 \left(\frac{\partial Q}{\partial T}\right)_V$$

Entropy(S)

$$S = R + R\ln(Q) + RT\left(\frac{\partial Q}{\partial T}\right)_V$$

Helmholtz free energy (F)

$$F = U - TS$$

Gibbs free energy (F)

$$G = F + pV$$

Translation

$$q_t = \left(\frac{2\pi m k_B T}{h^2}\right)^{3/2} \frac{k_B T}{P}$$

$$E_t = \frac{3}{2}RT$$

$$S_t = R\left(ln(q_t) + \frac{5}{2}\right)$$

Rotation

$$q_r = \frac{1}{\sigma}\left(\frac{T}{\Theta_r}\right)$$

$$E_r = RT$$

$$S_r = R\left(\ln(q_t) + 1\right)$$

Vibrations

$$q_{\mathrm{v}} = \prod_K \frac{e^{-\Theta_{\mathrm{v},K}/2T}}{1 - e^{-\Theta_{\mathrm{v},K}/T}}$$

$$E_{\mathrm{v}} = R\sum_K \Theta_{\mathrm{v},K}\left(\frac{1}{2} + \frac{1}{e^{\Theta_{\mathrm{v},K}/T} - 1}\right)$$

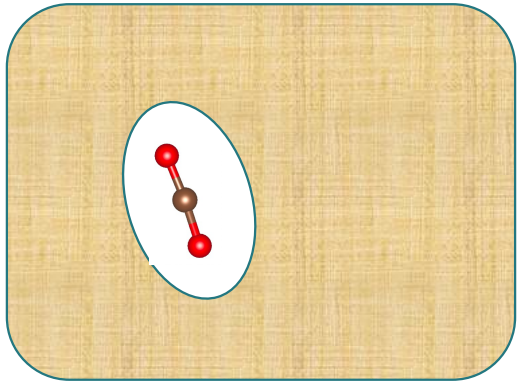
$$S_{\mathrm{v}} = R\left(\ln(q_{\mathrm{v}}) + T\left(\frac{\partial \ln q}{\partial T}\right)_V\right)$$

$$= R\sum_K \left(\frac{\Theta_{\mathrm{v},K}/T}{e^{\Theta_{\mathrm{v},K}/T} - 1} - \ln(1 - e^{-\Theta_{\mathrm{v},K}/T})\right)$$

Thermochemistry: effects of entropy, Temp &Press

- Gas phase CO_2 & N_2 vs dissolved in reline
- Gas phase CO_2:
  - 3 translations, 2 (or 3) rotations , 6 vibrations
- Gas phase N_2:
  - 3 translations, 2 rotations, 1-vibration
- CO_2 in reline:
  - 0 translations, 0 rotation, 9 vibrations
- N_2 in reline:
  - 0 translations, 0 rotations, 6 vibrations

Gas molecules trapped in void



Partition function: $Q=q_{rot}*q_{transl}*q_{vib}$

$$Q = \left[\frac{k_B T}{P}\left(\frac{2\pi m k_B T}{h^2}\right)^{3/2} \cdot \frac{T}{\sigma\theta_{rot}}\right]^{\delta} \cdot \left\{\prod_{j=1}^{N_{vib}} \frac{e^{-\theta_j^{vib}}/2T}{1-e^{-\theta_j^{vib}}/T}\right\}$$

Gas phase: δ =1, Nvib=5

In reline: δ =0, Nvib=9

Main contribution to E_{BE} : conversion of transl, rot ➔ vibrations

Thermochemistry: effects of entropy, Temp &Press

Partition function: $Q = q_{rot} * q_{transl} * q_{vib}$

$$Q = \left[\frac{k_B T}{P}\left(\frac{2\pi m k_B T}{h^2}\right)^{3/2} \cdot \frac{T}{\sigma\theta_{rot}}\right]^{\delta} \cdot \left\{\prod_{j=1}^{N_{vib}} \frac{e^{-\theta_j^{vib}/2T}}{1 - e^{-\theta_j^{vib}/T}}\right\}$$

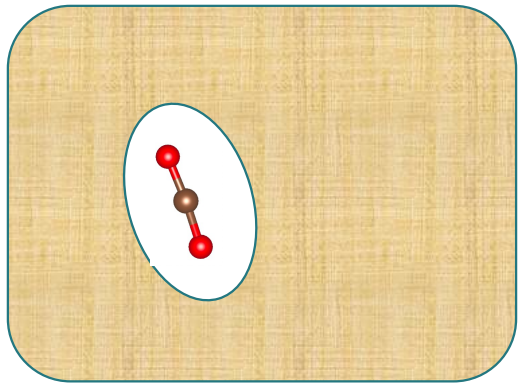
Gas phase: δ =1, Nvib=5

In reline: δ =0, Nvib=9

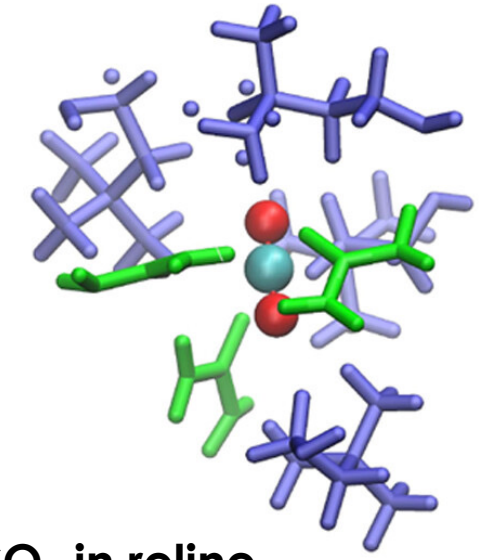
Main contribution to E_{BE} : conversion of transl, rot ➔ vibrations

Minimal Solvation model

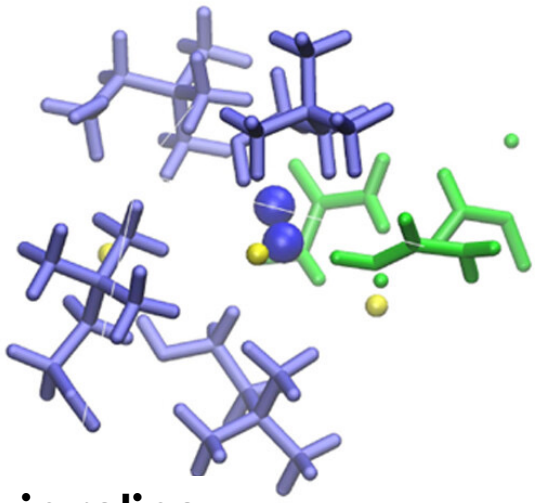
Gas molecules trapped in void



1st solvation shell model

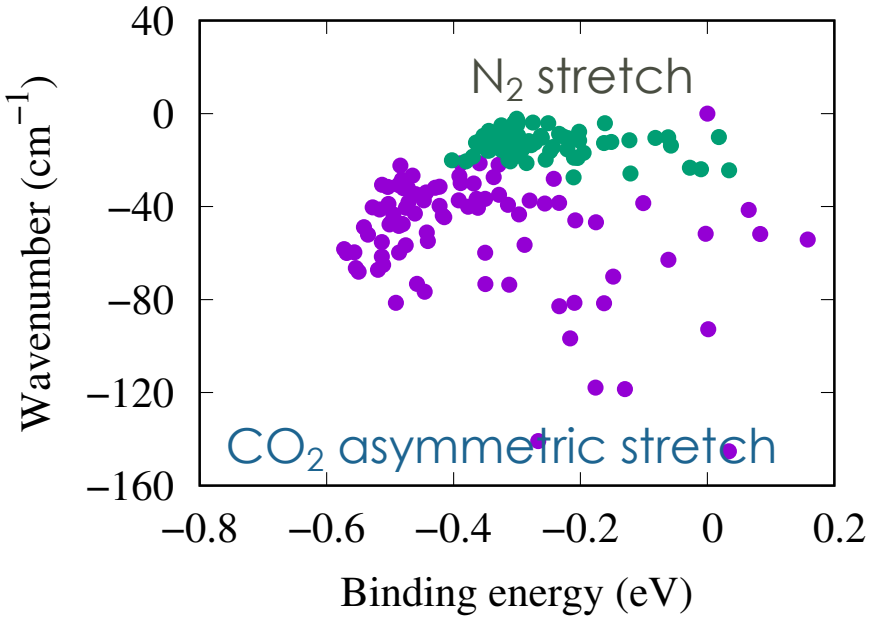


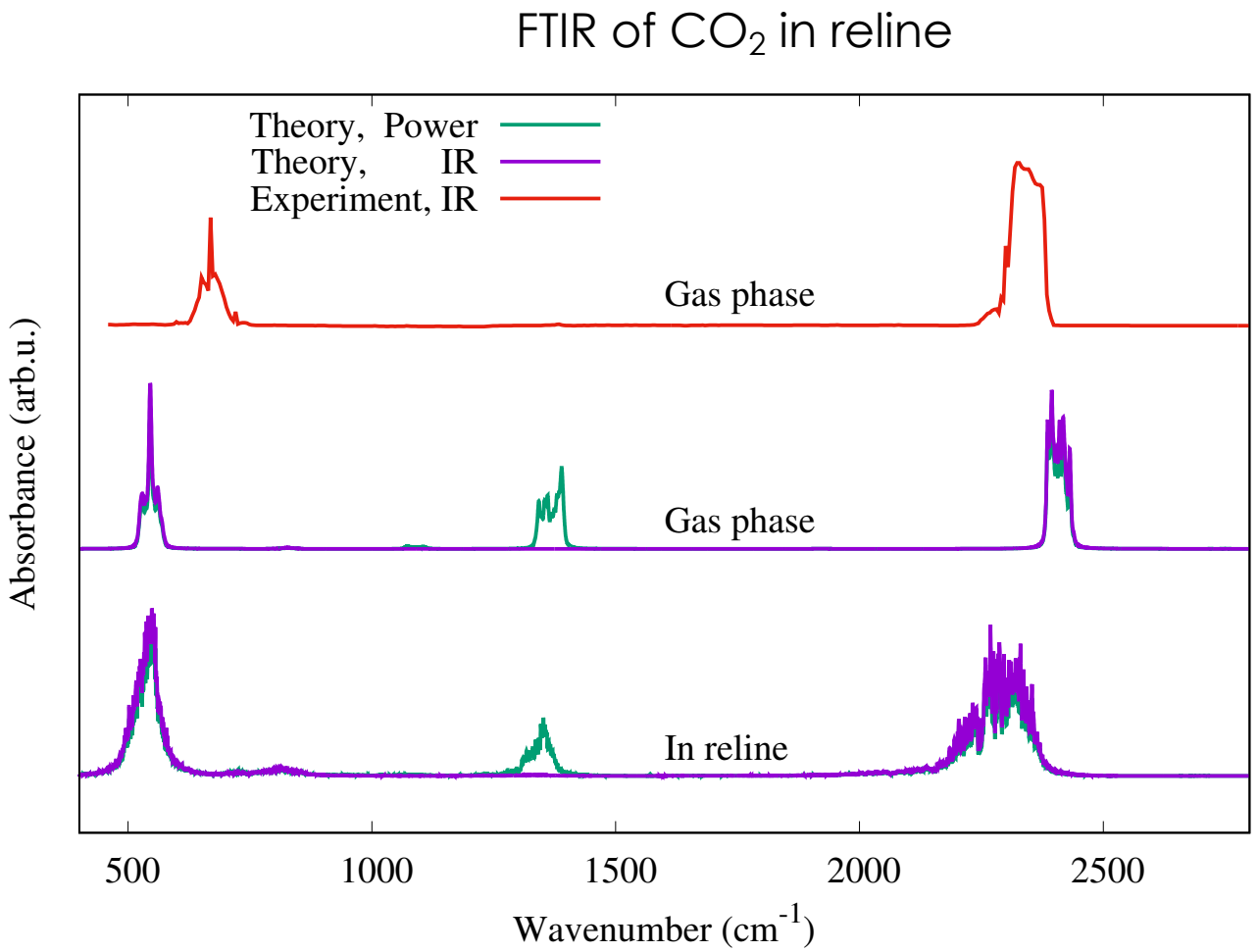
CO_2 in reline



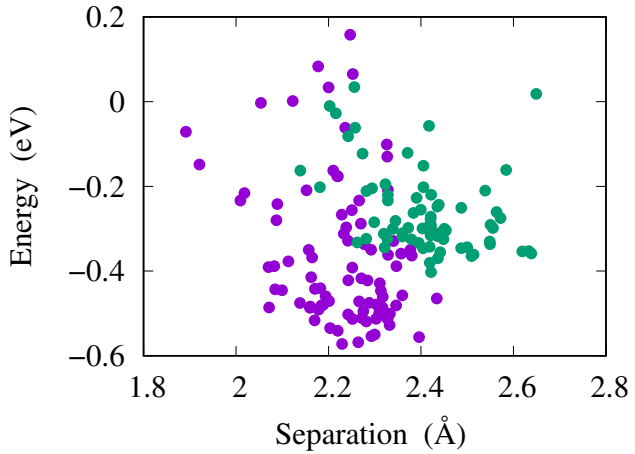
N_2 in reline

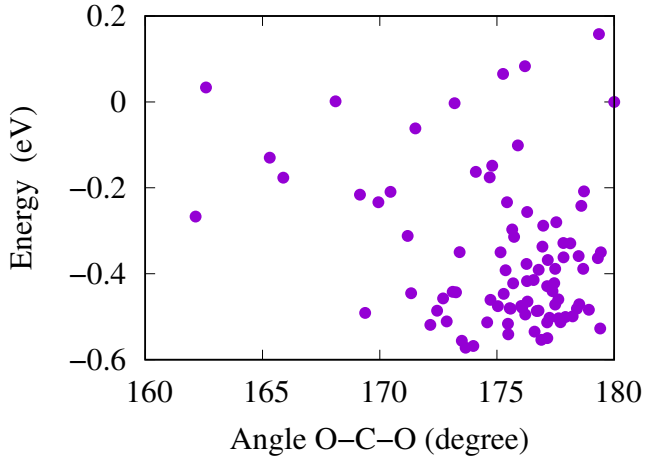
Correlation of vibrational modes, binding energy and structure descriptors

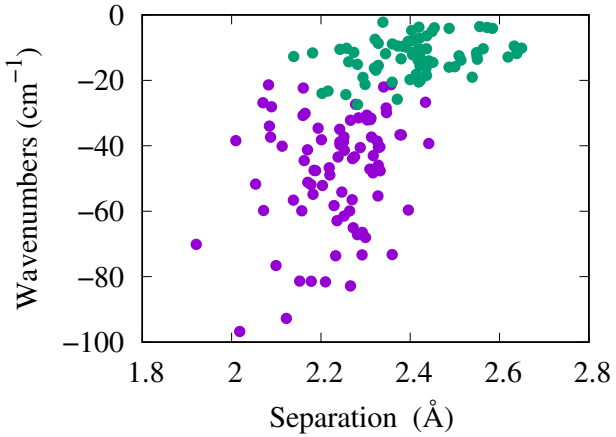


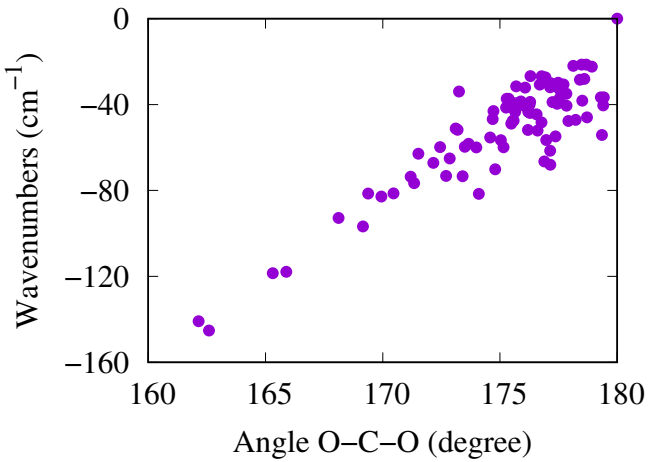


Correlation of vibrational modes, binding energy and structure descriptors







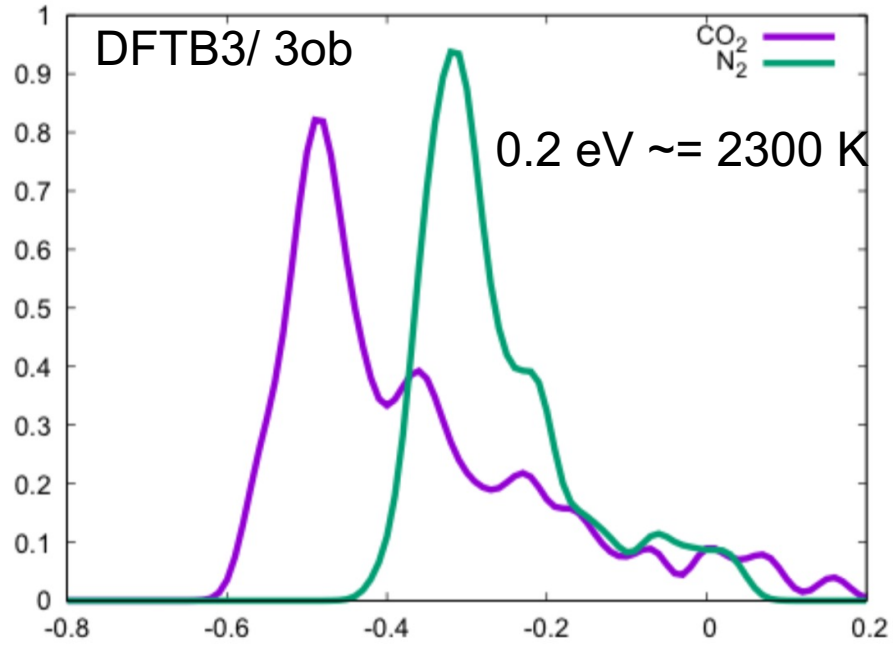


CO_2

N_2

Binding energy (BE)

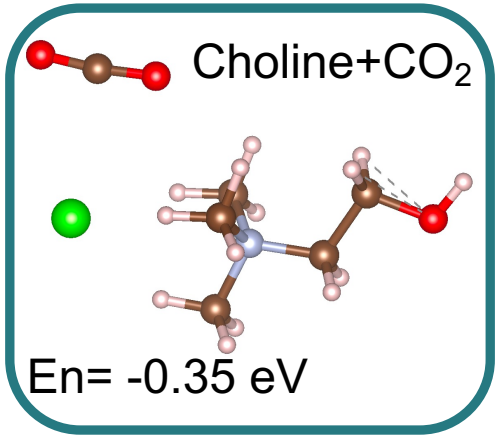
- Electronic energy only DFTB3/ 3ob
- No entropy /thermal effects
- Energy with respect to gas phase
- All structures optimized

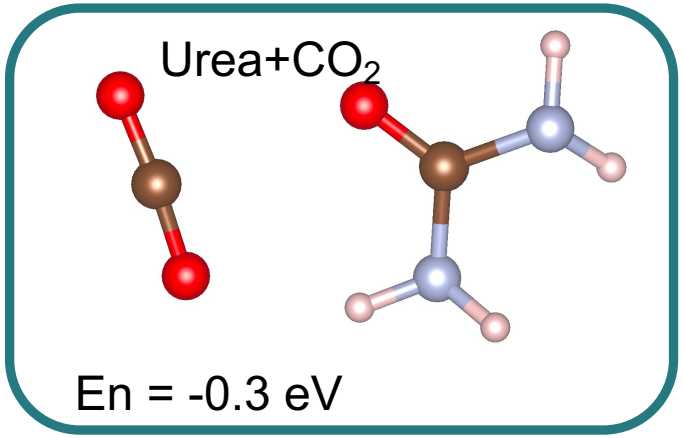


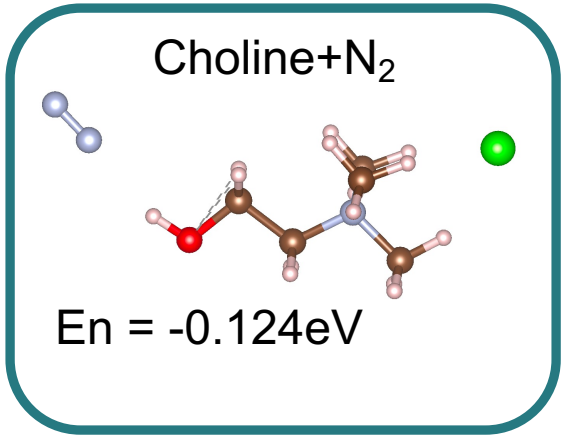
Binding Energy (eV)

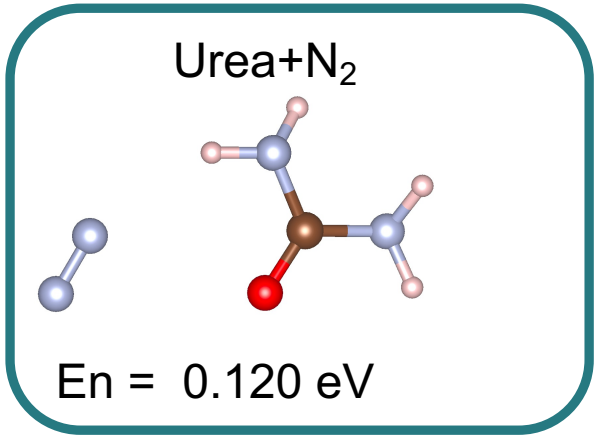
BE = E(gas+reline) – E(reline) –E(gas)

B3LYP/6-31G(d)



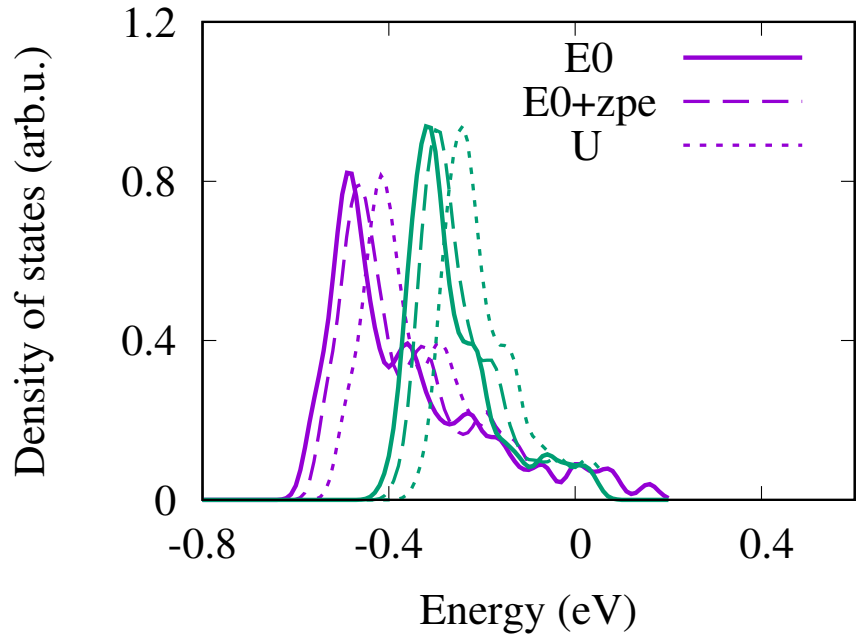






Binding energy

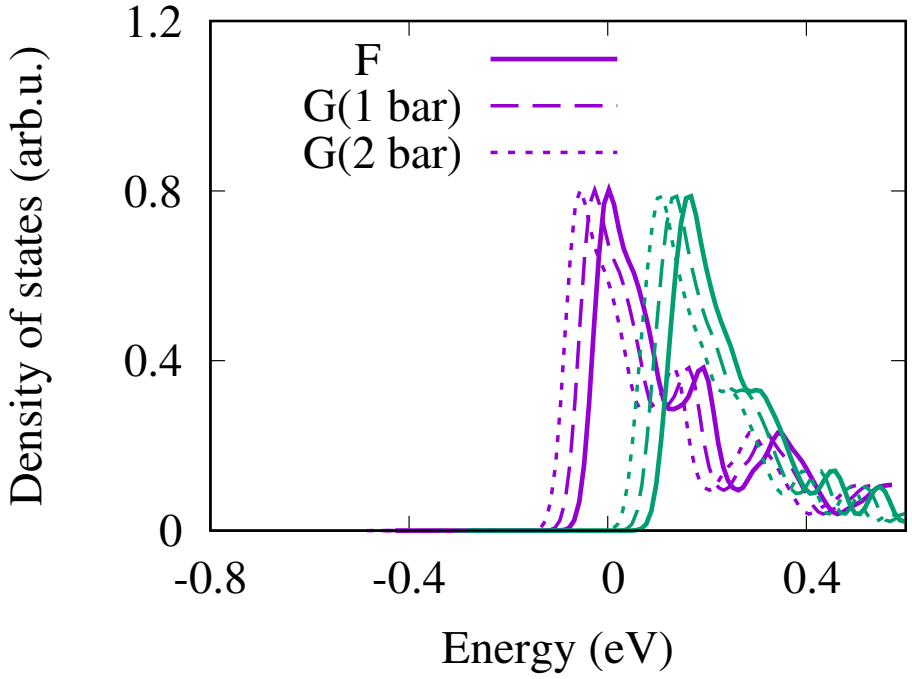
Electronic +vibrational corrections



CO_2

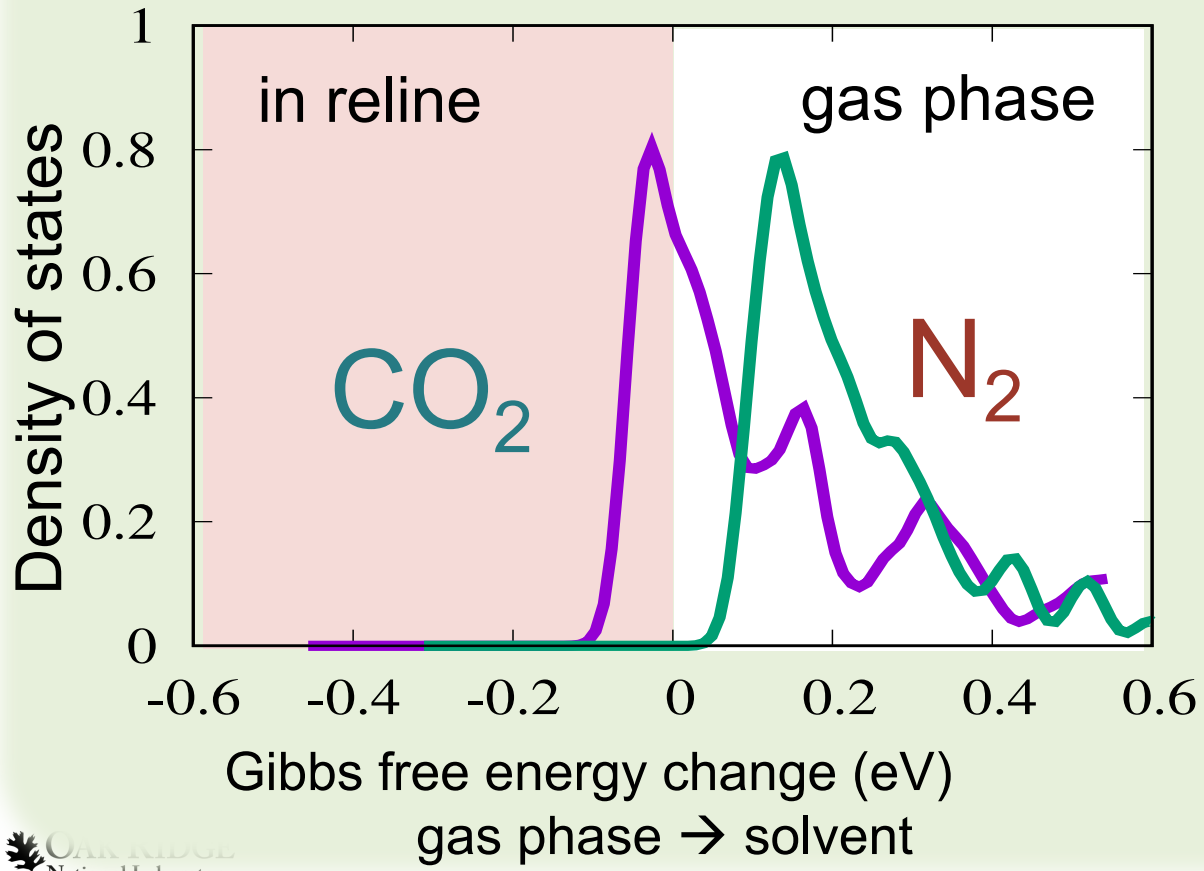
N_2

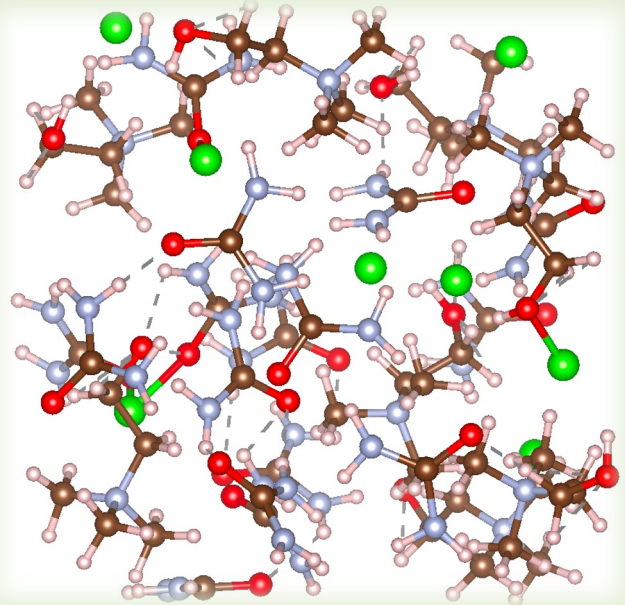
Entropy effects included



Summary of Results

Electronic and entropic effects lead to selective capture of CO_2 vs N_2 in reline (DES)

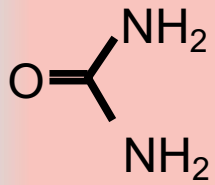




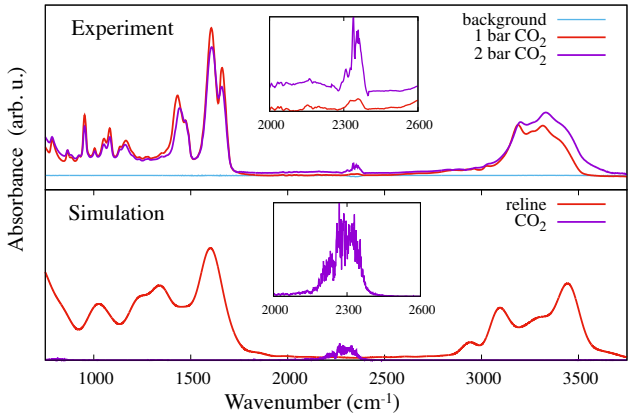
Experiment and simulations of CO2 capture in deep eutectic solvents

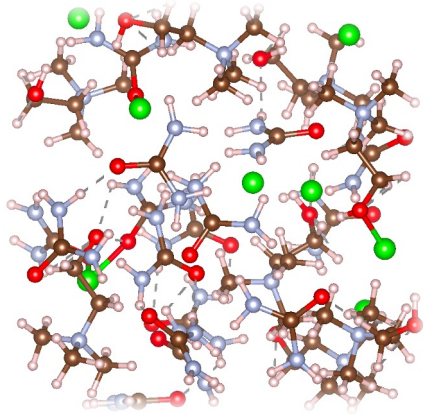
Reline is a mixture of 1:2 molar ratio of:

- choline chloride (HBA) + urea (HBD)

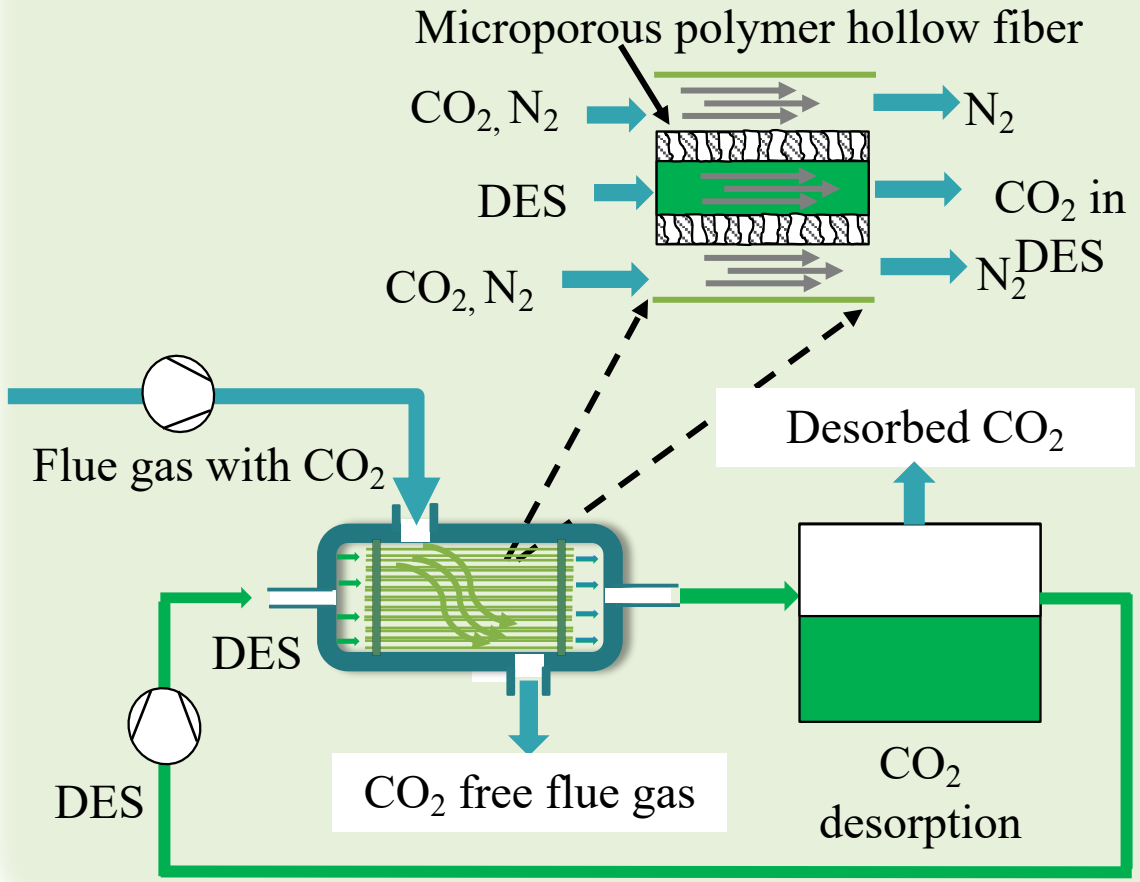


FTIR for CO_2 in reline





Polymer Hollow Fiber Membrane Contactor



Electronic and **entropic** effects lead to selective capture of CO_2 in reline (DES) with from CO_2/N_2 mixture with 97% purity

[1] S. Z.Islam, [Ind. & Eng. Chem. Res. (2023) 62, 10,4455
[2] J. Jakowski, et al. J. Phys. Chem. B, (2023), 127, 8888

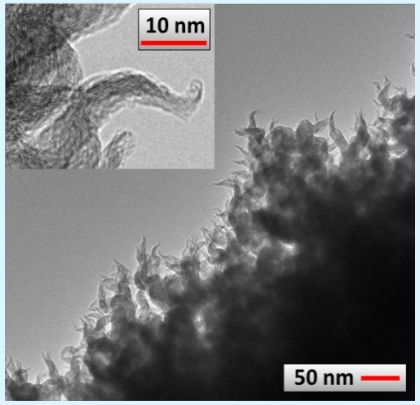
Part II. Towards modeling of CO_2 conversion from real time TDDFT

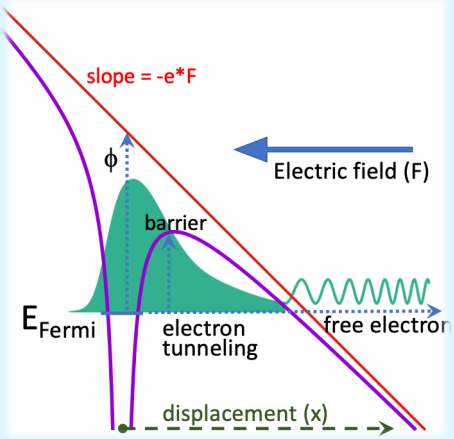
- Real-time TDDFT: electronic excitation, non-equilibrium processes
- Theory, implementation, benchmarking
- RMG-DFT program

Carbon dioxide conversion

- Needs for computational models:
  - non-equilibrium charge transfer, redox
  - electronically excited states during dynamics
  - interaction with UV-VIS, laser pulses
  - coupling between electrons and nuclei
  - charge transfer, nanoelectronics
  - applicable for large systems

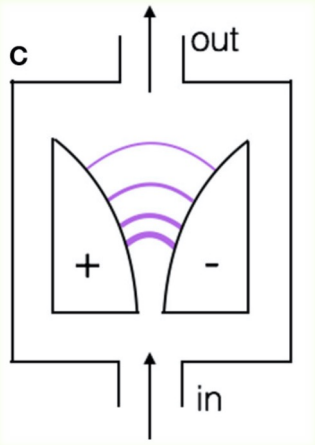
Electrochemical



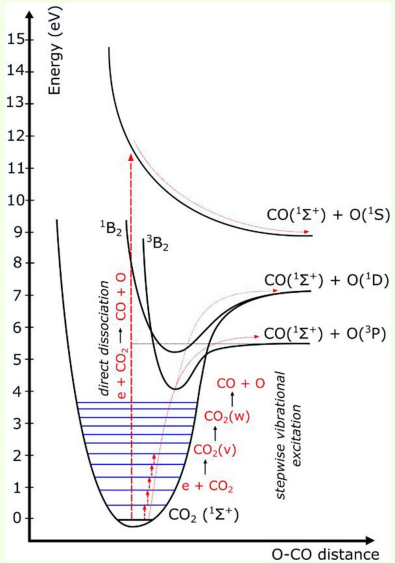


J. Electrochem. Soc. 161, H558 (2014).

Plasma technology

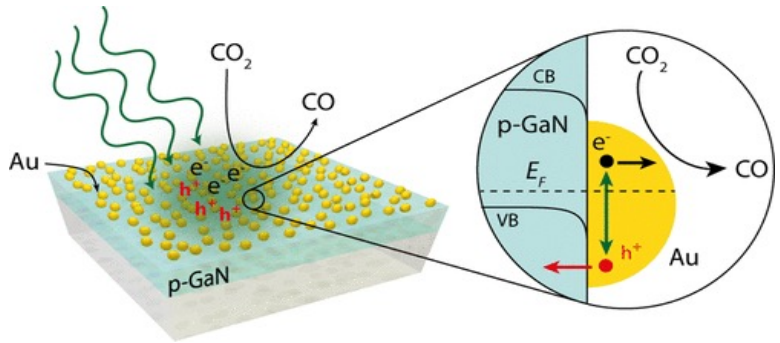


Gliding Arc Plasmatron reactor for CO_2 conversion



Front. Energy Res. 2020, 8:111

Plasmonics

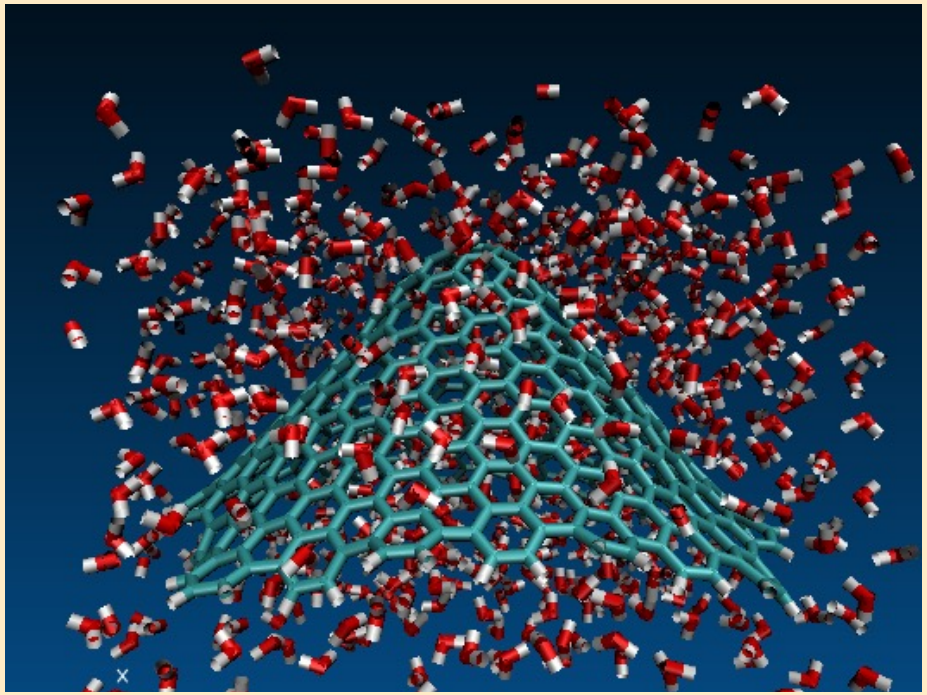


generation of non-equilibrium "hot" electron−hole pairs via surface plasmon decay within metal nanostructure

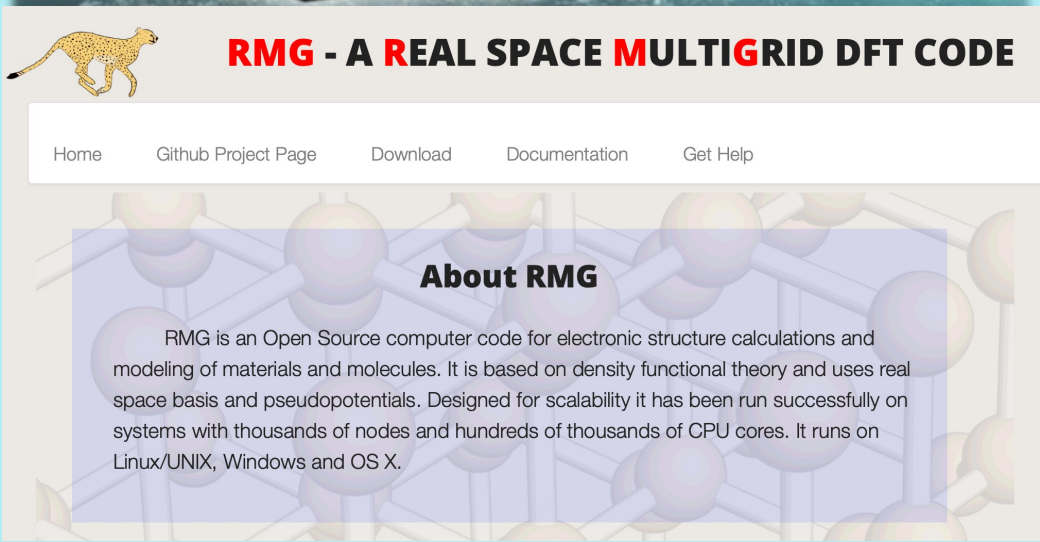
Nano Lett. 2018, 18, 4, 2545–2550

RMG-DFT calculations on Frontier

Graphene nanocone + waters:
2,979 atoms and 8,000 electrons



Important system for electric-field-assisted catalysis

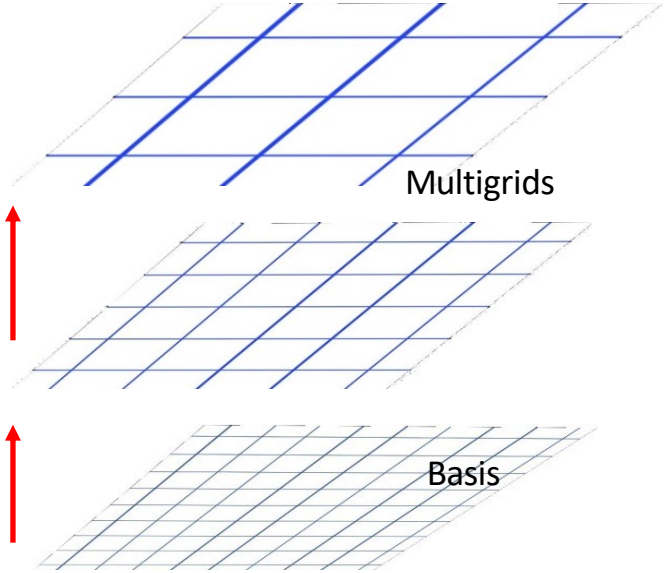


Collaboration with RMG-DFT team at NCSU:
J. Bernholc, Wenchang Lu and Emil Briggs

http://www.rmgdft.org

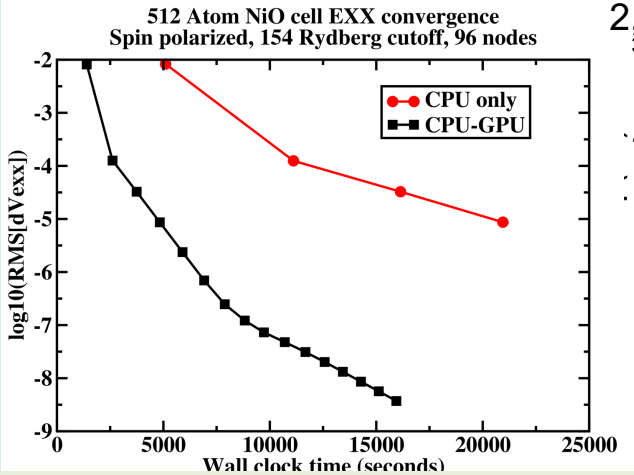
Real-space Multi-Grid method (RMG)

- Full-featured DFT/hybrid-DFT code: DFT equations solved directly on the grid.
- Multigrid techniques remove instabilities by working on one length scale at a time.
- Excellent parallelization via domain decomposition: multi-core CPUs, multiple GPUs/node, many nodes.
  Runs well on Frontier, Aurora, Summit, Perlmutter, Polaris, clusters, and workstations.
- Full Nvidia, AMD and Intel GPU support: uses all CPU cores and GPUs per node.
- Norm-conserving and ultrasoft pseudopotentials included in the distribution.
- High performance for all lattice types.
- Hybrid functionals, LDA+U, vdW-DF, Grimme, and spin-orbit coupling.
- Web interface for setting up input using cif, xyz, VASP, or Quantum Espresso files.
- Web interface for analyzing results.
- Very high accuracy vs. Quantum Espresso: μHa/atom.
- Supported by the Exascale Computing Project for large-scale DFT input to QMCPACK



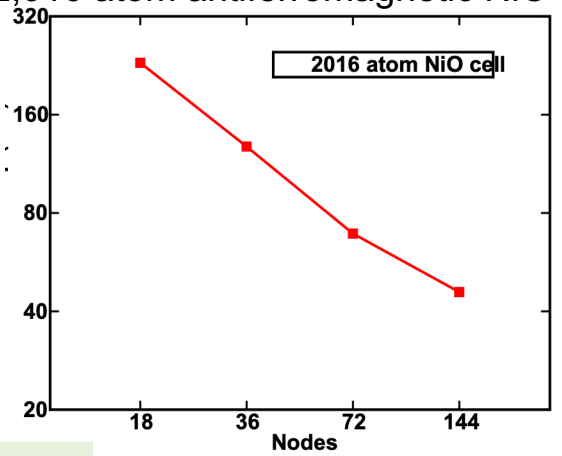
www.rmgdft.org

Summit



Frontier CPU-GPU

2,016 atom antiferromagnetic NiO



Ref: Briggs, Lu, Bernholc, *npj Comput. Mater.* (2024) 10, 17

Electron dynamics

- **Theory:**

- Magnus Expansion

- Density matrix propagation (von Neuman eq.)

- Commutator expansion

- **Implementation and benchmarks:**

- CPU/GPU

- Optical absorption spectra UV-VIS (benzene, plasmonics)

- timing information

Theory: Magnus expansion

- Evolution of density matrix for electrons

$$\frac{\partial P(t)}{\partial t} = -\frac{\imath}{\hbar}\left[H(t), P(t)\right]$$

- Formal solution through time-evolution operator

$$\mathcal{U}(t) = \exp\left(-\tfrac{\imath}{\hbar}\int_0^t H(t')dt'\right)$$

$$P(t) = \quad \mathcal{U}(t)\cdot P(0)\cdot \mathcal{U}(t)^{\dagger}$$

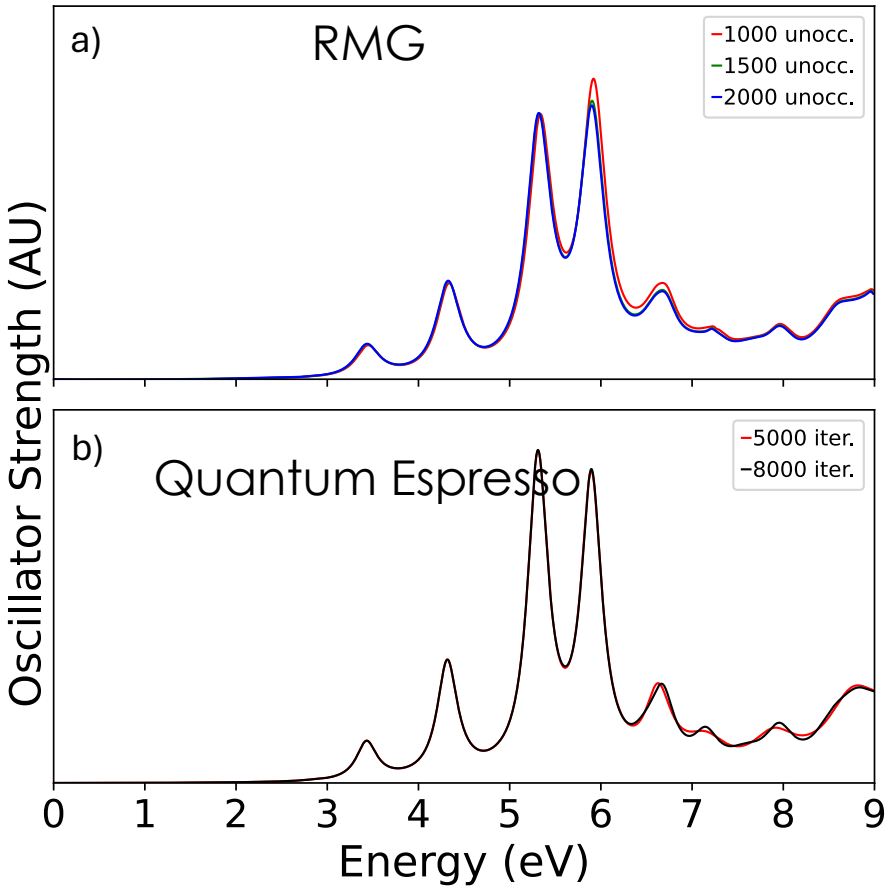
$$= \exp(\Omega)\cdot P(0)\cdot \exp(\Omega)^{\dagger}$$

  - where operator Ω is from **Magnus expansion**

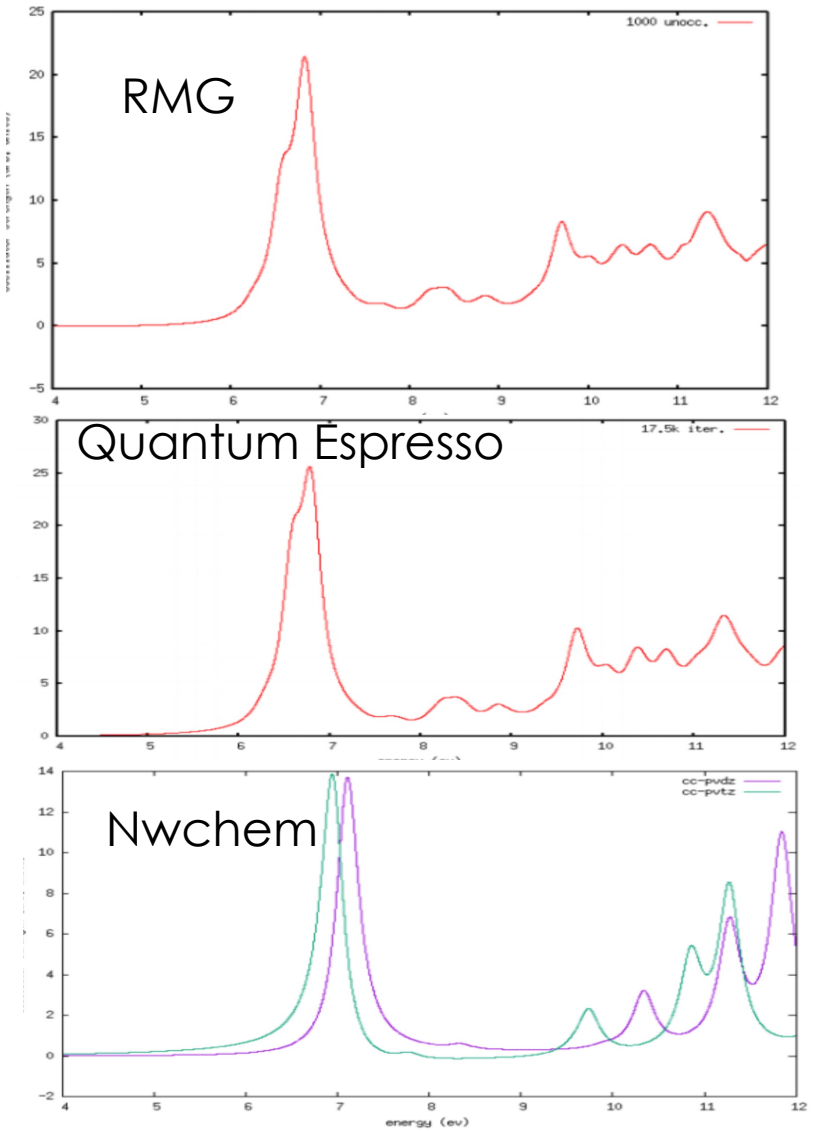
refs: 1) W. Magnus, Commun. Appl. Math 7,649 (1954)
2) J. Oteo, J. Ros, J. Math Physics 41, 3268 (2000)
3) Jakowski, Morokuma J. Chem. Phys. 130, 224106 (2009)

Comparison with other codes

C60



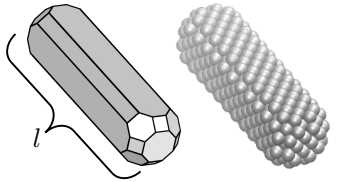
Benzene

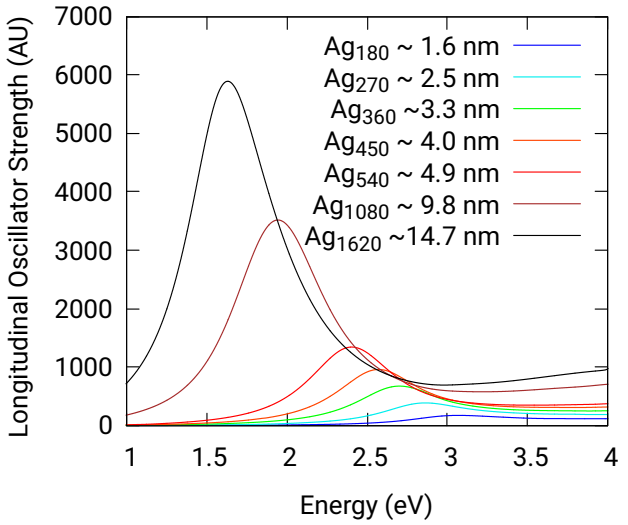


Real time TD-DFT simulations of plasmonic response of Ag nanorod

- **ORNL Frontier nodes:**
  CPU: 64 core AMD EPYC,
  GPU: 4x Radeon Instinct MI250X,
  total 8GPU per node)

- **System:** Ag nanorod, up 1620 atoms, (17,820 electrons), semicore (19e) vs frozen core calcs (11e)





- Investigating dipolar longitudinal localized surface plasmon.
  2,500 time steps, 0.2 AU time steps (=500 AU),
  walltime : TDDFT: 11s /step, SCF: 114 sec/ iteration

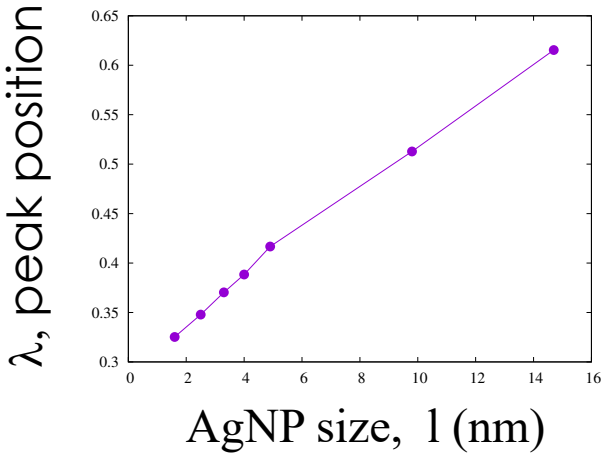
- **Redshifts of plasmon resonance peak with increasing size as expected.**

Empirical expression for plasmon peak position

$$\lambda = \lambda_0 + k \cdot l$$

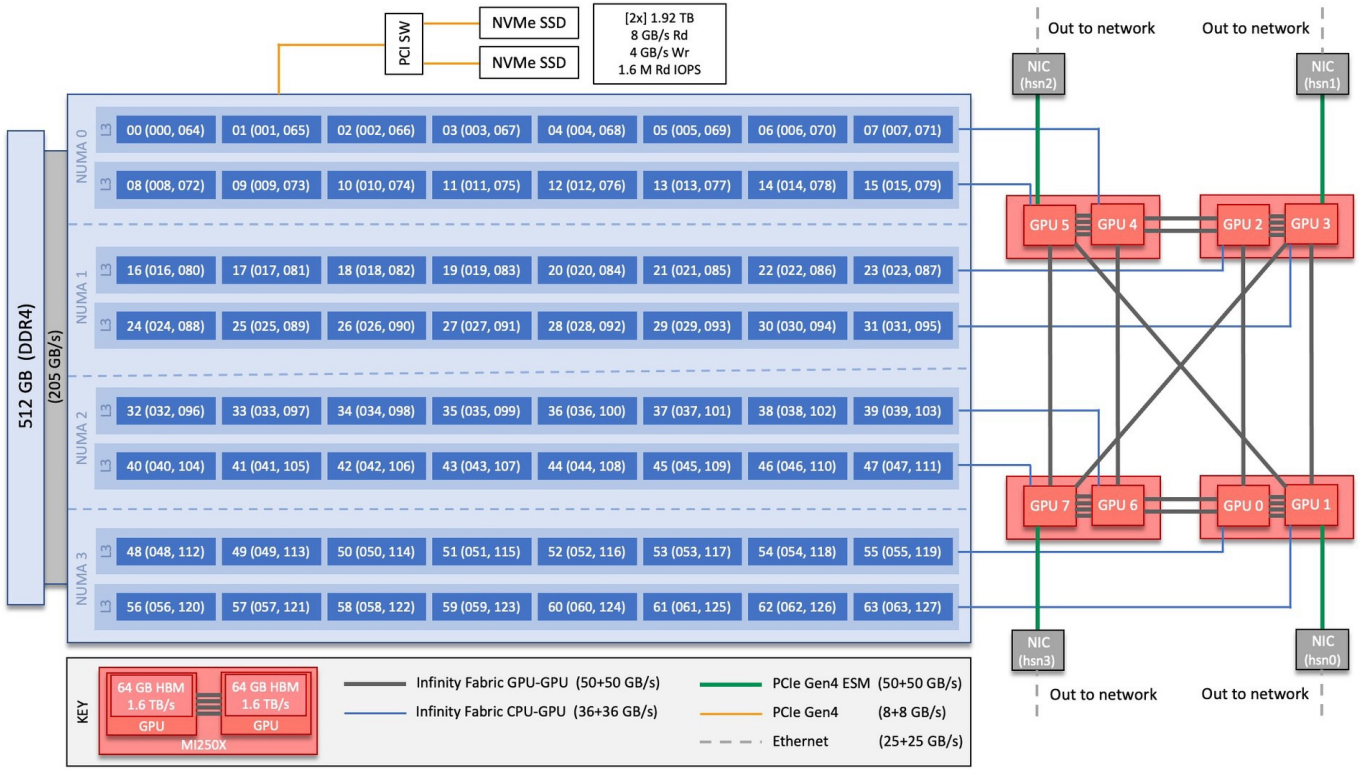
where

$$\lambda = 1/\omega$$



Ref: J. Chem. Theory Comput. (2024) - in preparation

Frontier



Frontier:
- 9,408 AMD compute nodes
- Hybrid CPU/GPU

Compute node:
- 64-core AMD "Optimized 3rd Gen EPYC" CPU
- Memory: 512 GB
- 4x accelerators AMD Radeon Instinct MI250X
- 8X GPUs per node
- 9,408 AMD compute nodes.

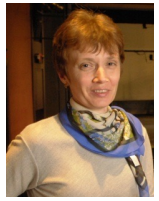
GPU accelerators:
- 4x AMD Radeon Instinct MI250X
- 2x GPU /acceleator
- 14,080 cores
- 128 GB
- 1000 Mhz
- 6nm tech

Acknowledgment

- ORNL

  - **Jingsong Huang**
  - **Syed Islam**
  - **Panchapakesan Ganesh**
  - **David Lingerfelt**
  - **Bobby G. Sumpter**
  - **David S. Sholl**

- University of South Carolina



  - **Sonya Garashchuk**
  - **Vitaly Rassolov**

- North Carolina State University (RMG-DFT)
  - **Jerry Bernholc**
  - **Wenchang Lu**
  - **Emil Briggs**

Spallation Neutron Source (SNS) &
Center for Nanophase Material Science (CNMS)

This work was performed at the Center for Nanophase Materials Sciences, a U.S. Department of Energy Office of Science User Facility.

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