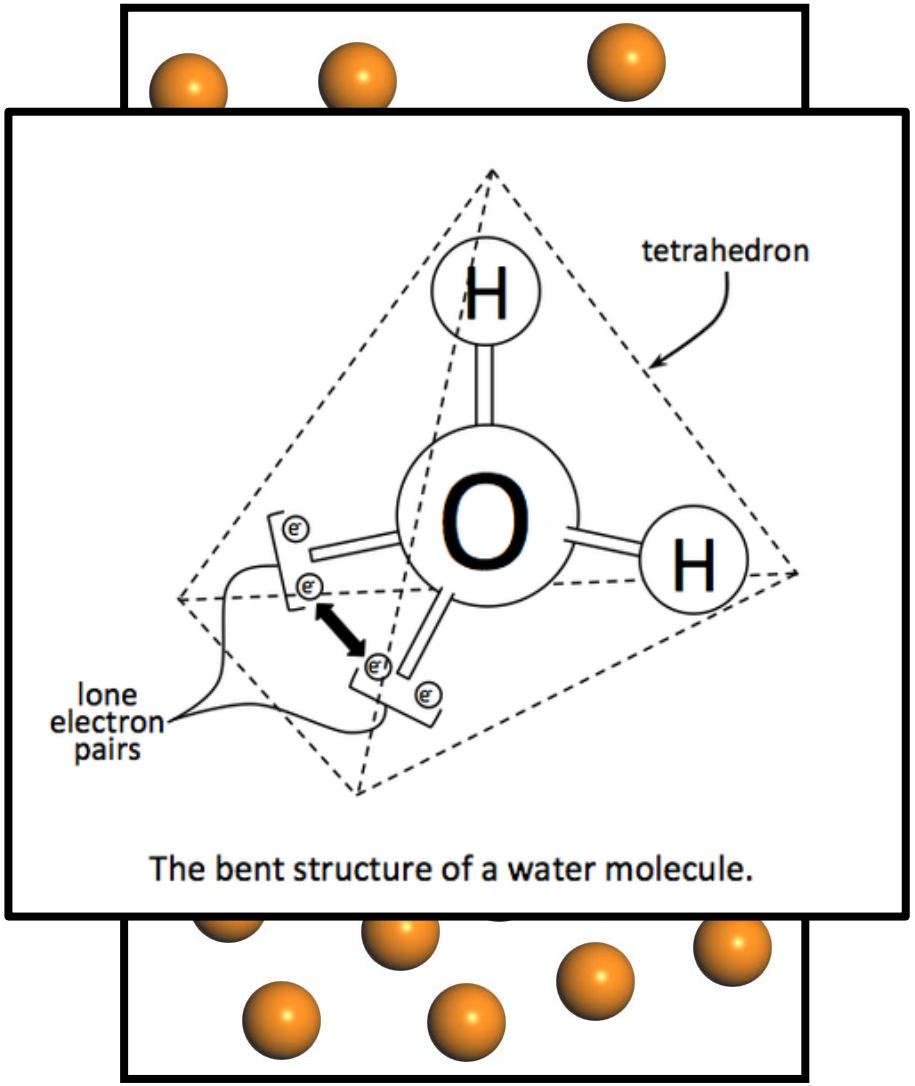
H-Bond Structure and Dynamics from Molecular Dynamics Simulations

Mark DelloStritto

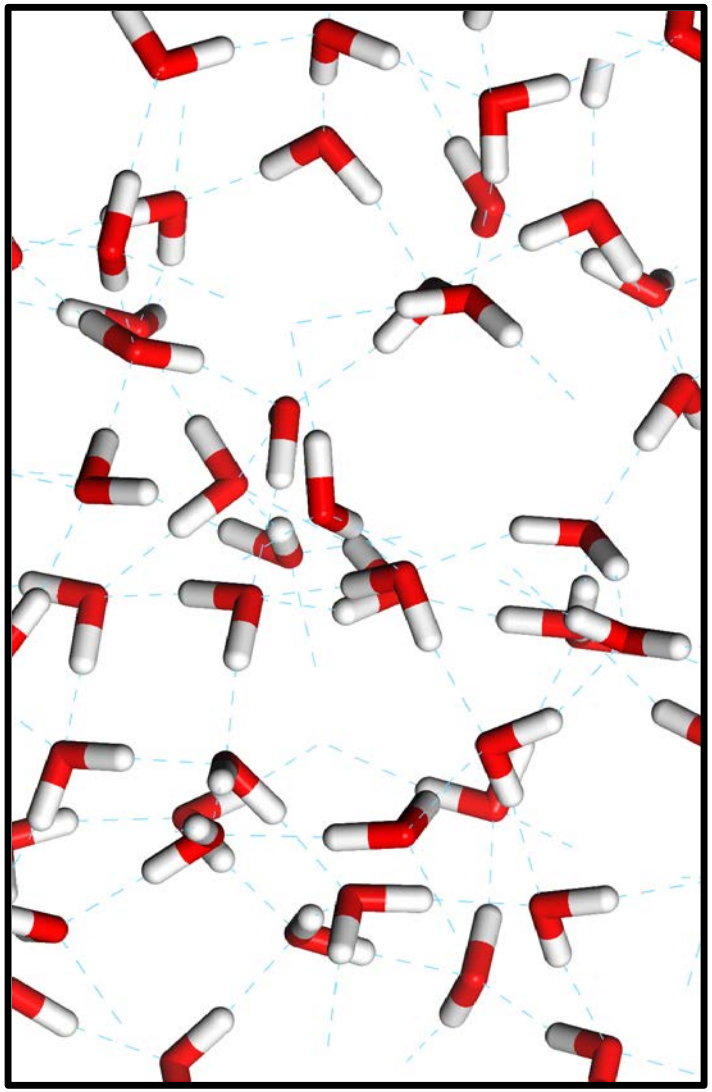
Temple University

Water - "Structured" Liquid

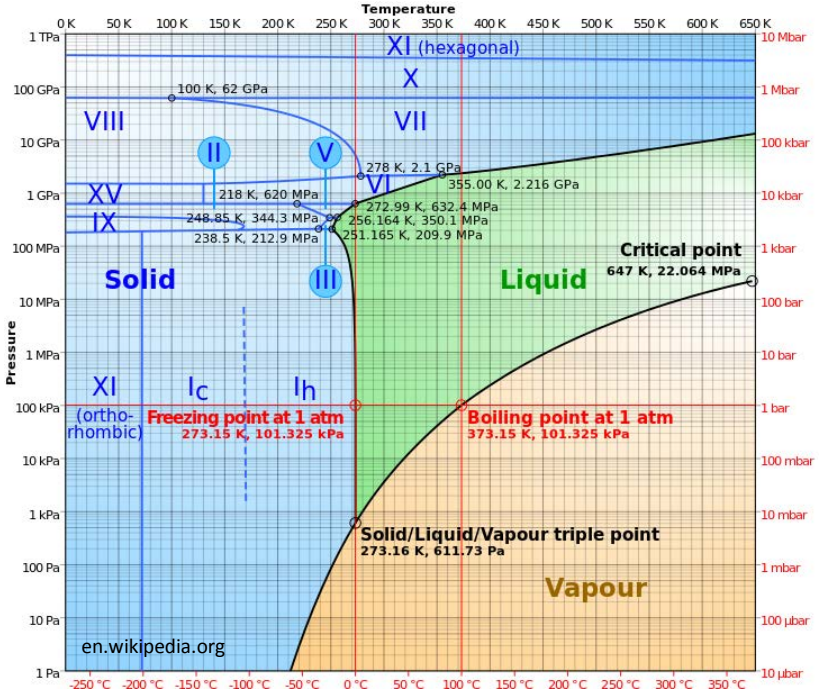
Lennard - Jones

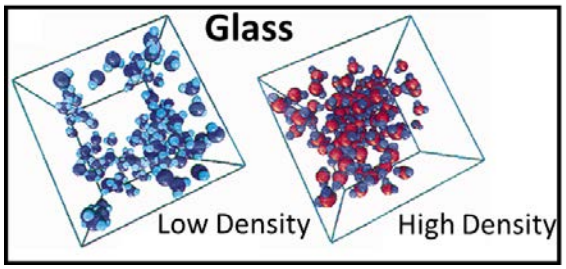


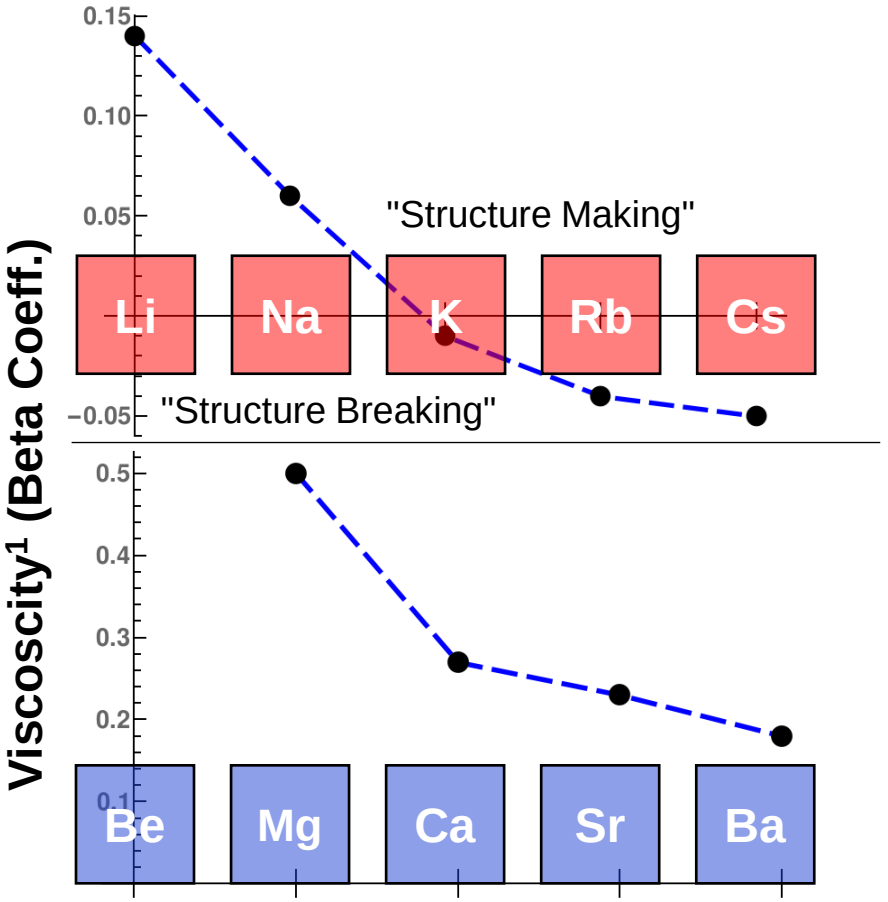
Water



Water - "Structured" Liquid

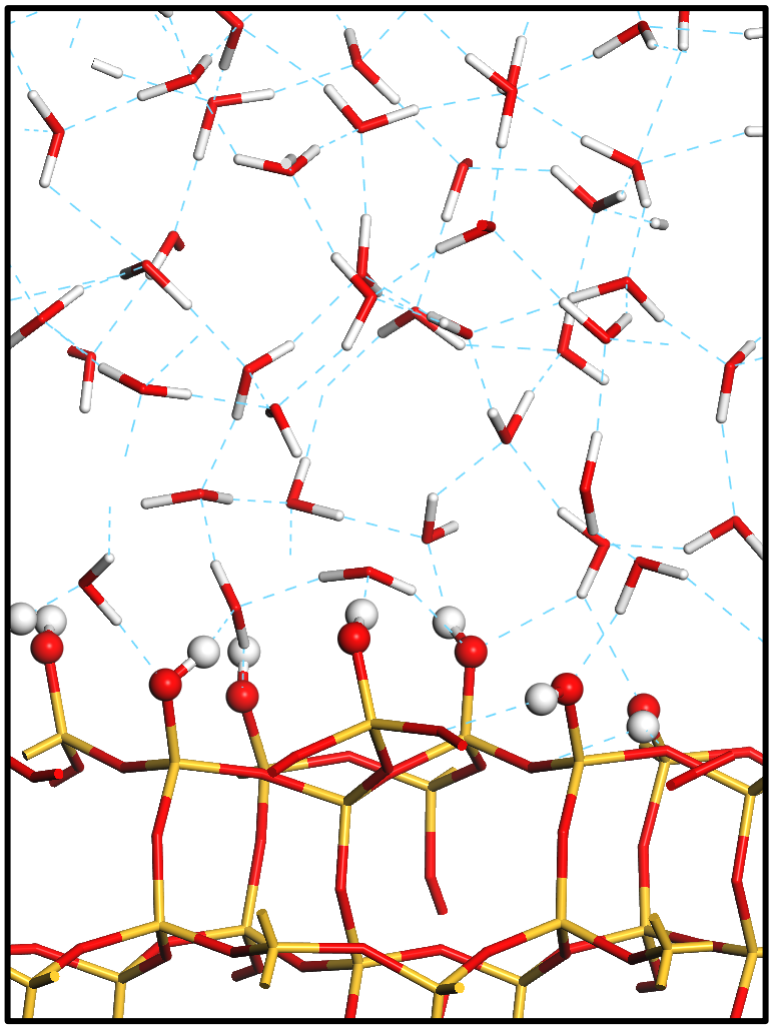






[1] Marcus, Y. Chem. Rev. 109, 1346–1370 (2009).

Structure and Dynamics at Interfaces



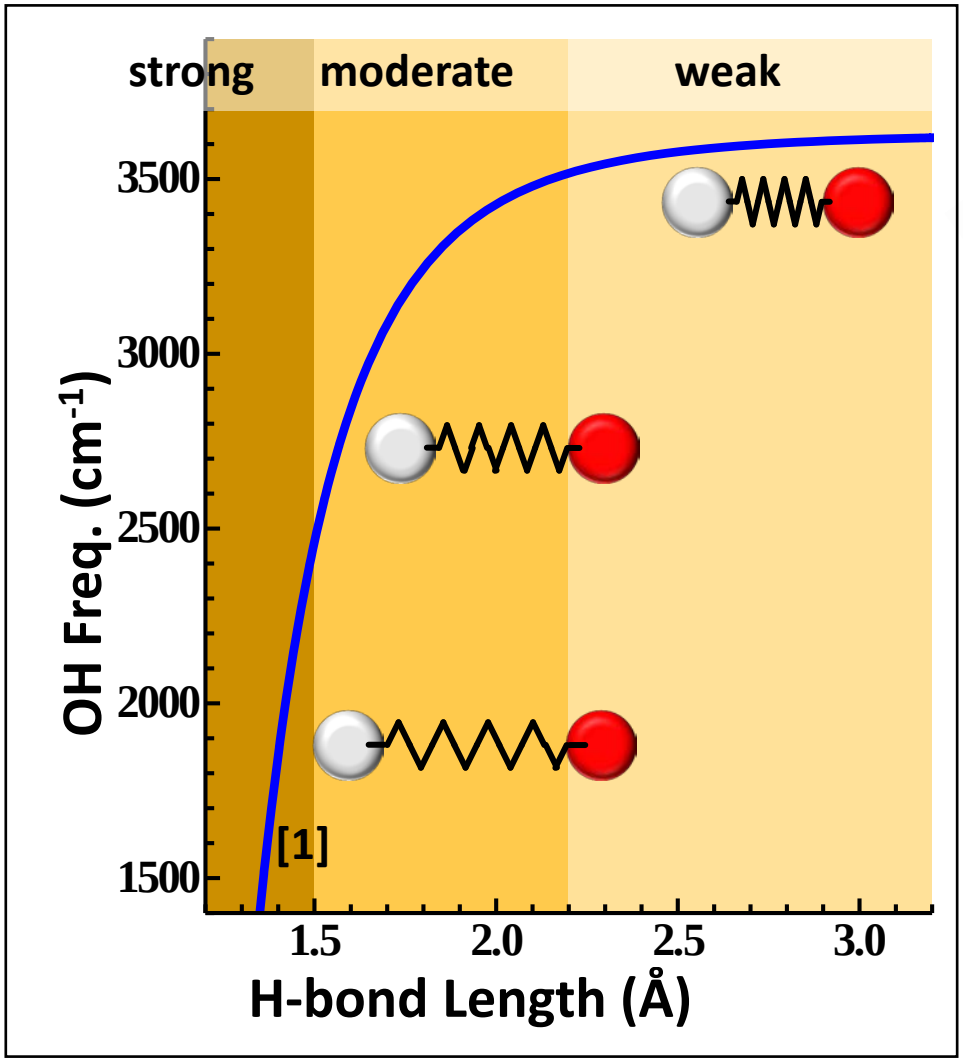
Bulk Water

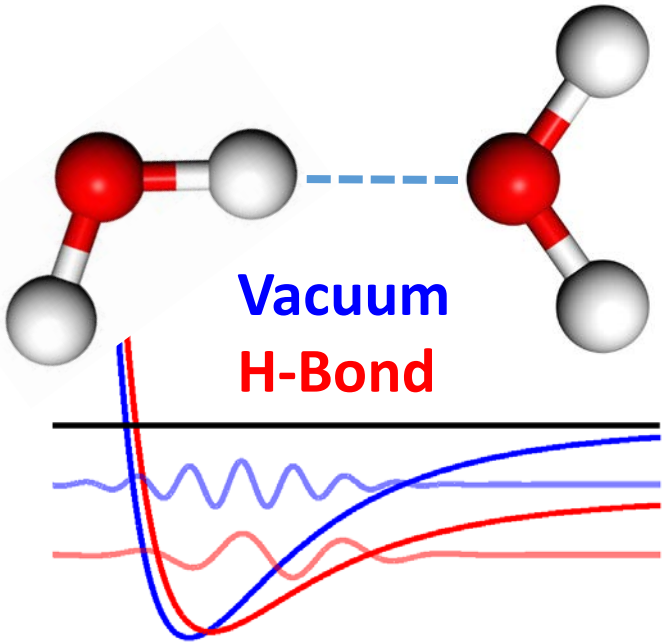
Interfacial Water

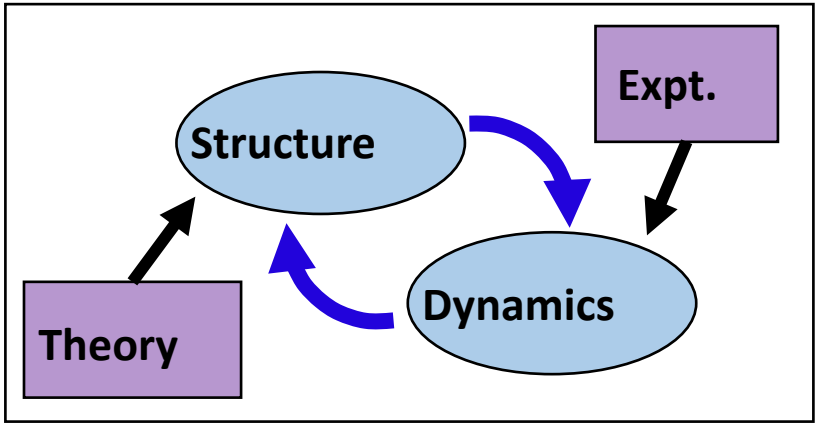
Surface OH Groups

Bulk Oxide

Structure - Dynamics - Spectroscopy





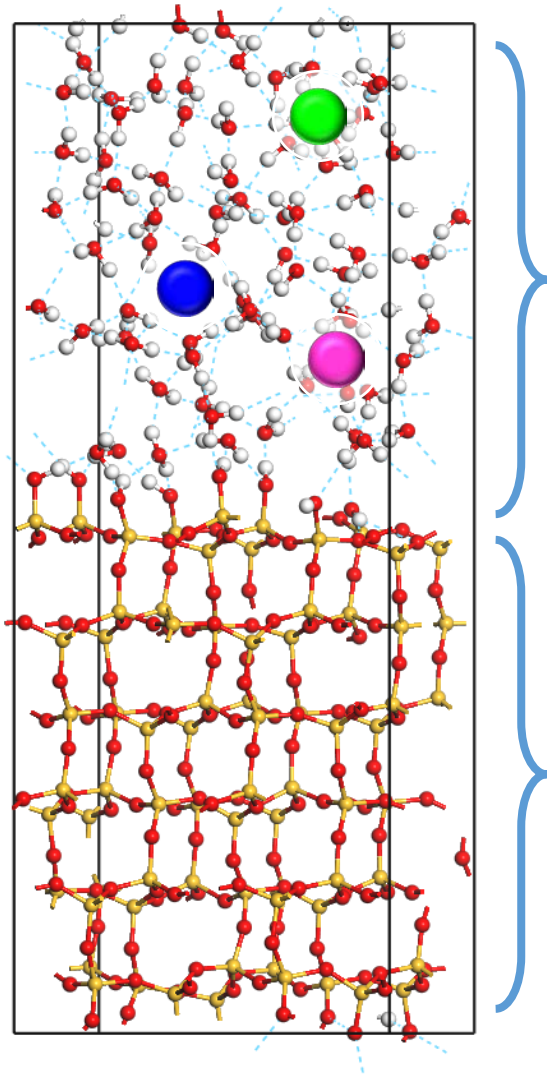


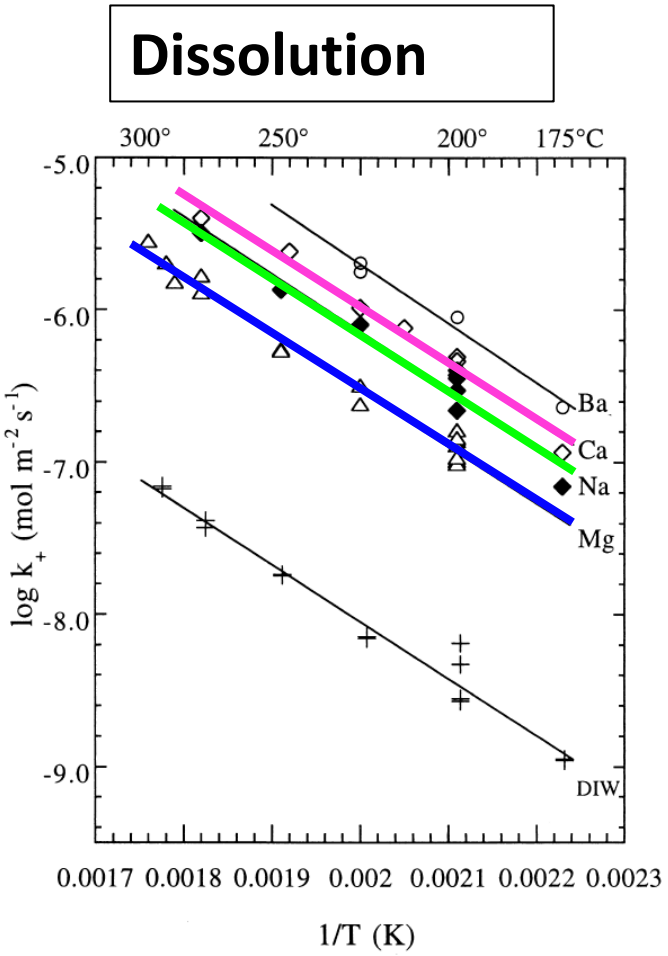
[1] Wang, Hsiu-Wen, Mark J. DelloStritto, et al. *J Phys Chem C* 118,(2014): 10805

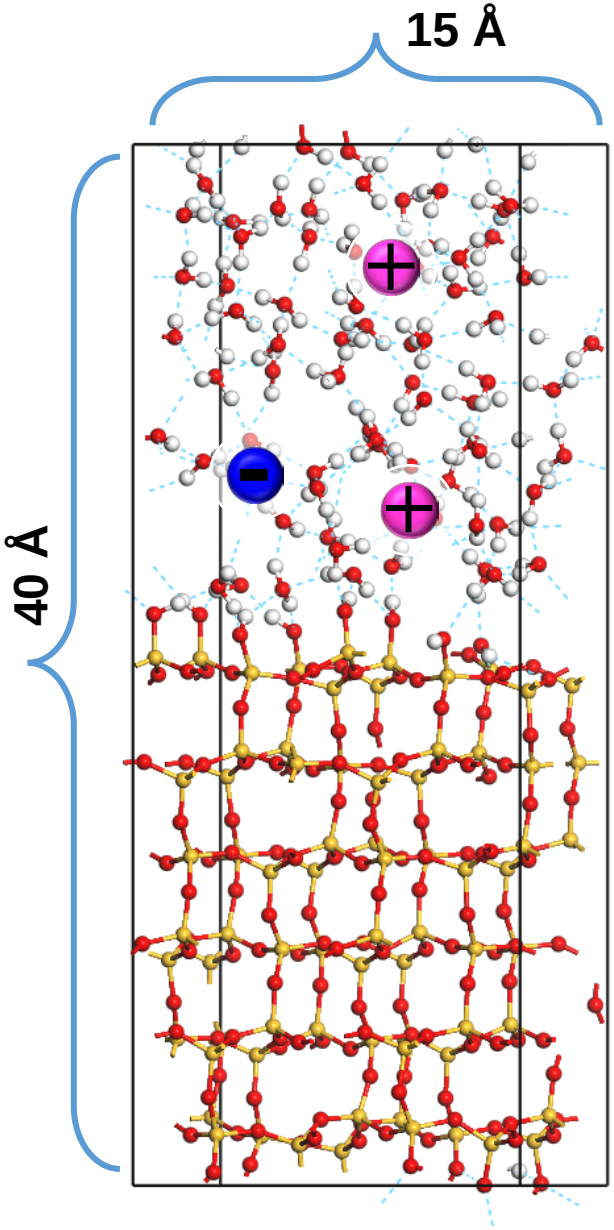
Outline

- $SiO_2(101)$-H_2O Interface
  - Connecting H-bond structure to dynamics
  - Graph description of H-bond network
- $Al_2O_3(0001)$-H_2O Interface
  - Sum Frequency Generation (SFG) Spectroscopy
  - Dynamics and Reproducibility
- $Al_2O_3(1120)$-H_2O Interface
  - SFG at a Disordered Surface
  - Effect of Functional
- Fe/Ni Oxyhydroxides
  - Applications for Water Splitting
  - Dynamics of Confined Water

$SiO_2(101)$-H_2O Interface

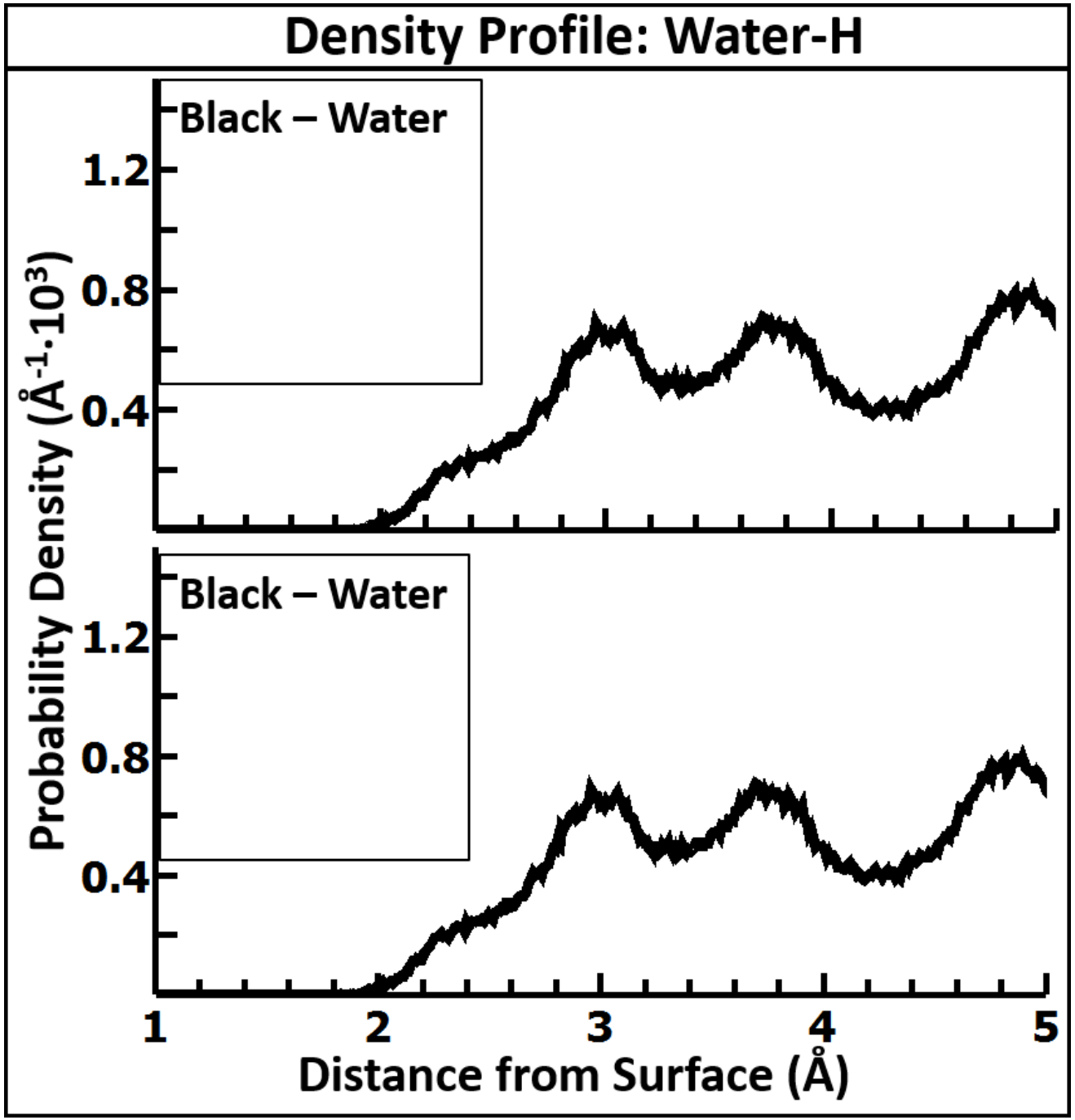


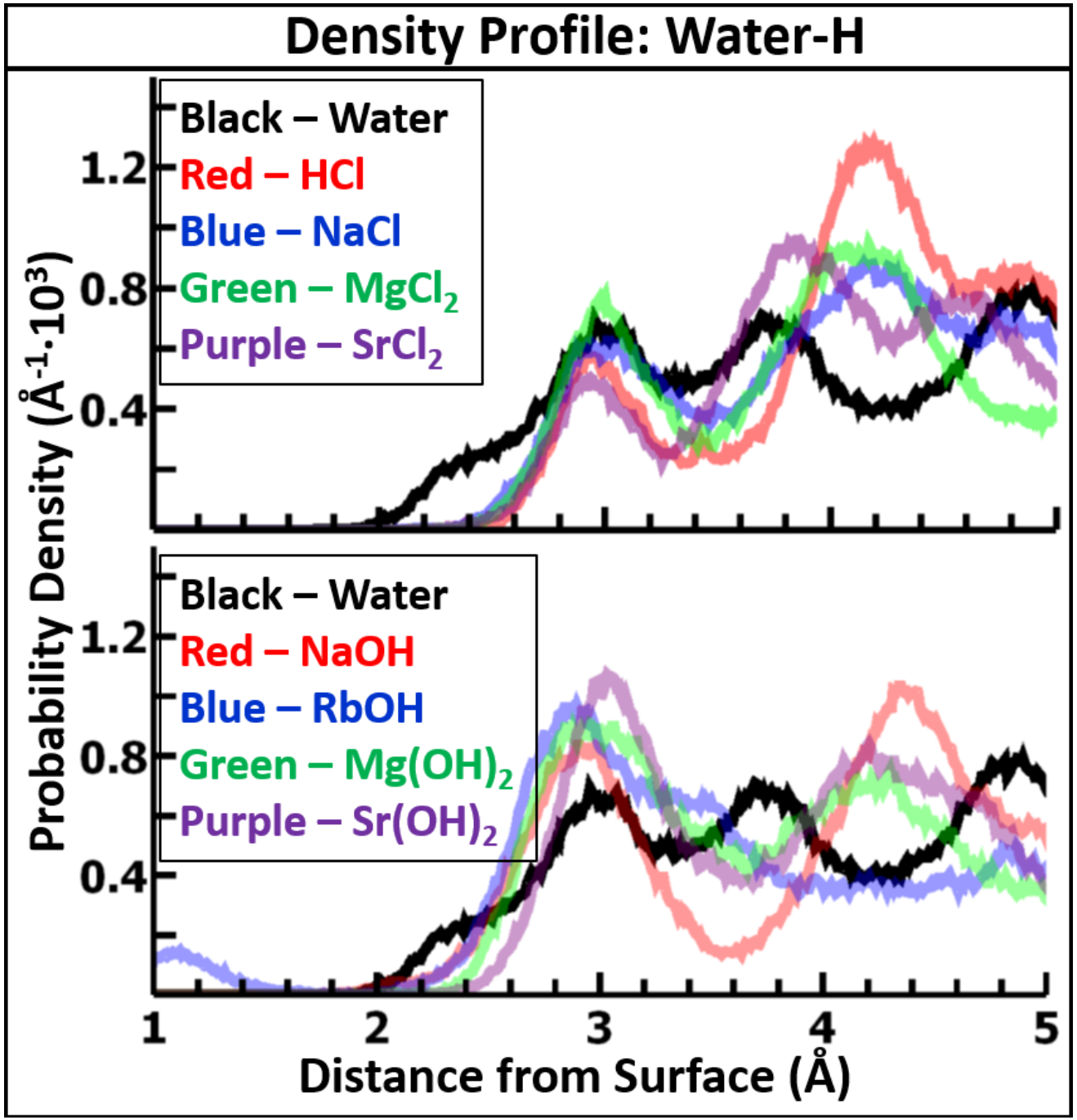


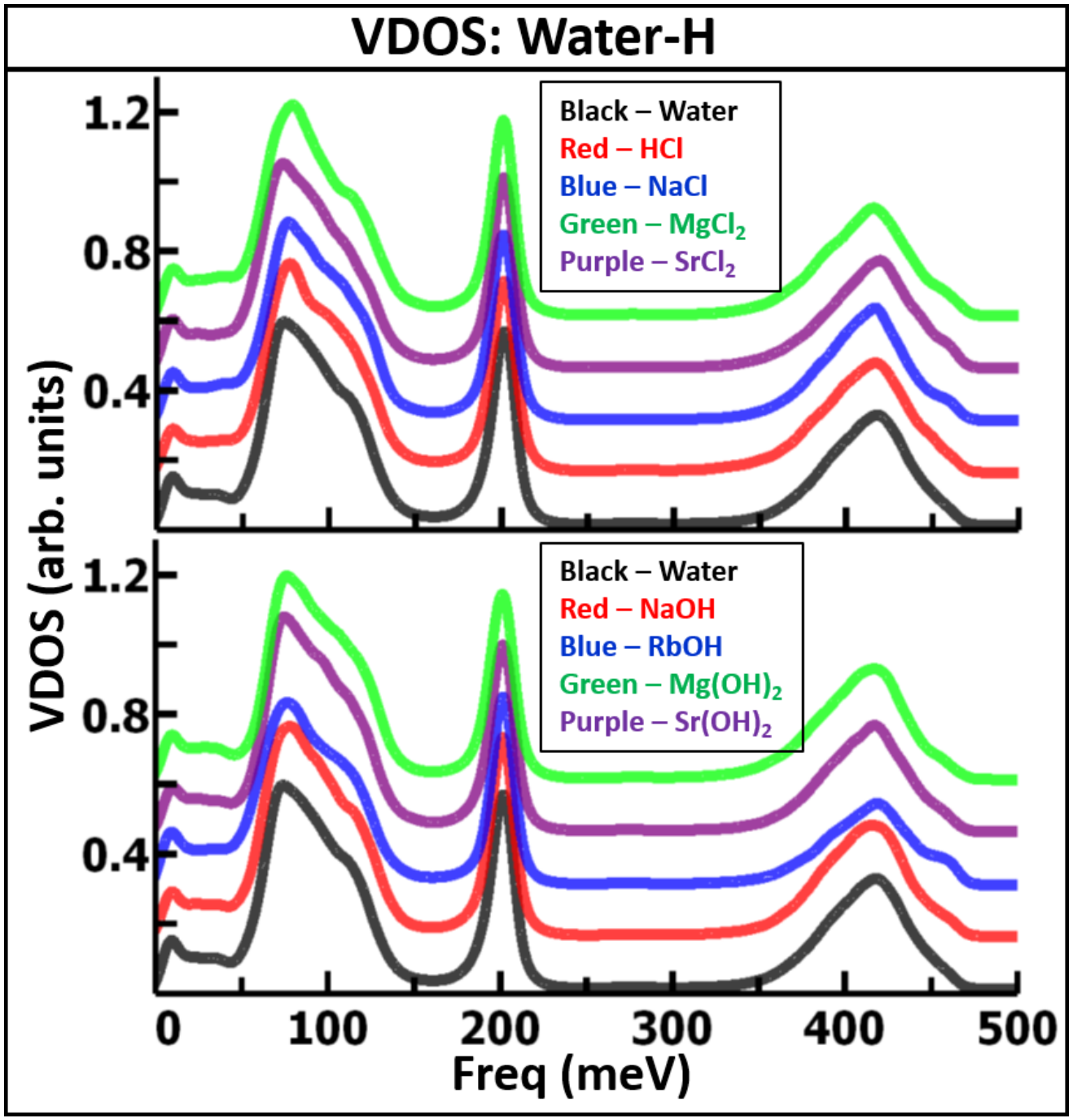


Ab-Initio Simulations

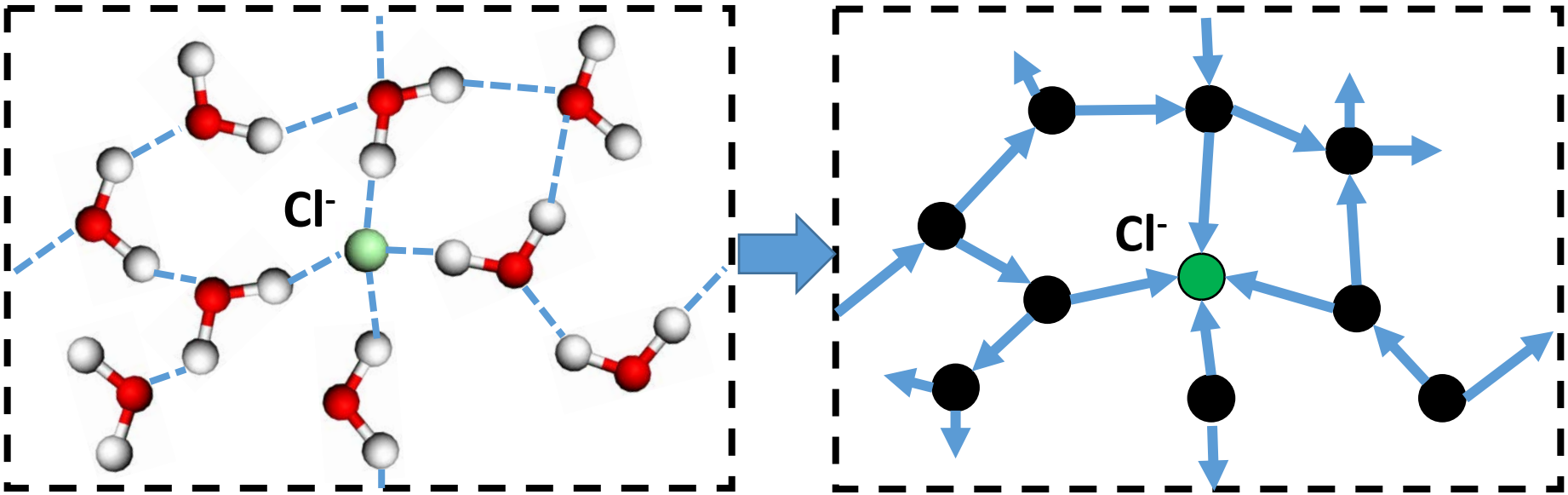
Acidic	Neutral	Basic	
HCl	$SrCl_2$	$Sr(OH)_2$	IIA
	$MgCl_2$	$Mg(OH)_2$	
	NaCl	Na(OH)	IA
		Rb(OH)	

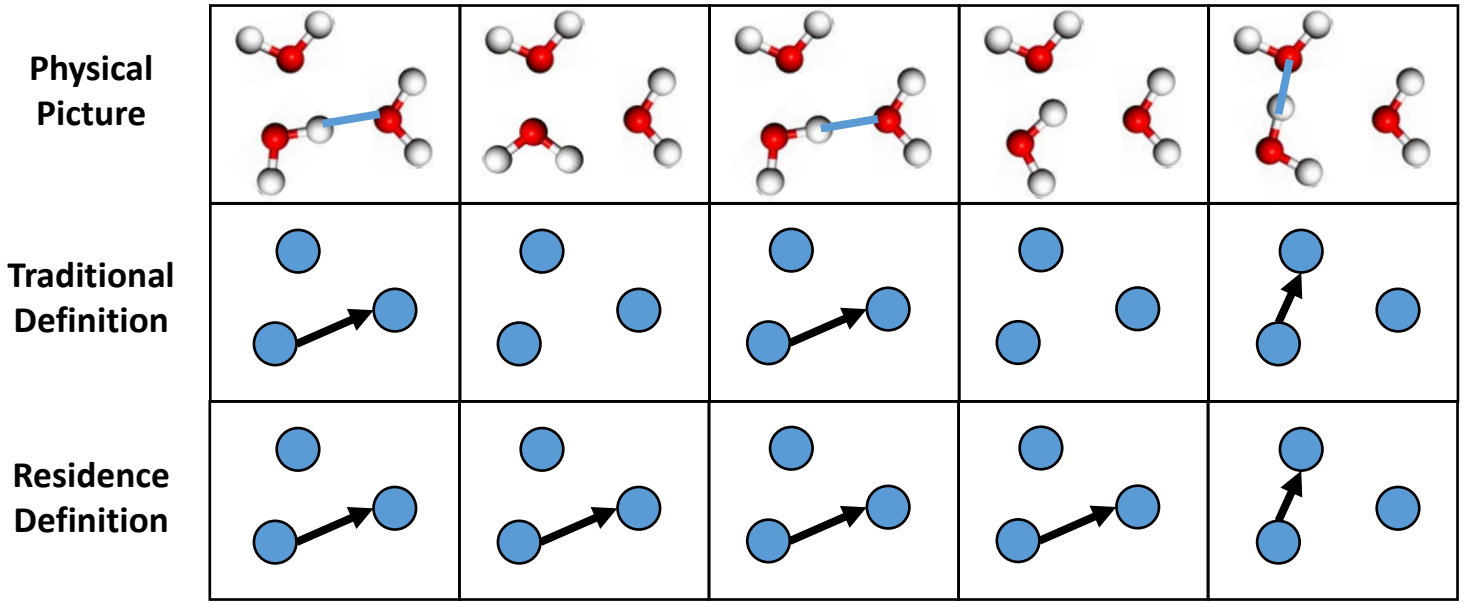

Density Profile: Water-H
Black – Water
1.2
0.8
0.4
Probability Density (Å-1.10³)
Black – Water
1.2
0.8
0.4
1
2
3
4
5
Distance from Surface (Å)


Density Profile: Water-H
Black – Water
Red – HCl
Blue – NaCl
Green – MgCl2
Purple – SrCl2
Black – Water
Red – NaOH
Blue – RbOH
Green – Mg(OH)2
Purple – Sr(OH)2
Probability Density (Å-1.10³)
1.2
0.8
0.4
1
2
3
4
5
Distance from Surface (Å)

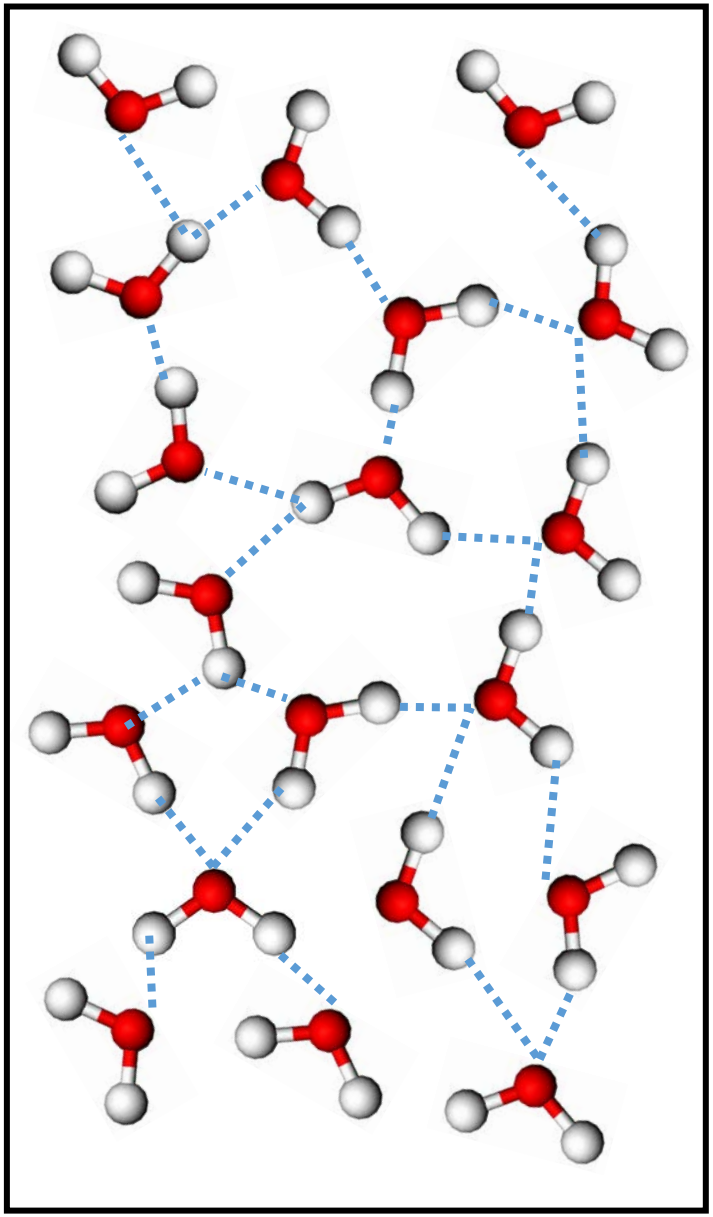

VDOS: Water-H
Black – Water
Red – HCl
Blue – NaCl
Green – MgCl2
Purple – SrCl2
Black – Water
Red – NaOH
Blue – RbOH
Green – Mg(OH)2
Purple – Sr(OH)2
VDOS (arb. units)
1.2
0.8
0.4
0
100
200
300
400
500
Freq (meV)

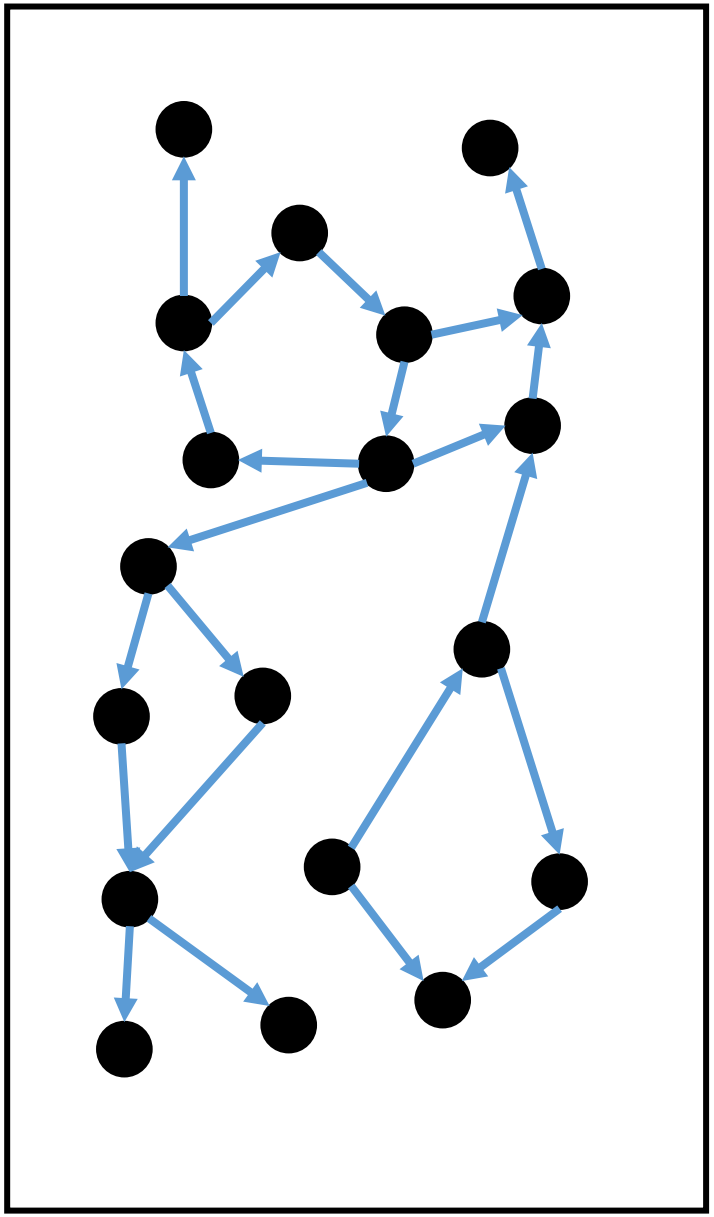
H-Bond Network: Graph Representation



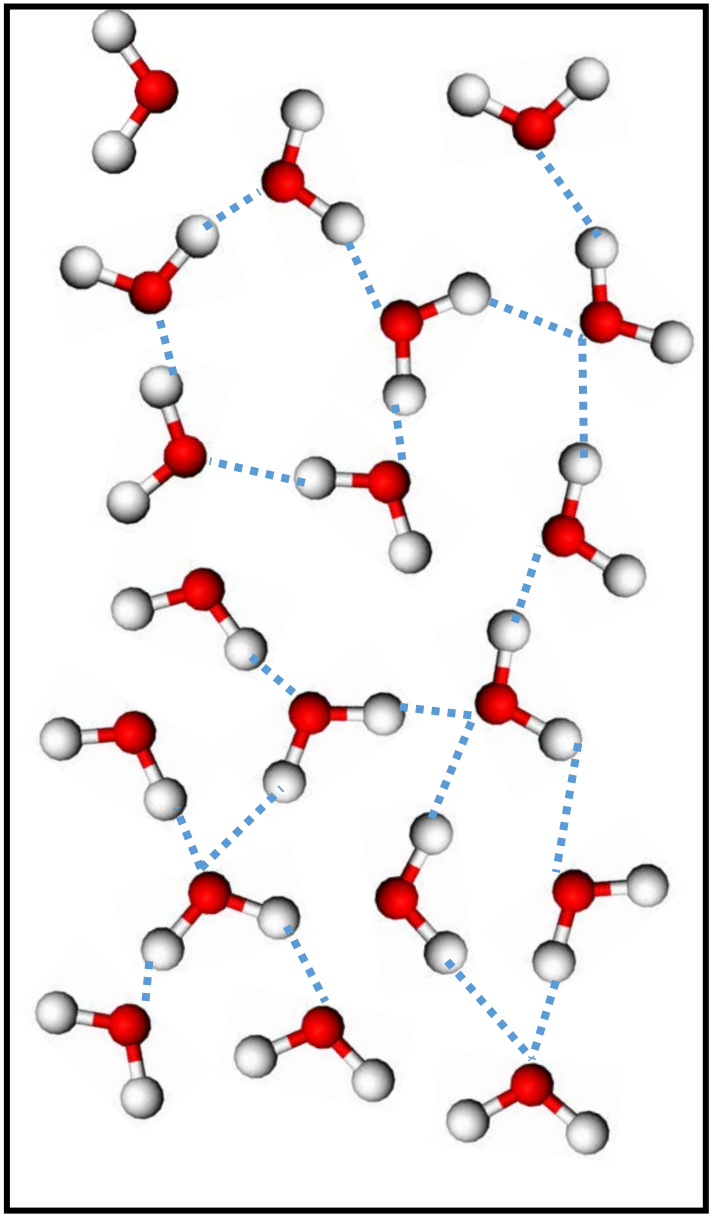


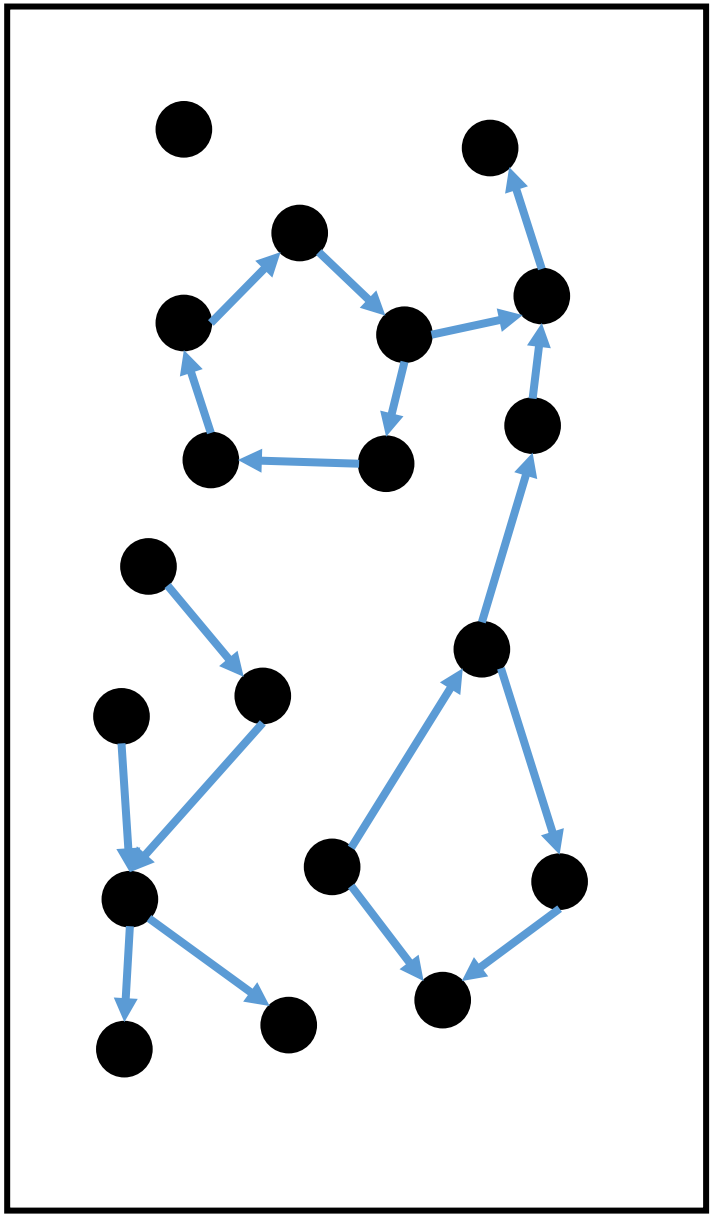
Network Correlation Function



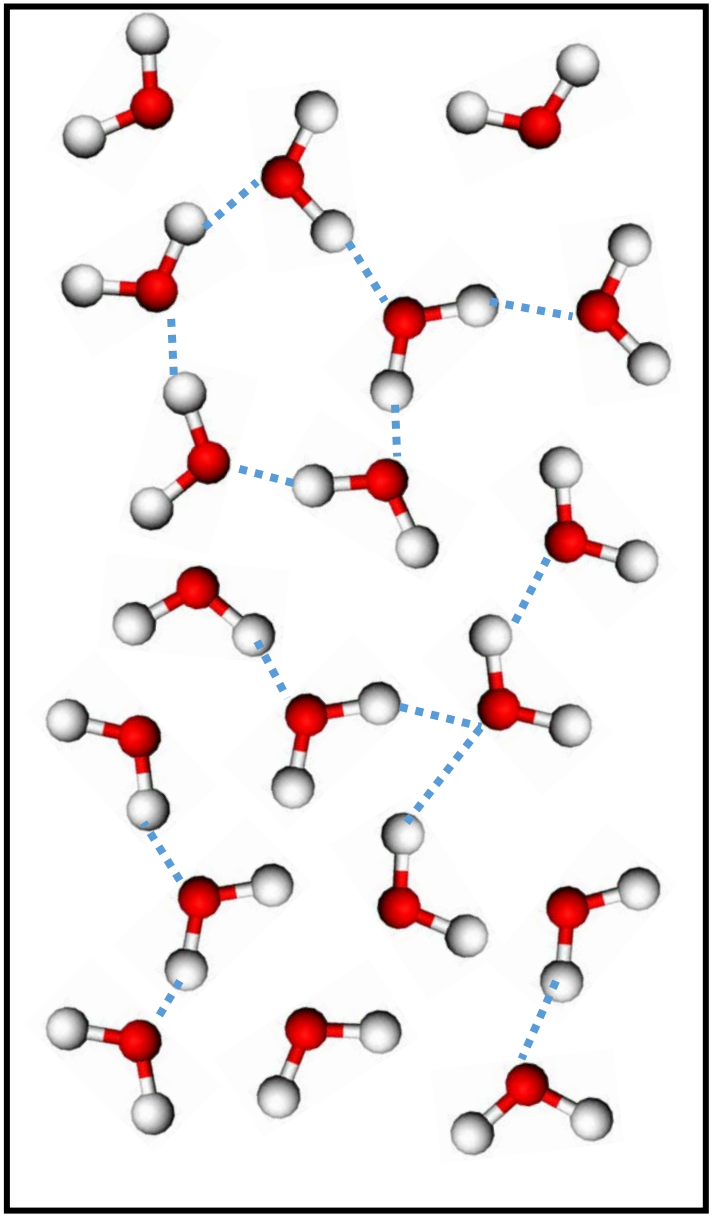


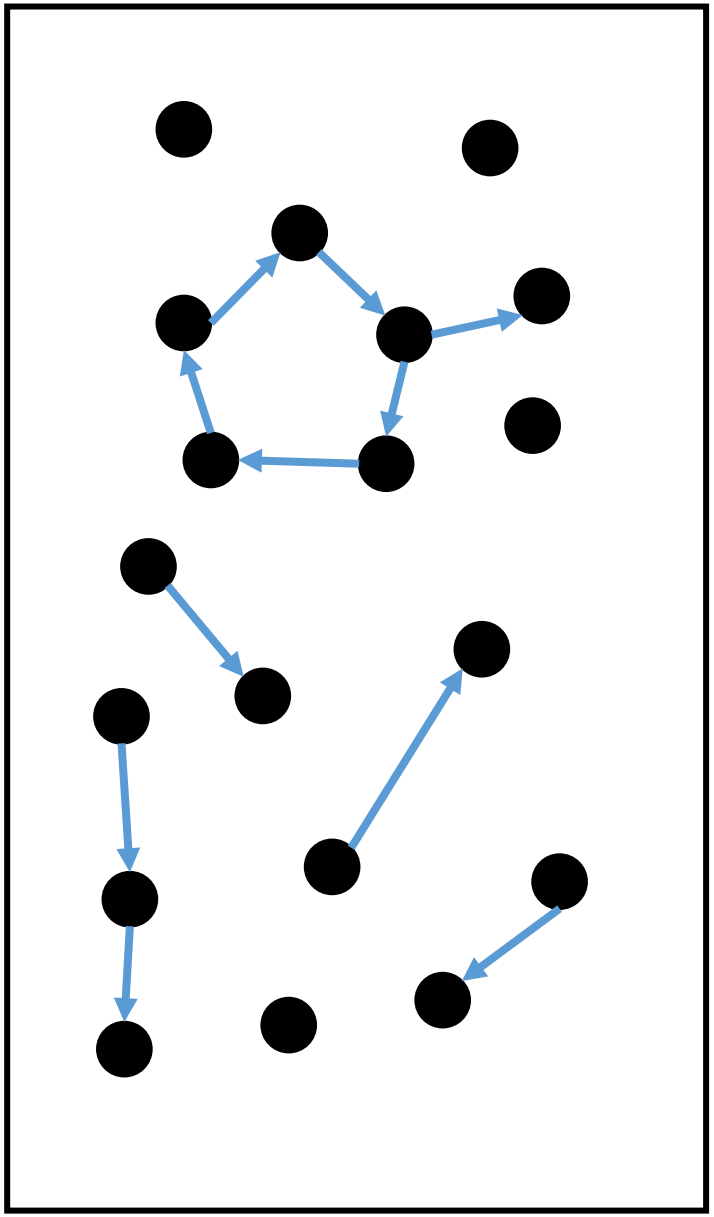
Network Correlation Function

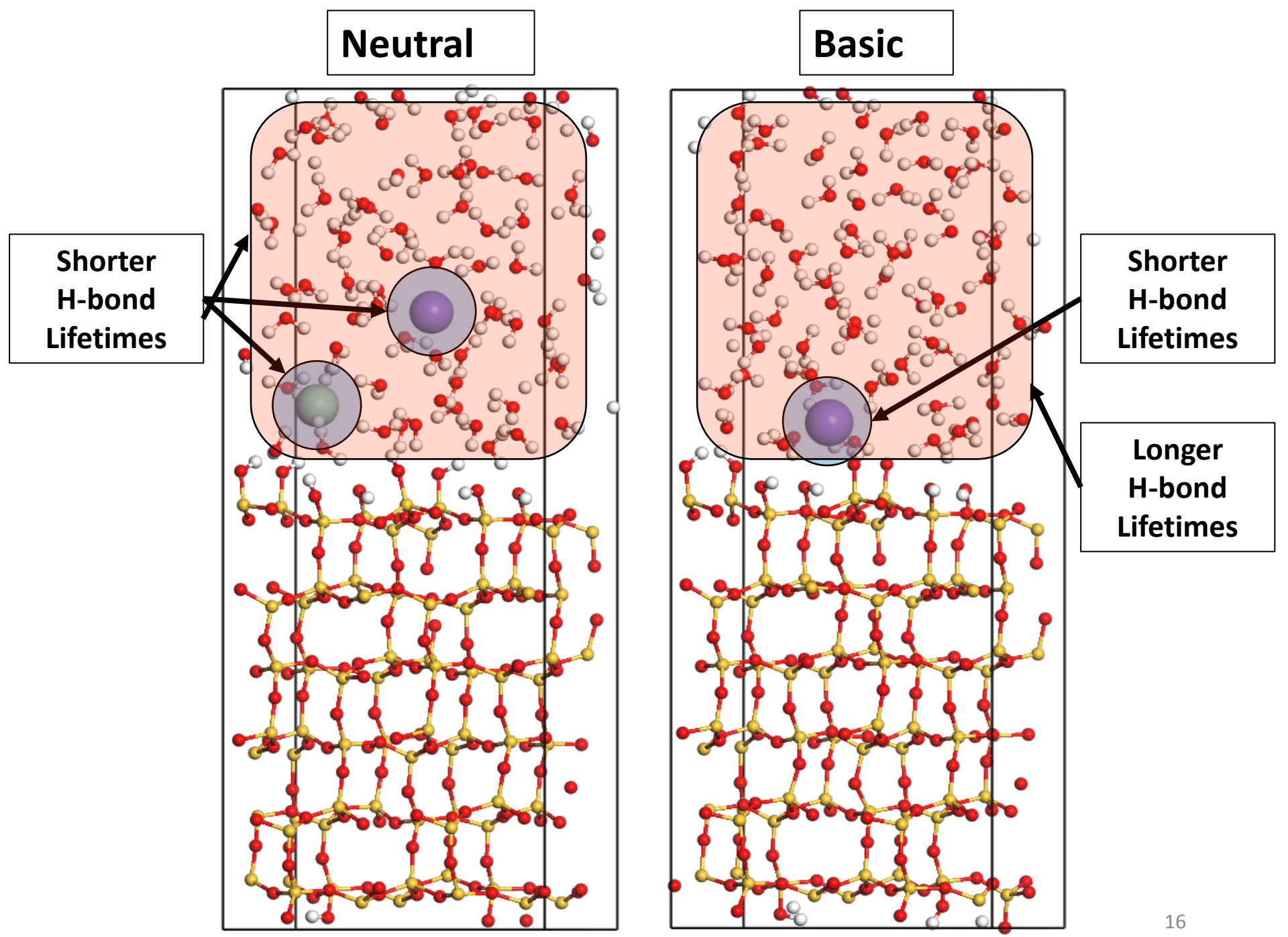




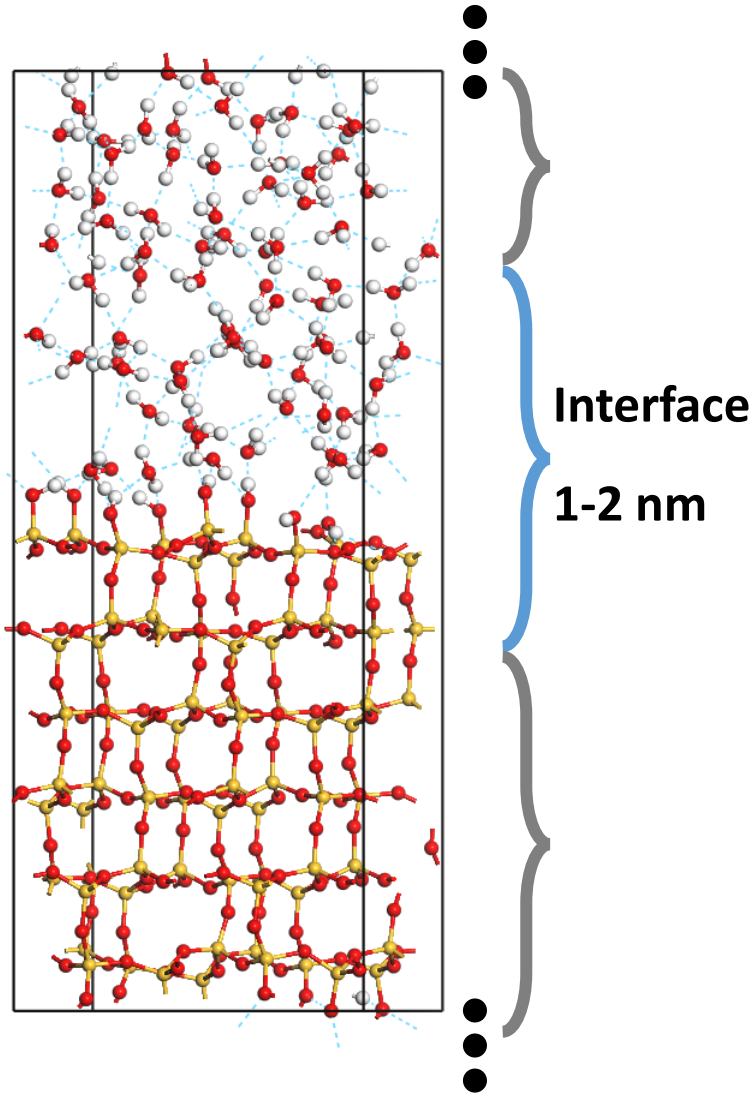
Network Correlation Function

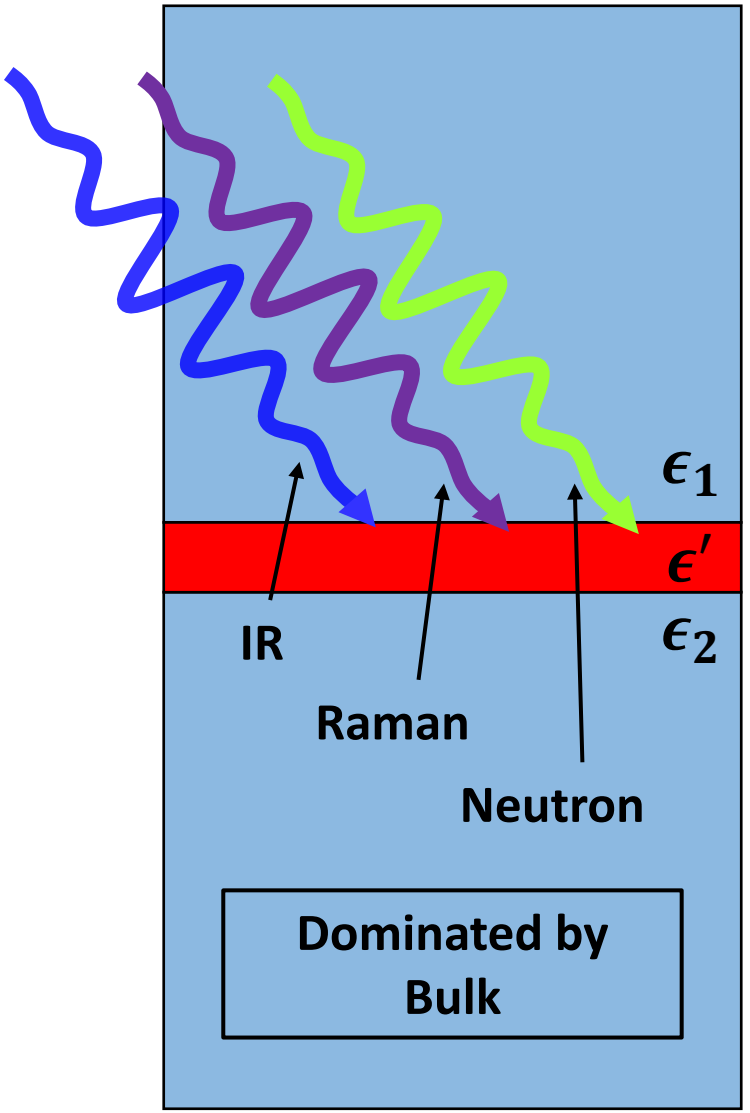




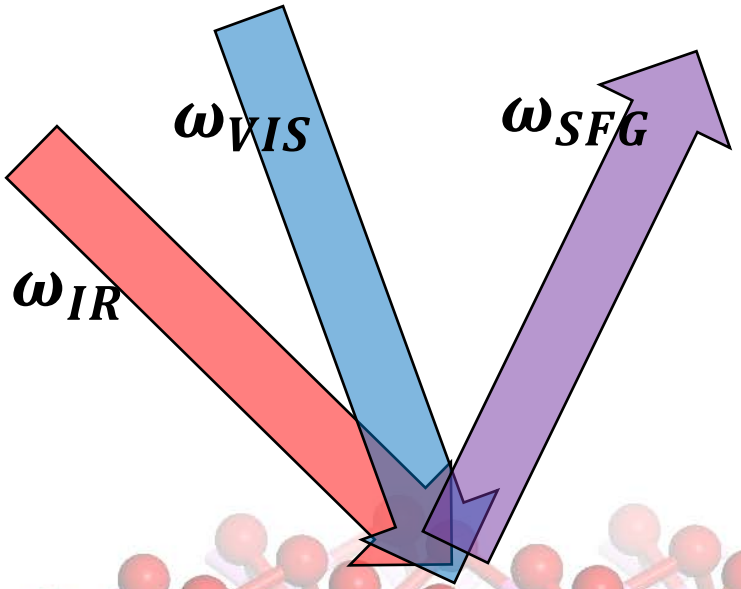

Neutral
Basic
Shorter H-bond Lifetimes
Shorter H-bond Lifetimes
Longer H-bond Lifetimes

Interface ≈ 2D





Sum Frequency Generation (SFG)



$$\vec{E}_{SFG} \propto \chi^{(2)} \vec{E}_{IR} \vec{E}_{vis}$$

$$\chi^{(2)}(\omega) \begin{cases} = 0 \; in \; bulk \\ \neq 0 \; at \; interface \end{cases}$$

Surface Specific Vibrational Probe

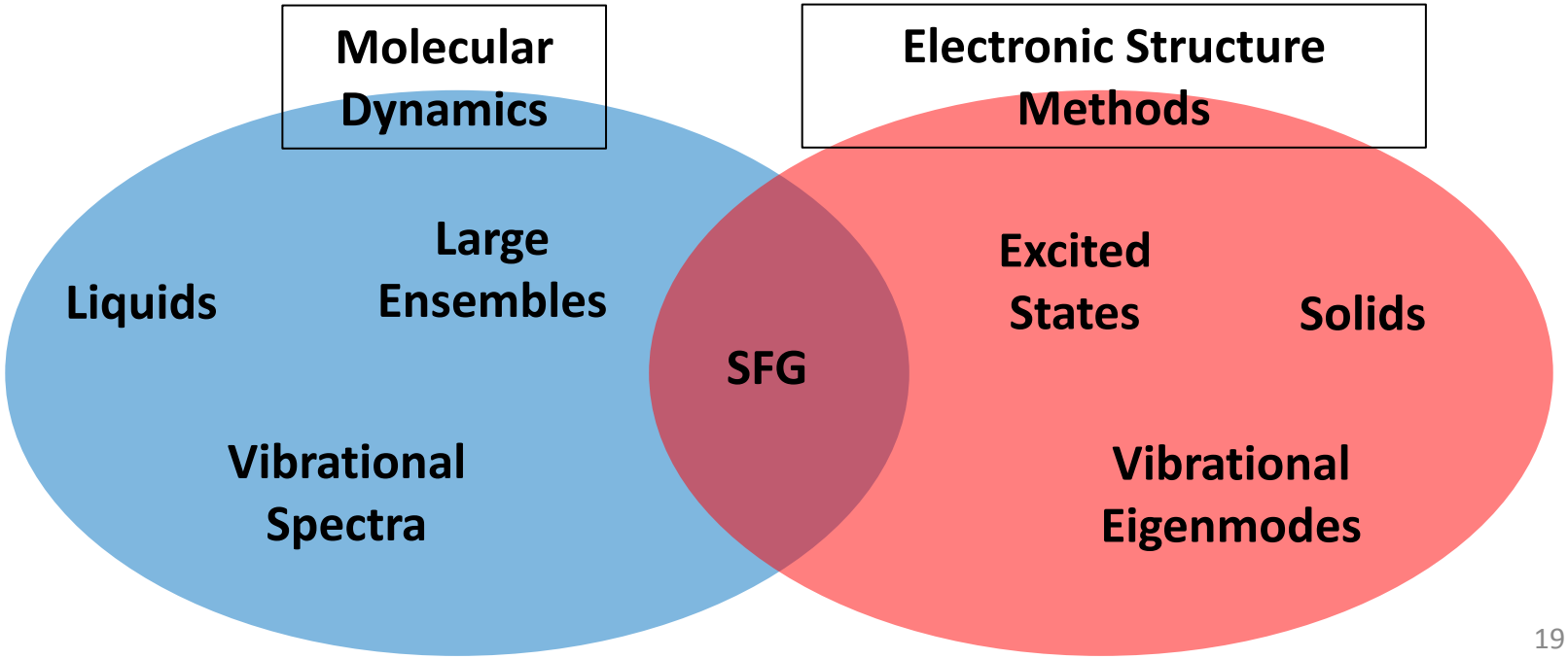
$$I(\omega_{IR}) \propto \left|\chi^{(2)}(\omega_{IR})\right|^2$$

$\chi^{(2)}(\omega)$ → **Surface Vib. Spectrum** → **H-bond Dynamics + Structure**

Calculation: Challenges

Linear: $\chi^{(1)}(\omega) = \sum_{nm} \frac{\mu_{nm}\mu_{mn}}{\omega - \omega_{nm}}$

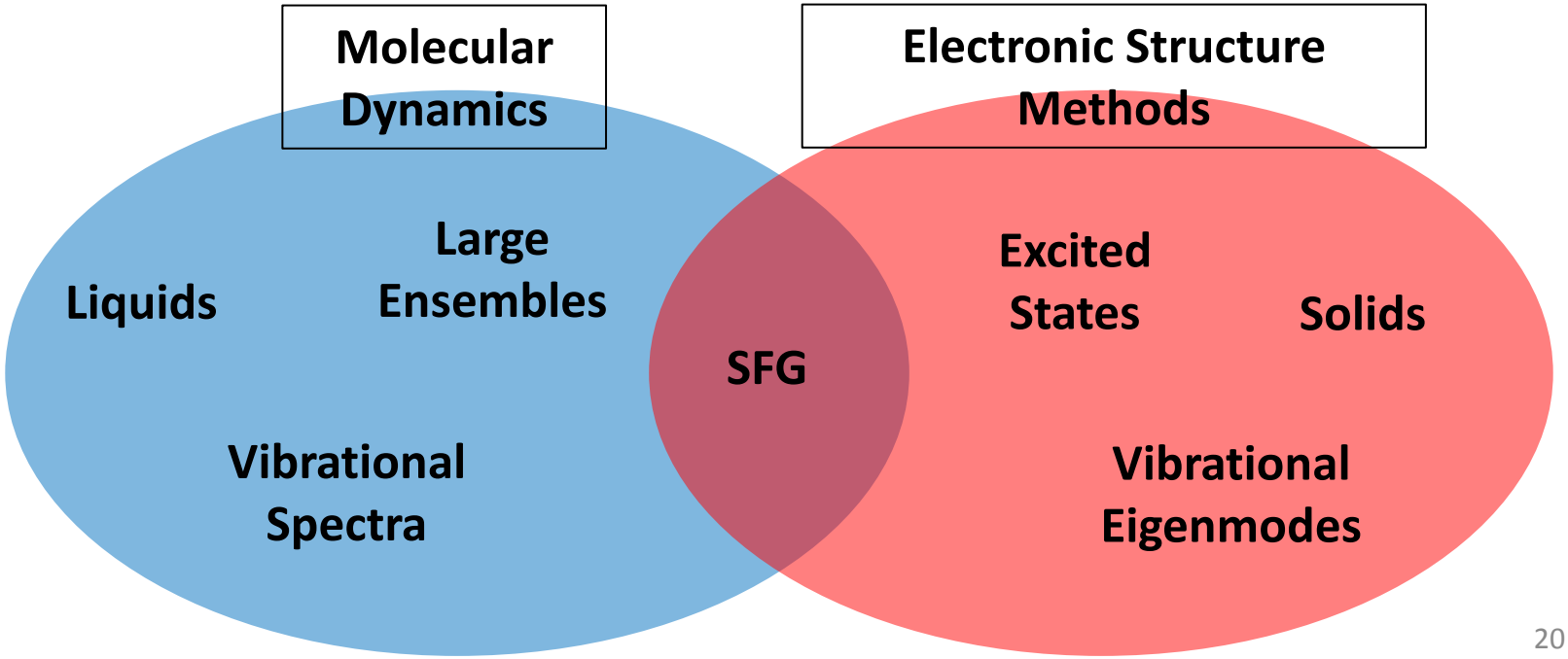
2nd Order: $\chi^{(2)}(\omega_{vis} + \omega_{IR}) = \sum_{nm} \frac{\alpha_{nm}\mu_{mn}}{(\omega_{IR} - \omega_{nm})(\omega_{IR} + \omega_{VIS} - \omega_{nm})}$



Calculation: Challenges

Linear: $\chi^{(1)}(\omega) \propto \int_0^\infty \langle \mu(t)\mu(0)\rangle e^{i\omega t} dt$

2nd Order: $\chi^{(2)}(\omega_{vis} + \omega_{IR}) \propto \int_0^\infty \langle \alpha(t)\mu(0)\rangle e^{i\omega_{IR} t} dt$

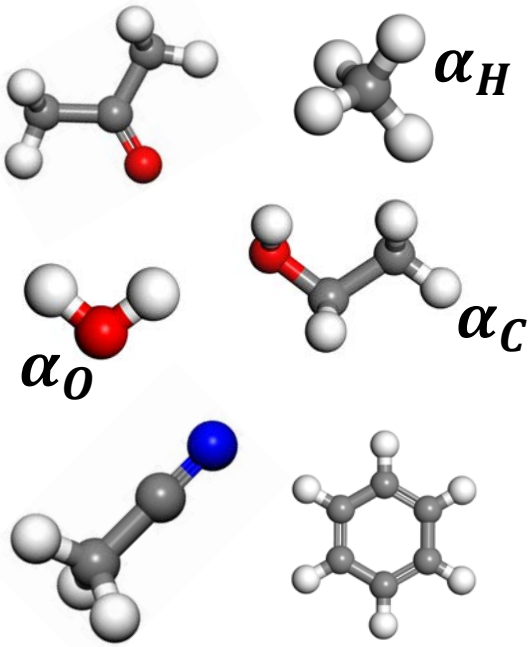


Calculation: Solutions

Separate the Atomic and Electronic Dynamics

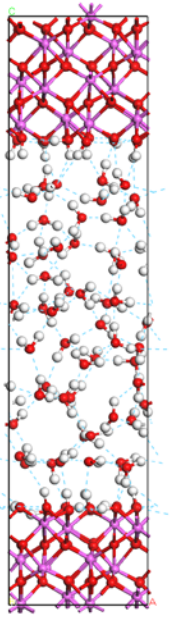
Pre-Processing

Fit atomic α to training set



Molecular Dynamics

Run MD Simulation



Post-Processing

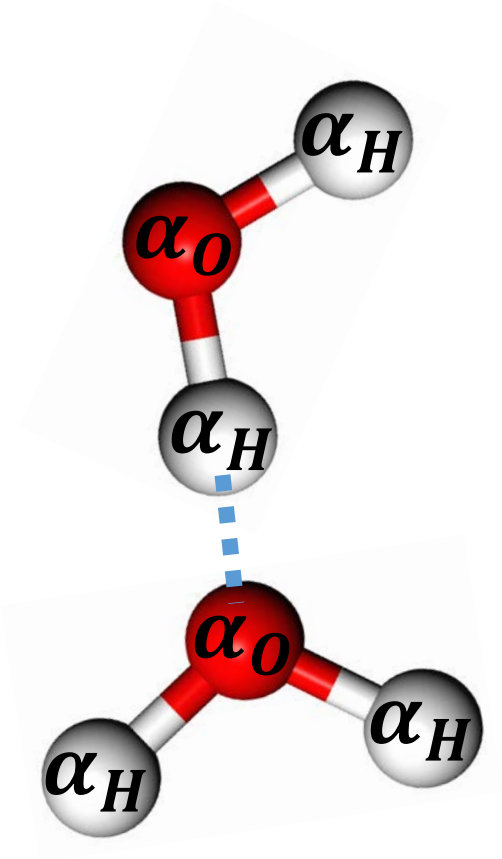
Find Effective α, Self-Consistent μ

$$\alpha_{Tot} = \sum_n \alpha_n^{(eff)}$$

$$\mu_{Tot} = \sum_n \mu_n^{(sc)}$$

$$\chi^{(2)}(\omega) \propto \Im[\langle \alpha_{Tot} \mu_{Tot} \rangle]$$

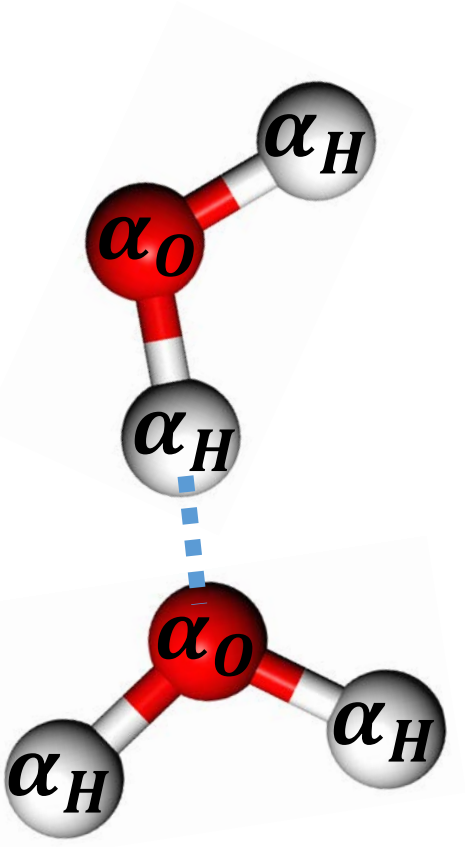
Effective Polarizabilities



$$\boldsymbol{\mu_i = \alpha_i(E + T_{ij}\mu_j)}$$

$$\boldsymbol{T_{ij} = \frac{3r_{ij}r_{ij}^T - Ir_{ij}^T r_{ij}}{r_{ij}^T r_{ij}}}$$

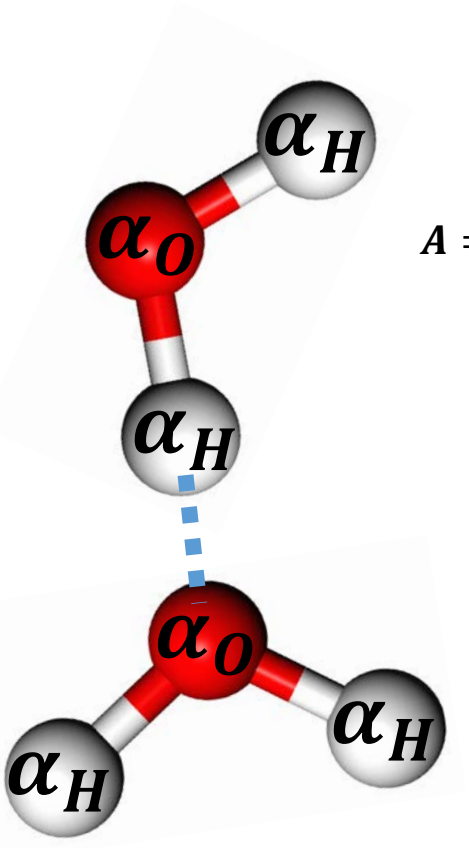
Effective Polarizabilities



$$\begin{pmatrix} \mu_O \\ \mu_H \\ \mu_H \\ \mu_O \\ \mu_H \\ \mu_H \end{pmatrix} = \begin{pmatrix} \alpha_O & 0 & 0 \\ 0 & \alpha_H & 0 \\ 0 & 0 & \alpha_H \end{pmatrix} \otimes \begin{pmatrix} I & 0 \\ 0 & I \end{pmatrix} \times$$

$$\left[\begin{pmatrix} E \\ E \\ E \\ E \\ E \\ E \end{pmatrix} + \begin{pmatrix} 0 & T_{OH} & T_{HH}T_{OO} & T_{OH} & T_{HH} \\ T_{OH} & 0 & T_{HH}T_{OH} & T_{HH} & T_{HH} \\ T_{HH} & T_{HH} & 0 \; T_{HH} & T_{HH} & T_{HH} \\ T_{OO} & T_{OH} & T_{HH} \; 0 & T_{OH} & T_{HH} \\ T_{OH} & T_{HH} & T_{HH}T_{OH} & 0 & T_{HH} \\ T_{HH} & T_{HH} & T_{HH}T_{HH} & T_{HH} & 0 \end{pmatrix} \times \begin{pmatrix} \mu_O \\ \mu_H \\ \mu_H \\ \mu_O \\ \mu_H \\ \mu_H \end{pmatrix} \right]$$

Effective Polarizabilities

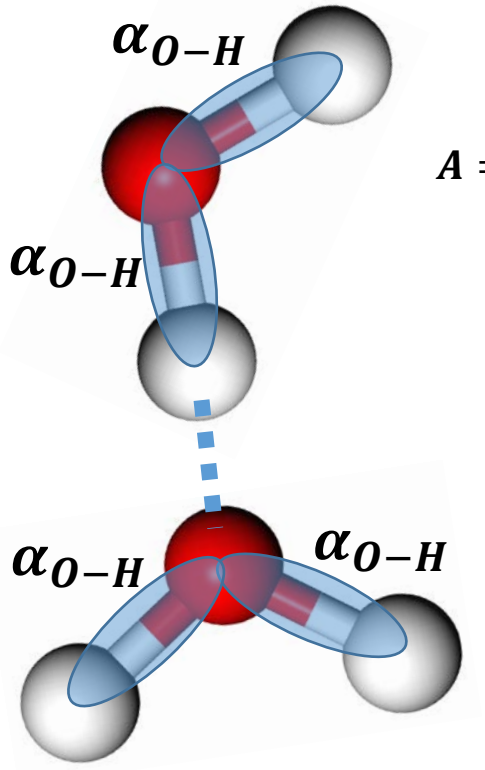


$$\boldsymbol{\mu = AE}$$

$$\boldsymbol{A = \left[\begin{pmatrix} \alpha_O^{-1} & T_{OH} & T_{OH} \\ T_{OH} & \alpha_H^{-1} & T_{HH} \\ T_{OH} & T_{HH} & \alpha_H^{-1} \end{pmatrix} \otimes \begin{pmatrix} I & 0 \\ 0 & I \end{pmatrix} + \begin{pmatrix} T_{OO} & T_{OH} & T_{OH} \\ T_{OH} & T_{HH} & T_{HH} \\ T_{OH} & T_{HH} & T_{HH} \end{pmatrix} \otimes \begin{pmatrix} 0 & I \\ I & 0 \end{pmatrix} \right]^{-1}}$$

$$\boldsymbol{\alpha_T} \leftarrow \begin{pmatrix} A_{11} & \cdots & A_{1n} \\ \vdots & \ddots & \vdots \\ A_{n1} & \cdots & A_{nn} \end{pmatrix} \rightarrow \boldsymbol{\alpha_1^{eff}}, \quad \boldsymbol{\alpha_n^{eff}}$$

Effective Polarizabilities



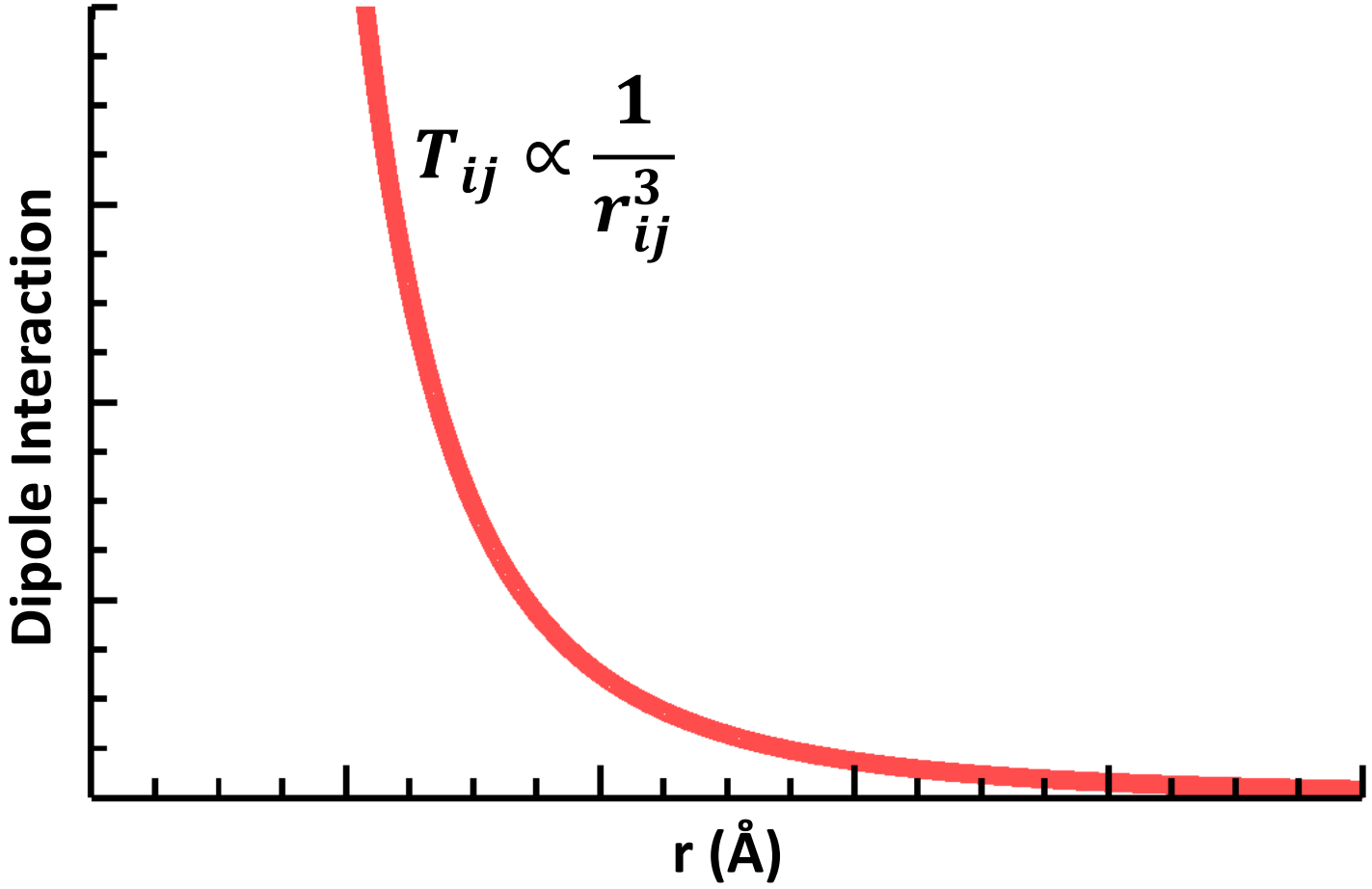
$$\boldsymbol{\mu = AE}$$

$$\boldsymbol{A = \left[\begin{pmatrix} \alpha_O^{-1} & T_{OH} & T_{OH} \\ T_{OH} & \alpha_H^{-1} & T_{HH} \\ T_{OH} & T_{HH} & \alpha_H^{-1} \end{pmatrix} \otimes \begin{pmatrix} I & 0 \\ 0 & I \end{pmatrix} + \begin{pmatrix} T_{OO} & T_{OH} & T_{OH} \\ T_{OH} & T_{HH} & T_{HH} \\ T_{OH} & T_{HH} & T_{HH} \end{pmatrix} \otimes \begin{pmatrix} 0 & I \\ I & 0 \end{pmatrix} \right]^{-1}}$$

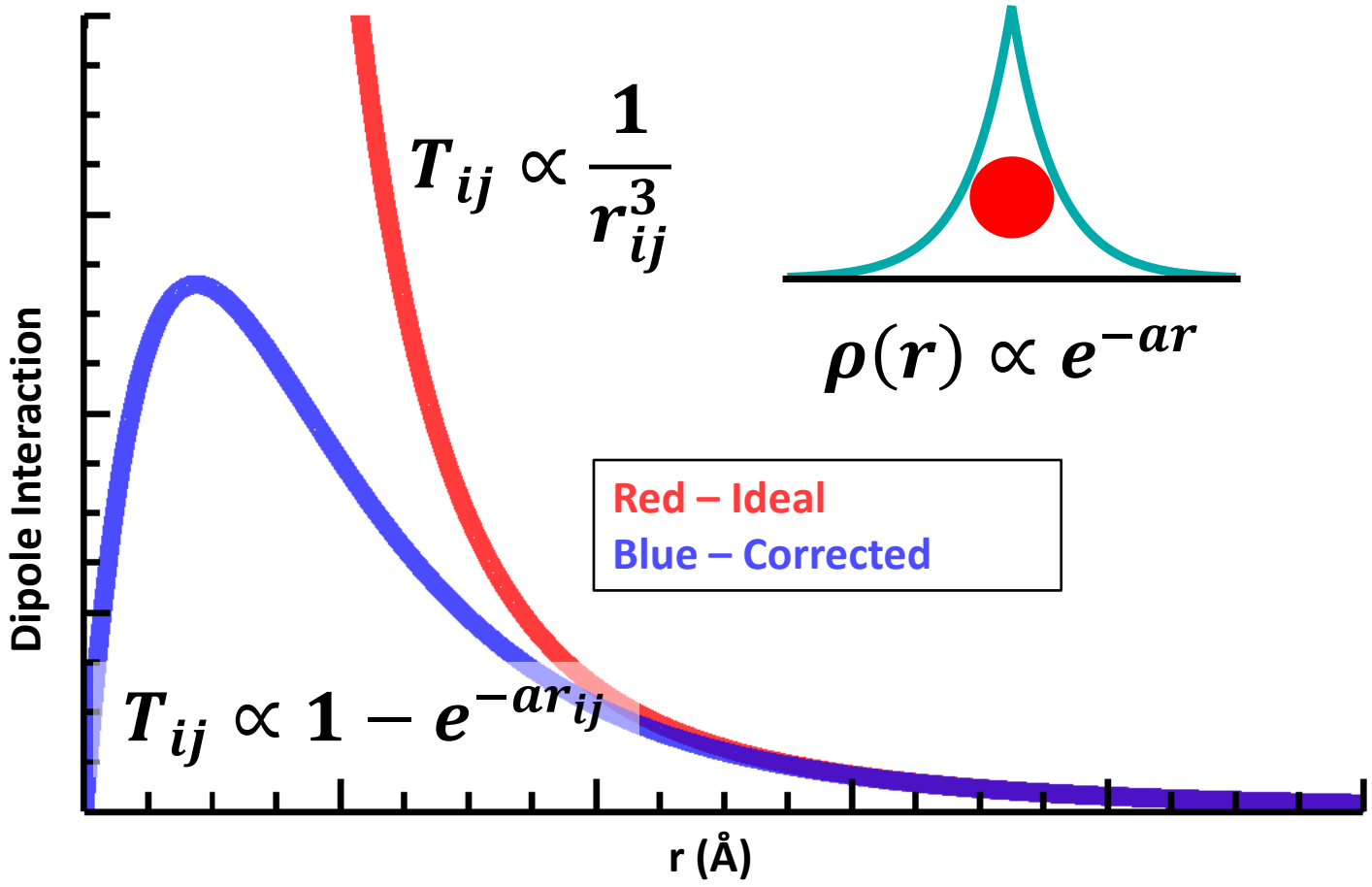
$\boldsymbol{\alpha_T}$ $\leftarrow$ $\begin{pmatrix} A_{11} & \cdots & A_{1n} \\ \vdots & \ddots & \vdots \\ A_{n1} & \cdots & A_{nn} \end{pmatrix}$ $\rightarrow$ $\boldsymbol{\alpha_1^{eff}}$, $\boldsymbol{\alpha_n^{eff}}$

$$\boldsymbol{\alpha_{O-H} = \frac{1}{2}\alpha_O + \alpha_H}$$

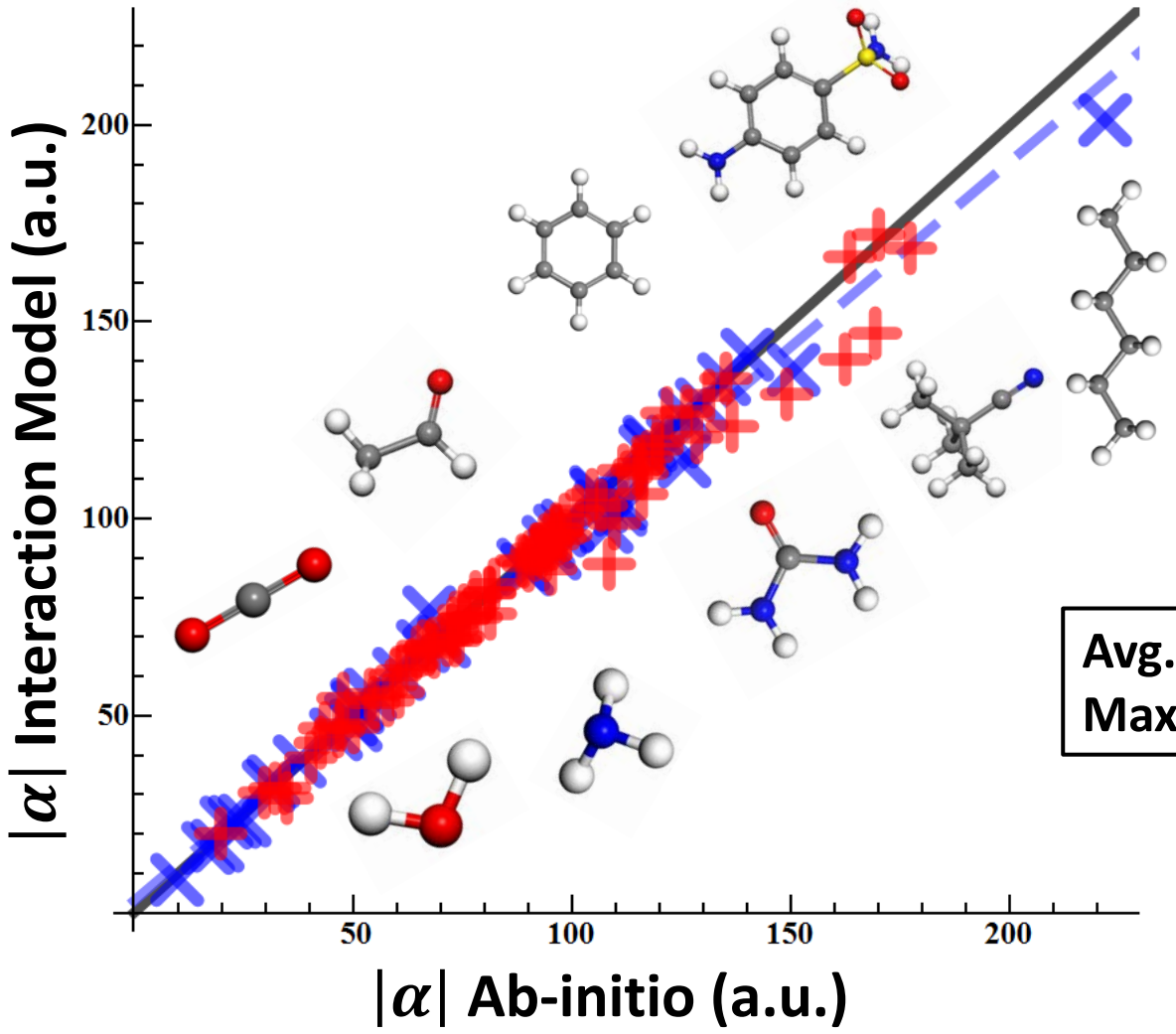
Dipole Interactions: Corrections



Dipole Interactions: Corrections



Effective Polarizabilities: Performance (H,C,O,N,S)



Training Set

Test Set

Unit Slope

Best Fit

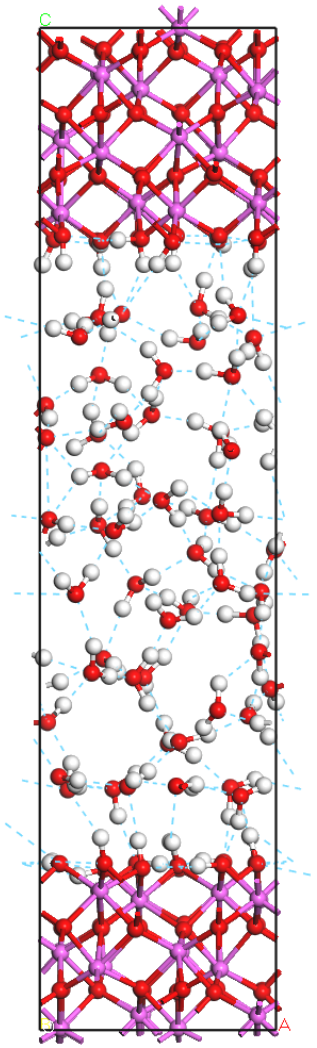
m = 0.94

r^2 = 0.98

Avg. % Error = 6.5

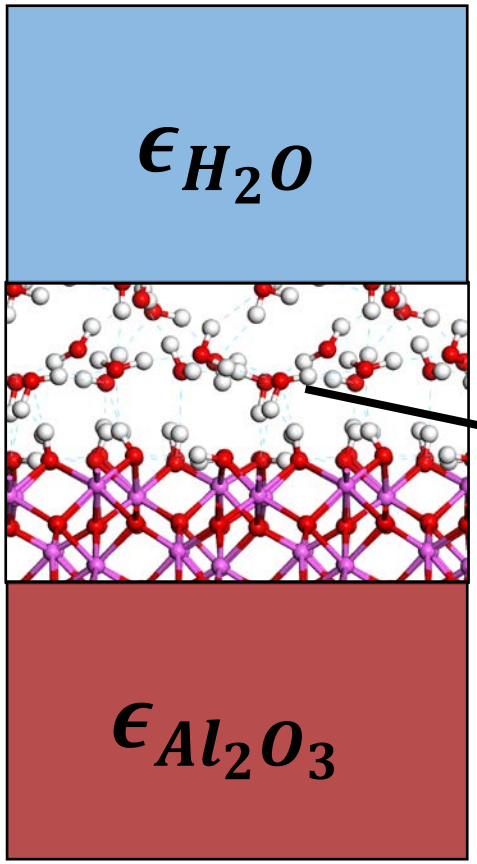
Max % Error = 22.8

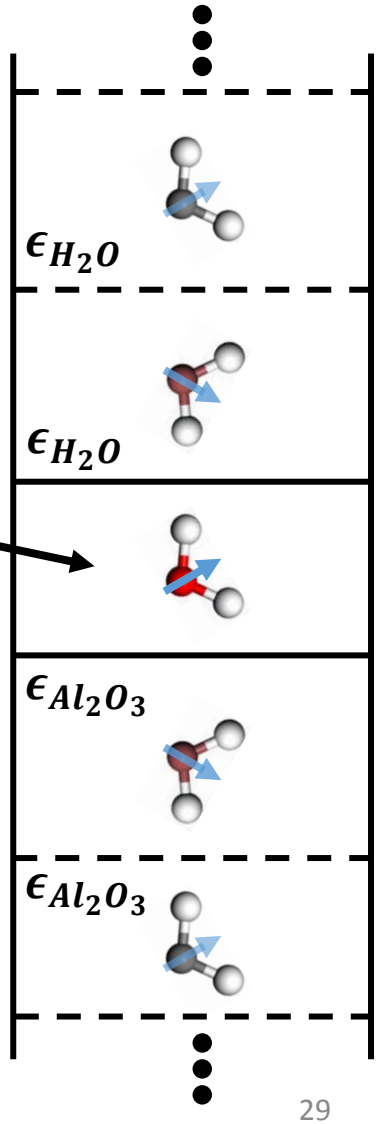
Three-Layer Dielectric Model



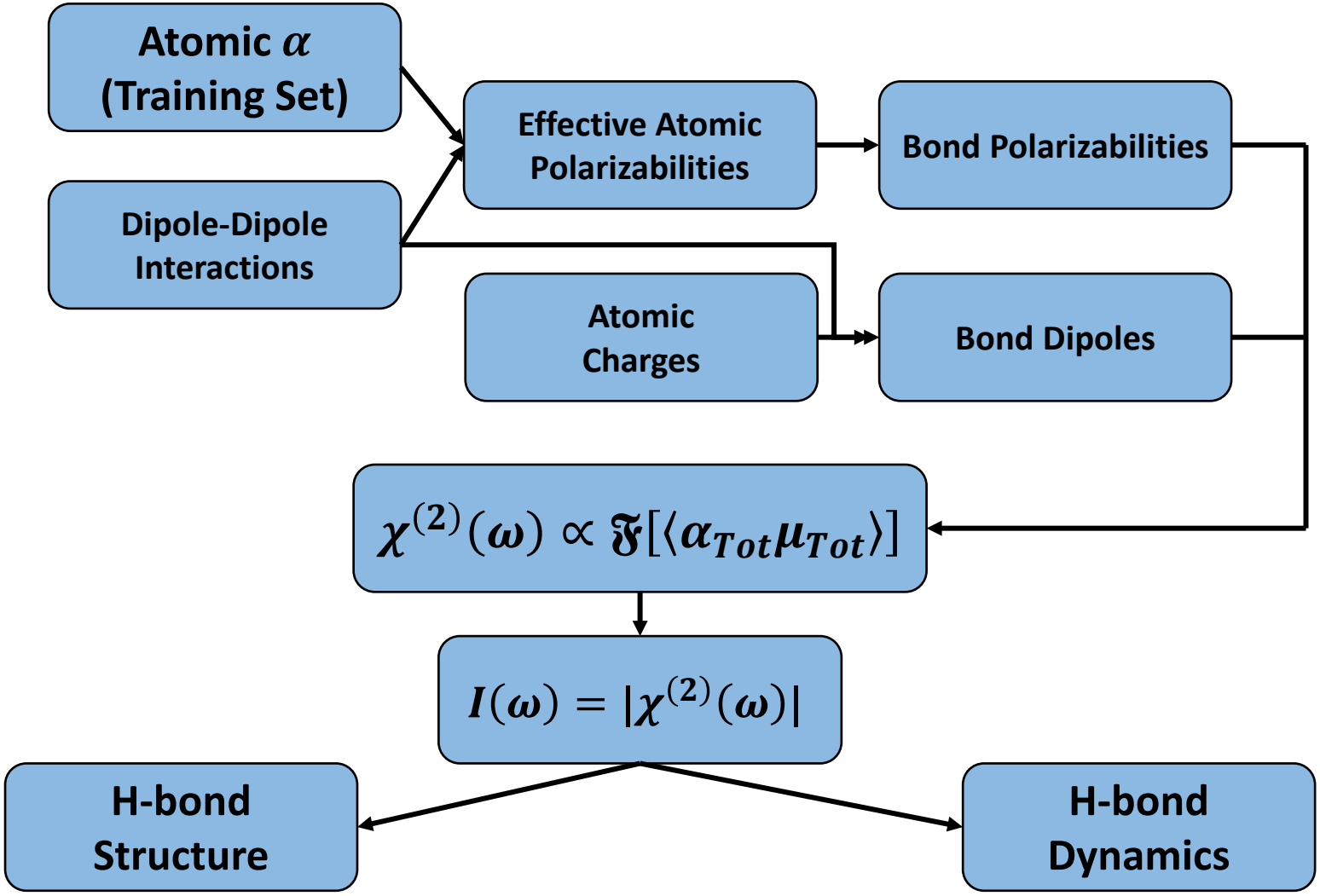
$$\alpha_{Tot} \approx 0$$
$$\mu_{Tot} \approx 0$$

$$\alpha_I \neq 0$$
$$\mu_I \neq 0$$





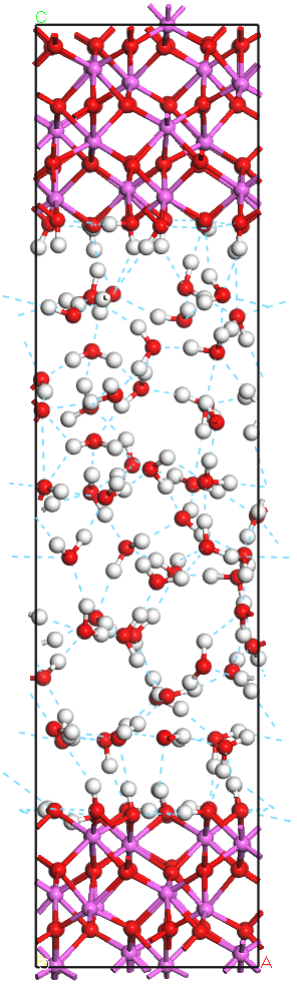
SFG: Summary


Atomic α (Training Set)
Dipole-Dipole Interactions
Effective Atomic Polarizabilities
Bond Polarizabilities
Atomic Charges
Bond Dipoles
$\chi^{(2)}(\omega) \propto \Im[\langle \alpha_{Tot} \mu_{Tot} \rangle]$
$I(\omega) = |\chi^{(2)}(\omega)|$
H-bond Structure
H-bond Dynamics

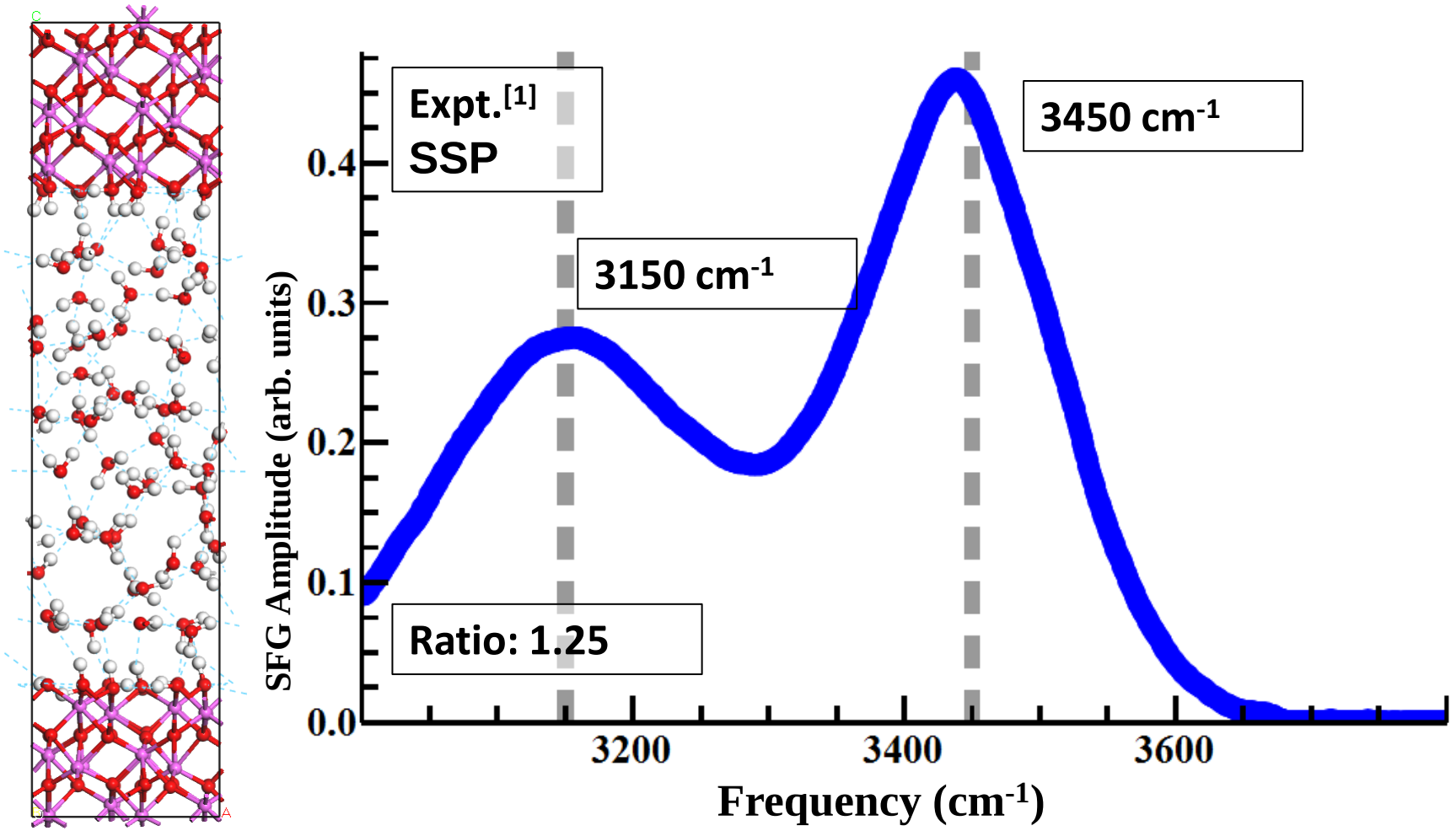
Test System: Al_2O_3-H_2O

- **Al_2O_3**
  - **Well known surface structure**
  - **Well known surface-water interactions**
  - **Stable (doesn't readily dissolve)**
- **Simulation:**
  - **DFT – PBE – VASP**
  - **15 ps production runs**
  - **Cell = 8.24 x 9.52 x 35 Å**
  - **Six Layers of Al_2O_3**
  - **52 H_2O ($\rho = 1.035\ g/cm^2$)**

en.wikipedia.org

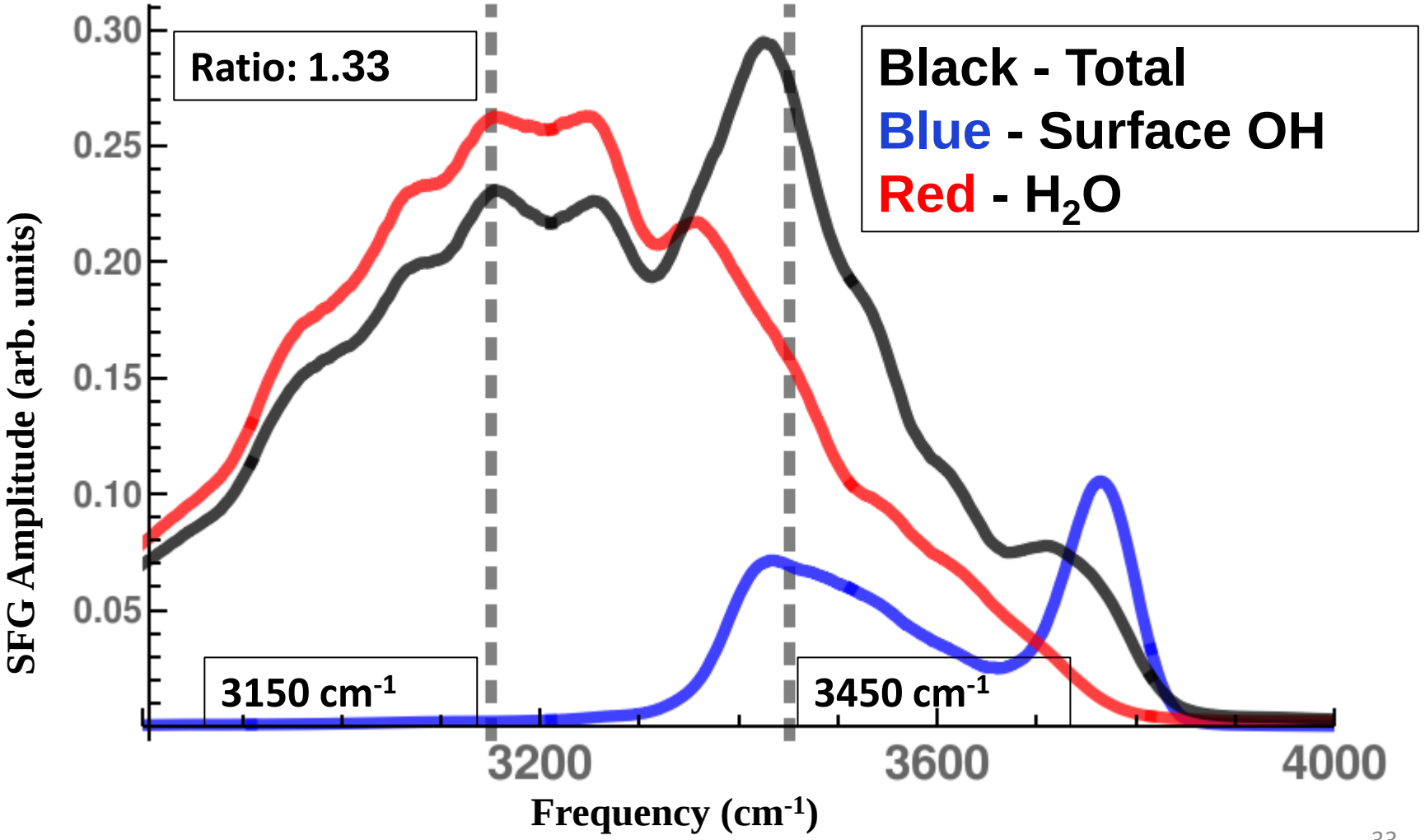


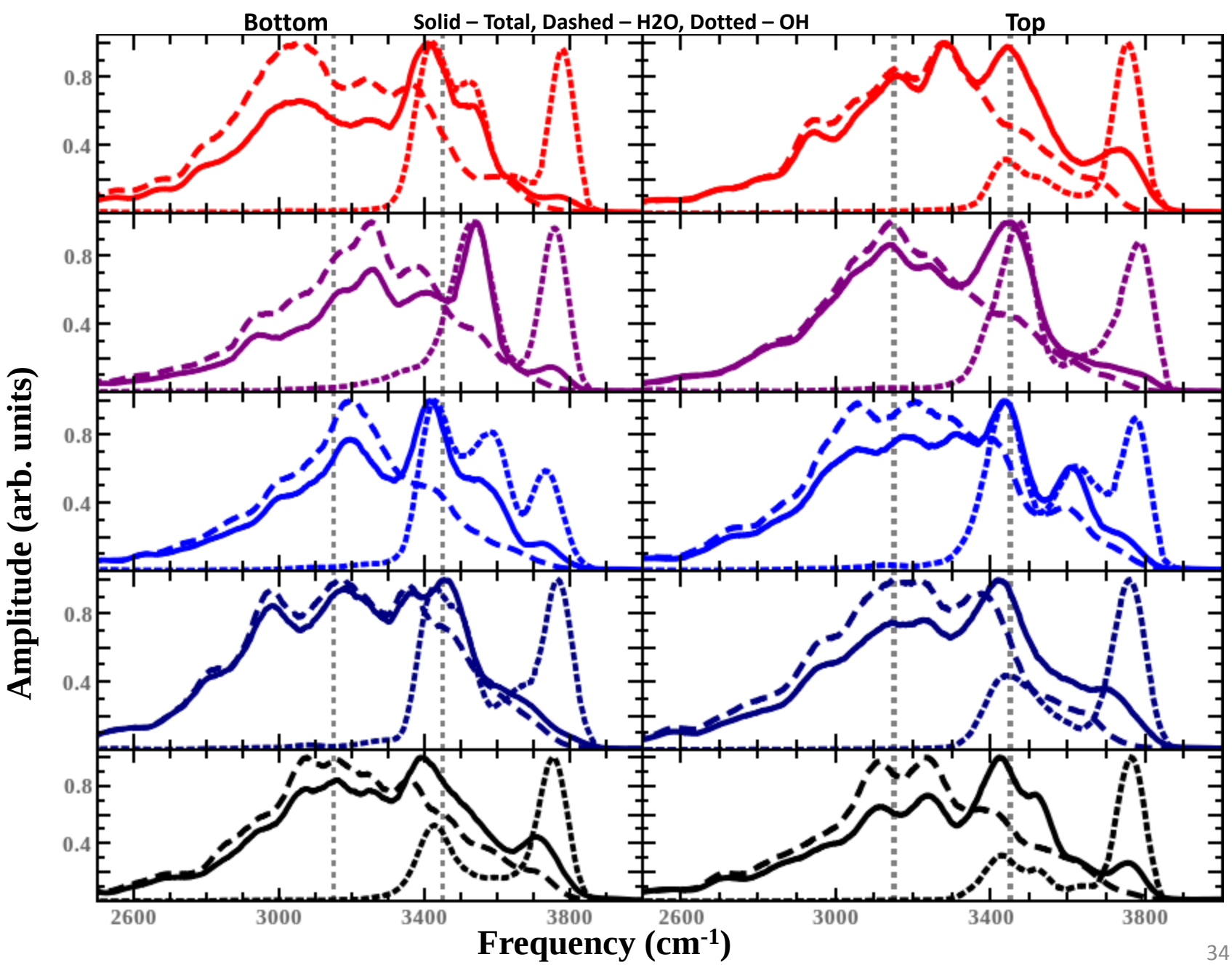
SFG Spectrum: Expt. $Al_2O_3(0001)$-H_2O Interface

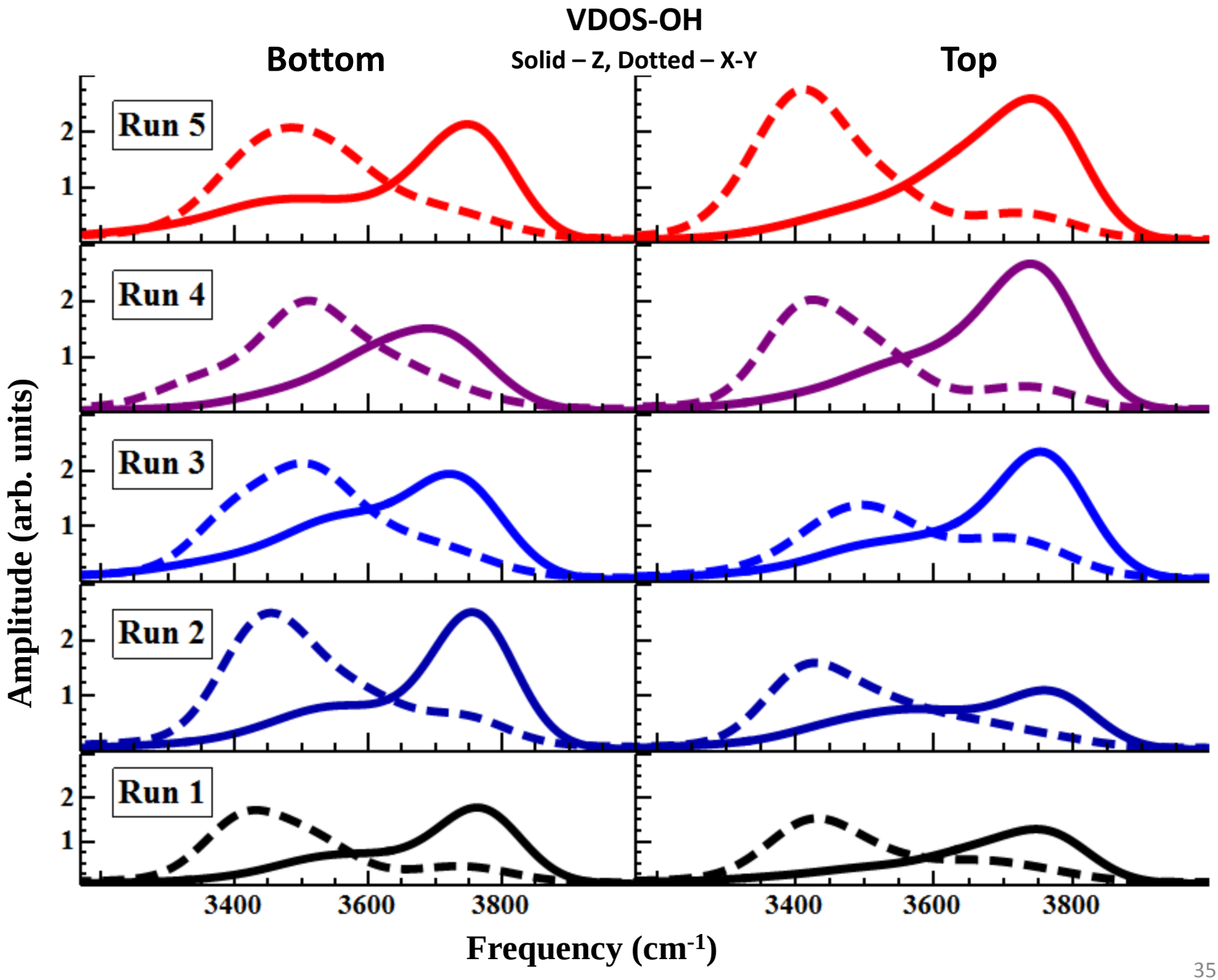


[1] Braunschweig, et al. *Phys Chem C* 112, (2008): 1751

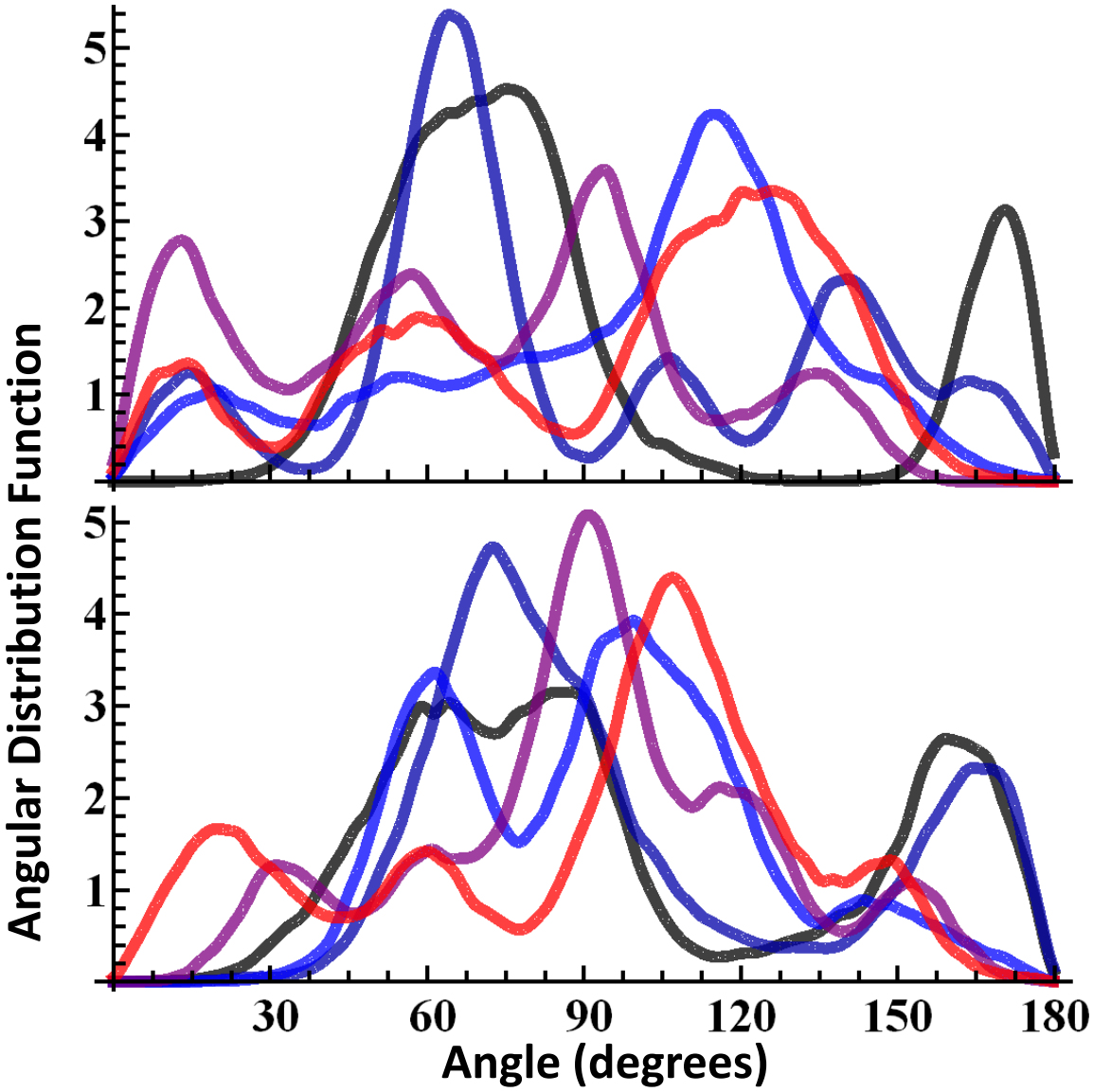
SFG Spectrum: Calc. $Al_2O_3(0001)$-H_2O Interface

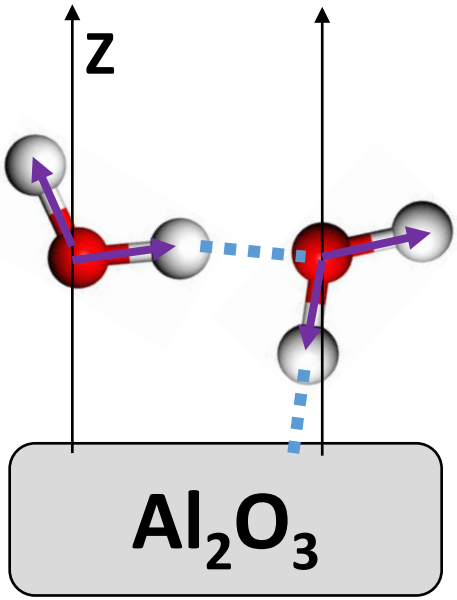



SFG Spectrum (SSP)
Bottom
Solid – Total, Dashed – H2O, Dotted – OH
Top
Amplitude (arb. units)
0.8
0.4
2600
3000
3400
3800
Frequency (cm-1)

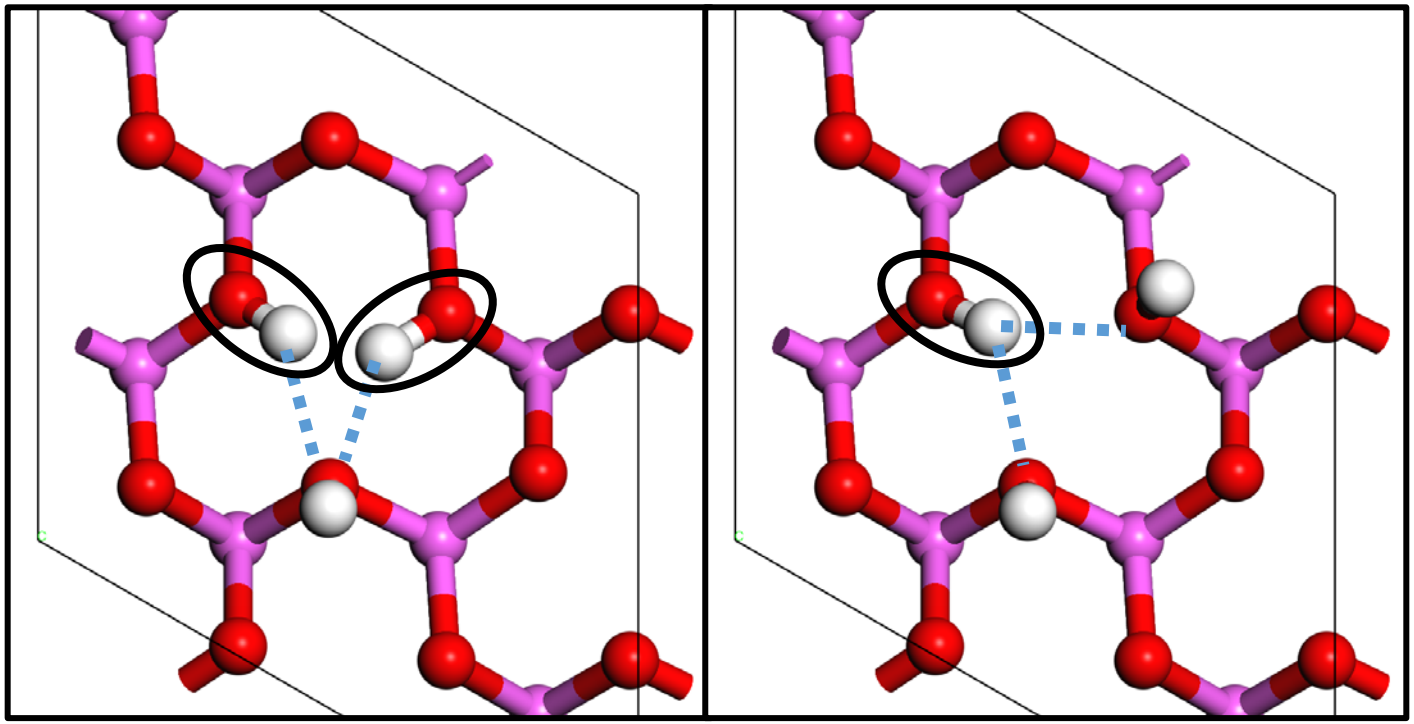

VDOS-OH
Bottom
Solid – Z, Dotted – X-Y
Top
Run 5
Run 4
Run 3
Run 2
Run 1
Amplitude (arb. units)
Frequency (cm-1)
3400
3600
3800

Variability: H_2O Configurations





Surface H-bond Configurations

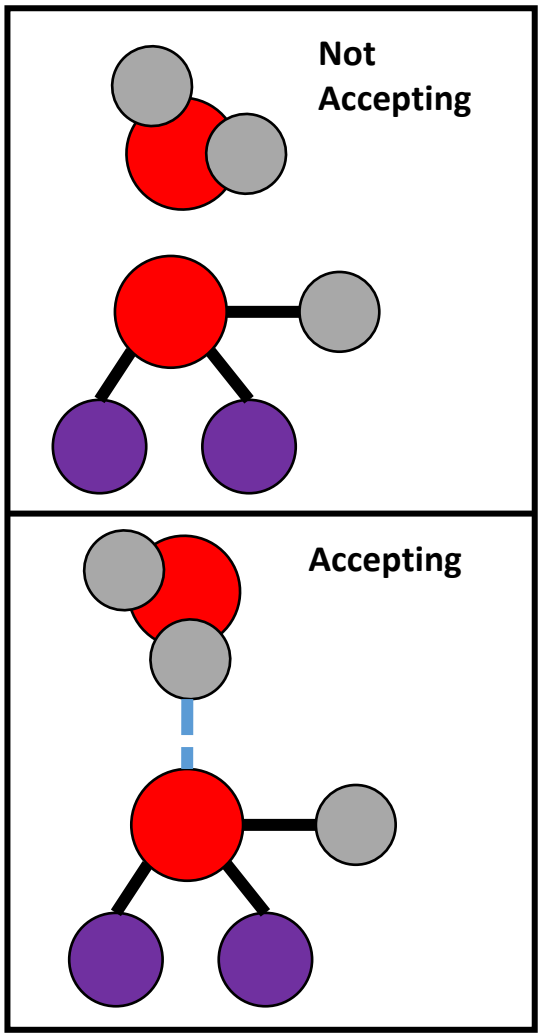


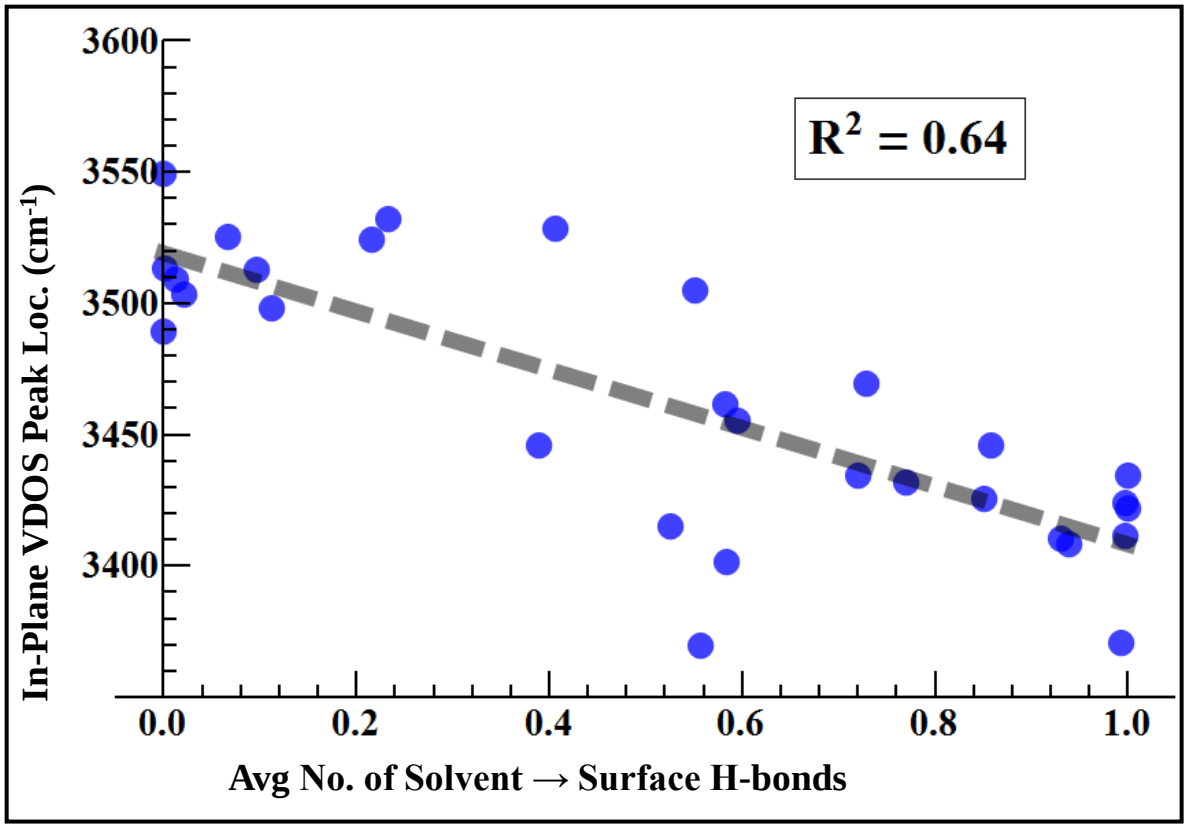
Double In-Plane
Freq: 3550±60 cm^{-1}

Single In-Plane
Freq: 3460±50 cm^{-1}

Contributes to ~3400 cm^{-1} peak

H-Bonds b/w H_2O and Surface

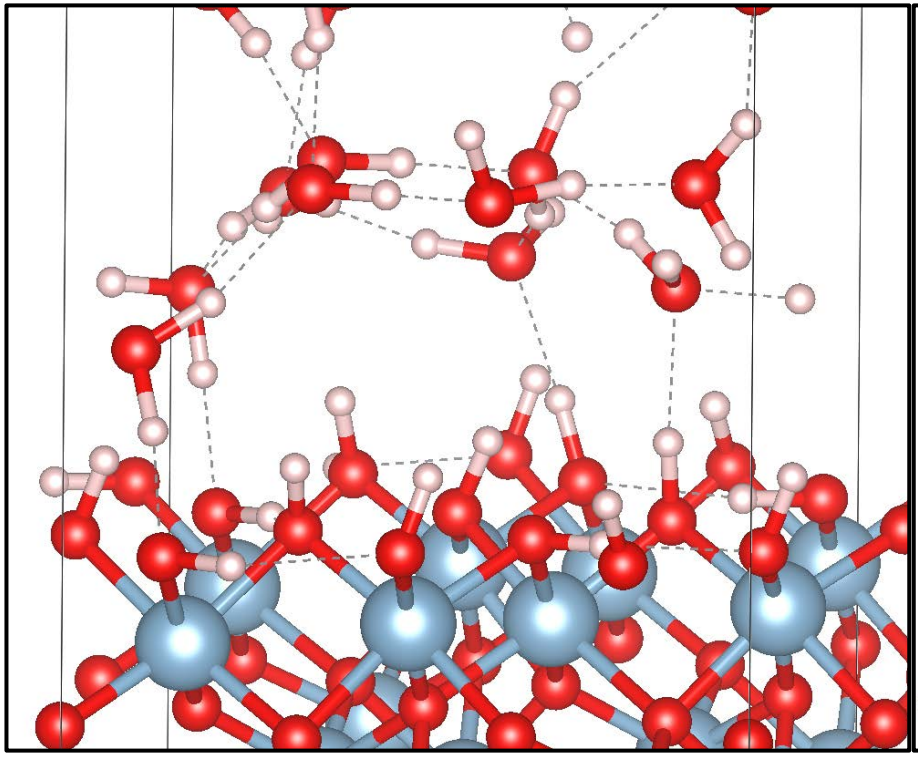




Accepting a H-bond => Lower Frequency

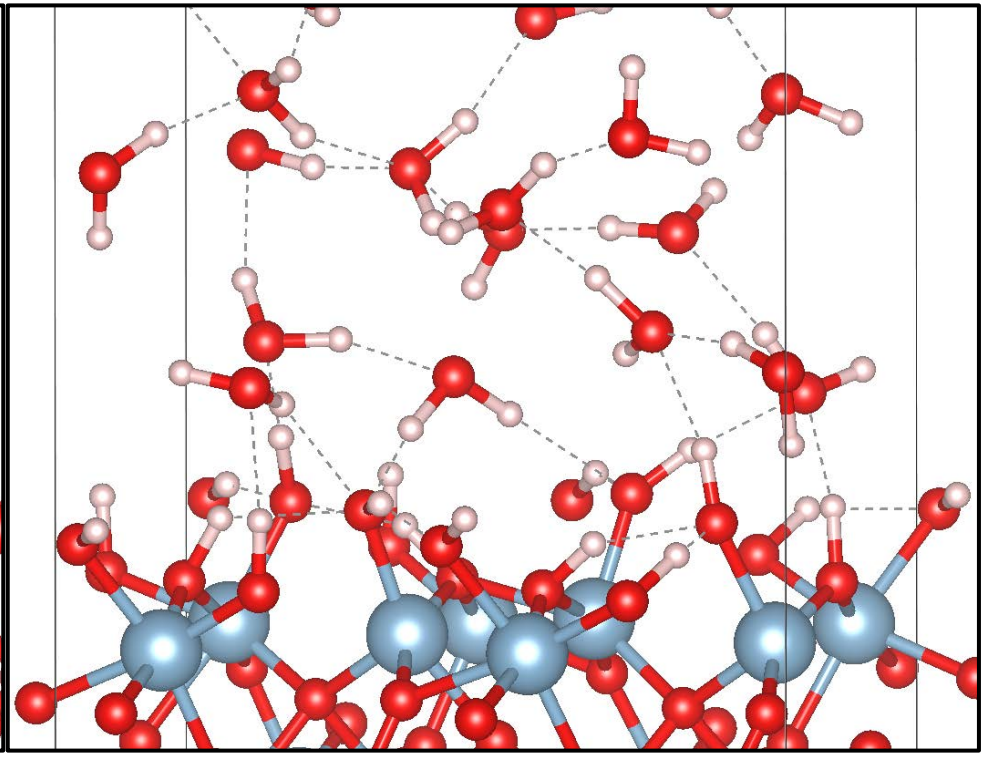
Surface Structure <-> Spectroscopy

$Al_2O_3(0001)$-H_2O

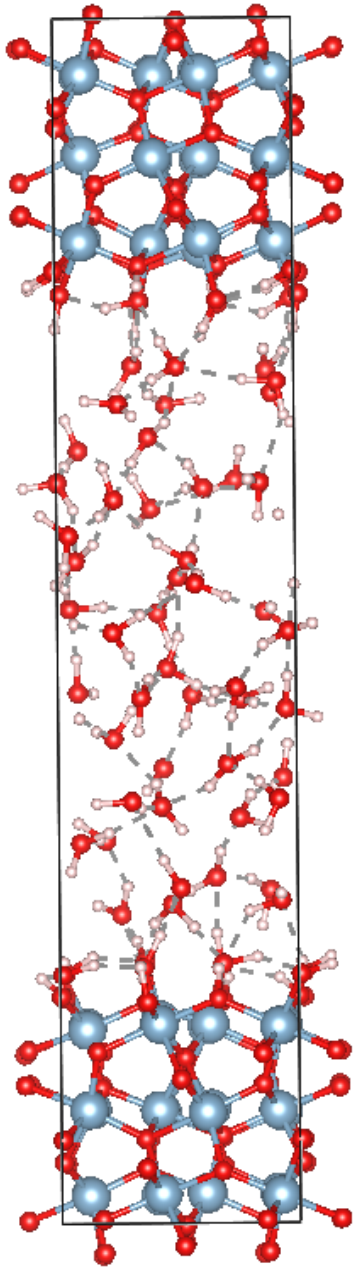


- Single OH Group
- Highly Ordered
- Few H_2O-OH bonds

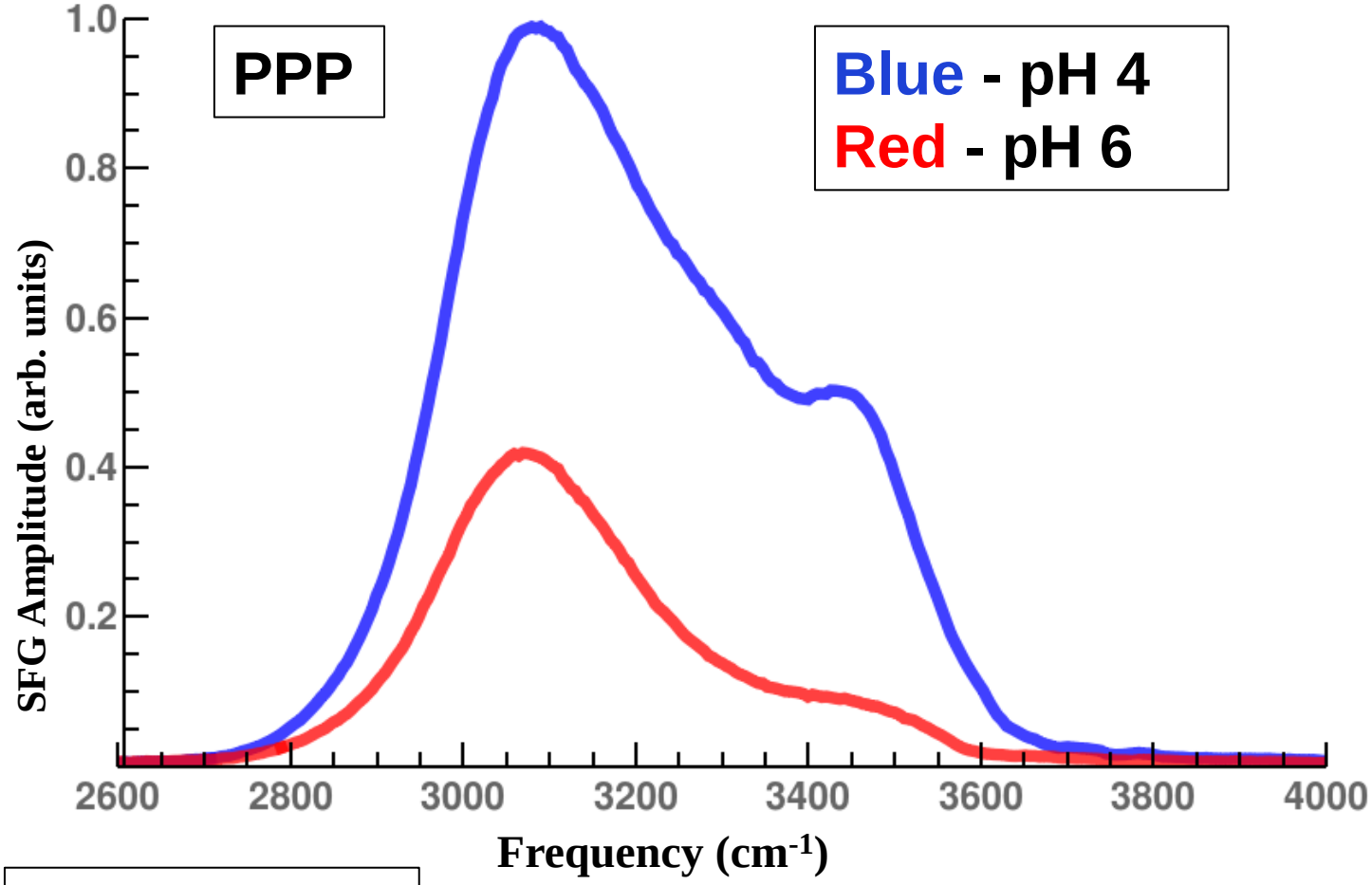
$Al_2O_3(1120)$-H_2O



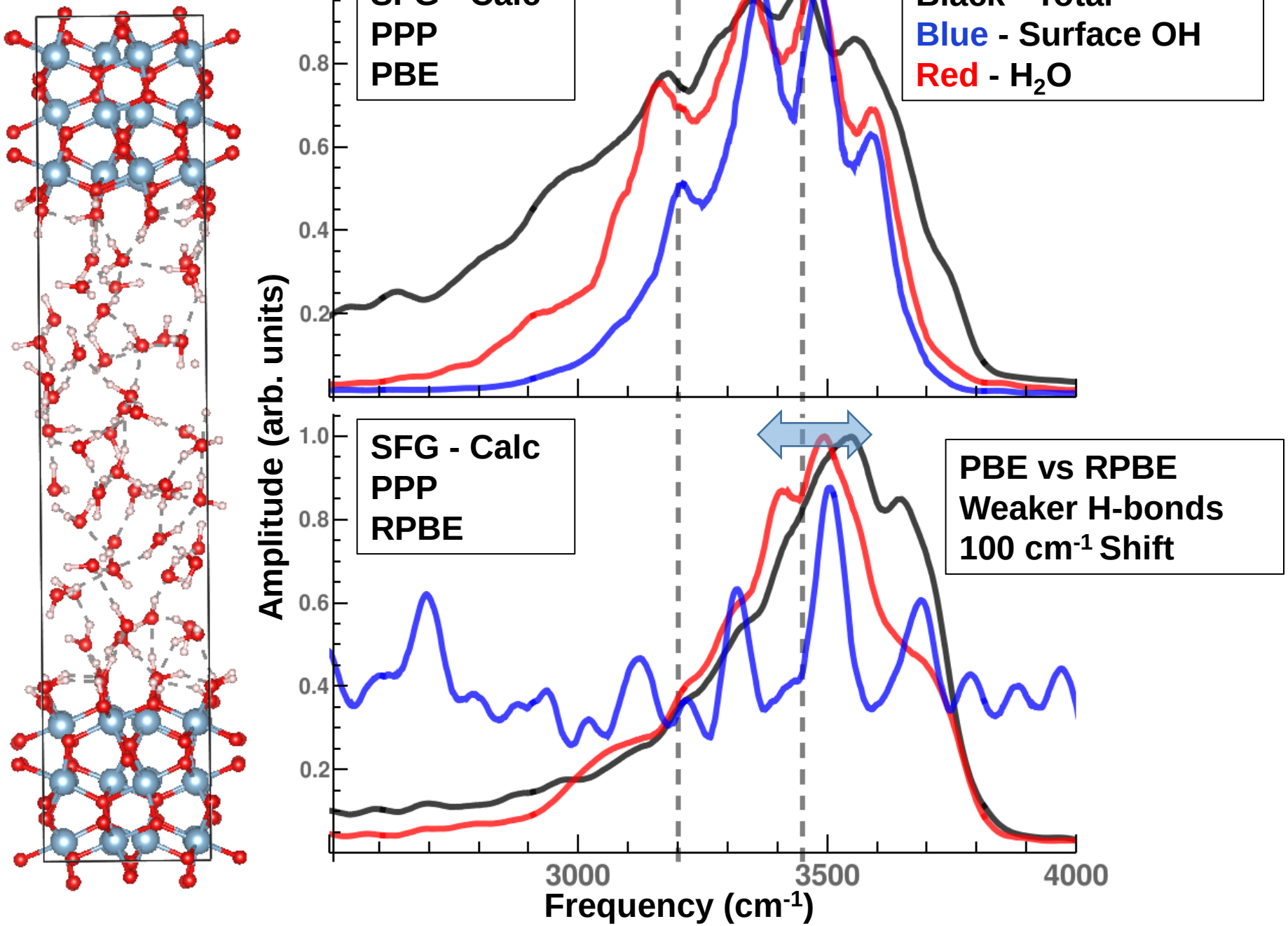
- Multiple OH Groups
- Highly Disordered
- Many H_2O-OH bonds

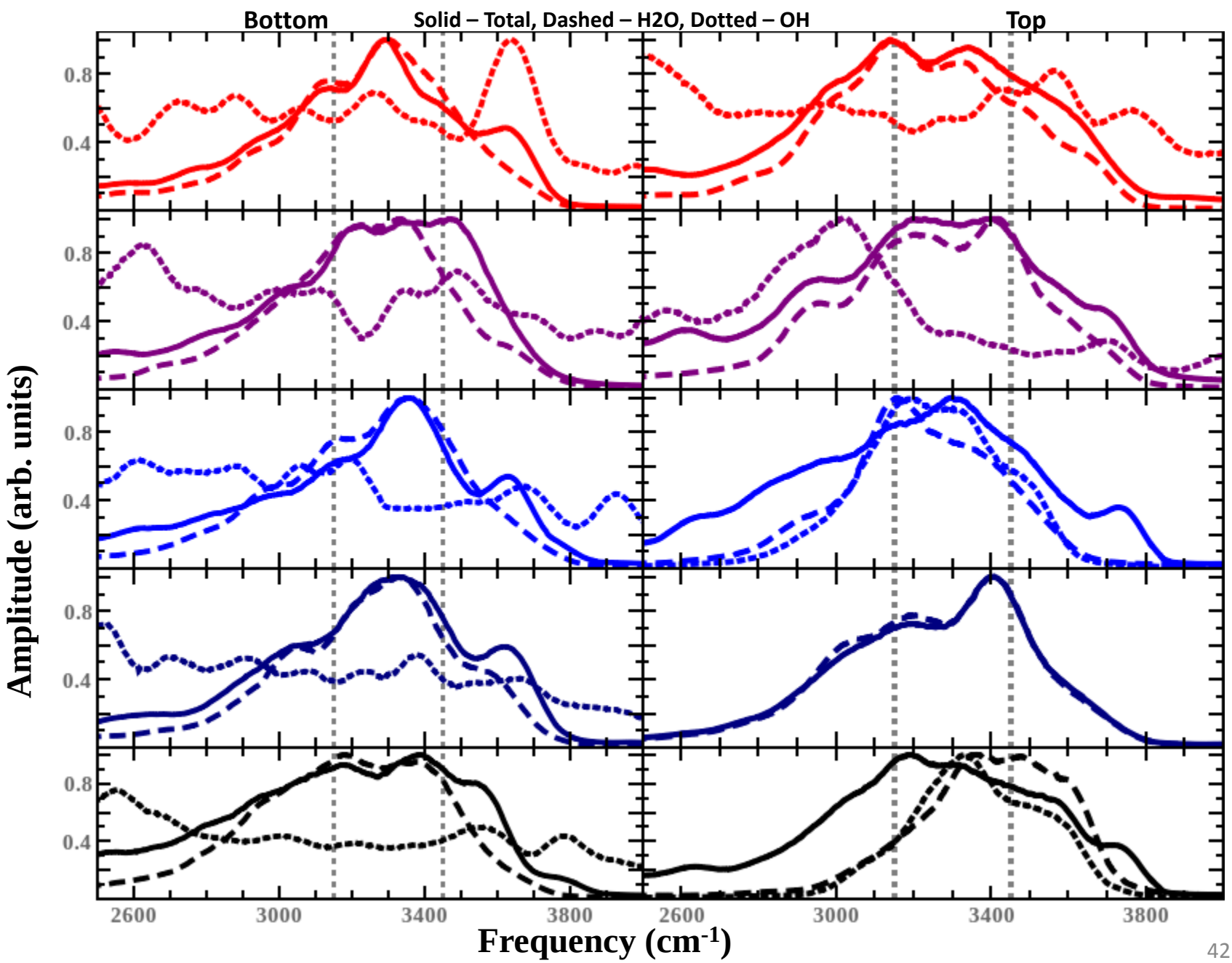


SFG Spectrum: Expt.
Al_2O_3(**1120**)-H_2O Interface



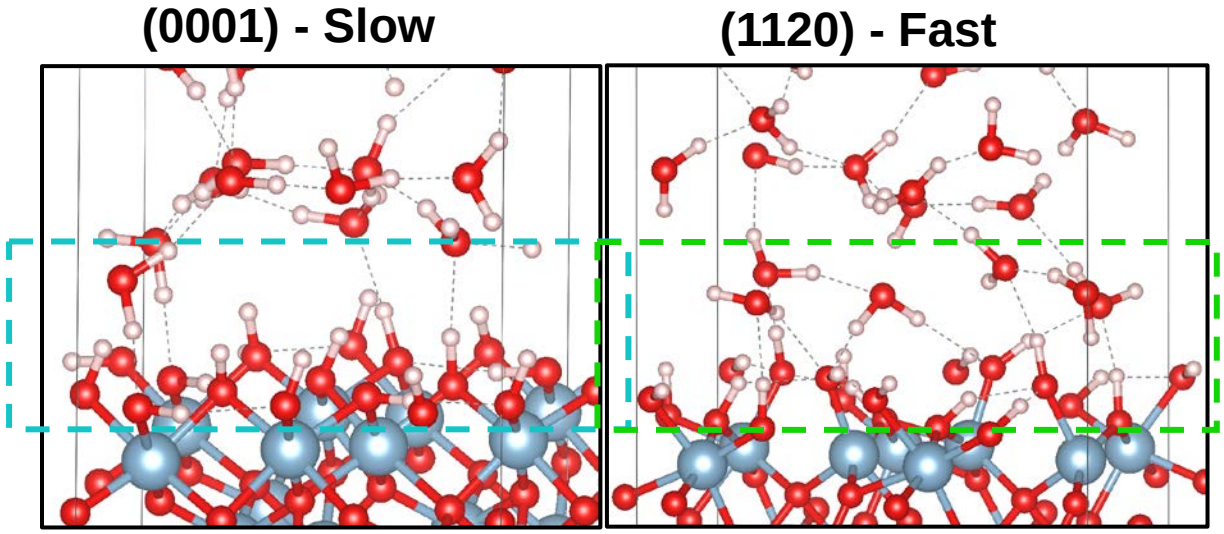
Borguet Group

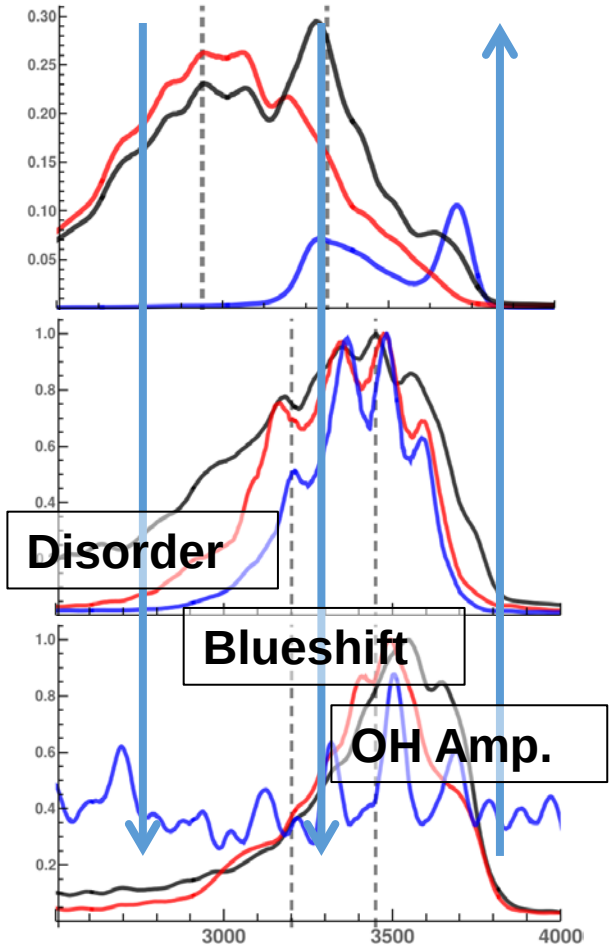

SFG - Calc
PPP
PBE
Black - Total
Blue - Surface OH
Red - H2O
SFG - Calc
PPP
RPBE
PBE vs RPBE
Weaker H-bonds
100 cm-1 Shift
Amplitude (arb. units)
Frequency (cm-1)
1.0
0.8
0.6
0.4
0.2
3000
3500
4000


SFG Spectrum (SSP)
Bottom
Solid – Total, Dashed – H2O, Dotted – OH
Top
Amplitude (arb. units)
0.8
0.4
2600
3000
3400
3800
Frequency (cm-1)

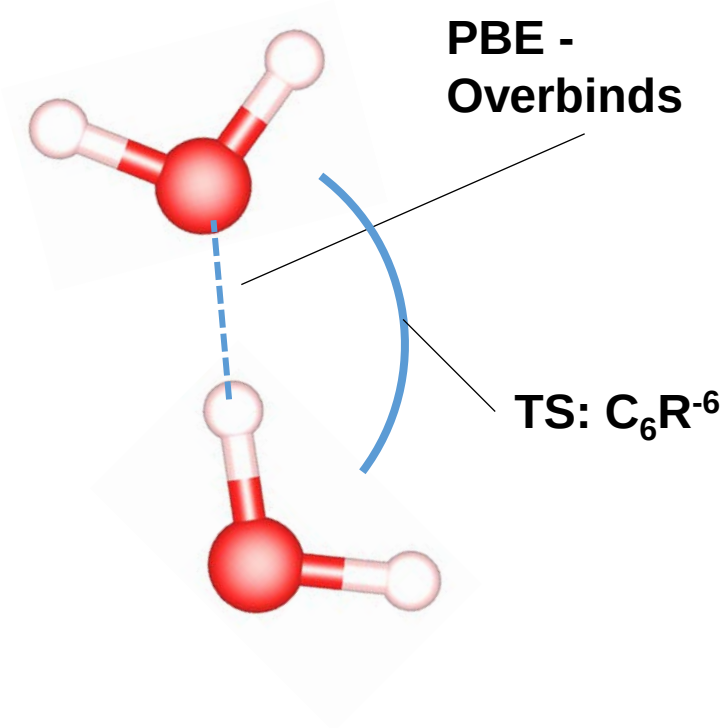
Structure <-> Dynamics <-> Spectroscopy

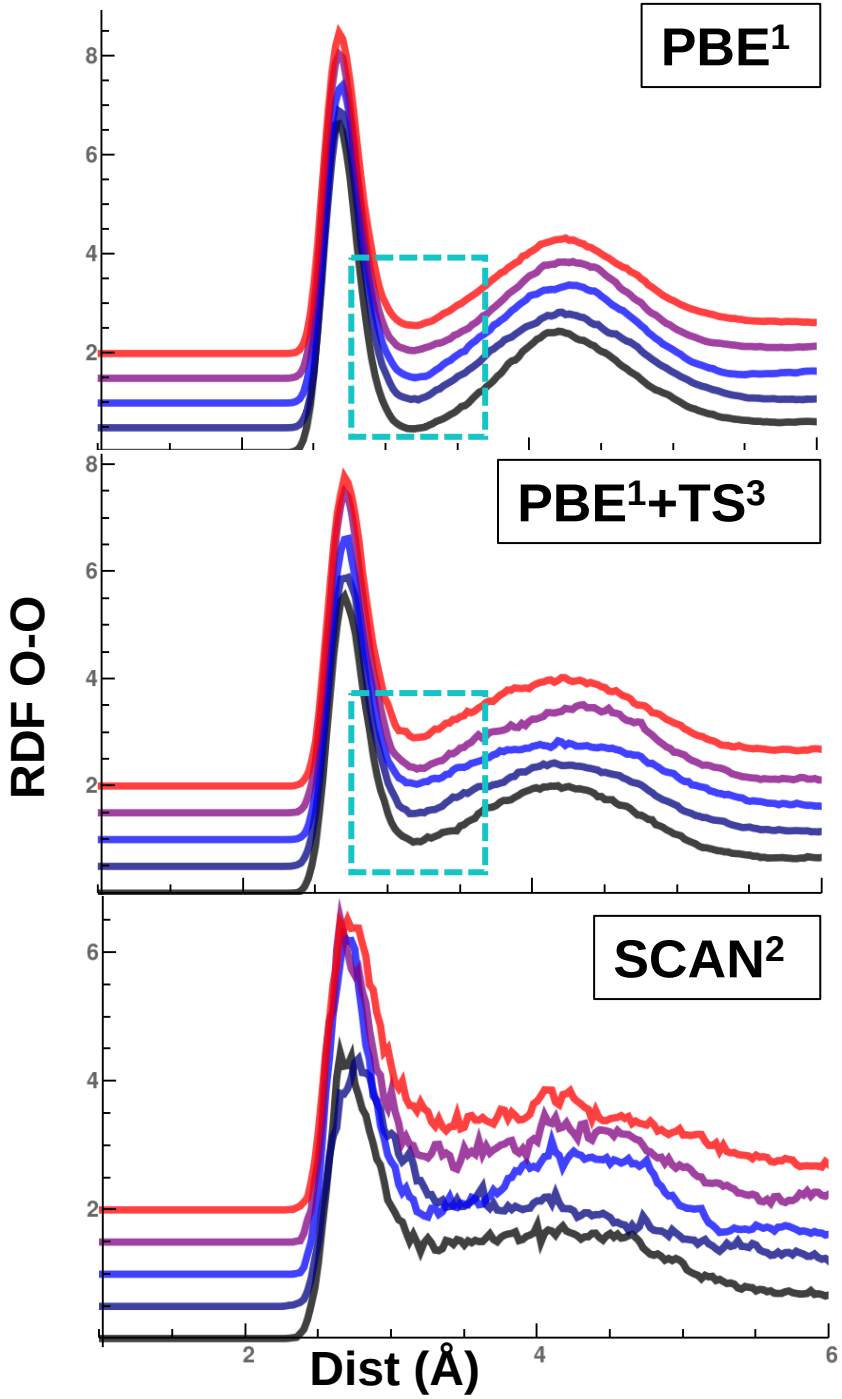
H-Bond T	(0001)-PBE	(1120)-PBE	(1120)-RPBE
Run1	2.31	0.89	0.29
Run2	1.17	0.9	0.21
Run3	1.21	0.76	0.33
Run4	1.38	0.72	0.2
Run5	1.32	1.09	0.52





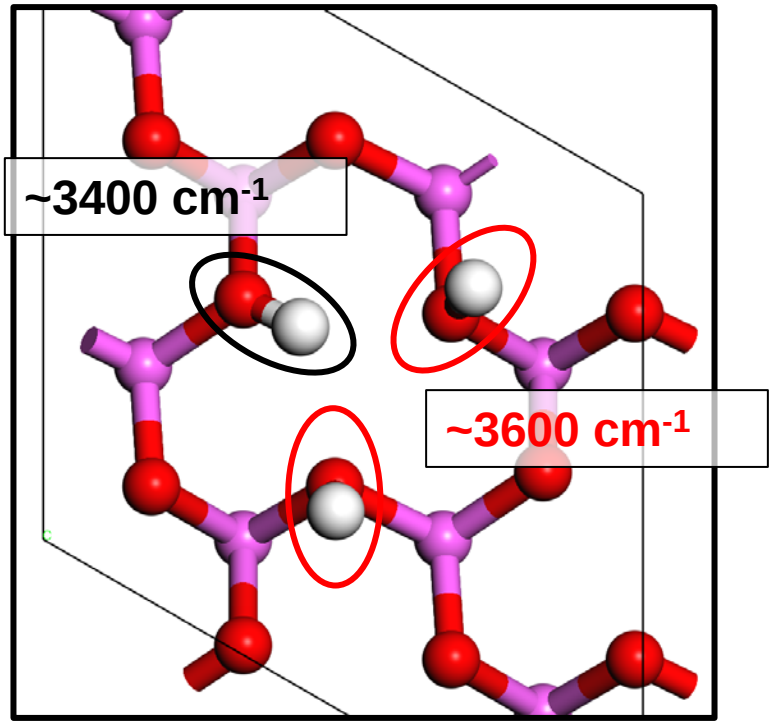
Effect of Functional - Structure

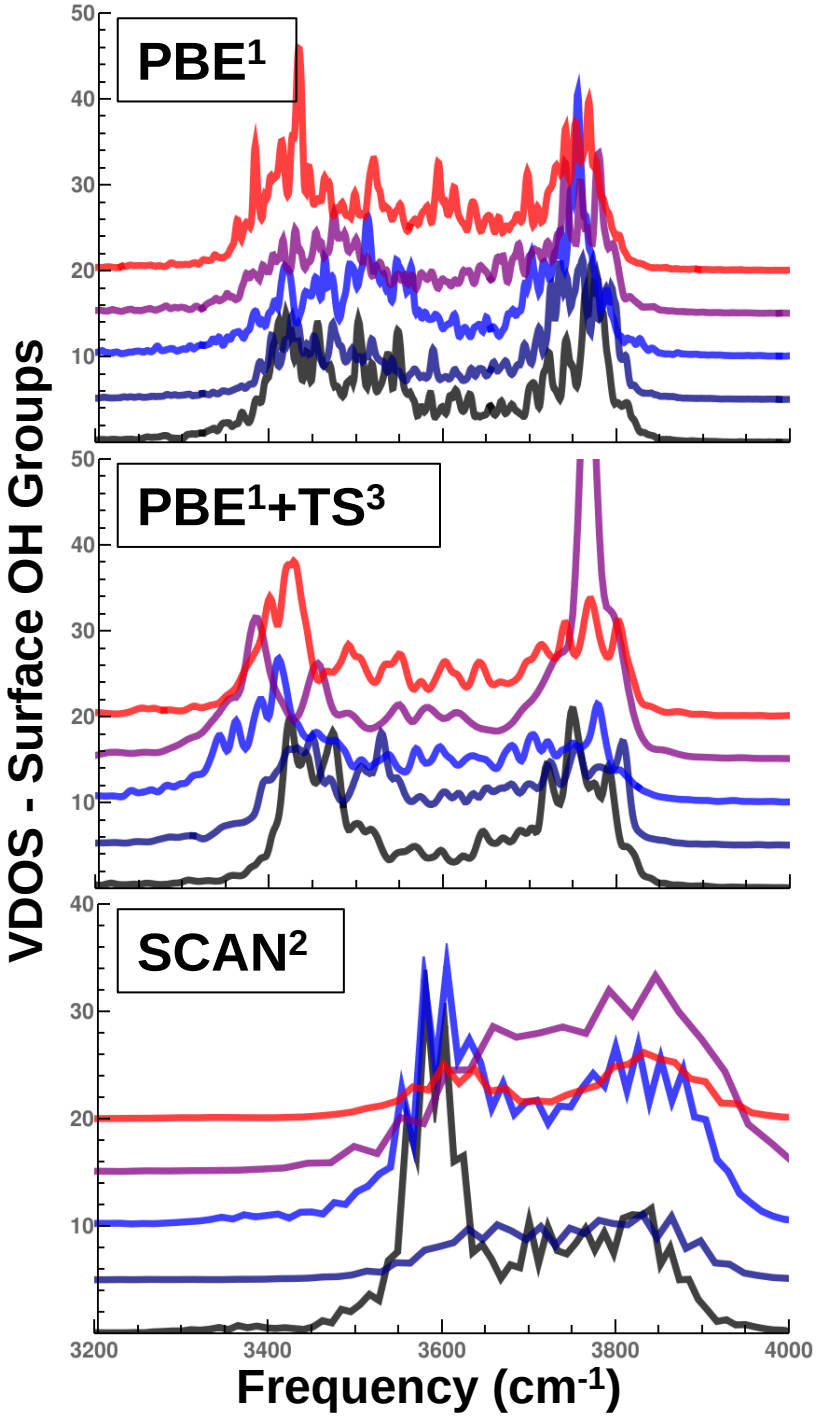




[1] Perdew, J. P., Burke, K. & Ernzerhof, M. PRL 77, 3865–3868 (1996).
[2] Sun, J., Ruzsinszky, A. & Perdew, J. P. PRL 115, 036402 (2015).
[3] Tkatchenko, A. & Scheffler, M. PRL 102, 073005 (2009)

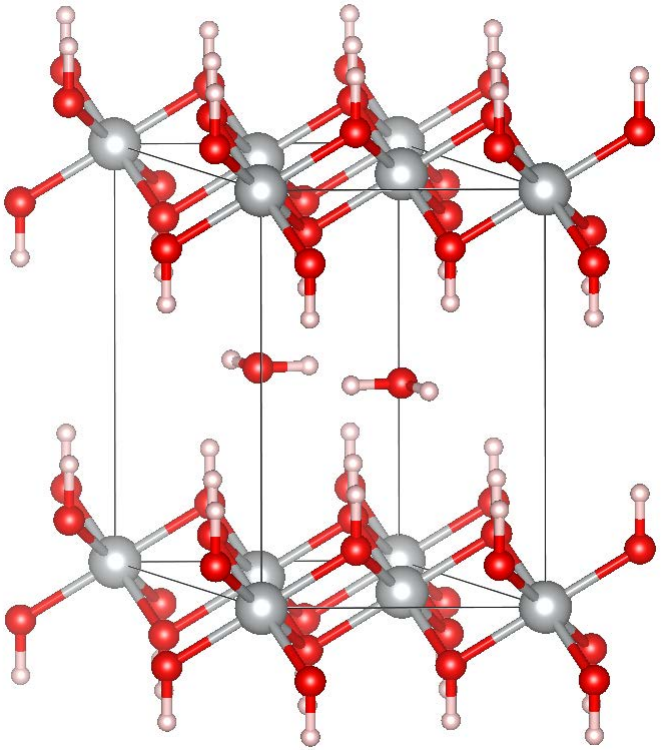
Effect of Functional - Dynamics

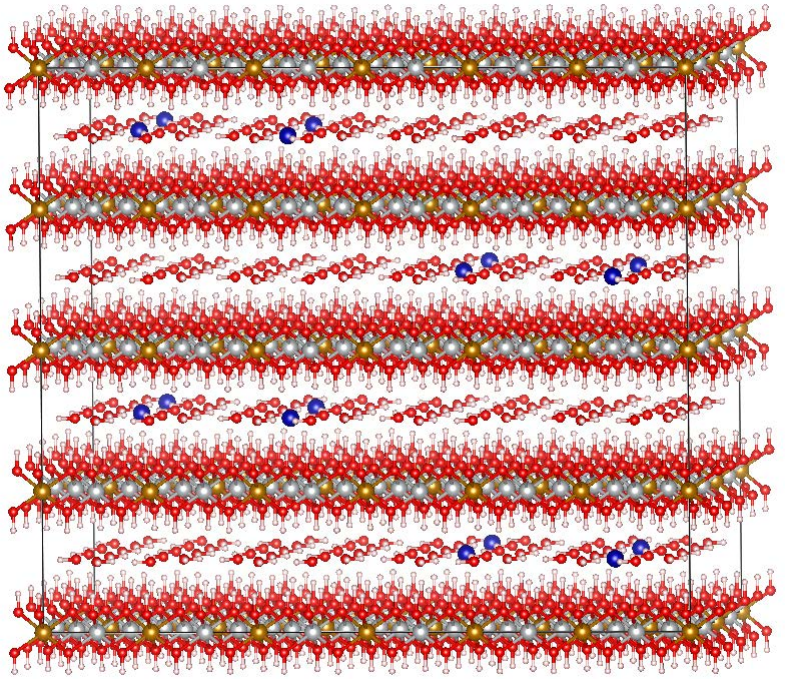




[1] Perdew, J. P., Burke, K. & Ernzerhof, M. PRL 77, 3865–3868 (1996).
[2] Sun, J., Ruzsinszky, A. & Perdew, J. P. PRL 115, 036402 (2015).
[3] Tkatchenko, A. & Scheffler, M. PRL 102, 073005 (2009)

NiFeOH-H_2O: Dynamics of Confined Water

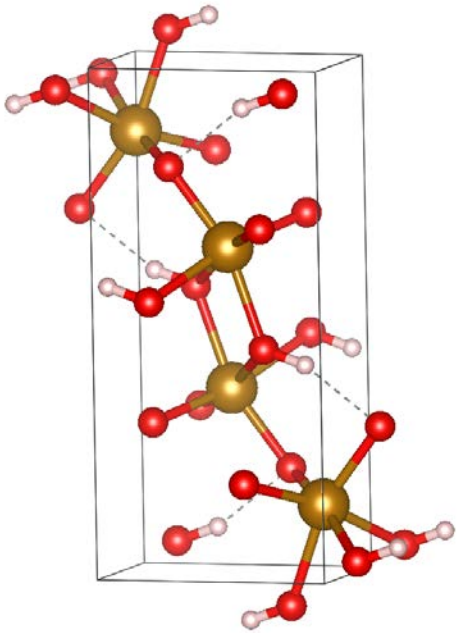




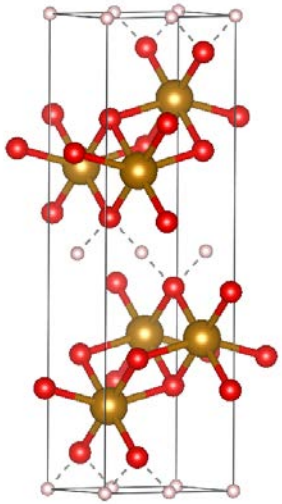
NiFeOH-H_2O: Dynamics of Confined Water

Fe(a.u.):
- ε = 2.712E-05
- σ = 4.000526

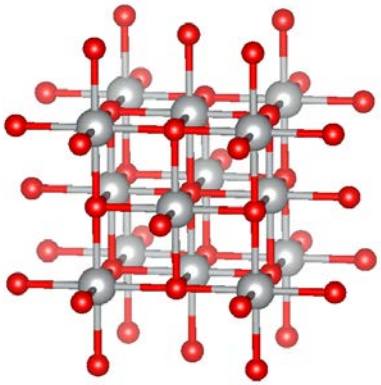
Ni(a.u.):
- ε = 1.422E-05
- σ = 4.388900



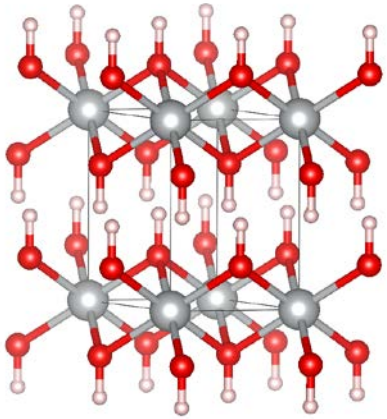
Geothite



Lepridocosite

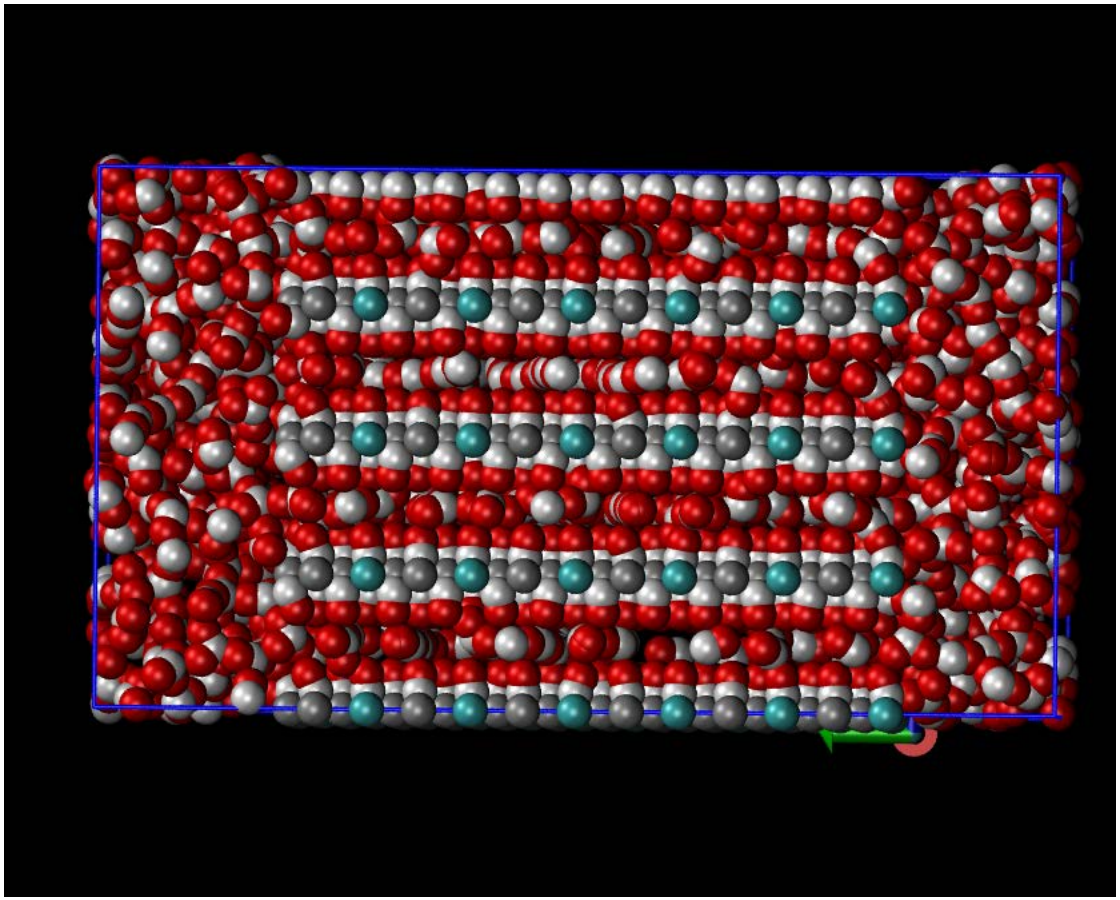


Bunsenite



Thephrastite

NiFeOH-H_2O: Dynamics of Confined Water



Acknowledgements

- Thesis Advisor - Penn State - Jorge Sofo
- Postdoc Advisor - Temple - Michael Klein
- Experimental Collaborators
  - Eric Borguet
  - Dan Strongin
  - Akila Thenuwara
- Theory Collaborators
  - Rick Remsing
  - Himanshu Chakraborty