Vibrational Analysis of Water Using the SPC Force Field Model

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CHEM 279

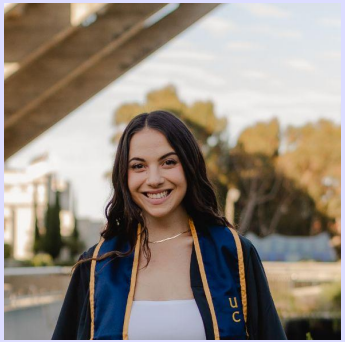
01

Project Introduction

Team

Jesse Maki

Implemented:
Lennard-Jones Potential
Angle Potential Energy
Hessian Matrix
Plotting



Emma Brugman

Implemented:
Coulombic energy
Bond Angle Energy
Mass-weighting & Diagonalization
Plotting

Topic & Objectives

Vibrational Analysis of Water Using the SPC Force Field Model

Objectives:

1. Input Geometry to Building the Atomic System
2. Initialize SPC/E Model and Compute Force and Energy Calculations
3. Hessian Matrix Calculation
4. Mass-weighted Hessian Matrix
5. Initialize SPC/FW Model and Compute Vibrational Modes (Eigenvalues & Wavelengths)

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Methodology

Input Files & Geometry

- Provides initial atomic coordinates of water molecules.
- H2O files are already defined as theoretical optimum due to rigid model constraints.

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3
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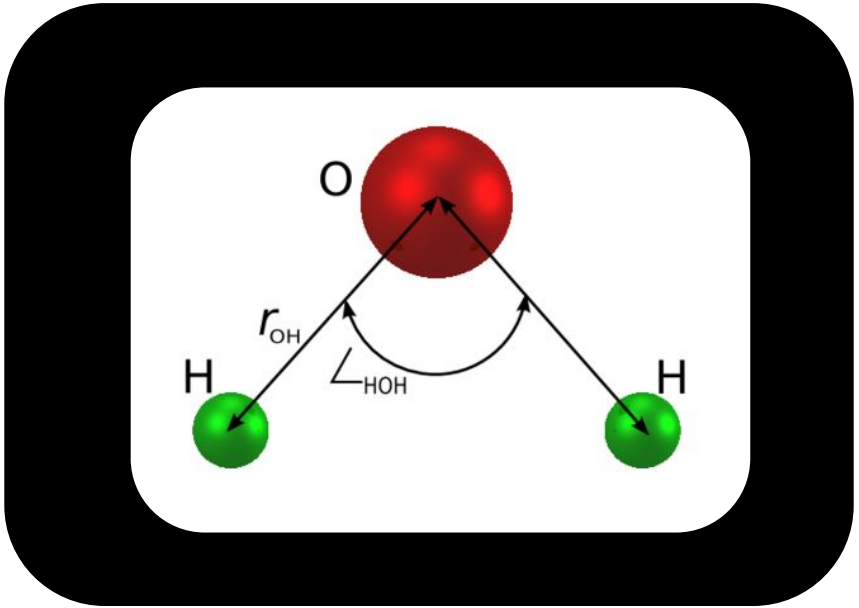
1 0.000000 1.012000 0.000000
1 0.000000 -0.405300 0.927300
```



SPC/E

- Models water as a rigid isosceles triangle with fixed geometry.
- Bond length: 1.0 Å (O-H); H-O-H angle: 109.47°
- Coulombic + Lennard-Jones Energy

$$E_{LJ} = \sum_{i<j,\ O-O\ Pairs} 4\varepsilon_O\left[\left(\frac{\sigma_O}{r_{ij}}\right)^{12} - \left(\frac{\sigma_o}{r_{ij}}\right)^{6}\right],\ for\ r_{ij} < r_{cutoff}$$

$$E_{coulomb} = \sum_{i<j} \frac{q_i q_j}{r_{ij}},\ for\ r_{ij} > 0\ and\ r_{ij} < r_{cutoff}$$

Parameter	Original Theoretical Values	Converted to Atomic Units
σ_{OO}	3.166 Å	5.9819129309 Bohr
ε_{OO}	0.650 $kJ\ mol^{-1}$	0.000247572 Hartrees
r_{OH}	1.000 Å	1.88973 Bohr
$<_{HOH}$	109.47°	1.91061193 Radian
q_O	-0.8476e	-0.8476e
q_H	0.4238	0.4238e
Polarization Constant	1.25 $kcal/mol$	0.001992 Hartree

http://www.sklogwiki.org/SklogWiki/index.php/SPC/E_model_of_water

SPC/FW

- Models water as a flexible 3-site molecule with harmonic bond and angle potentials
- Bond length (O-H): 1.012 Å ; H-O-H angle: 113.24°
- Intermolecular Coulombic + Lennard Jones + Bond Energy + Angle Energy

Parameter	Value	Converted to Atomic Units
σ_{OO}	3.165492 Å	5.982 Bohr
ε_{OO}	0.1554253 $kcal\,mol^{-1}$	0.000247 Hartrees
q_O	-0.82 e	-0.82 e
q_H	0.41e	0.41 e
k_b	1059.162 $kcal.\,mol^{-1}Å^{-2}$	0.474 $Hartree/Bohr^2$
r^{eq}_{OH}	1.012 Å	1.912 Bohr
k_a	75.90 $kcal.\,mol^{-1}rad^{-2}$	0.145 $Hartree/Radians^2$
$\vartheta^{eq}<_{HOH}$	113.24°	1.976 Radians

$$V^{\text{inter}} = \sum_{ij}^{\text{all pairs}} \left\{ 4\epsilon_{ij} \left[\left(\frac{\sigma_{ij}}{R_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{R_{ij}} \right)^{6} \right] + \frac{q_i q_j}{R_{ij}} \right\}$$

$$V_{\text{bond}} = \frac{1}{2} k_r (r - r_0)^2 \quad V_{\text{angle}} = \frac{1}{2} k_\theta (\theta - \theta_0)^2$$

http://www.sklogwiki.org/SklogWiki/index.php/SPC/Fw_model_of_water

Forces & Hessian Matrix

Force Calculation: $F_i \approx -\frac{E(x_i+h) - E(x_i-h)}{2h}$

- Method: Central difference approximation for numerical derivatives.
- Gradient of potential energy, used to compute the Hessian.

Hessian Matrix: $H_{ij} \approx -\frac{F_i(x_j+h) - F_i(x_j-h)}{2h}$

- Method: Central difference approximation for numerical derivatives
- Captures curvature of energy surface

```
========= Force Calculation ========

Central Difference Forces (Hartree/Bohr):
             0             0             0
  -3.6361e-04  -1.9095e-04   5.5455e-04
  -5.4853e-04   5.1940e-04   2.9030e-05
```

```
======== Hessian Calculation ========

Numerical Hessian (Hartree/Bohr^2):
  -6.0769e-04             0             0   3.0618e-04             0             0   3.0401e-04             0             0
             0   5.8320e-01  -1.2257e-01             0  -4.7400e-01  -3.6600e-02             0  -1.0920e-01   1.5917e-01
             0  -1.2257e-01   4.7605e-01             0  -2.7182e-04  -5.5631e-02             0   1.2284e-01  -4.2042e-01
   3.0618e-04             0             0  -1.1333e-05             0             0  -2.9610e-04             0             0
             0  -4.7400e-01  -2.7182e-04             0   4.7400e-01   2.7159e-04             0  -2.3308e-17  -1.4343e-17
             0  -3.6600e-02  -5.5631e-02             0   2.7159e-04   3.9752e-02             0   3.6328e-02   1.5878e-02
   3.0401e-04             0             0  -2.9610e-04             0             0  -9.1623e-06             0             0
             0  -1.0920e-01   1.2284e-01             0  -2.3308e-17   3.6328e-02             0   1.0920e-01  -1.5917e-01
             0   1.5917e-01  -4.2042e-01             0  -1.4343e-17   1.5878e-02             0  -1.5917e-01   4.0455e-01
```

Mass-weighting & Diagonalization

Mass-weighting

- Rescales Hessian using atomic masses: $$\tilde{H}_{ij} = \frac{H_{ij}}{\sqrt{m_i m_j}}$$

Diagonalization

- Solves for eigenvalues (ω^2) to get normal modes
- Eigenvalues > 0: vibrational frequency
- Eigenvalues < 0: imaginary frequency
- Converts eigenvalues (ω^2) to frequencies in wavenumbers (cm^-1) using the conversion factor: 5140.484532 cm^-1

$$\nu_i = \sqrt{\lambda_i} \times 5140.484532$$

Mode classification

- Degrees of freedom (H2O): 3N = 9
- 3 translational modes + 3 rotational modes = 6
- So, 9-6 = 3 vibrational modes

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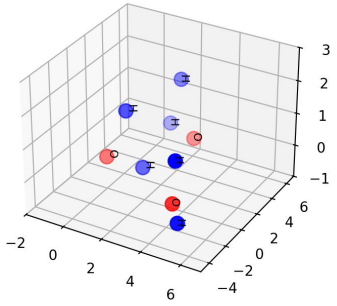
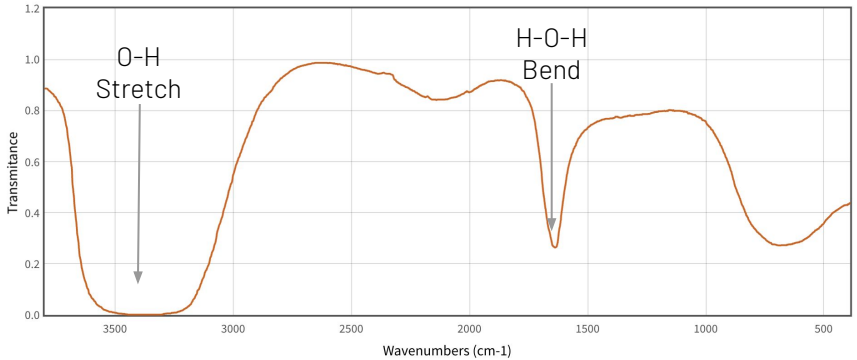
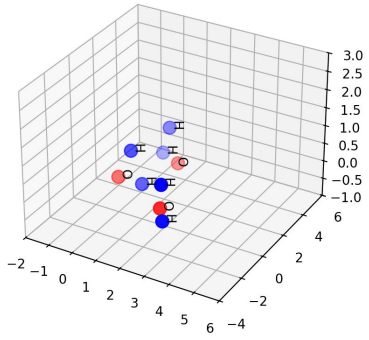
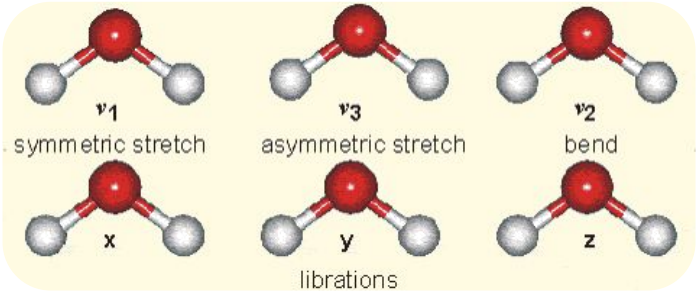
Results



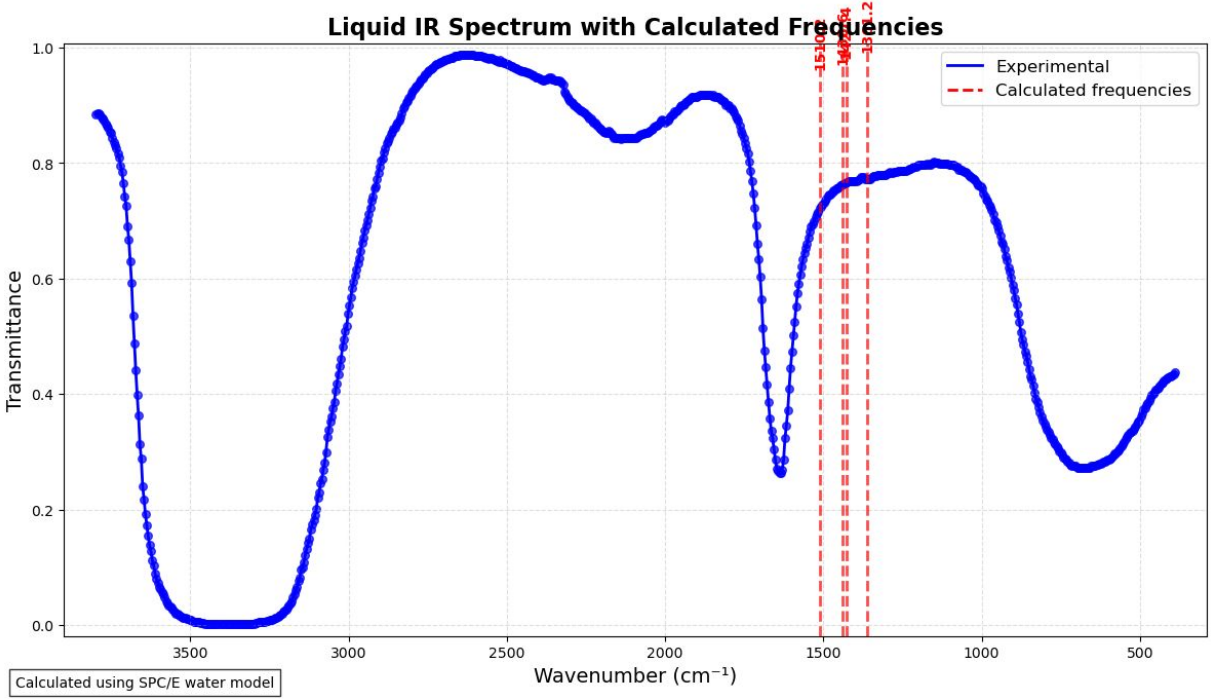






- Each absorption peak corresponds to a vibrational mode
  - Bending mode: ~1600 cm^-1
  - O-H Stretch (symmetric and asymmetric): ~3200-3650 cm^-1
- Libarations: ~400–900 cm^-1
- Water's IR spectrum is widely researched, making it ideal for validating computational models

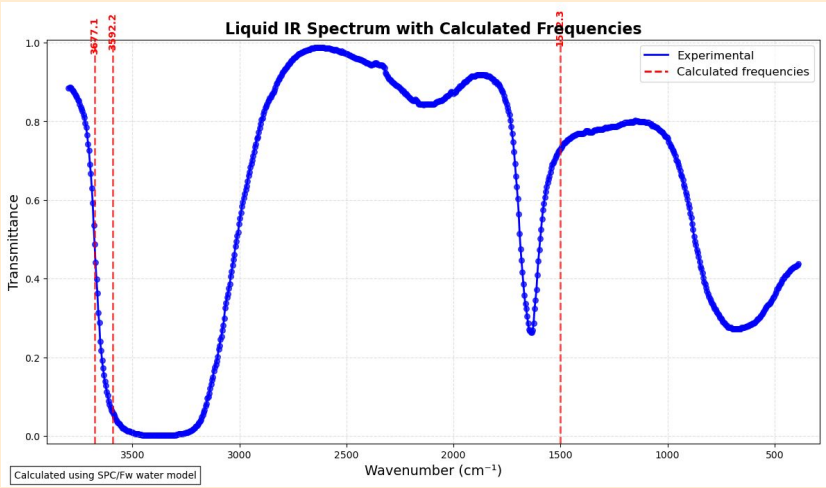
IR Spectroscopy




```
Frequencies (cm^-1):
  Imaginary (-0.15959)
  Imaginary (-0.06901)
  Imaginary (-0.00597)
  Imaginary (-0.00434)
  214.00076 cm^-1
  1361.21608 cm^-1
  1427.41430 cm^-1
  1438.60926 cm^-1
  1510.15642 cm^-1
```

SPC/E

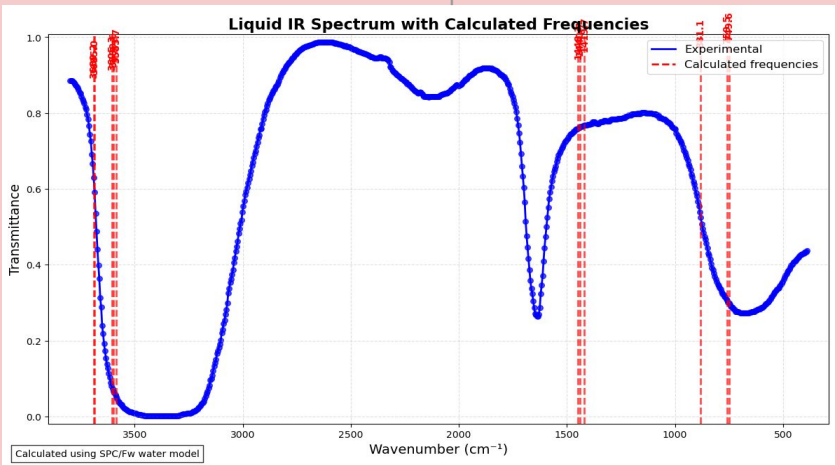
SPC/FW




```
Frequencies (cm^-1):
  Imaginary (-0.00034)
  Imaginary (-0.00000)
  Imaginary (-0.00000)
  0.12060 cm^-1
  53.22013 cm^-1
  86.56577 cm^-1
  1502.25602 cm^-1
  3592.24853 cm^-1
  3677.14667 cm^-1
```

1 H2O molecule

3 H2O molecules - 3 A apart

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Frequencies (cm^-1):
  Imaginary (-0.07333)
  Imaginary (-0.07311)
  Imaginary (-0.06828)
  Imaginary (-0.00626)
  Imaginary (-0.00347)
  Imaginary (-0.00097)
  Imaginary (-0.00019)
  Imaginary (-0.00004)
  Imaginary (-0.00002)
  Imaginary (-0.00000)
  0.00456 cm^-1
  0.01218 cm^-1
  84.78354 cm^-1
  144.88435 cm^-1
  203.18281 cm^-1
  749.55308 cm^-1
  759.53739 cm^-1
  881.06060 cm^-1
  1419.65401 cm^-1
  1440.73534 cm^-1
  1448.32118 cm^-1
  3585.65498 cm^-1
  3599.59959 cm^-1
  3605.34397 cm^-1
  3685.00090 cm^-1
  3689.19799 cm^-1
  3698.80347 cm^-1
```

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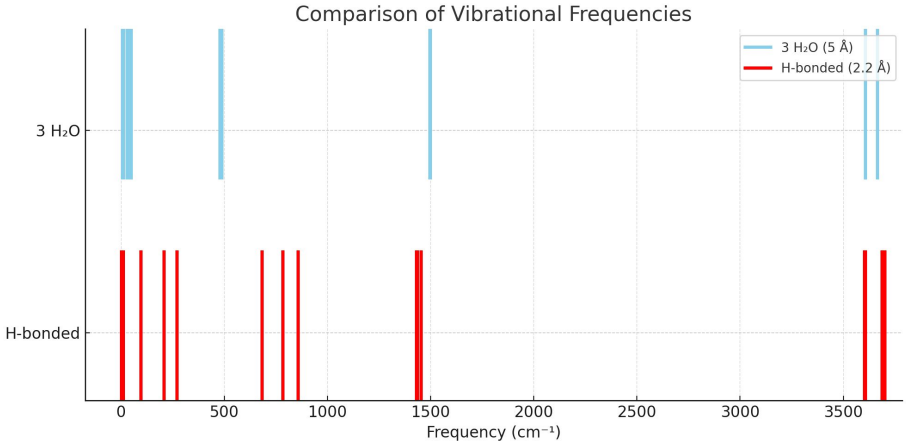
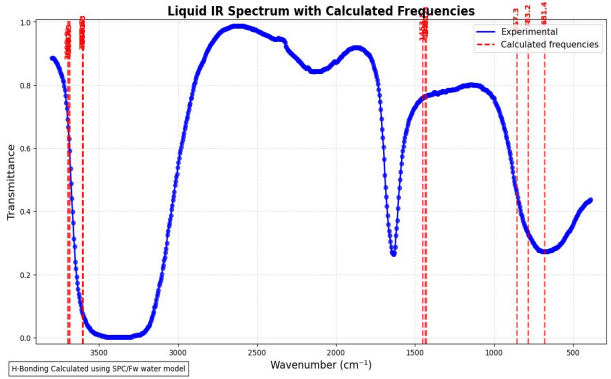
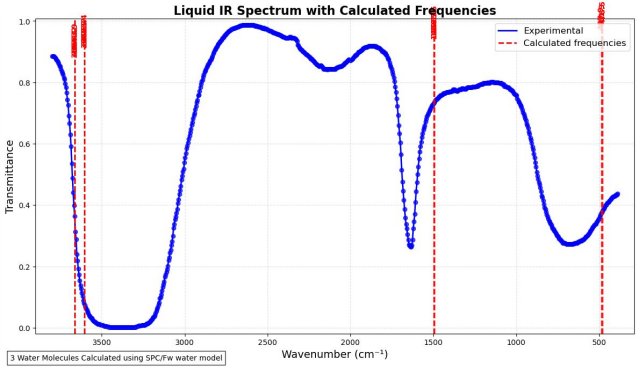
Discussion

Hydrogen Bonding

Mode	3 H_2O Molecules (cm^{-1})	H-Bonded System (cm^{-1})	Assignment
1–10	Imaginary	Imaginary	Rotations / Translations
11	5.36	0.00514	Low-frequency translation
12	10.73	0.00618	Low-frequency vibration
13	28.03	8.87	Intermolecular vibration
14	37.56	94.79	Intermolecular bend
15	47.80	207.10	Intermolecular bend
16	478.48	270.95	Bending (HOH) mode
17	481.90	681.42	Bending (HOH) mode
18	487.93	783.23	Bending (HOH) mode
19	1495.52	857.31	Bending mode
20	1496.04	1431.32	Bending $mode
21	1496.85	1435.15	Bending mode
22	3605.38	3601.30	Stretching (OH)
23	3605.68	3603.87	Stretching (OH)
24	3605.90	3605.55	Stretching (OH)
25	3663.86	3687.49	Free OH stretch
26	3664.18	3691.61	Free OH stretch
27	3664.39	3699.93	Free OH stretch







3 H2O molecule - 2.2 A

3 H2O molecule – 5 A

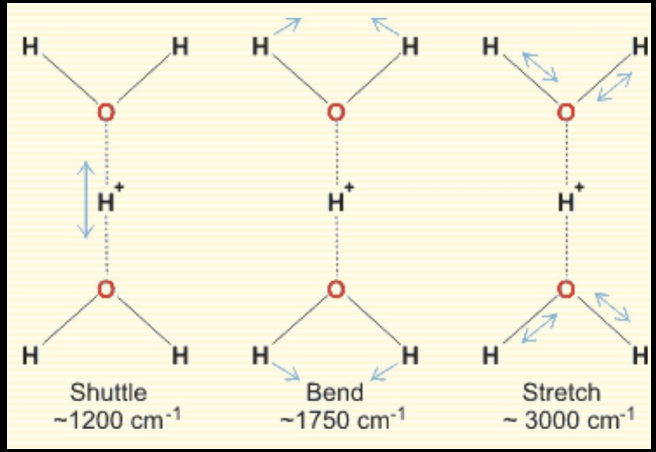
Thank You

Questions?

References

1. http://www.sklogwiki.org/SklogWiki/index.php/SPC/E_model_of_water
2. http://www.sklogwiki.org/SklogWiki/index.php/SPC/Fw_model_of_water
3. https://en.wikipedia.org/wiki/Water_model
4. https://water.lsbu.ac.uk/water/water_vibrational_spectrum.html
5. https://www.colby.edu/chemistry/PChem/Hartree.html
6. https://pubmed.ncbi.nlm.nih.gov/17115765/

Future Directions



Expand the theory to allow ion analysis (Zundel Cation)